CHM1664: Topics in Statistical Mechanics:
The Foundations of Molecular Simulation

Lecture notes written by J. Schofield and R. van Zon

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About the course

The Foundations of Molecular Simulation

This course covers the basic principles involved in simulating chemical and physical systems in the condensed phase. Simulations are a means to evaluate equilibrium properties such free energies as well as dynamical properties such as transport coefficients and reaction rates. In addition, simulations allow one to gain insight into molecular mechanisms. After presenting the theoretical basis of Monte Carlo and molecular dynamics simulations, particular attention is given to recent developments in this field. These include the hybrid Monte Carlo method, parallel tempering, and symplectic and other integration schemes for rigid, constrained, and unconstrained systems.

Organizational details

Location: Online via Zoom or Bb Collaborate
Dates and Time: TBD

Instructor

- Prof. Jeremy Schofield
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  - Office hours: By appointment

Grading

1. 4 problem sets — 70%
2. Short literature report (3500 word limit) or simulation project — 30%

Suggested reference books

- D. A. McQuarrie, *Statistical Mechanics*
- D. Frenkel and B. Smit, *Understanding Molecular Dynamics: From Algorithms to Applications* (Academic Press, 2002) 2nd ed.:
  `https://www.sciencedirect.com/book/9780122673511/understanding-molecular-simulation`
- D. C. Rapaport, *The Art of Molecular Dynamics Simulations* (Cambridge U. P., 2011) 2nd ed.
  `https://doi.org/10.1017/CBO9780511816581`
- W. H. Press, S. A. Teukolvsky, W. T. Vettering, and C. P. Flannery, *Numerical Recipes: The Art of Scientific Computing* (Cambridge University Press, 2007) 3rd ed.
  `https://dx.doi.org/10.1145/1874391.187410`
  `www.nrbook.com`

Contents

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Review

1.1 Classical Mechanics

- 1-Dimensional system with 1 particle of mass m
  - Newton's equations of motion for position $x(t)$ and momentum $p(t)$:

$$\begin{aligned}
\dot{x}(t) &\equiv \frac{dx}{dt} \qquad\qquad p = m\dot{x} \\
F(t) &= ma(t) \qquad\qquad a(t) = \ddot{x}(t) \\
F(t) &= -\frac{dV}{dx} \\
\dot{p}(t) &= m\ddot{x}(t) = F(t) = -\frac{dV}{dx}
\end{aligned}$$

  - Define an energy function called the *Hamiltonian* $H(x,p) = \frac{p^2}{2m} + V(x)$.
  - Introduce terminology

$$\frac{p^2}{2m} = \text{kinetic energy} \qquad V(x) = \text{potential energy}$$

  - Newton's laws can then be expressed as:

$$\dot{x} = \frac{p}{m} = \frac{\partial H}{\partial p} \qquad \dot{p} = -\frac{dV}{dx} = -\frac{\partial H}{\partial x}.$$

  - These are coupled ordinary differential equations whose solution is uniquely specified by specifying two conditions, such as $x_0 = x(0)$ and $p_0 = p(0)$ at some reference time $t_0 = 0$.

- 3-dimensional system of 1 particle
  - Notation: $\mathbf{r} = (x, y, z)$ and $\mathbf{p} = (p_x, p_y, p_z)$. Also, $\mathbf{p} \cdot \mathbf{p} = p_x^2 + p_y^2 + p_z^2$.
  - The Hamiltonian is: $\frac{\mathbf{p}\cdot\mathbf{p}}{2m} + V(\mathbf{r})$.
  - The equations of motion are:

$$\begin{aligned} \dot{\mathbf{r}} &= \frac{\partial H}{\partial \mathbf{p}} = \frac{\mathbf{p}}{m} \quad \xrightarrow{\text{shorthand for}} \quad \begin{pmatrix} \dot{r_x} \\ \dot{r_y} \\ \dot{r_z} \end{pmatrix} = \frac{1}{m} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} \\ \dot{\mathbf{p}} &= -\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial V}{\partial \mathbf{r}} \end{aligned}$$

- 2 particles in 3-dimensions
  - Hamiltonian: $H = \frac{\mathbf{p}_1\cdot\mathbf{p}_1}{2m_1} + \frac{\mathbf{p}_2\cdot\mathbf{p}_2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2)$
  - Equations of motion are:

$$\begin{aligned} \dot{\mathbf{r}_1} &= \frac{\partial H}{\partial \mathbf{p}_1} = \frac{\mathbf{p}_1}{m_1} \qquad & \dot{\mathbf{r}_2} &= \frac{\partial H}{\partial \mathbf{p}_2} = \frac{\mathbf{p}_2}{m_2} \\ \dot{\mathbf{p}_1} &= -\frac{\partial H}{\partial \mathbf{r}_1} & \dot{\mathbf{p}_2} &= -\frac{\partial H}{\partial \mathbf{r}_2} \end{aligned}$$

  - Introduce generalized notation: $\mathbf{r}^{(2)} = (\mathbf{r}_1, \mathbf{r}_2)$ and $\mathbf{p}^{(2)} = (\mathbf{p}_1, \mathbf{p}_2)$.

$$\mathbf{p}^{(2)} \cdot \mathbf{p}^{(2)} = \mathbf{p}_1 \cdot \mathbf{p}_1 + \mathbf{p}_2 \cdot \mathbf{p}_2$$

  - Equations of motion in this notation:

$$\dot{\mathbf{r}}^{(2)} = \frac{\partial H}{\partial \mathbf{p}^{(2)}} \qquad \dot{\mathbf{p}}^{(2)} = -\frac{\partial H}{\partial \mathbf{r}^{(2)}}.$$

- N particle system in 3-D
  - Equation of motion in generalized notation:

$$\dot{\mathbf{r}}^{(N)} = \frac{\partial H}{\partial \mathbf{p}^{(N)}} \qquad \dot{\mathbf{p}}^{(N)} = -\frac{\partial H}{\partial \mathbf{r}^{(N)}}.$$

  - A total of $6N$ equations!
  - At each point in time, the system is specified by $6N$ coordinates $(\mathbf{r}^{(N)}(t), \mathbf{p}^{(N)}(t)) \equiv \mathbf{x}^{(N)}(t)$ called the *phase point*.
  - The set of all phase points is called *phase space*.
  - Classical dynamics describes a path through the $6N$-Dimensional phase space.

- Special properties of path through phase space:
  1. Certain quantities remain unchanged during the evolution of system.
     * Examples: energy, momentum and angular momentum may be *conserved* (constant) along the path or *trajectory* of the system.
     * Path remains on a hyper-surface of constant energy in phase space.
  2. Paths never cross in phase space. Each disjoint path, labelled by initial conditions, passes arbitrarily close to any point on the constant energy hypersurface.
     * Amount of time for the trajectory of the system from a given initial point in phase space to pass arbitrarily close to the initial point is called the *recurrence time*: Absolutely enormous for large, interacting systems.

- Consider an arbitrary function G of the phase space coordinate $\boldsymbol{x}^{(N)}$,

$$G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = G(\mathbf{x}^{(N)}, t).$$

Taking the time derivative,

$$\begin{aligned}
\frac{dG(\mathbf{x}^{(N)}, t)}{dt} &= \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{r}^{(N)}} \cdot \dot{\mathbf{r}}^{(N)} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{p}^{(N)}} \cdot \dot{\mathbf{p}}^{(N)} \\
&= \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}}.
\end{aligned}$$

- We can define the *Liouville operator* $\mathcal{L}$ to be:

$$\mathcal{L} = \frac{\partial H}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial}{\partial \mathbf{r}^{(N)}} - \frac{\partial H}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial}{\partial \mathbf{p}^{(N)}}$$

so that in terms of a general function B

$$\mathcal{L}B = \frac{\partial B}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial B}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}}.$$

- In terms of the Liouville operator,

$$\frac{dG(\mathbf{x}^{(N)}, t)}{dt} = \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \mathcal{L}G(\mathbf{x}^{(N)}, t).$$

- Functions of the phase space coordinate G that are not explicit functions of time t are conserved by the dynamics if $\mathcal{L}G = 0$.
- Formal solution of evolution is then

$$G(\boldsymbol{x}^{(N)}, t) = e^{\mathcal{L}t} G(\boldsymbol{x}^{(N)}, 0).$$

- In particular,
$$\boldsymbol{x}^{(N)}(t) = e^{\mathcal{L}t}\boldsymbol{x}^{(N)}(0).$$
- Note that $\mathcal{L}H = 0$.
- Can also define the *Poisson bracket* operator via
$$\{A, B\} \equiv \frac{\partial A}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{p}^{(N)}} - \frac{\partial A}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{r}^{(N)}}.$$
- The relationship between the Poisson bracket and Liouville operators is
$$\mathcal{L}B = \{B, H\} \qquad \text{so} \qquad \frac{dG(\mathbf{x}^{(N)}, t)}{dt} = \frac{\partial G(\mathbf{x}^{(N)}, t)}{\partial t} + \{G(\mathbf{x}^{(N)}, t), H(\boldsymbol{x}^{(N)})\}.$$

- Important property:
$$e^{\mathcal{L}t}\left(A(\boldsymbol{x}^{(N)})B(\boldsymbol{x}^{(N)})\right) = \left(e^{\mathcal{L}t}A(\boldsymbol{x}^{(N)})\right)\left(e^{\mathcal{L}t}B(\boldsymbol{x}^{(N)})\right) = A(\boldsymbol{x}^{(N)}(t))B(\boldsymbol{x}^{(N)}(t)).$$

1.2 Ensembles and Observables

- Consider some arbitrary dynamical variable $G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = G(\boldsymbol{x}^{(N)})$ (function of phase space coordinates and hence possibly evolving in time).

- An experimental measurement of quantity corresponds to a *time* average of some (possibly short) sampling interval τ.
$$G_{\text{obs}}(t) = \overline{G(t)} \equiv \frac{1}{\tau}\int_0^\tau d\sigma\ G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right).$$
  - $\tau \gg \tau_m$. where τ_m is a *microscopic time scale*. Hence fluctuations on microscopic time scale a smoothed out.
  - For most systems, evolution of $G(t)$ cannot be solved analytically and so must resort to
    1. Numerically solving evolution (computer simulation)
    2. Developing a new theoretical framework relating time averages to something that can be calculated.

- Ensemble Average: Infinite/long time average of dynamical variable corresponds to an average over a properly weighted set of points of phase space (called an *ensemble*). The statistical average is called an *ensemble average*.
  - Each point in phase space corresponds to a different configuration of the system.

– Ensemble average therefore corresponds to a weighted average over different configurations of the system.

- Define a probability density for phase space (often loosely called the "distribution function')':

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) \quad = \quad \text{distribution function}$$

and hence

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \quad = \quad \text{prob. of finding a system in ensemble with coordinates between } (\mathbf{r}^{(N)}, \mathbf{r}^{(N)} + d\mathbf{r}^{(N)}) \text{ and } (\mathbf{p}^{(N)}, \mathbf{p}^{(N)} + d\mathbf{p}^{(N)}) \text{ at time } t.$$

– Note that the distribution function is normalized:

$$\int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\, f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = 1$$

- The *ensemble average* is defined as:

$$\langle G(t) \rangle \equiv \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\, G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})\, f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t).$$

- *microcanonical ensemble*: All systems in ensemble have the same total energy.
  – All dynamical trajectories with same energy compose a set of states in microcanonical ensemble.
  – Technically, all conserved quantities should also be the same.

What is the connection between the ensemble average and the experimental observation (time average)?

- **Quasi-ergodic hypothesis:** As $\mathbf{t} \to \infty$, a dynamical trajectory will pass arbitrarily close to each point in the constant-energy (if only conserved quantity) hypersurface of phase space (metrically transitive).
  – Another statement: For all initial states except for a set of zero measure, the phase space is connected through the dynamics.
  – Hypersurfaces of phase space covered by trajectory.

- So in some sense, as $\tau \to \infty$:, we expect

$$G_{\text{obs}}(t) = \frac{1}{\tau}\int_0^{\tau} d\sigma\, G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right) = \frac{1}{\Omega}\int' d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\, G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$$

  where

$$\Omega = \int' d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} = \int_{E<H(\boldsymbol{x}^{(N)})<E+\delta E} d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}$$

  hence

$$G_{\text{obs}}(t) = \overline{G}(t) = \int G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t)\, d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \quad \text{if } f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = 1/\Omega.$$

  - All points on hypersurface have the same weight (equally probable).
  - Ensemble analogy: each point in restricted phase space corresponds to a configuration of the system with the same macroscopic properties.

- Can utilize an axiomatic approach to find equilibrium distributions: Maximize statistical entropy subject to constraints.

- Alternate method: Asymptotic solution of the Boltzmann equation for distribution functions - describes collisions of pairs from Newton's equations and adds an assumption of statistical behavior (molecular chaos).

  - System naturally evolves from an initial state to states with static macroscopic properties corresponding to "equilibrium" properties - Can model this with simple spin systems like the Kac ring model.
  - Measure of disorder, the statistical entropy, increases as the system evolves: maximized in equilibrium (H theorem).

Canonical Ensemble

- Remove restriction of defining probability only on constant energy hypersurface.

- Allow total energy of systems in ensemble to vary (hopefully) narrowly around a fixed average value.

$$f(\boldsymbol{x}^{(N)}) = \frac{1}{N!h^{3N}} \exp\{\beta(A - H(\boldsymbol{x}^{(N)}))\}$$

- A is the Helmholtz free energy.

- We define the *partition function* $Q_N(T,V)$ by

$$Q_N(T,V) = \frac{1}{N!h^{3N}} \int d\boldsymbol{x}^{(N)} \ \exp\{-\beta H(\boldsymbol{x}^{(N)})\} = \exp\{-\beta A\}$$

so by normalization

$$f(\boldsymbol{x}^{(N)}) = \frac{1}{N!h^{3N}} \exp\{\beta(A - H(\boldsymbol{x}^{(N)}))\} = \frac{1}{N!H^{3N}} \frac{\exp\{-\beta H(\boldsymbol{x}^{(N)})\}}{Q_N(T,V)}.$$

- Relation $A = -kT \ln Q_N(T,V)$ gives thermodynamic connection: For example

1. The pressure is:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left(\frac{\partial \ln Q_N}{\partial V}\right)_T.$$

2. The chemical potential is:

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

3. The energy is:

$$\begin{aligned}
\overline{E} &= \frac{\exp\{\beta A\}}{N!h^{3N}} \int d\boldsymbol{x}^{(N)} \ H(\boldsymbol{x}^{(N)}) \exp\{-\beta H(\boldsymbol{x}^{(N)})\} \\
&= \frac{\exp\{\beta A\}}{N!h^{3N}} - \frac{\partial}{\partial \beta} \int d\boldsymbol{x}^{(N)} \ \exp\{-\beta H(\boldsymbol{x}^{(N)})\} \\
&= -\frac{1}{Q_N}\frac{\partial Q_N}{\partial \beta} = -\frac{\partial \ln Q_N}{\partial \beta}.
\end{aligned}$$

- We can write the canonical partition function as:

$$\begin{aligned}
Q_N(T,V) &= \frac{1}{N!h^{3N}} \int d\boldsymbol{x}^{(N)} \ \exp\{-\beta H(\boldsymbol{x}^{(N)})\} \\
&= \int_0^\infty dE \frac{1}{N!h^{3N}} \int d\boldsymbol{x}^{(N)} \ \exp\{-\beta H(\boldsymbol{x}^{(N)})\}\delta(E - H(\boldsymbol{x}^{(N)})) \\
&= \int_0^\infty dE \ \exp\{-\beta E\} \left(\frac{1}{N!h^{3N}} \int d\boldsymbol{x}^{(N)} \ \delta(E - H(\boldsymbol{x}^{(N)}))\right) \\
Q_N(T,V) &= \int_0^\infty dE \ \exp\{-\beta E\} N(E)
\end{aligned}$$

where

$$\begin{aligned}
N(E) &\equiv \frac{1}{N!h^{3N}} \int d\boldsymbol{x}^{(N)} \ \delta(E - H(\boldsymbol{x}^{(N)})) \\
&= \text{density of } \textit{unique} \text{ states at energy } E \text{ (microcanonical partition function).}
\end{aligned}$$

Relationship between ensemble averages

- How likely are we to observe a system in the canonical ensemble with an energy very different from the average energy $\overline{E} = \langle H(\boldsymbol{x}^{(N)})\rangle$? From the Tchebycheff inequality, we find that

$$Pr\left(\left|H(\boldsymbol{x}^{(N)}) - \overline{E}\right| \geq \lambda\overline{E}\right) \leq \frac{\sigma_E^2}{\lambda^2\overline{E}^2}$$

- Now the variance in the energy is:

$$\sigma_E^2 = \left\langle H(\boldsymbol{x}^{(N)})^2\right\rangle - \langle H(\boldsymbol{x}^{(N)})\rangle^2 = \frac{\partial^2 \ln Q_N}{\partial\beta^2} = -\frac{\partial\overline{E}}{\partial\beta} = kT^2C_v$$

and hence

$$Pr\left(\left|H(\boldsymbol{x}^{(N)}) - \overline{E}\right| \geq \lambda\overline{E}\right) \leq \frac{kT^2C_v}{\lambda^2\overline{E}^2}$$

- For an ideal gas system, $\overline{E} = 3/2NkT$ and hence $C_v = 3/2Nk$.
- Typically, $\overline{E} \sim N$ and $C_v \sim N$.

$$Pr\left(\left|H(\boldsymbol{x}^{(N)}) - \overline{E}\right| \geq \lambda\overline{E}\right) \leq \frac{kT^2C_v}{\lambda^2\overline{E}^2} \sim \frac{1}{N\lambda^2}$$

  - As N increases, it becomes less and less likely to observe a system with energy very different from $\overline{E}$,

$$\langle B(\boldsymbol{x}^{(N)})\rangle_{\text{canon}} = \int dE\ P(E)\langle B(\boldsymbol{x}^{(N)})\rangle_{\text{micro at } E} \approx \langle B(\boldsymbol{x}^{(N)})\rangle_{\text{micro at } \overline{E}}\left(1 + O(1/N)\right).$$

- $P(E)$ is sharply-peaked around $E = \overline{E}$: Can show

$$P(E) \quad\approx\quad P(\overline{E})\left(\frac{1}{2\pi\sigma_E^2}\right)^{1/2} \exp\left\{-\frac{(E-\overline{E})^2}{2kT^2C_v}\right\}$$

- Relative spread of energy $\sigma_E/\overline{E} \sim N^{-1/2}$.

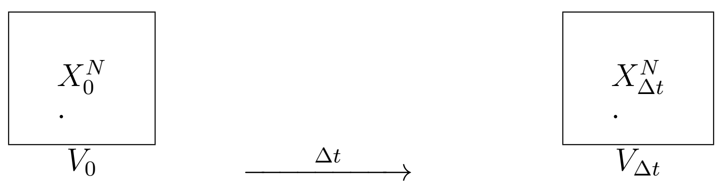
1.3 Liouville Equation for Hamiltonian Systems

Define small volume element V_0 in phase space.

- How does probability of finding the system in this region change in time?

$$P(V_0) = \int_{V_0} dX_0^N \; f(X_0^N, 0)$$

- Allow system to evolve according to dynamics:



  - Volume changes shape in mapping:

$$\begin{aligned} X_0^N \to X_{\Delta t}^N &\simeq X_0^N + \dot{X}_0^N \Delta t \\ &\equiv X_0^N + \delta X^N \end{aligned}$$

  - Maybe changes volume as well.
  - Number of states is V_0 and $V_{\Delta t}$ is same since we follow all points in original volume.
    - Can only change if some points in V_0 aren't in $V_{\Delta t}$ (flow out of volume).

- So $P(V_0, 0) = P(V_{\Delta t}, \Delta t)$: Conservation of probability (like fluid where particles aren't created or destroyed.)

- Changing variables from X_0^N to $X_{\Delta t}^N$,

$$\begin{aligned} P(V_0) &= \int_{V_0} dX_0^N \; f(X_0^N, 0) = \int_{V_{\Delta t}} dX_{\Delta t}^N \; J(X^N; X_{\Delta t}^N) f(X_{\Delta t}^N - \delta X^N, \Delta t - \Delta t) \\ &= P_{\Delta t}(V_{\Delta t}) \quad \text{since } P(V_0, 0) = P(V_{\Delta t}, \Delta t). \end{aligned}$$

- Recall that $X_{\Delta t}^N - X_0^N \equiv \delta X_0^N$.

- Evaluation of the Jacobian is a bit complicated, but gives

$$\begin{aligned} J(X_0^N; X_{\Delta t}^N) &= \text{Jacobian for transform } \; X_0^N = X_{\Delta t}^N - \delta X^N \\ &= \left| \frac{\partial X_0^N}{\partial X_{\Delta t}^N} \right| = 1 - \nabla_{X^N} \cdot \delta X^N \end{aligned}$$

So

$$P_{\Delta t}(V_{\Delta t}) = P(V_0) = \int_{V_{\Delta t}} dX_{\Delta t}^N \left(1 - \nabla_{X^N} \cdot \delta X^N\right) \, f\left(X_{\Delta t}^N - \delta X^N, \Delta t - \Delta t\right)$$

for small δX^N.

- What is δX^N?
  - For Hamiltonian systems $\;X_{\Delta t}^N \simeq X_0^N + \dot{X}_0^N \Delta t$, or $\delta X^N = \dot{X}_0^N \Delta t$.
  - Expanding for small displacements δX_0^N and small time intervals Δt:

$$f\left(X_{\Delta t}^N - \delta X^N, \Delta t - \Delta t\right) \simeq f\left(X_{\Delta t}^N, \Delta t\right)$$
$$-\frac{\partial f}{\partial t}\,\Delta t - \left(\nabla_{X^N} f\right) \cdot \delta X^N + \frac{1}{2}\left(\nabla_{X^N}^2 f\right)(\delta X^N)^2 + \ldots$$

  - Inserting this in previous equation for $P_{\Delta t}(V_{\Delta t}) = P(V_0)$, we get

$$\begin{aligned} P_{\Delta t}(V_{\Delta t}) &= P_{\Delta t}(V_{\Delta t}) + \int_{V_{\Delta t}} dX_{\Delta t}^N \\ & \quad \left(-\frac{\partial f}{\partial t}\,\Delta t - \nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f (\delta X^N)^2\right) \end{aligned}$$

  or

$$\int_{V_{\Delta t}} dX_{\Delta t}^N \left(-\frac{\partial f}{\partial t}\,\Delta t - \nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f (\delta X^N)^2\right) = 0$$

  - Since this holds arbitrary volume $V_{\Delta t}$, the integrand must vanish.

$$\frac{\partial f}{\partial t}\,\Delta t = -\nabla_{X^N} \cdot (\delta X^N f) + \frac{1}{2}\nabla_{X^N}^2 f (\delta X^N)^2 + \cdots$$

  - Now, let us evaluate this for $\delta X^N = \dot{X}_0^N \Delta t$
    * To linear order in Δt

$$\nabla_{X^N} \cdot \left(\dot{X}_0^N f\right) \Delta t = \left(\dot{X}^N \cdot \nabla_{X^N} f + \nabla_{X^N} \cdot \dot{X}^N f\right) \Delta t$$

    but

$$\nabla_{X^N} \cdot \dot{X}^N = \frac{\partial \dot{R}^N}{\partial R^N} + \frac{\partial \dot{P}^N}{\partial P^N} = \frac{\partial H}{\partial R^N \partial P^N} - \frac{\partial H}{\partial P^N \partial R^N} = 0!$$

  * Note that this implies the volume element does not change with normal Hamiltonian propagation:

$$dX_0^N = dX_{\Delta t}^N \, J(X^N; X_{\Delta t}^N) = dX_{\Delta t}^N \left(1 - \nabla_{X^N} \cdot \dot{X}^N \Delta t\right) = dX_{\Delta t}^N.$$

- Also, $(\delta X^N)^2 \sim O(\Delta t)^2$ since $\delta X^N \sim \Delta t$, so

$$\frac{\partial f}{\partial t}\Delta t = -\dot{X}^N \cdot \nabla_{X^N} f \Delta t + O(\Delta t)^2$$

- In the short-time limit,

$$\boxed{\frac{\partial f}{\partial t} = -\dot{X}^N \cdot \nabla_{X^N} f}$$

Recall

$$\begin{aligned} \dot{X}^N \cdot \nabla_{X^N} G &= \left(\dot{R}^N \cdot \nabla_{R^N} + \dot{P}^N \cdot \nabla_{P^N}\right) \mathrm{G} \\ &= \left(\frac{\partial H}{\partial P^N} \cdot \nabla_{R^N} - \frac{\partial H}{\partial R^N} \cdot \nabla_{P^N}\right) \mathrm{G} \equiv \mathcal{L}\mathrm{G} = \{\mathrm{G},\mathrm{H}\} \end{aligned}$$

So we obtain the **Liouville equation:**

$$\boxed{\frac{\partial f}{\partial t} = -\mathcal{L} f = -\{f, \mathrm{H}\}}.$$

- The formal solution is:

$$f(\boldsymbol{x}^{(N)}, t) = e^{-\mathcal{L}t} f(\boldsymbol{x}^{(N)}, 0).$$

- Also note:

$$\frac{\partial f}{\partial t} + \dot{X}^N \cdot \nabla_{X^N} f = \frac{df(X^N, t)}{dt} = 0.$$

- Interpretation:

$$\begin{aligned} f(\mathbf{r}^{(N)}(0), \mathbf{p}^{(N)}(0), 0) &= f(\mathbf{r}^{(N)}(t), \mathbf{p}^{(N)}(t), t) \\ f(\mathbf{r}^{(N)}(0), \mathbf{p}^{(N)}(0), t) &= f(\mathbf{r}^{(N)}(-t), \mathbf{p}^{(N)}(-t), 0). \end{aligned}$$

- If follow an initial phase point from time 0 to time t, probability density doesn't change (i.e. you go with the flow).

- Probability density near phase point $\boldsymbol{x}^{(N)}(0)$ at time t is the same as the *initial* probability density at backward-evolved point $\boldsymbol{x}^{(N)}(-t)$.

1.3.1 Alternate derivation of Liouville equation

The time average of an evolving microscopic variable is

$$\overline{A}(t) = \lim_{T\to\infty}\frac{1}{T}\int_0^T d\tau A(\mathbf{x}(t+\tau)) = \langle A\rangle_t = \int d\boldsymbol{x}_0^{(N)}\,\rho(\boldsymbol{x}_0^{(N)})A(\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)})),$$

where $\rho(\mathbf{x}_0)$ is the density at the phase point $\mathbf{x}_0$ at time $t=0$.

- Note that

$$\begin{aligned}
\langle A\rangle_t &= \int d\boldsymbol{x}^{(N)}d\boldsymbol{x}_0^{(N)}\,\delta(\boldsymbol{x}^{(N)}-\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)}))\,\rho(\boldsymbol{x}_0^{(N)})A(\boldsymbol{x}^{(N)})\\
&= \int d\boldsymbol{x}^{(N)}\,\langle\delta(\boldsymbol{x}^{(N)}-\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)}))\rangle_0\;A(\boldsymbol{x}^{(N)})\\
&= \int d\boldsymbol{x}^{(N)}\,\rho(\boldsymbol{x}^{(N)},t)\;A(\boldsymbol{x}^{(N)}),
\end{aligned}$$

  Hence, the time dependent probability density can be written in general terms as $\rho(\boldsymbol{x}^{(N)},t) = \langle\delta(\boldsymbol{x}^{(N)}-\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)}))\rangle_0 = \int d\boldsymbol{x}_0^{(N)}\,\rho(\boldsymbol{x}_0^{(N)})\delta(\boldsymbol{x}^{(N)}-\boldsymbol{x}^{(N)}(t;\mathbf{x}_0))$, where $\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)})$ is the phase point at time t given that at time $t=0$ it was at point $\boldsymbol{x}_0^{(N)}$ (i.e. the solution of the phase space trajectory).

- The equation of motion for $\rho(\boldsymbol{x}^{(N)},t)$, the Liouville equation, follows from

$$\begin{aligned}
\frac{\partial\rho(\boldsymbol{x}^{(N)},t)}{\partial t} &= \frac{d}{dt}\left\langle\delta(\boldsymbol{x}^{(N)}-\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)}))\right\rangle_0\\
&= \left\langle\dot{\boldsymbol{x}^{(N)}}(t;\boldsymbol{x}_0^{(N)})\cdot\nabla_{\boldsymbol{x}^{(N)}(t)}\delta(\boldsymbol{x}^{(N)}-\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)}))\right\rangle_0\\
&= -\nabla_{\boldsymbol{x}^{(N)}}\cdot\left\langle\dot{\boldsymbol{x}^{(N)}}(t;\boldsymbol{x}_0^{(N)})\delta(\boldsymbol{x}^{(N)}-\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)}))\right\rangle_0\\
&= -\nabla_{\boldsymbol{x}^{(N)}}\cdot\left(\dot{\boldsymbol{x}}^{(N)}\left\langle\delta(\boldsymbol{x}^{(N)}-\boldsymbol{x}^{(N)}(t;\boldsymbol{x}_0^{(N)}))\right\rangle_0\right)\\
&= -\nabla_{\boldsymbol{x}^{(N)}}\cdot\left(\dot{\boldsymbol{x}}^{(N)}\;\rho(\boldsymbol{x}^{(N)},t)\right)\\
&= -\dot{\boldsymbol{x}}^{(N)}\cdot\nabla_{\boldsymbol{x}^{(N)}}\rho(\boldsymbol{x}^{(N)},t)
\end{aligned}$$

  if $\nabla_{\boldsymbol{x}^{(N)}}\cdot\dot{\boldsymbol{x}}^{(N)}=0$ as it does for a Hamiltonian system as shown above.

1.3.2 Equilibrium (stationary) solutions of Liouville equation

- Not a function of time, meaning $f(R^N,P^N,t)=f(R^N,P^N)$ or

$$\frac{\partial f}{\partial t} = -\mathcal{L}f = -\{f,H\} = \{H,f\} = 0.$$

- Recall that we showed that energy is conserved by the dynamics so $\frac{dH}{dt} = 0$.
- Suppose $f(R^N, P^N, t)$ is an *arbitrary* function of $H(R^N, P^N)$.

$$\frac{\partial f}{\partial t} = \{H, f(H)\} = \frac{\partial H}{\partial R^N} \cdot \frac{\partial f}{\partial P^N} - \frac{\partial H}{\partial P^N} \cdot \frac{\partial f}{\partial R^N}$$

but

$$\frac{\partial f}{\partial P^N} = \frac{\partial f}{\partial H} \frac{\partial H}{\partial P^N} \qquad \frac{\partial f}{\partial R^N} = \frac{\partial f}{\partial H} \frac{\partial H}{\partial R^N}$$

$$\frac{\partial f}{\partial t} = \left(\frac{\partial H}{\partial R^N} \cdot \frac{\partial H}{\partial P^N} - \frac{\partial H}{\partial P^N} \cdot \frac{\partial H}{\partial R^N} \right) \frac{\partial f}{\partial H} = 0$$

Thus any funct. of H is stationary solution of Liouville equation!

- In particular, both the microcanonical and canonical distribution functions are solutions of the Liouville equation.

1.3.3 Time-dependent Correlation Functions

Consider the *time-dependent correlation function* $C_{AB}(t)$ in the canonical ensemble

$$\left\langle A(\boldsymbol{x}^{(N)}, t) B(\boldsymbol{x}^{(N)}, 0) \right\rangle = \int d\boldsymbol{x}^{(N)} A(\boldsymbol{x}^{(N)}, t) B(\boldsymbol{x}^{(N)}, 0) f(\boldsymbol{x}^{(N)}).$$

- From the form of the Liouville operator, for arbitrary functions A and B of the phase space coordinates

$$A(\boldsymbol{x}^{(N)}, t) B(\boldsymbol{x}^{(N)}, t) = \left(e^{\mathcal{L}t} A(\boldsymbol{x}^{(N)}, 0) \right) \left(e^{\mathcal{L}t} B(\boldsymbol{x}^{(N)}, 0) \right) = e^{\mathcal{L}t} \left(A(\boldsymbol{x}^{(N)}, 0) B(\boldsymbol{x}^{(N)}, 0) \right).$$

- It can be shown by integrating by parts that:

$$\left\langle \left(\mathcal{L} A(\boldsymbol{x}^{(N)}) \right) B(\boldsymbol{x}^{(N)}) \right\rangle = - \left\langle A(\boldsymbol{x}^{(N)}) \left(\mathcal{L} B(\boldsymbol{x}^{(N)}) \right) \right\rangle.$$

- Consequence:

$$\left\langle A(\boldsymbol{x}^{(N)}, t) B(\boldsymbol{x}^{(N)}, 0) \right\rangle = \left\langle A(\boldsymbol{x}^{(N)}) B(\boldsymbol{x}^{(N)}, -t) \right\rangle.$$

- The *autocorrelation* function $C_{AA}(t)$ is therefore an even function of time.

- Also,

$$\begin{aligned}\int d\boldsymbol{x}^{(N)} \left(e^{\mathcal{L}t} A(\boldsymbol{x}^{(N)}, 0)\right) f(\boldsymbol{x}^{(N)}, 0) &= \int d\boldsymbol{x}^{(N)} A(\boldsymbol{x}^{(N)}, 0) \left(e^{-\mathcal{L}t} f(\boldsymbol{x}^{(N)}, 0)\right) \\ &= \int d\boldsymbol{x}^{(N)} A(\boldsymbol{x}^{(N)}, 0) f(\boldsymbol{x}^{(N)}, t)\end{aligned}$$

  - For an equilbrium system where $f(\boldsymbol{x}^{(N)}, t) = f(\boldsymbol{x}^{(N)})$,

$$\begin{aligned}\langle A(t)\rangle &= \langle A(0)\rangle \\ \langle A(t+\tau)B(\tau)\rangle &= \langle A(t)B(0)\rangle\,.\end{aligned}$$

2

Numerical integration and importance sampling

2.1 Quadrature

Consider the numerical evaluation of the integral

$$I(a,b) \;=\; \int_a^b dx\, f(x)$$

- Rectangle rule: on small interval, construct interpolating function and integrate over interval.
  - Polynomial of degree 0 using mid-point of interval:

    $$\int_{ah}^{(a+1)h} dx\, f(x) \approx h\, f\left((ah+(a+1)h)/2\right).$$

  - Polynomial of degree 1 passing through points $(a_1, f(a_1))$ and $(a_2, f(a_2))$: Trapezoidal rule

    $$f(x) = f(a_1) + \frac{x-a_1}{a_2-a_1}\left(f(a_2)-f(a_1)\right) \;\longrightarrow\; \int_{a_1}^{a_2} dx\, f(x) = \left(\frac{a_2-a_1}{2}\right)\left(f(a_1)+f(a_2)\right).$$

  - Composing trapezoidal rule n times on interval (a,b) with even sub-intervals $[kh,(k+1)h]$ where $k = 0,\ldots,n-1$ and $h = (b-a)/n$ gives estimate

    $$\int_a^b dx\, f(x) \approx \frac{b-a}{n}\left(\frac{f(a)+f(b)}{2} + \sum_{k=1}^{n-1} f(a+kh)\right).$$

- Simpsons rule: interpolating function of degree 2 composed n times on interval (a, b):

$$\int_a^b dx\, f(x) \approx \frac{b-a}{3n}\left[f(a) + 4f(a+h) + 2f(a+2h) + 4f(a+3h) + 2f(a+4h) + \cdots + f(b)\right].$$

  - Error bounded by

$$\frac{h^4}{180}(b-a)\left|f^{(4)}(\xi)\right|.$$

    where $\xi \in (a, b)$ is the point in the domain where the magnitude of the 4th derivative is largest.

2.1.1 Gaussian quadrature

For a fixed choice n of evaluations of the integrand, judicious choices of un-even divisions of the domain of integration can reduce the error bounds on integration. The schemes are based on the approximation,

$$I(a, b) = \int_a^b F(x)dx \approx \sum_{i=1}^{n} w_i F_i,$$

where $w_i = w(x_i)$ and $F_i = F(x_i)$ with choice of x_i and w_i are based on the definite integral of polynomials of higher order.

- Example is Gaussian quadrature with n points based on polynomial of degree $2n-1$. Consider a general integral $I(a, b) = \int_a^b F(y)dy$ We can rewrite this integral to extend over the domain $[-1, 1]$ using the mapping

$$y = \frac{1}{2}\left((b-a)x + a + b\right) \qquad x = \frac{2y - a - b}{b - a},$$

so that $I(a, b) = \int_{-1}^{1} f(x; a, b)dx$ where $f(x; a, b) = \frac{b-a}{2}F(\frac{b-a}{2}x + \frac{a+b}{2})$. This integral can be approximated as $I(a, b) = \sum_{i=1}^{n} w_i f_i$ where $f_i = f(x_i; a, b)$.

Suppose $f(x)$ is a polynomial of degree $2n-1$ or less. We can write this polynomial in the form $f(x) = Q(x)P_n(x) + R(x)$, where $P_n(x)$ is a polynomial of degree n and both $Q(x)$ and $R(x)$ are polynomials of lower degree than n (i.e of maximum degree $n-1$). In fact, we know that the degree of $R(x)$ is lower than that of $Q(x)$. In particular, we can choose $P_n(x)$ to be the nth-Legendre polynomial, which is of degree n. The

Legendre polynomials have the property that they are orthonormal when integrated over the domain $[-1, 1]$:

$$\int_{-1}^{1} P_m(x)P_n(x)dx = \delta_{m,n}.$$

This property implies that

$$I(a, b) = \int_{-1}^{1} R(x)dx$$

since $Q(x)$ is of lower degree than $P_n(x)$. This the integral is exactly equal to the integral of the integrand of a polynomial of degree $n - 1$ or less.

A *Lagrange polynomial* of degree $n - 1$ that passes through all n points $(x_i, R(x_i))$ is

$$R(x) = \sum_{i=1}^{n} R(x_i)L_i(x),$$

where

$$L_i(x) = \prod_{\substack{j=1 \\ j\neq i}}^{n} \frac{x - x_j}{x_i - x_j}.$$

If $R(x)$ is a polynomial of degree $n - 1$ or less this representation is exact.

The integral $I(a, b)$ is then exactly given by:

$$I(a, b) = \int_{-1}^{1} \sum_{i=1}^{n} R(x_i)L_i(x)dx = \sum_{i=1}^{n} R(x_i)w_i,$$

where

$$w_i = \int_{-1}^{1} L_i(x)dx = \int_{-1}^{1} \prod_{\substack{j=1 \\ j\neq i}}^{n} \frac{x - x_j}{x_i - x_j}\, dx.$$

- This is true for any choice of points x_i, but for arbitrary choices we must be able to evaluate the polynomial $R(x)$.
- The set of weights w_i can be evaluated and tabulated for any choice of points x_i.

- If we *choose* the points x_i such that $P_n(x_i) = 0$ (i.e. the set of n zeroes of the Legendre polynomial), then $f_i = R(x_i)$ and the integral is exactly given by

$$I(a,b) = \sum_{i=1}^{n} f_i w_i.$$

- Example: 5-point quadrature based on $P_5(x) = (63x^5 - 70x^3 + 15x)/16$.

$$\begin{aligned} x_i &= \{0, \pm 0.538..., \pm 0.906..\} \\ w_i &= \{0.56888, 0.478629..., 0.236926..\} \end{aligned}$$

- If $f(x)$ is not a polynomial of degree $2n-1$ or lower, then the Lagrange representation that interpolates $R(x)$ using the $L_i(x)$ is only an approximation, though it can be quite accurate if n is large enough. This depends on the specific form of the integrand $f(x)$.
- Error bounds for n-point Gaussian quadrature are

$$\frac{(b-a)^{2n+1}}{(2n+1)!}\frac{(n!)^4}{[(2n)!]^3}\left|F^{(2n)}(\xi)\right| \text{ for } \xi \in (a,b)..$$

- Must map limits onto the finite interval $[-1,1]$ even if original limits are infinite.
  - For the integral

$$\int_0^\infty \frac{dy}{y^5\left(e^{1/y}-1\right)},$$

    we can map the domain onto a finite interval by the transformation $y = \tan\theta$ so that the integral is

$$\int_0^{\pi/2} \frac{\cot^5\theta + \cot^3\theta}{e^{\cot\theta}-1} d\theta,$$

    which can then be mapped onto the domain $[-1,1]$.
- Example of Gaussian quadrature: Evaluate the integral

$$I = \int_0^1 \frac{x^4}{\sqrt{2(1+x^2)}} = \frac{\sqrt{18}\ln(1+\sqrt{2})-2}{16}.$$

  - Simpson's rule requires 89 points for 9-significant digit acccuracy.
  - Gaussian quadrature requires only 7 points.
- For multi-dimensional integrals, must place n_i grid points along each i dimension.
  - Number of points in hyper-grid grows exponentially with dimension.
  - Unsuitable for high-dimensional integrals.

2.2 Importance Sampling and Monte Carlo

Suppose integrand $f(\mathbf{x})$ depends on multi-dimensional point $\mathbf{x}$ and that integral over hyper-volume

$$I = \int_V d\mathbf{x}\, f(\mathbf{x})$$

is non-zero only in specific regions of the domain.

- We should place higher density of points in region where integrand is large.
- Define a weight function $w(\mathbf{x})$ that tells us which regions are significant.
  - Require property $w(\mathbf{x}) > 0$ for any point $\mathbf{x}$ in volume.
  - Sometimes use normalized weight function so $\int_V d\mathbf{x}\, w(\mathbf{x}) = 1$, though not strictly necessary.
  - Re-express integral as:

    $$I = \int_V d\mathbf{x}\, \frac{f(\mathbf{x})}{w(\mathbf{x})}\, w(\mathbf{x}).$$

- Idea: Draw a set of N points $\{\mathbf{x}_1, \ldots, \mathbf{x}_N\}$ from the weight function $w(\mathbf{x})$ then

  $$\overline{I} = \frac{1}{N}\sum_{i=1}^{N} \frac{f(\mathbf{x}_i)}{w(\mathbf{x}_i)}.$$

- As $N \to \infty$, $\overline{I} \to I$.
- How does this improve the rate of convergence of the calculation of I? We will see that the statistical uncertainty is related to the variance $\sigma_{\overline{I}}^2$ of the estimate of I, namely

  $$\sigma_{\overline{I}}^2 \;=\; \frac{1}{N}\sum_{i}^{N} \langle \Delta I_i \Delta I_i \rangle \qquad \text{where} \qquad \Delta I_i = \frac{f(\mathbf{x}_i)}{w(\mathbf{x}_i)} - \overline{I}.$$

  and we have assumed that the random variables ΔI_i are statistically independent. Here $\langle \cdots \rangle$ represents the average over the true distribution of f/w that is obtained in the limit $N \to \infty$.
  - Vastly different values of ratio $f(\mathbf{x}_i)/w(\mathbf{x}_i)$ lead to large uncertainty.
- The error is minimized by minimizing $\sigma_{\overline{I}}^2$.

- If $\alpha\, w(\mathbf{x}_i) = f(\mathbf{x}_i)$, then $f(\mathbf{x}_i)/w(\mathbf{x}_i) = \alpha$ and

  $$\left\langle \frac{f(\mathbf{x}_i)}{w(\mathbf{x}_i)} \right\rangle = I = \alpha \qquad \left\langle \left(\frac{f(\mathbf{x}_i)}{w(\mathbf{x}_i)} \right)^2 \right\rangle = \alpha^2,$$

  and $\sigma_{\overline{I}}^2 = 0$.
- Note that writing $w(\mathbf{x}_i) = f(\mathbf{x}_i)/\alpha$ requires knowing $\alpha = I$, the problem we are trying to solve.
- Generally desire all $f(\mathbf{x}_i)/w(\mathbf{x}_i)$ to be roughly the same for all sampled points $\mathbf{x}_i$ to mimimize $\sigma_{\overline{I}}^2$.

• Example in 1-dimensional integral $I = \int_a^b dx\, f(x) = \int_a^b dx\, \frac{f(x)}{w(x)}\, w(x)$.

- **Monte-Carlo** sampling: use random sampling of points x with weight $w(x)$ to estimate ratio $f(x)/w(x)$.
- How do we draw sample points with a given weight $w(x)$? Consider simplest case of a uniform distribution on interval (a, b):

  $$w(x) = \begin{cases} \frac{1}{b-a} & \text{if } x \in (a, b). \\ 0 & \text{otherwise.} \end{cases}$$

- Use a *random number generator* that gives a pseudo-random number *rand* in interval $(0, 1)$.

  $$x_i = a + (b - a) \times rand,$$

  then $\{x_i\}$ are distributed uniformly in the interval (a, b).
- We find that the estimator of f is then:

  $$\overline{I} = \frac{1}{N} \sum_{i=1}^{N} \frac{f(x_i)}{w(x_i)} = \frac{b-a}{N} \sum_{i=1}^{N} f(x_i) = \frac{1}{N} \sum_{k=1}^{N} I_k,$$

  where each $I_k = (b - a)\, f(x_k)$ is an independent estimate of the integral.
- Like trapezoidal integration but with randomly sampled points $\{x_i\}$ from (a, b) each with uniform weight.

• How about other choices of weight function $w(x)$?

- It is easy to draw uniform $y_i \in (0, 1)$. Now suppose we map the y_i to x_i via

  $$y(x) = \int_a^x dz\, w(z).$$

- Note that $y(a) = 0$ and $y(b) = 1$ if $w(x)$ is normalized over (a, b).

- How are the x distributed? Since the y are distributed uniformly over $(0,1)$, the probability of finding a value of y in the interval is

  $$dy(x) = w(x)\,dx,$$

  so the x are distributed with weight $w(x)$.
- It then follows that the one-dimensional integral can be written in the transformed variables y as:

  $$I = \int_a^b dx\, w(x)\,\frac{f(x)}{w(x)} = \int_{y(a)}^{y(b)} dy\,\frac{f(x(y))}{w(x(y))} = \int_0^1 dy\,\frac{f(x(y))}{w(x(y))}$$

- Integral easily evaluated by selecting uniform points y and then solving $x(y)$. Must be able to solve for $x(y)$ to be useful.

- Procedure:

  1. Select N points y_i uniformly on $(0,1)$ using $y_i = rand$.
  2. Compute $x_i = x(y_i)$ by inverting $y(x) = \int_a^x dz\, w(z)$.
  3. Compute estimator for integral $\overline{I} = \frac{1}{N}\sum_{i=1}^N f(x_i)/w(x_i)$.

- This procedure is easy to do using simple forms of $w(x)$. Suppose the integrand is strongly peaked around $x = x_0$. One good choice of $w(x)$ might be a Gaussian weight

  $$w(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_0)^2}{2\sigma^2}},$$

  where the variance (width) of the Gaussian is treated as a parameter.

  - If $I = \int_{-\infty}^{\infty} dx\, f(x) = \int_{-\infty}^{\infty} dx\, w(x) f(x)/w(x)$, can draw randomly from the Gaussian weight by:

    $$\begin{aligned} y(x) &= \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{x} d\tilde{x}\, e^{-\frac{(\tilde{x}-x_0)^2}{2\sigma^2}} \\ &= \frac{1}{2} + \frac{1}{\sqrt{2\pi\sigma^2}} \int_0^x d\tilde{x}\, e^{-\frac{(\tilde{x}-x_0)^2}{2\sigma^2}} \\ &= \frac{1}{2} + \frac{1}{\sqrt{\pi}} \int_0^{\frac{x-x_0}{\sqrt{2}\sigma}} dw\, e^{-w^2} = \frac{1}{2}\left(1 + \operatorname{erf}\left(\frac{x-x_0}{\sqrt{2}\sigma}\right)\right). \end{aligned}$$

  - Inverting gives $x_i = x_0 + \sqrt{2}\sigma\,\operatorname{ierf}(2y_i - 1)$, where ierf is the inverse error function with series representation

    $$\operatorname{ierf}(z) = \frac{\sqrt{\pi}}{2}\left(z + \frac{\pi}{12} z^3 + \frac{7\pi^2}{480} z^5 + \ldots\right)$$

- The estimator of the integral is therefore

$$\overline{I} = \frac{1}{N}\sqrt{2\pi\sigma^2}\sum_{i=1}^{N} f(x_i)e^{\frac{(x_i-x_0)^2}{2\sigma^2}}.$$

- This estimator reduces the variance $\sigma^2_{\overline{I}}$ if $w(x_i)$ and $f(x_i)$ resemble one another.

- Another way to draw from a Gaussian:
  - Draw 2 numbers, y_1 and y_2 uniformly on $(0, 1)$. Define $R = \sqrt{-2\ln y_1}$ and $\theta = 2\pi y_2$. Then $x_1 = R\cos\theta$ and $x_2 = R\sin\theta$ are distributed with density

$$w(x_1, x_2) = \frac{1}{2\pi}e^{-x_1^2/2}e^{-x_2^2/2}$$

since

$$dy_1 dy_2 = \begin{vmatrix} \frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} \\ \frac{\partial y_2}{\partial x_1} & \frac{\partial y_2}{\partial x_2} \end{vmatrix} dx_1 dx_2 = w(x_1, x_2)dx_1 dx_2$$

  - Show this!

2.3 Markov Chain Monte Carlo

2.3.1 Ensemble averages

- Generally, we cannot find a simple way of generating the $\{\mathbf{x}_i\}$ according to a known $w(\mathbf{x}_i)$ for high-dimensional systems by transforming from a uniform distribution.
  - Analytical integrals for coordinate transformation may be invertable only for separable coordinates.
  - Many degrees of freedom are coupled so that joint probability is complicated and not the product of single probabilities.
- Typical integrals are ensemble averages of the form:

$$\langle A \rangle = \frac{1}{Z}\int_V d\mathbf{r}^{(N)}e^{-\beta u(\mathbf{r}^{(N)})}A(\mathbf{r}^{(N)}) = \frac{\int_V d\mathbf{r}^{(N)}e^{-\beta u(\mathbf{r}^{(N)})}A(\mathbf{r}^{(N)})}{\int_V d\mathbf{r}^{(N)}e^{-\beta u(\mathbf{r}^{(N)})}}$$

  - Typical potentials are complicated functions of configuration $\mathbf{r}^{(N)}$.
  - A good importance sampling weight would set $w(\mathbf{r}^{(N)}) = e^{-\beta u(\mathbf{r}^{(N)})}$.
- How do we sample configurations from a general, multi-dimensional weight?

- **Goal:** Devise a method to generate a sequence of configurations $\{\mathbf{r}_1^{(N)}, \ldots, \mathbf{r}_n^{(N)}\}$ in which the probability of finding a configuration $\mathbf{r}_i^{(N)}$ in the sequence is given by $w(\mathbf{r}_i^{(N)})d\mathbf{r}_i^{(N)}$.

- We will do so using a stochastic procedure based on a random walk.

2.3.2 Markov Chains

We will represent a general, multi-dimensional configurational coordinate that identifies the state by the vector $\mathbf{X}$. We wish to generate a sequence of configurations $\mathbf{X}_1, \ldots, \mathbf{X}_n$ where each $\mathbf{X}_t$ is chosen with probability density $P_t(\mathbf{X}_t)$. To generate the sequence, we use a *discrete-time, time-homogeneous, Markovian random walk*.

- Consider the configuration $\mathbf{X}_1$ at an initial time labelled as 1 that is treated as a random variable drawn from some known initial density $P_1(\mathbf{X})$.

- We assume the stochastic dynamics of the random variable is determined by a *time-independent* transition function $\mathsf{K}(\mathbf{Y} \to \mathbf{X})$, where the transition function defines the probability density of going from state $\mathbf{Y}$ to state $\mathbf{X}$ in a time step.

- Since K is a probability density, it must satisfy

$$\int d\mathbf{X}\, \mathsf{K}(\mathbf{Y} \to \mathbf{X}) = 1 \qquad\qquad \mathsf{K}(\mathbf{Y} \to \mathbf{X}) \geq 0.$$

- The state $\mathbf{X}_t$ at time t is assumed to be obtained from the state at time $\mathbf{X}_{t-1}$ by a realization of the dynamics, where the probability of all transitions is determined by K.

- At the second step of the random walk, the new state $\mathbf{X}_2$ is chosen from $P_2(\mathbf{X}|\mathbf{X}_1) = \mathsf{K}(\mathbf{X}_1 \to \mathbf{X})$. At the third step, the state $\mathbf{X}_3$ is chosen from $P_3(\mathbf{X}|\mathbf{X}_2) = \mathsf{K}(\mathbf{X}_2 \to \mathbf{X})$, and so on, generating the random walk sequence $\{\mathbf{X}_1, \ldots, \mathbf{X}_n\}$.

- If infinitely many realizations of the dynamics is carried out, we find that the distribution of $\mathbf{X}_i$ for each of the i steps are

$$\begin{array}{ll}
P_1(\mathbf{X}) & \text{for } \mathbf{X}_1 \\
P_2(\mathbf{X}) = \int d\mathbf{Y}\, \mathsf{K}(\mathbf{Y} \to \mathbf{X}) P_1(\mathbf{Y}) & \text{for } \mathbf{X}_2 \\
P_3(\mathbf{X}) = \int d\mathbf{Y}\, \mathsf{K}(\mathbf{Y} \to \mathbf{X}) P_2(\mathbf{Y}) & \text{for } \mathbf{X}_3 \\
\quad\vdots & \quad\vdots \\
P_t(\mathbf{X}) = \int d\mathbf{Y}\, \mathsf{K}(\mathbf{Y} \to \mathbf{X}) P_{t-1}(\mathbf{Y}) & \text{for } \mathbf{X}_t.
\end{array}$$

- The transition function K is *ergodic* if any state $\mathbf{X}$ can be reached from any state $\mathbf{Y}$ in a finite number of steps in a non-periodic fashion.

- If K is ergodic, then the *Perron-Frobenius Theorem* guarantees the existence of a unique *stationary distribution* $P(\mathbf{X})$ that satisfies

$$P(\mathbf{X}) = \int d\mathbf{Y}\, \mathsf{K}(\mathbf{Y} \to \mathbf{X}) P(\mathbf{Y}) \qquad \text{and} \qquad \lim_{t\to\infty} P_t(\mathbf{X}) = P(\mathbf{X}).$$

- Implications

  1. From any initial distribution of states $P_1(\mathbf{X})$, an ergodic K guarantees that states $\mathbf{X}_t$ will be distributed according to the unique stationary distribution $P(\mathbf{X})$ for large t (many steps of random walk).
  2. $P(\mathbf{X})$ is like an eigenvector of "matrix" K with eigenvalue $\lambda = 1$.
  3. Goal is then to design an ergodic transition function K so that the stationary or *limit distribution* is the Bolztmann weight $w(\mathbf{X})$.

Finite State Space

To make the Markov chain more concrete, consider a finite state space in which only m different configurations of the system exist. The phase space then can be enumerated as $\{\mathbf{X}_1, \ldots \mathbf{X}_m\}$.

- The transition function is then an $m \times m$ matrix K, where the element $\mathsf{K}_{ij} \geq 0$ is the transition probability of going from state $\mathbf{X}_j$ to state $\mathbf{X}_i$.

- Since the matrix elements represent transition probabilities, for any fixed value of j,

$$\sum_{i=1}^{m} \mathsf{K}_{ij} = 1.$$

- The distribution $P_t(\mathbf{X})$ corresponds to a column vector $\mathbf{P}_t = \mathrm{col}[a_t^{(1)}, \ldots a_t^{(m)}]$, where $a_t^{(i)}$ is the probability of state $\mathbf{X}_i$ at time t.

- The distribution evolves under the random walk as $\mathbf{P}_t = \mathsf{K} \cdot \mathbf{P}_{t-1}$.

- The matrix K is *regular* if there is an integer t_0 such that K^{t_0} has all positive (non-zero) entries. Then K^t for $t \geq t_0$ has all positive entries.

- Suppose the matrix K is a regular transition matrix. The following properties hold:

Statements following from the Frobenius-Perron theorem

1. The multiplicity of the eigenvalue $\lambda = 1$ is one (i.e. the eigenvalue is *simple*.)

   Proof. Since K is regular, there exists a transition matrix $\mathcal{K} = \mathsf{K}^{t_0}$ with all positive elements. Note that if $\mathsf{K}\mathbf{e} = \lambda\mathbf{e}$, then $\mathcal{K}\mathbf{e} = \lambda^{t_0}\mathbf{e}$, so that all eigenvectors of K with eigenvalue λ are also eigenvectors of $\mathcal{K}$ with eigenvalue λ^{t_0}. Let $\mathbf{e}_1 = \mathrm{col}[1, 1, \ldots, 1]/m$. Since $\sum_i \mathsf{K}_{ij} = 1$ for any j, we have $\sum_i (\mathsf{K} \cdot \mathsf{K})_{ij} = 1$, and hence $\sum_i \mathcal{K}_{ij} = 1$ for any j. The transpose of $\mathcal{K}$ therefore satisfies $\sum_i \mathcal{K}^T_{ji} = 1$ for all j. The vector $\mathbf{e}_1$ is the right eigenvector with eigenvalue $\lambda = 1$ since $(\mathcal{K}^T\mathbf{e}_1)_j = 1/m \sum_i \mathcal{K}^T_{ji}$, and hence $\mathcal{K}^T\mathbf{e}_1 = e_1$. Now both $\mathcal{K}$ and $\mathcal{K}^T$ are $m \times m$ square matrices and have the same eigenvalues (since the characteristic equation is invariant to the transpose operation), so $\lambda = 1$ is an eigenvalue of both $\mathcal{K}$ and $\mathcal{K}^T$. Now suppose $\mathcal{K}^T\mathbf{v} = \mathbf{v}$ and all components v_j of $\mathbf{v}$ are not equal. Let k be the index of the largest component, v_k, which we can take to be positive without loss of generality. Thus, $v_k \geq |v_j|$ for all j and $v_k > |v_l|$ for some l. It then follows that $v_k = \sum_j \mathcal{K}^T_{kj} v_j < \sum_j \mathcal{K}^T_{kj} v_k$, since all components of $\mathcal{K}^T$ are non-zero and positive. Thus we conclude that $v_k < v_k$, a contradiction. Hence all v_k must be the same, corresponding to eigenvector $\mathbf{e}_1$. Hence $\mathbf{e}_1$ is a unique eigenvector of $\mathcal{K}^T$ and $\lambda = 1$ is a simple root of the characterstic equation. Hence $\mathcal{K}$ has a single eigenvector with eigenvalue $\lambda = 1$. $\square$

2. If the eigenvalue $\lambda \neq 1$ is real, then $|\lambda| < 1$.

   Proof. Suppose $\mathcal{K}^T\mathbf{v} = \lambda^{t_0}\mathbf{v}$, with $\lambda^{t_0} \neq 1$. It then follows that there is an index k of vector $\mathbf{v}$ such that $v_k \geq |v_j|$ for all j and $v_k > |v_l|$ for some l. Now $\lambda^{t_0} v_k = \sum_j \mathcal{K}^T_{kj} v_j < \sum_j \mathcal{K}^T_{kj} v_k = v_k$, or $\lambda^{t_0} v_k < v_k$. Thus $\lambda^{t_0} < 1$, and hence $\lambda < 1$, since λ is real. Similarly, following the same lines of argument and using the fact that $-v_k < v_l$ for some l, we can establish that $\lambda > -1$. Hence $|\lambda| < 1$. A similar sort of argument can be used if λ is complex. $\square$

3. Under the dynamics of the random walk $\mathbf{P}_t = \mathsf{K}\mathbf{P}_{t-1}$, $\lim_{t\to\infty} \mathbf{P}_t = \mathbf{P}_1$, where $\mathbf{P}_1$ is the right eigenvector of K with simple eigenvalue $\lambda = 1$.

   Proof. If the matrix K is diagonalizable, the eigenvectors of K form a complete basis (since it can be put in *Jordan canonical form*). Thus, any initial distribution $\mathbf{P}_s$ can be expanded in terms of the complete, linearly independent basis $\{\mathbf{P}_1, \mathbf{P}_2, \ldots \mathbf{P}_m\}$ of eigenvectors as $\mathbf{P}_s = b_1\mathbf{P}_1 + \cdots + \mathbf{b}_m\mathbf{P}_m$, where $\mathsf{K}\mathbf{P}_i = \lambda_i\mathbf{P}_i$ with $\lambda_1 = 1$ and $|\lambda_i| < 1$. Now $\mathbf{P}_t = \mathbf{b}_1\mathbf{P}_1 + b_2\lambda_2^t\mathbf{P}_2 + \cdots + \mathbf{b}_m\lambda_m^t\mathbf{P}_m$, but $\lim_{t\to\infty} \lambda_i^t = 0$ exponentially fast for $i \geq 2$. Thus, $\lim_{t\to\infty} \mathsf{K}^t\mathbf{P}_s = b_1\mathbf{P}_1$. Note that if $\sum_i (\mathbf{P}_s)_i = 1$, then $\sum_i (\mathbf{P}_t)_i = 1$ as K maintains the norm. This implies that $b_1 = (\sum_i (\mathbf{P}_1)_i)^{-1}$. It turns out that the condition of *detailed balance*, which we will define to mean $\mathsf{K}_{ij}(\mathbf{P}_1)_j = \mathsf{K}_{ji}(\mathbf{P}_1)_i$ allows one to define a symmetric transition matrix K', which is necessarily diagonalizable.

More generally, any square matrix is similar to a matrix of Jordan form, with isolated blocks of dimension of the multiplicity of the eigenvalue. Thus the matrix K can be written as $\mathsf{K} = \mathsf{P}\tilde{\mathsf{K}}\mathsf{P}^{-1}$ where the columns of P are the (generalized) eigenvectors of K and $\tilde{\mathsf{K}}$ is of form

$$\tilde{\mathsf{K}} = \begin{pmatrix} 1 & & & \\ & J_1 & & \\ & & J_2 & \\ & & & J_3 \end{pmatrix} \qquad J_i = \begin{pmatrix} \lambda_i & 1 & 0 & 0 \\ 0 & \lambda_i & 1 & 0 \\ 0 & 0 & \lambda_i & 1 \\ 0 & 0 & 0 & \lambda_i \end{pmatrix}$$

for an eigenvalue λ_i of multiplicity 4. It is easily shown that the nth power of a block J_i has elements bounded by $\binom{n}{k}\lambda_i^{n-k}$ for a block of size k, which goes to zero exponentially has n goes to infinity. Hence, the matrix $\tilde{\mathsf{K}}$ goes to

$$\tilde{\mathsf{K}} = \begin{pmatrix} 1 & & & \\ & 0 & & \\ & & 0 & \\ & & & 0 \end{pmatrix}$$

Thus it follows that as n goes to infinity

$$(\mathsf{K}^n)_{\alpha\beta} = \left(\mathsf{P}\tilde{\mathsf{K}}^n\mathsf{P}^{-1}\right)_{\alpha\beta} \to \mathsf{P}_{\alpha 1}\mathsf{P}^{-1}_{1\beta} = (\mathbf{P}_1)_\alpha,$$

where $\mathbf{P}_1$ is the stationary distribution, since the matrix $\mathsf{P}^{-1}_{1\beta}$ is the β component of the left eigenvector of K with eigenvalue of 1, which is the constant vector. □

- Consider the explicit case $m = 3$, with K_{ij} given by

$$\mathsf{K} = \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{3} \\ 0 & \frac{1}{2} & \frac{1}{3} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{3} \end{pmatrix}.$$

  - $(\mathsf{K}\cdot\mathsf{K})_{ij} > 0$ for all i and j, so K is regular. Note also that $\sum_i \mathsf{K}_{ij} = 1$ for all j.
  - The eigenvalues and eigenvectors of K are

$$\begin{aligned} \lambda &= 1 \implies \mathbf{P}_1 = (2/7, 2/7, 3/7) \\ \lambda &= -\frac{1}{6} \implies \mathbf{P}_2 = (-3/14, -3/14, 6/14) \\ \lambda &= \frac{1}{2} \implies \mathbf{P}_3 = (-3/7, 3/7, 0). \end{aligned}$$

– If initially $\mathbf{P}_s = (1,0,0)$, then $\mathbf{P}_2 = (1/2, 0, 1/2)$ and

$$\mathbf{P}_{10} = (0.28669\cdots, 0.28474\cdots, 0.42857\cdots),$$

which differs from $\mathbf{P}_1$ by 0.1%.

2.3.3 Construction of the transition matrix $\mathsf{K}(y \to x)$

We wish to devise a procedure so that the limiting (stationary) distribution of the random walk is the Boltzmann distribution $P_{eq}(x)$.

- Break up the transition matrix into two parts, generation of trial states $\mathsf{T}(y \to x)$ and acceptance probability of trial state $\mathsf{A}(y \to x)$

$$\mathsf{K}(y \to x) = \mathsf{T}(y \to x)\mathsf{A}(y \to x).$$

  – Will consider definition of acceptance probability given a specified procedure for generating trial states with condition probability $\mathsf{T}(y \to x)$.

- Write dynamics in term of probabilities at time t

$$\begin{aligned}
\text{Probability of starting in } y \text{ and ending in } x &= \int dy\, P_t(y)\, \mathsf{K}(y \to x) \\
\text{Probability of starting in } x \text{ and remaining in } x &= P_t(x)\left(1 - \int dy\, \mathsf{K}(x \to y)\right)
\end{aligned}$$

so

$$\begin{aligned}
P_{t+1}(x) &= \int dy\, P_t(y)\, \mathsf{K}(y \to x) + P_t(x)\left(1 - \int dy\, \mathsf{K}(x \to y)\right) \\
&= P_t(x) + \int dy \left(P_t(y)\mathsf{K}(y \to x) - P_t(x)\mathsf{K}(x \to y)\right).
\end{aligned}$$

- Thus, to get $P_{t+1}(x) = P_t(x)$, we want

$$\int dy \left(P_t(y)\mathsf{K}(y \to x) - P_t(x)\mathsf{K}(x \to y)\right) = 0.$$

- This can be accomplished by requiring *microscopic reversibility* or *detailed balance*:

$$\begin{aligned}
P_t(y)\mathsf{K}(y \to x) &= P_t(x)\mathsf{K}(x \to y) \\
P_t(y)\mathsf{T}(y \to x)\mathsf{A}(y \to x) &= P_t(x)\mathsf{T}(x \to y)\mathsf{A}(x \to y).
\end{aligned}$$

  - We desire $P_t(x) = P_{t+1}(x) = P_{eq}(x)$. This places restriction on the acceptance probabilities

$$\frac{\mathsf{A}(y \to x)}{\mathsf{A}(x \to y)} = \frac{P_{eq}(x)\mathsf{T}(x \to y)}{P_{eq}(y)\mathsf{T}(y \to x)}.$$

  - Note that $P_{eq}(x)\mathsf{K}(x \to y)$ is the probability of observing the sequence $\{x, y\}$ in the random walk. This must equal the probability of the sequence $\{y, x\}$ in the walk.

- Metropolis Solution: Note that if $P_{eq}(x)\mathsf{T}(x \to y) > 0$ and $P_{eq}(y)\mathsf{T}(y \to x) > 0$, then we can define

$$\begin{aligned}
\mathsf{A}(y \to x) &= \min\left(1, \frac{P_{eq}(x)\mathsf{T}(x \to y)}{P_{eq}(y)\mathsf{T}(y \to x)}\right) \\
\mathsf{A}(x \to y) &= \min\left(1, \frac{P_{eq}(y)\mathsf{T}(y \to x)}{P_{eq}(x)\mathsf{T}(x \to y)}\right).
\end{aligned}$$

  - This definition satisfies details balance.

    Proof. Verifying explicitly, we see that

$$\begin{aligned}
P_{eq}(y)\mathsf{T}(y \to x)\mathsf{A}(y \to x) &= \min\left(P_{eq}(y)\mathsf{T}(y \to x), P_{eq}(x)\mathsf{T}(x \to y)\right) \\
P_{eq}(x)\mathsf{T}(x \to y)\mathsf{A}(x \to y) &= \min\left(P_{eq}(x)\mathsf{T}(x \to y), P_{eq}(y)\mathsf{T}(y \to x)\right) \\
&= P_{eq}(y)\mathsf{T}(y \to x)\mathsf{A}(y \to x)
\end{aligned}$$

    as required. □

  - Procedure guaranteed to generate states with probability proportional to Boltzmann distribution if proposal probability $\mathsf{T}(y \to x)$ generates an ergodic transition probability K.

Simple example

- Suppose we want to evaluate the equilibrium average $\langle A \rangle$ at inverse temperature β of some dynamical variable $A(x)$ for a 1-dimensional harmonic oscillator system with potential energy $U(x) = kx^2/2$.

$$\langle A(x) \rangle = \int_{-\infty}^{\infty} dx\, P_{eq}(x) A(x) \qquad P_{eq}(x) = \frac{1}{Z} e^{-\beta k x^2/2}$$

- Monte-Carlo procedure

1. Suppose the current state of the system is x_0. We define the proposal probability of a configuration y to be

$$\mathsf{T}(x_0 \to y) \quad = \quad \begin{cases} \frac{1}{2\Delta x} & \text{if } y \in [x_0 - \Delta x, x_0 + \Delta x] \\ 0 & \text{otherwise} \end{cases}$$

   - Δx is fixed to some value representing the maximum displacement of the trial coordinate.
   - y chosen uniformly around current value of x_0.
   - Note that if y is selected, then $\mathsf{T}(x_0 \to y) = 1/(2\Delta x) = \mathsf{T}(y \to x_0)$ since x_0 and y are within a distance Δx of each other.

2. Accept trial y with probability

$$\mathsf{A}(x_0 \to y) = \min\left(1, \frac{\mathsf{T}(y \to x_0)P_{eq}(y)}{\mathsf{T}(x_0 \to y)P_{eq}(x_0)}\right) = \min\left(1, e^{-\beta\Delta U}\right),$$

   where $\Delta U = U(y) - U(x_0)$.

   - Note that if $\Delta U \leq 0$ so the proposal has lower potential energy than the current state, $\mathsf{A}(x_0 \to y) = 1$ and the trial y is always accepted as the next state $x_1 = y$.
   - If $\Delta U > 0$, then $\mathsf{A}(x_0 \to y) = e^{-\beta\Delta U} = q$. We must accept the trial y with probability $0 < q < 1$. This can be accomplished by picking a random number r uniformly on $(0, 1)$ and then:
     (a) If $r \leq q$, then accept configuration $x_1 = y$
     (b) If $r > q$, then reject configuration and set $x_1 = x_0$ (keep state as is).

3. Repeat steps 1 and 2, and record states $\{x_i\}$.

- Markov chain of states (the sequence) $\{x_i\}$ generated, with each x_i appearing in the sequence with probability $P_{eq}(x_i)$ (after some number of equilibration steps).

- After collecting N total configurations, the equilibrium average $\langle A\rangle$ can be estimated from

$$\langle A\rangle = \frac{1}{N}\sum_{i=1}^{N} A(x_i)$$

  since the importance function $w(x) = P_{eq}(x)$.

- Rejected states **are** important to generate states with correct weight.

- Typically, should neglect the first N_s points of Markov chain since it takes some iterations of procedure to generate states with stationary distribution of $\mathsf{K}(y \to x)$.

  - Called equilibration or "burn in" time.
  - Often have correlation among adjacent states. Can record states every N_{corr} Monte-Carlo steps (iterations).

- Why must rejected states be counted? Recall that $\mathsf{K}(x \to y)$ must be normalized to be a probability (or probability density).

$$\int dy\, \mathsf{K}(x \to y) \;\; = \;\; 1 = \int dy\; [\delta(x-y) + (1 - \delta(x-y))]\, \mathsf{K}(x \to y)$$

hence, the probability to remain in the current state is

$$\mathsf{K}(x \to x) = 1 - \int dy\, (1 - \delta(x-y))\, \mathsf{K}(x \to y)$$

  - $\mathsf{K}(x \to x)$ is non-zero to insure normalization, so we **must** see the sequence $\{\ldots, x, x, \ldots\}$ in the Markov chain.

2.4 Statistical Uncertainties

We would like some measure of the reliability of averages computed from a finite set of sampled data. Consider the average $\overline{x}$ of a quantity x constructed from a finite set of N measurements $\{x_1, \ldots, x_N\}$, where the x_i are random variables drawn from a density $\rho(x)$.

$$\overline{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$$

- Suppose the random variables x_i are drawn independently, so that the joint probability satisfies

$$\rho(x_1, \ldots x_N) = \rho(x_1)\rho(x_2)\cdots\rho(x_N).$$

- Suppose that the intrinsic mean $\langle x \rangle$ of the random variable is $\langle x \rangle = \int dx\, x\rho(x)$ and that the intrinsic variance is σ^2, where

$$\sigma^2 = \int dx\, \big(x - \langle x \rangle\big)^2 \rho(x).$$

- A measure of reliability is the standard deviation of $\overline{x}$, also known as the *standard error* $\sigma_E = \sqrt{\sigma_E^2}$, where σ_E^2 is the variance of the finite average $\overline{x}$ around $\langle x \rangle$ in the finite set $\{x_1, \ldots, x_N\}$

$$\sigma_E^2 = \langle \big(\overline{x} - \langle x \rangle\big)^2 \rangle.$$

- We expect
  1. Variance (error) decreases with increasing N
  2. Error depends on the intrinsic variance σ^2 of the density ρ. Larger variance should mean slower convergence of $\overline{x}$ to $\langle x\rangle$.

Suppose all the intrinsic moments $\langle x^n\rangle$ of $\rho(x)$ exist. If we define the dimensionless variable

$$z = \frac{\overline{x} - \langle x\rangle}{\sigma_E},$$

and note that the probability density of z can be written as

$$\begin{aligned} P(\tilde{z}) &= \langle \delta(z-\tilde{z})\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\,\langle e^{-it(z-\tilde{z})}\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{it\tilde{z}}\langle e^{-itz}\rangle \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{it\tilde{z}}\chi_N(t), \end{aligned} \tag{2.1}$$

where $\chi_N(t)$ is the *characteristic function* of $P(z)$. Using the fact that $\sigma_E = \sigma/\sqrt{N}$, as will be shown shortly, z can be expressed as

$$z = \frac{\sqrt{N}}{N}\sum_{i=1}^{N}\frac{x_i - \langle x\rangle}{\sigma} = \frac{1}{\sqrt{N}}\sum_{i=1}^{N}\left(\frac{x_i-\langle x\rangle}{\sigma}\right),$$

and hence

$$\chi_N(t) = \left\langle e^{\dfrac{-it}{\sqrt{N}}\sum_{i=1}^{N}\left(\dfrac{x_i-\langle x\rangle}{\sigma}\right)}\right\rangle = \left(\left\langle e^{\frac{-it}{\sqrt{N}}\left(\frac{x-\langle x\rangle}{\sigma}\right)}\right\rangle\right)^N = \chi(t/\sqrt{N})^N,$$

where

$$\chi(u) = \left\langle e^{-iu(x-\langle x\rangle)/\sigma}\right\rangle,$$

which, for small arguments u can be expanded as $\chi(u) = 1 - u^2/2 + iu^3\kappa_3/(6\sigma^3) + \ldots$, where κ_3 is the *third cumulant* of the density $\rho(x)$. Using this expansion, we find $\ln\chi_N(t) = -t^2/2 + O(N^{-1/2})$, and hence $\chi_N(t) = e^{-t^2/2}$ for large N. Inserting this form in Eq. (2.1) gives

$$P(\tilde{z}) = \frac{1}{\sqrt{2\pi}}e^{-\tilde{z}^2/2}$$

and hence we find the *central limit theorem* result that the averages $\overline{x}$ are distributed around the intrinsic mean according to the normal distribution

$$N(\overline{x};\langle x\rangle,\sigma_E^2) = \frac{1}{\sqrt{2\pi}\sigma_E}e^{-\frac{(\overline{x}-\langle x\rangle)^2}{2\sigma_E^2}},$$

provided the number of samples N is large and all intrinsic moments (and hence cumulants) of $\rho(x)$ are finite.

- If the central limit theorem holds so that the finite averages are *normally distributed* as above, then the standard error can be used to define confidence intervals since the probability p that the deviations in the average, $\overline{x} - \langle x \rangle$, lie within a factor of c times the standard error is given by

$$\int_{-c\sigma_E}^{c\sigma_E} d(\overline{x} - \langle x \rangle) N(\overline{x}; \langle x \rangle, \sigma_{\overline{x}}^2) = p.$$

- If $p = 0.95$, defining the 95% confidence intervals, then we find that $c = 1.96$, and hence the probability that the intrinsic mean $\langle x \rangle$ lies in the interval $(\overline{x} - 1.96\sigma_E, \overline{x} + 1.96\sigma_E)$ is $P(\overline{x} - 1.96\sigma_E \leq \langle x \rangle \leq \overline{x} + 1.96\sigma_E) = 0.95$.

- If the data are not normally distributed, then higher cumulants of the probability density may be needed (skewness, kurtosis, ...). The confidence intervals are defined in terms of integrals of the probability density.

- How do we calculate σ_E or σ_E^2? We defined the variance as

$$\sigma_E^2 = \langle \left(\overline{x} - \langle x \rangle\right)^2 \rangle \qquad \text{where} \qquad \overline{x} = \frac{1}{N} \sum_i x_i$$

- Expanding the square, we get $\sigma_E^2 = \langle \overline{x}^2 \rangle - \langle x \rangle^2$ but

$$\begin{aligned} \langle \overline{x}^2 \rangle &= \frac{1}{N^2} \sum_{i,j} \langle x_i x_j \rangle = \frac{1}{N^2} \left(\sum_i \langle x_i^2 \rangle + \sum_i \sum_{j \neq i} \langle x_i \rangle \langle x_j \rangle \right) \\ &= \frac{1}{N^2} \left(N(\sigma^2 + \langle x \rangle^2) + N(N-1)\langle x \rangle^2 \right) = \frac{\sigma^2}{N} + \langle x \rangle^2, \end{aligned}$$

  hence $\sigma_E^2 = \sigma^2/N$.

- However we don't really know what σ^2 is, so we must estimate this quantity. One way to do this is to define the estimator of the standard deviation $\hat{\sigma}^2$:

$$\hat{\sigma}^2 = \frac{1}{N} \sum_i \left(x_i - \overline{x}\right)^2.$$

- The average of this estimator is

$$\langle \hat{\sigma}^2 \rangle = \frac{1}{N} \sum_i \langle (x_i - \overline{x})^2 \rangle = \frac{1}{N} \sum_i \langle x_i^2 - 2x_i\overline{x} + \overline{x}^2 \rangle.$$

  but using the facts that

$$\langle x_i \overline{x} \rangle = \frac{\langle x^2 \rangle}{N} + \frac{N-1}{N} \langle x \rangle^2 \qquad \langle \overline{x}^2 \rangle = \frac{\sigma^2}{N} + \langle x \rangle^2,$$

  we get $\langle \hat{\sigma}_E^2 \rangle = (N-1)\sigma^2/N$ and hence $\sigma^2 = N\langle \hat{\sigma}^2 \rangle/(N-1)$.

- The standard error can therefore be estimated by

$$\sigma_E = \frac{\sqrt{\hat{\sigma}^2}}{\sqrt{N-1}}$$

- Note that σ_E decreases as $1/\sqrt{N-1}$
  - Narrowing confidence intervals by a factor of 2 requires roughly 4 times more data.
  - If the x_i are **not** indepenent, then $N \sim N_{eff}$, where N_{eff} is the effective number of independent configurations. If τ_c is the correlation length (number of Monte-Carlo steps over which correlation $\langle x_i x_j \rangle$ differs from $\langle x \rangle^2$), then $N_{eff} = N/\tau_c$.

- Another way to estimate the intrinsic variance σ^2 is to use the Jackknife Method: see B. Efron, *The annals of statistics* **7**, 1 (1979).
  - Jackknife procedure is to form N averages from the set $\{x_1, \ldots, x_N\}$ by omitting one data point. For example, the jth average is defined to be

$$\overline{x}^{(j)} = \frac{1}{N-1} \sum_{i \neq j}^{N} x_i$$

    The result is to form a set of averages $\{\overline{x}^{(1)}, \overline{x}^{(2)}, \ldots \overline{x}^{(N)}\}$.
  - The average $\overline{x}$ over this Jackknifed set is the same as before since

$$\overline{x} = \frac{1}{N} \sum_{j=1}^{N} \overline{x}^{(j)} = \frac{1}{N(N-1)} \sum_{j=1}^{N} \sum_{i \neq j} x_i = \frac{1}{N} \sum_{i=1}^{N} x_i.$$

- We define an estimator of the variance Σ^2 of the Jackknifed set to be

$$\Sigma^2 = \frac{1}{N}\sum_{j=1}^{N}\left(\overline{x}^{(j)} - \overline{x}\right)^2.$$

which converges to $\langle\Sigma^2\rangle$ as N gets large.

- Inserting the definitions of $\overline{x}^{(j)}$ and $\overline{x}$ and using the independence of the x_i, we see that the estimator is related to the intrinsic variance by

$$\langle\Sigma^2\rangle = \left(\frac{1}{N-1} - \frac{1}{N}\right)\sigma^2 = \frac{\sigma^2}{N(N-1)} \qquad \sigma^2 = N(N-1)\langle\Sigma^2\rangle.$$

- The standard error can therefore be estimated using the Jackknifed set as

$$\Sigma_E = \sqrt{\frac{N-1}{N}\sum_{j=1}^{N}\left(\overline{x}^{(j)} - \overline{x}\right)^2}.$$

2.4.1 Error estimates of multivariable functions of random variables

Sometimes after data collection we are interested in evaluating the statistical uncertainty of functions of averages we have calculated via numerical methods.

- For example, to evaluate the transition-state theory estimate of a rate constant, one can perform Monte-Carlo simulations to generate a set of independent configurations $\mathbf{x}_i$ distributed by their Boltzmann weight $P(\mathbf{x}_i)e^{-\beta U(\mathbf{x}_i)}/Z$.

  - The estimated rate constant is the ratio of two expectations

$$\begin{aligned} k_{TST} &= \sqrt{\frac{k_B T}{2\imath m}}\frac{\int d\mathbf{x}\, e^{-\beta U(\mathbf{x})}w(\mathbf{x})\delta(q(\mathbf{x}))}{\int d\mathbf{x}\, e^{-\beta U(\mathbf{x})}H(q(\mathbf{x}))} \\ &= \sqrt{\frac{k_B T}{2\imath m}}\frac{\left\langle \hat{J}_1\right\rangle}{\left\langle \hat{J}_2\right\rangle}, \end{aligned}$$

where $q(\mathbf{x})$ is the "reaction coordinate", $\left\langle \hat{J}_1\right\rangle = \sum_i w(\mathbf{x}_i)\Delta(q(\mathbf{x}_i))$ is the average of a weight function $w(\mathbf{x})$ over a restricted set of points of the set where the configuration is near the transition state dictated by the condition $\Delta(q(\mathbf{x}))$ and $\left\langle \hat{J}_2\right\rangle = \sum_i H(q(\mathbf{x}_i))$ is the average over all points where the reaction coordinate is smaller than the transition state value.

– From the simulation, we can compute the empirical averages of $\hat{J}_1$, $\hat{J}_2$ and the covariance matrix $\sigma_{ij}^2 = \left\langle \left(\hat{J}_i - \langle \hat{J}_i \rangle\right) \left(\hat{J}_j - \langle \hat{J}_j \rangle\right) \right\rangle$.

– We must compute the variance of the estimates of k_{TST} to estimate the statistical uncertainties of this quantity.

- Consider a general function $f(\mathbf{X})$ of random variables $\mathbf{X} = (\hat{J}_1, \hat{J}_2)$ with mean $\boldsymbol{\theta} = \left(\left\langle \hat{J}_1 \right\rangle, \left\langle \hat{J}_2 \right\rangle\right)$ and covariance matrix $\boldsymbol{\sigma}^2$. We require that $\sigma_{ij}^2 \ll \left\langle \hat{J}_i \right\rangle, \left\langle \hat{J}_j \right\rangle$, as is usually the case.

- To estimate the statistical uncertainty in our estimates of the function $f(\mathbf{X})$ in terms of the estimates of $\boldsymbol{\theta}$, we must compute the variance of $f(\mathbf{X})$.

  To approximate this variance, we first Taylor-expand the random function $f(\mathbf{X})$ around the mean $\boldsymbol{\theta}$,

$$f(\mathbf{X}) \quad = \quad f(\boldsymbol{\theta}) + (\mathbf{X} - \boldsymbol{\theta}) \cdot \frac{\partial f(\boldsymbol{\theta})}{\partial \boldsymbol{\theta}} + \frac{1}{2} (\mathbf{X} - \boldsymbol{\theta}) \cdot \frac{\partial^2 f(\boldsymbol{\theta})}{\partial \boldsymbol{\theta} \partial \boldsymbol{\theta}} \cdot (\mathbf{X} - \boldsymbol{\theta}) + \ldots$$

  The expectation value of this random function is

$$E[f(\mathbf{X})] \quad = \quad \langle f(\mathbf{X}) \rangle = f(\boldsymbol{\theta}) + \frac{1}{2} \frac{\partial^2 f(\boldsymbol{\theta})}{\partial \boldsymbol{\theta} \partial \boldsymbol{\theta}} : \boldsymbol{\sigma}^2 + \ldots$$

  The expectation of $g(\mathbf{X}) = f(\mathbf{X})^2$ is therefore

$$E[g(\mathbf{X})] \quad = \quad \langle g(\mathbf{X}) \rangle = \left\langle f(\mathbf{X})^2 \right\rangle = g(\boldsymbol{\theta}) + \frac{1}{2} \frac{\partial^2 g(\boldsymbol{\theta})}{\partial \boldsymbol{\theta} \partial \boldsymbol{\theta}} : \boldsymbol{\sigma}^2 + \ldots$$

  and hence since

$$\frac{\partial^2 g(\boldsymbol{\theta})}{\partial \boldsymbol{\theta} \partial \boldsymbol{\theta}} = 2 \frac{\partial f(\mathbf{X})}{\partial \boldsymbol{\theta}} \frac{\partial f(\mathbf{X})}{\partial \boldsymbol{\theta}} + 2 f(\boldsymbol{\theta}) \frac{\partial^2 f(\boldsymbol{\theta})}{\partial \boldsymbol{\theta} \partial \boldsymbol{\theta}},$$

  we find the variance of $f(\mathbf{X})$ is approximately

$$\mathrm{Var}[f(\mathbf{X})] = \sigma_f^2 = \left\langle f(\mathbf{X})^2 \right\rangle - \langle f(\mathbf{X}) \rangle^2 = \frac{\partial f(\boldsymbol{\theta})}{\partial \boldsymbol{\theta}} \frac{\partial f(\boldsymbol{\theta})}{\partial \boldsymbol{\theta}} : \boldsymbol{\sigma}^2.$$

- This variance can be used to compute the standard error and the confidence interval of the average of f.

- For the special case of $f(\mathbf{X}) = \hat{J}_1 / \hat{J}_2$, we find that

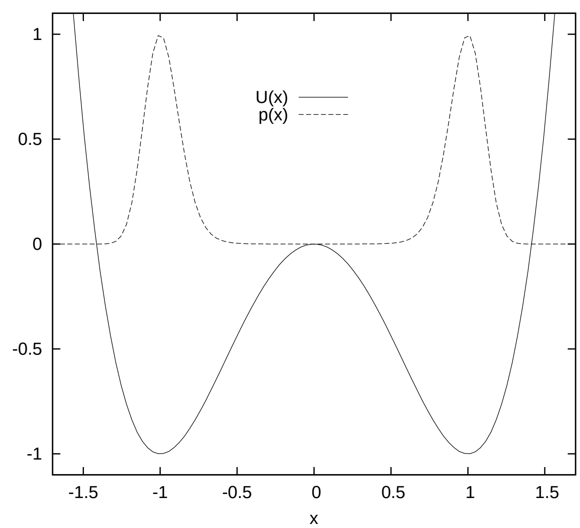
$$\sigma_f^2 = \frac{\left\langle \hat{J}_1 \right\rangle^2}{\left\langle \hat{J}_2 \right\rangle^2} \left[\frac{\sigma_{11}^2}{\left\langle \hat{J}_1 \right\rangle^2} - 2 \frac{\sigma_{12}^2}{\left\langle \hat{J}_1 \right\rangle \left\langle \hat{J}_2 \right\rangle} + \frac{\sigma_{22}^2}{\left\langle \hat{J}_2 \right\rangle^2} \right].$$

3

Applications of the Monte Carlo method

3.1 Quasi-ergodic sampling

- Detailed balance condition and ergodic transition matrix imply that random walk Monte-Carlo method correctly generates distribution of configurations.
- Says nothing about the *rate* of convergence, which depends on implementation (eigenvalue spectrum of transition matrix).
- Consider a 1-dimensional system with a quartic potential $U(x) = x^2(x^2 - 2)$.
- For $\beta = 10$, probability density $P(x) \sim e^{-\beta U(x)}$ is bimodal with small relative probability to be found near $x = 0$.



  - Note that $P(1)/P(0) = e^{10}$.

- Consider the simple Metropolis Monte-Carlo scheme discussed previously with:

$$\mathsf{T}(x \to y) = \begin{cases} \frac{1}{2\Delta x} & \text{if } y \in [x - \Delta x, x + \Delta x] \\ 0 & \text{otherwise.} \end{cases}$$

  - If maximum displacement Δx is small ($\Delta x \ll 1$), then if x is in the region near $x = 1$, the probability of proposing y near -1 is zero, and the proposal is very unlikely to propose a configuration y which is in a different mode from x.
  - Random walk dynamics consists of long periods of x being localized in one of the modes, with only rare transitions between the modes (roughly every e^{10} steps). Overall, an equal amount of time must be spent in both of the modes.
  - Rare transitions between modes leads to very slow convergence of distribution of states to $P(x)$.
  - Easy to fix here since we know where the modes lie: increasing Δx will allow proposals between modes.

3.2 Umbrella sampling

- Origin of quasi-ergodic sampling problem is poor movement in random walk dynamics between different modes of high probability density.

- Sampling can be improved if one improves the transition probability between modes by either improving the proposal of trial moves or by modifying the acceptance criterion (i.e. sampling with a different importance function).

- **Umbrella sampling** is based on using a modified version of the Boltzmann distribution, typically specified by an additional potential energy term that encourages movement between modes.

- Consider the quartic system discussed in the last section. We define the *umbrella potential* $U_b(x) = kx^2$ and the importance function $\Pi(x) = e^{-\beta U(x)} e^{-\beta U_b(x)}$ and define the transition matrix so that Π is the limit distribution of the random walk.

  - Any canonical average can be written as an average over Π

$$\langle A(x) \rangle = \int dx\, P(x) A(x) = \int dx\, \Pi(x) \left(A(x) \frac{P(x)}{\Pi(x)} \right)$$

  provided that $\Pi(x) \neq 0$ at any point where $P(x) \neq 0$.

- Generate Markov chain of states $\{x_1, \ldots, x_N\}$ according to $\Pi(x)$ so that an estimator of the average is

$$\langle A(x) \rangle = \frac{1}{N} \sum_{i=1}^{N} A(x_i) \frac{P(x_i)}{\Pi(x_i)} = \frac{1}{N} \sum_{i=1}^{N} A(x_i) w(x_i) = \frac{1}{N} \sum_{i=1}^{N} A(x_i) e^{\beta U_b(x_i)}.$$

- Weight factor $w(x_i) = e^{\beta U_b(x_i)}$ accounts for bias introduced by the umbrella potential. In this case, it will assign greater weight to regions around the modes at $x = \pm 1$ since the biased random walk attaches less signficance to these regions.
- The parameter k in the umbrella potential can be adjusted to minimize the statistical uncertainties.

- Disadvantage of umbrella approach: Must know a way in which to enhance movement between all modes of system in order to define an effective umbrella potential.

3.3 Simulated annealing and parallel tempering

3.3.1 High temperature sampling

- At high temperatures ($\beta \ll 1$), the equilibrium distribution $P_h(x)$ is only weakly bimodal.
  - Transition rate between modes depends exponentially on $\beta \Delta U$, where ΔU is the barrier height of the potential separating different modes.
  - If β is small so that $\beta \Delta U \ll 1$, then the system moves easily between modes.

- Can use high-temperature distribution $P_h(x)$ as an importance function $\Pi(x)$, resulting in weight function $w(x_i)$ given by

$$w(x_i) = \frac{P(x_i)}{\Pi(x_i)} = e^{-(\beta - \beta_h) U(x_i)} = e^{-\Delta \beta U(x_i)}.$$

  - If $\Delta\beta$ is large, points near barrier $x_i = 0$ receive little weight since $w(x_i) \ll 1$.
  - Advantage of this approach is that we don't need to know barrier locations since high average potential energy overcomes barriers.
  - Disadvantage: For high-dimensional systems, the number of accessible states is large (high entropy) for high temperatures. Many configurations sampled at high temperatures therefore receive little weight, leading to sampling inefficiency and large statistical uncertainties.

3.3.2 Extended state space approach: "Simulated Tempering", Marinari and Parisi, 1992

- Large temperature gaps in high temperature sampling approach lead to inefficient sampling due to a difference in density of states (entropy), while small temperature gaps are typically insufficient to enhance the passage between modes.

- Idea of extended state space approaches is to use a ladder of different temperatures (or other parameter) to allow the system to gradually move out of modes in an efficient manner.

- We augment the phase space point $\mathbf{r}^{(N)}$ with a parameter β_i from a set of m values $\{\beta_i\}$ and define a target limit distribution $\Pi(\mathbf{r}^{(N)}, \beta_i) = W_i e^{-\beta_i U(\mathbf{r}^{(N)})}$ on the extended state space $(\mathbf{r}^{(N)}, \beta_i)$, where W_i is an adjustable parameter.

- Monte-carlo procedure is standard, but with extended state space:

  1. Carry out sequence of a specified number of updates at fixed β_i using normal Metropolis scheme.
  2. Randomly and uniformly select a temperature index j, with corresponding parameter β_j, for a Monte-Carlo update. Accept change of parameter with probability $\mathsf{A}(i \to j)$, where

$$\mathsf{A}(i \to j) = \min\left(1, \frac{\Pi(\mathbf{r}^{(N)}, \beta_j)}{\Pi(\mathbf{r}^{(N)}, \beta_i)}\right) = \min\left(1, \frac{W_j}{W_i} e^{-(\beta_j - \beta_i)U(\mathbf{r}^{(N)})}\right).$$

  - Generate chain of states of extended phase space $\{(\mathbf{r}_1^{(N)}, i_1), \ldots, (\mathbf{r}_n^{(N)}, i_n)\}$. If target average is at temperature $\beta = \beta_1$, averages are given by estimator

$$\langle A(\mathbf{r}^{(N)}) \rangle = \frac{1}{n} \sum_{k=1}^{n} A(\mathbf{r}_k^{(N)}) \frac{W_1}{W_{i_k}} e^{-(\beta_1 - \beta_{i_k})U(\mathbf{r}_k^{(N)})}.$$

- Drawbacks:

  - Must specify the parameter set $\{\beta_i\}$ properly to ensure the proper movement between modes.
  - Must know how to choose weights W_k for a given set of $\{\beta_k\}$. This can be done iteratively, but requires a fair amount of computational effort.

3.3.3 Parallel Tempering or Replica Exchange, C.J. Geyer, 1991

- Use an extended state space composed of replicas of the system to define a Markov chain $\mathbf{X} = (\mathbf{r}_1, \ldots \mathbf{r}_m)$, where each $\mathbf{r}_i$ is a complete configuration of the system.

- Design a transition matrix so that limiting distribution is

$$P(\mathbf{X}) = \Pi_1(\mathbf{r}_1) \ldots \Pi_m(\mathbf{r}_m)$$

  - The (statistically independent) individual components i of the extended state space vector can be assigned any weight Π_i. One choice is to use a Boltzmann distribution $\Pi_i(\mathbf{r}_i) = e^{-\beta_i U(\mathbf{r}_i)}$ with inverse temperature β_i.

- The Monte-Carlo process on the extended state space can be carried out as follows:

  1. Carry out a fixed number of updates on all replicas, each with a transition matrix K_i that has a limit distribution Π_i.
  2. Attempt a swap move, in which different components of the extended state space vector (replicas) are swapped.
     - For example, any pair of components, possibly adjacent to one another, can be selected from a set of all possible pairs with uniform probability. Suppose one picks components 2 and 3, so that the original configuration $\mathbf{X}_i$ and proposed configuration $\mathbf{Y}_i$ are

$$\mathbf{X}_i = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \\ \vdots \\ \mathbf{r}_m \end{pmatrix} \qquad \mathbf{Y}_i = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_3 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_m \end{pmatrix}$$

     - The proposed configuration $\mathbf{Y}_i$ should be accepted with probability $\mathsf{A}(\mathbf{X}_i \to \mathbf{Y}_i)$ given by

$$\mathsf{A}(\mathbf{X}_i \to \mathbf{Y}_i) = \min\left(1, \frac{P(\mathbf{Y}_i)}{P(\mathbf{X}_i)}\right) = \min\left(1, \frac{\Pi_2(\mathbf{r}_3)\Pi_3(\mathbf{r}_2)}{\Pi_2(\mathbf{r}_2)\Pi_3(\mathbf{r}_3)}\right)$$

     - Note that no adjustable weight factors W_i are needed.
     - If $\Pi_i = e^{-\beta_i U(\mathbf{r}_i)}$, then

$$\frac{\Pi_2(\mathbf{r}_3)\Pi_3(\mathbf{r}_2)}{\Pi_2(\mathbf{r}_2)\Pi_3(\mathbf{r}_3)} = \frac{e^{-\beta_2 U(\mathbf{r}_3)}}{e^{-\beta_2 U(\mathbf{r}_2)}} \frac{e^{-\beta_3 U(\mathbf{r}_2)}}{e^{-\beta_3 U(\mathbf{r}_3)}} = e^{-(\beta_2-\beta_3)U(\mathbf{r}_3)} e^{(\beta_2-\beta_3)U(\mathbf{r}_2)} = e^{\Delta\beta\Delta U},$$

       where $\Delta\beta = \beta_3 - \beta_2$ and $\Delta U = U(\mathbf{r}_3) - U(\mathbf{r}_2)$.

- Each component of $\mathbf{X}_i$ in Markov chain of extended states $\{\mathbf{X}^{(1)}, \ldots \mathbf{X}^{(N)}\}$ is distributed with weight Π_i

- Averages at any of the temperatures are therefore readily computed using

$$\langle A \rangle_{\beta_i} = \frac{1}{N} \sum_{k=1}^{N} A(\mathbf{X}_i^{(k)}),$$

  where $\mathbf{X}_i^{(k)}$ is the ith component of the extended configuration $\mathbf{X}^{(k)}$ (the kth configuration in the Markov chain).

- Advantages: Quasi-ergodic sampling is mitigated by using a range of parameters such as β_i. The parameters should be defined such that their extreme values (such as highest temperature) should demonstrate no trapping in single modes.

- Disadvantages: There must be some overlap in adjacent densities Π_i and Π_{i+1} if a swap move is to be accepted with significant probability. Ideally, the parameters β_i should be chosen so that any given labelled configuration spends an equal amount of time at all parameter values.

  – Sometimes requires many replicas, which means that it takes many Monte-Carlo exchange moves for a given configuration to cycle through the parameters.

- One of the major advantages of the replica exchange method is the ease with which one can parallelize the algorithm.

  – Normal single-chain algorithm cannot be parallelized efficiently because of sequential nature of random walk procedure.

  – Can parallelize the generation of many trial configurations and use an asymmetric proposal procedure to select one preferentially.

  – Can parallelize computation of energy, if this is a rate-determining step.

- The exchange frequency between replicas can be optimized to suit the computer architecture.

- Each processor can deal with a single replica, or sub-sets of replicas.

4

Molecular dynamics

4.1 Basic integration schemes

4.1.1 General concepts

- Aim of Molecular Dynamics (MD) simulations:
  compute *equilibrium* and *transport* properties of *classical many body systems*.

- Basic strategy: numerically solve equations of motions.

- For many classical systems, the equations of motion are of Newtonian form

  $$\dot{R}^N = \frac{1}{m} P^N$$
  $$\dot{P}^N = F^N = -\frac{\partial U}{\partial R^N},$$

  or

  $$\dot{X}^N = \mathcal{L} X^N, \text{ with } \mathcal{L} A = \{A, \mathcal{H}\},$$

  where $X^N = (R^N, P^N)$.
  The energy $\mathcal{H} = \frac{P^N \cdot P^N}{2m} + U(R^N)$ is conserved under this dynamics.
  The potential energy is typically of the form of a sum of pair potentials:

  $$U(R^N) = \sum_{(i,j)} \varphi(r_{ij}) = \sum_{i=1}^{N} \sum_{j=1}^{i-1} \varphi(r_{ij}),$$

  which entails the following expression for the forces F^N:

  $$\mathbf{F}_i = -\sum_{j \neq i} \frac{\partial}{\partial \mathbf{r}_i} \varphi(r_{ij}) = -\sum_{j \neq i} \varphi'(r_{ij}) \frac{\partial r_{ij}}{\partial \mathbf{r}_i} = \sum_{j \neq i} \underbrace{\varphi'(r_{ij}) \frac{\mathbf{r}_j - \mathbf{r}_i}{r_{ij}}}_{\mathbf{F}_{ij}}$$

- Examples of quantities of interest:

  1. Radial distribution function (structural equilibrium property)

  $$g(r) = \frac{2V}{N(N-1)} \sum_{(i,j)} \langle \delta(\mathbf{r}_i - \mathbf{r}_j - \mathbf{r}) \rangle ,$$

  where

  $$\begin{aligned} \langle A \rangle &= \frac{\int dX^N\, A(X^N) e^{-\beta \mathcal{H}(X^N)}}{\int dX^N\, e^{-\beta \mathcal{H}(X^N)}} && \text{(canonical ensemble)} \\ \text{or} \quad &= \frac{\int dX^N\, A(X^N)\, \delta(E - \mathcal{H}(X^N))}{\int dX^N\, \delta(E - \mathcal{H}(X^N))} && \text{(microcanonical ensemble).} \end{aligned}$$

  2. Pressure (thermodynamic equilibrium property):

  $$pV = NkT + \frac{1}{3} \sum_{(i,j)} \langle \mathbf{F}_{ij} \cdot \mathbf{r}_{ij} \rangle$$

  which can be written in terms of $g(r)$ as well.

  3. Mean square displacement (transport property):

  $$\left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle \to 6Dt \text{ for long times } t,$$

  where D is the self diffusion coefficient.

  4. Time correlation function (relaxation properties)

  $$C(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$$

  which is related to D as well:

  $$D = \frac{1}{3} \lim_{t \to \infty} \lim_{N,V \to \infty} \int_0^t C(\tau)\, d\tau$$

- If the system is ergodic then time average equals the microcanonical average:

$$\lim_{t_{\text{final}} \to \infty} \frac{1}{t_{\text{final}}} \int_0^{t_{\text{final}}} dt\, A(X^N(t)) = \frac{\int dX^N\, A(X^N)\, \delta(E - \mathcal{H}(X^N))}{\int dX^N\, \delta(E - \mathcal{H}(X^N))}.$$

- For large N, microcanonical and canonical averages are equal for many quantities A.

- Need long times t_{final}!

- The equations of motion to be solved are ordinary differential equations.

- There exist general algorithms to solve ordinary differential equations numerically (see e.g. *Numerical Recipes* Ch. 16), such as Runge-Kutta and predictor/correction algorithms. Many of these are too costly or not stable enough for long simulations of many-particle systems. In MD simulations, it is therefore better to use algorithms specifically suited for systems obeying Newton's equations of motion, such as the Verlet algorithm.

- However, we first want to explore some general properties of integration algorithms. For this purpose, consider a function x of t which satisfies

$$\dot{x} = f(x, t). \tag{4.1}$$

- We want to solve for the trajectory $x(t)$ numerically, given the initial point $x(0)$ at time $t = 0$.

- Similar to the case of integration, we restrict ourselves to a discrete set of points, separated by a <u>*small time step* Δt</u>:

$$\begin{aligned} t_n &= n\Delta t \\ x_n &= x(t_n), \end{aligned}$$

  where $n = 0, 1, 2, 3, \ldots$.

- To transform equation (4.1) into a closed set of equations for the x_n, we need to express the time derivative $\dot{x}$ in terms of the x_n. This can only be done approximately.

- Using that Δt is small:

$$\dot{x}(t_n) \approx \frac{x(t_n + \Delta t) - x(t_n)}{\Delta t} = \frac{x_{n+1} - x_n}{\Delta t}.$$

- Since this should be equal to $f(x(t), t) = f(x_n, t_n)$:

$$\frac{x_{n+1} - x_n}{\Delta t} \approx f(x_n, t_n) \Rightarrow$$

$$\boxed{x_{n+1} = x_n + f(x_n, t_n)\Delta t} \quad \underline{\textit{Euler Scheme}}. \tag{4.2}$$

  This formula allows one to generate a time series of points which are an approximation to the real trajectory. A simple MD algorithm in pseudo-code could look like this:[1]

[1] Pseudo-code is an informal description of an algorithm using common control elements found in most programming language and natural language; it has no exact definition but is intended to make implementation in a high-level programming language straightforward.

```
EULER ALGORITHM
SET x to the initial value x(0)
SET t to the initial time
WHILE t < tfinal
   COMPUTE f(x,t)
   UPDATE x to x+f(x,t)*dt
   UPDATE t to t+dt
END WHILE
```

DO NOT USE THIS ALGORITHM!

- It is easy to show that the error in the Euler scheme is of order Δt^2, since

$$x(t + \Delta t) = x(t) + f(x(t), t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2 + \ldots,$$

so that

$$x_{n+1} = x_n + f(x_n, t_n)\Delta t + \underbrace{\mathcal{O}(\Delta t^2)}_{\text{local error}}. \tag{4.3}$$

The strict meaning of the "big O" notation is that if $A = \mathcal{O}(\Delta t^k)$ then $\lim_{\Delta t\to 0} A/\Delta t^k$ is finite and nonzero. For small enough Δt, a term $\mathcal{O}(\Delta t^{k+1})$ becomes smaller than a term $\mathcal{O}(\Delta t^k)$, but the big O notation cannot tell us what magnitude of Δt is small enough.

- A numerical prescription such as (4.3) is called an *integration algorithm*, *integration scheme*, or *integrator*.

- Equation (4.3) expresses the error after one time step; this is called the *local truncation error*.

- What is more relevant is the *global error* that results after a given physical time t_f of order one. This time requires $M = t_f/\Delta t$ MD steps to be taken.

- Denoting $f_k = f(x_k, t_k)$, we can track the errors of subsequent time steps as follows:

$$\begin{aligned}
x_1 &= x_0 + f_0\Delta t + \mathcal{O}(\Delta t^2)\\
x_2 &= [x_0 + f_0\Delta t + \mathcal{O}(\Delta t^2)] + f_1\Delta t + \mathcal{O}(\Delta t^2)\\
&= x_0 + (f_0 + f_1)\Delta t + \mathcal{O}(\Delta t^2) + \mathcal{O}(\Delta t^2)\\
&\ \ \vdots\\
x_M &= x_0 + \sum_{k=1}^{M} f_{k-1}\Delta t + \sum_{k=1}^{M} \mathcal{O}(\Delta t^2);
\end{aligned}$$

but as $M = t_f/\Delta t$:

$$x(t) = x_M = x_0 + \sum_{k=1}^{t_f/\Delta t} f_{k-1}\Delta t + \underbrace{\sum_{k=1}^{t_f/\Delta t} \mathcal{O}(\Delta t^2)}_{\text{global error}}.$$

- Since $t_f = \mathcal{O}(1)$, the accumulated error is

$$\sum_{k=1}^{t_f/\Delta t} \mathcal{O}(\Delta t^2) = \mathcal{O}(\Delta t^2)\mathcal{O}(t_f/\Delta t) = \mathcal{O}(t_f \Delta t), \tag{4.4}$$

which is of first order in the time step Δt.

- Since the global error goes as the first power of the time step Δt, we call equation (4.3) a *first order* integrator.

- In absence of further information on the error terms, this constitutes a general principle: If in a single time step of an integration scheme, the local truncation error is $\mathcal{O}(\Delta t^{k+1})$, then the globally accumulated error over a time t_f is $\mathcal{O}(t_f \Delta t^k) = \mathcal{O}(\Delta t^k)$, i.e., the scheme is kth order.

- Equation (4.4) also shows the possibility that the error grows with physical time t_f: *Drift*.

- Illustration of local and global errors:
Let $f(x,t) = -\alpha x$, so that equation (4.1) reads

$$\dot{x} = -\alpha x,$$

whose solution is exponentially decreasing with a rate α:

$$x(t) = e^{-\alpha t} x(0). \tag{4.5}$$

The numerical scheme (4.3) gives for this system

$$x_{n+1} = x_n - \alpha x_n \Delta t. \tag{4.6}$$

Note that the true relation is $x(t + \Delta t) = e^{-\alpha\Delta t} x(t) = x(t) - \alpha \Delta t x(t) + \mathcal{O}(\Delta t^2)$, i.e., the local error is of order Δt^2.

Equation (4.6) is solved by

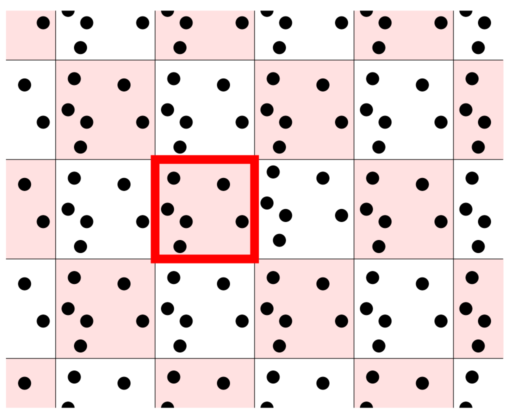
$$x_n = (1 - \alpha\Delta t)^n x_0 = (1 - \alpha \Delta t)^{t/\Delta t} = e^{[\ln(1-\alpha\Delta t)/\Delta t]t}. \tag{4.7}$$

By comparing equations (4.5) and (4.7), we see that the behaviour of the numerical solution is similar to that of the real solution but with the rate α replaced by $\alpha' = -\ln(1-\alpha\Delta t)/\Delta t$. For small Δt, one gets for the numerical rate $\alpha' = \alpha + \alpha^2 \Delta t/2 + \cdots = \alpha + \mathcal{O}(\Delta t)$, thus the global error is seen to be $\mathcal{O}(\Delta t)$, which demonstrates that the Euler scheme is a first order integrator. Note that the numerical rate diverges at $\Delta t = 1/\alpha$, which is an example of a numerical instability.

4.1.2 Ingredients of a molecular dynamics simulation

1. *Boundary conditions*

 - We can only simulate finite systems.
 - A wall potential would give finite size effects and destroy translation invariance.
 - More benign boundary conditions: *Periodic Boundary Conditions:*
 - Let all particles lie in a simulation box with coordinates between $-L/2$ and $L/2$.
 - A particle which exits the simulation box, is put back at the other end.
 - Infinite checkerboard picture (easiest to visualize in two dimensions):



 - The box with thick boundaries is our simulation box.
 - All other boxes are copies of the simulation box, called periodic images.
 - The other squares contain particles with shifted positions

$$\mathbf{r}' = \mathbf{r} + \begin{pmatrix} iL \\ jL \\ kL \end{pmatrix},$$

 for any negative or positive integers i, j, and k. Thus, if a particle moves out of the simulation box, another particle will fly in from the other side.

Conversely, for any particle at position $\mathbf{r}'$ not in the simulation box, there is a particle in the simulation box at

$$\mathbf{r} = \begin{pmatrix} (x' + \frac{L}{2}) \bmod L - \frac{L}{2} \\ (y' + \frac{L}{2}) \bmod L - \frac{L}{2} \\ (z' + \frac{L}{2}) \bmod L - \frac{L}{2} \end{pmatrix}, \tag{4.8}$$

- Yet another way to view this is to say that the system lives on a torus.

2. Forces

- Usually based on pair potentials.
- A common pair potential is the Lennard-Jones potential

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right],$$

  - σ is a measure of the range of the potential.
  - ε is its strength.
  - The potential is positive for small r: repulsion.
  - The potential is negative for large r: attraction.
  - The potential goes to zero for large r: short-range.
  - The potential has a minimum of $-\varepsilon$ at $2^{1/6}\sigma$.
- Computing all forces in an N-body system requires the computation of $N(N-1)/2$ (the number of pairs in the system) forces $\mathbf{F}_{ij}$
- Computing forces is often the most demanding part of MD simulations.
- A particle i near the edge of the simulation box will feel a force from the periodic images, which can be closer to i than their original counter-parts.
- A consistent way to write the potential is

$$U = \sum_{i,j,k} \sum_{n=1}^{N} \sum_{m=1}^{n-1} \varphi(|\mathbf{r}_n - \mathbf{r}_m + iL\hat{\mathbf{x}} + jL\hat{\mathbf{y}} + kL\hat{\mathbf{z}}|). \tag{4.9}$$

- While this converges for most potentials φ, it is very impractical to have to compute an infinite sum to get the potential and forces.
- To fix this, one can modify the potential such that it becomes zero beyond a certain cut-off distance r_c:

$$\varphi'(r) = \begin{cases} \varphi(r) - \varphi(r_c) & \text{if } r < r_c \\ 0 & \text{if } r \geq r_c \end{cases}$$

  where the subtraction of $\varphi(r_c)$ is there to avoid discontinuities in the potential which would cause violations of energy conservation.

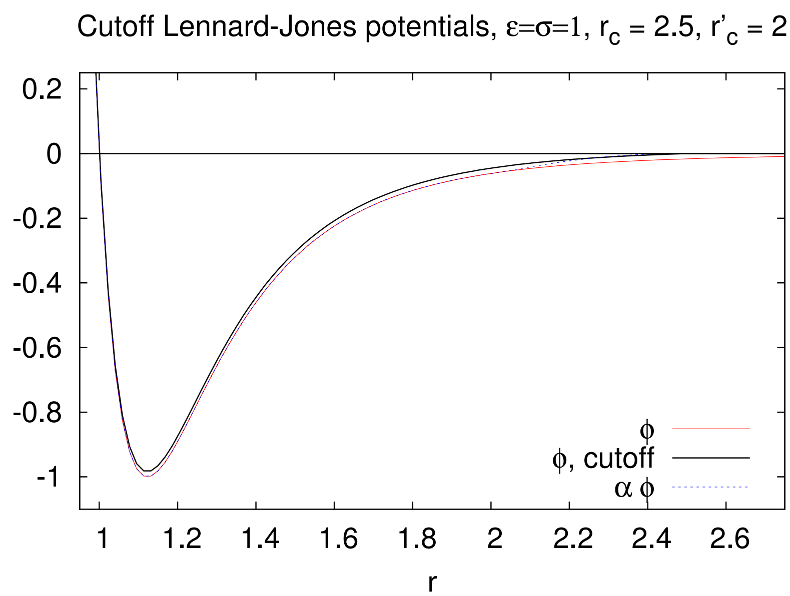
- To also avoid discontinuities in derivatives, one can use a schemes such as

$$\varphi''(r) = \alpha(r)\varphi(r) \tag{4.10}$$

where

$$\alpha(r) = \begin{cases} 1 & r < r'_c \\ \frac{(r_c - r)^2(r_c - 3r'_c + 2r)}{(r_c - r'_c)^3} & r'_c \leq r \leq r_c \\ 0 & r > r_c \end{cases} . \tag{4.11}$$

Here is an example of these procedures applied to the Lennard-Jones potential:



- Once the potential is zero beyond a point, the sums over i, j, and k in equation (4.9) become finite.
- In fact, if $r_c < L/2$, the sum contains at most one non-zero contribution for each pair of particles (i, j). This pair is either in the same box, or one of them is in the adjacent boxes.
- For any pair, the correct distance vector can be found from the original distance vector $\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j$ using equation (4.8).

3. <u>Initial conditions</u>

- The initial conditions are to some extent not important if the system naturally tends to equilibrium (ergodicity).
- Nonetheless, one would not want too extreme an initial configuration.

- Starting the system with the particles on a lattice and drawing initial momenta from a uniform or Gaussian distribution is typically a valid starting point.
- One often makes sure that the kinetic energy has the target value $\frac{3}{2}NkT$, while the total momentum is set to zero to avoid the system moving as a whole.

4. *Integration scheme*

- Needed to solve the *dynamics* as given by the equations of motion.
- Below, we will discuss in detail on how to construct or choose an appropriate integration scheme.

5. *Equilibration/Burn-in*

- Since we do not start the system from an equilibrium state, a certain number of time steps are to be taken until the system has reached an equilibrium.
- One can check for equilibrium by seeing if quantities like the potential energy are no longer changing in any systematic fashion and are just fluctuating around a mean values.
- The equilibrium state is microcanonical at a given total energy $E_{tot} = E_{pot} + E_{kin}$.
- Since $E_{kin} > 0$, the lattice initialization procedure outlined cannot reach all possible values of the energy, i.e. $E_{tot} > E_{pot}(lattice)$.
- To reach lower energies, one can periodically rescale the momenta (a rudimentary form of a so called *thermostat*).
- Another way to reach equilibrium is to generate initial conditions using the Monte Carlo method.

6. *Measurements*

- Construct estimators for physical quantities of interest.
- Since there are correlations along the simulated trajectory, one needs to take sample points that are far apart in time.
- Although when one is interested in dynamical quantities, all points should be used. In the statistical analysis there correlations should be taken into account.

Given these ingredients, the outline of an MD simulation could look like this:

```
OUTLINE MD PROGRAM
SETUP INITIAL CONDITIONS
PERFORM EQUILIBRATION by INTEGRATING over a burn-in time B
SET time t to 0
PERFORM first MEASUREMENT
WHILE t < tfinal
    INTEGRATE over the measurement interval
    PERFORM MEASUREMENT
END WHILE
```

in which the integration step from t1 to t1+T looks as follows (assuming t=t1 at the start):

```
OUTLINE INTEGRATION
WHILE t < t1+T
     COMPUTE FORCES on all particles
     COMPUTE new positions and momenta according to INTEGRATION SCHEME
     APPLY PERIODIC BOUNDARY CONDITIONS
     UPDATE t to t+dt
END WHILE
```

Note: we will encounter integration schemes in which the forces need to be computed in intermediate steps, in which case the separation between force computation and integration is not as strict as this outline suggests.

4.1.3 Desirable qualities for a molecular dynamics integrator

- *Accuracy:*
  Accuracy means that the trajectory obeys the equations of motion to good approximation. This is a general demand that one would also impose on integrators for general differential equations. The accuracy in principle improves by decreasing the time step Δt. But because of the exponential separation of near-by trajectories in phase space (Lyapunov instability), this is of limited help.

  Furthermore, one cannot decrease Δt too far in many particle systems for reasons of

- *Efficiency:*
  It is typically quite expensive to compute the inter-particle forces F^N, and taking smaller time steps Δt requires more force evaluations per unit of physical time.

- *Respect physical laws:*
  - Time reversal symmetry
  - Conservation of energy
  - Conservation of linear momentum
  - Conservation of angular momentum
  - Conservation of phase space volume

  provided the simulated system also has these properties, of course.

  Violating these laws poses serious doubts on the ensemble that is sampled and on whether the trajectories are realistic.

  Unfortunately, there is no general algorithm that obeys all of these conservation laws exactly for an interacting many-particle system. At best, one can find time-reversible, volume preserving algorithms that conserve linear momentum and angular momentum, but that conserve the energy only approximately.

  Note furthermore that with periodic boundary conditions:
  - Translational invariance and thus conservation of momentum is preserved.
  - There is no wall potential, so the energy conservation is not affected either.
  - But rotational invariance is broken: No conservation of angular momentum.

- *Stability:*
  Given that the energy is only conserved approximately, when studying dynamics on large time scales, or when sampling phase space using MD, it is important that the simulation is stable, i.e., that the algorithm does not exhibit *energy drift*, since otherwise, it would not even sample the correct microcanonical energy shell.

Remarks:

- Since the computational cost thus limits the time step, the accuracy of the algorithm has to be assessed at a fixed time step.

- Since Δt is not necessarily small, higher order algorithms need not be more accurate.

- The most efficient algorithm is then the one that allows the largest possible time step for a given level of accuracy, *while maintaining stability and preserving conservation laws.*

- All integration schemes become *numerically* unstable for large time steps Δt, even if they are stable at smaller time steps. A large step may can the system to a region of large potential energy. With infinite precision, this would just cause a large restoring force that pushes the system back into the low energy region. But with finite precision, the low energies cannot be resolved anymore, and the system remains in the high energy state.

- The dominance of the force evaluations means that the efficiency of a simulation can greatly be improved by streamlining the evaluation of the forces, using

  1. Cell divisions:

     - Divide the simulation box into cells larger than the cutoff r_c.
     - Make a list of all particles in each cell.
     - In the sum over pairs in the force computation, only sum pairs of particles in the same cell or in adjacent cells.
     - When 'adjacent' is properly defined, this procedure automatically picks out the right periodic image.
     - Draw-backs:
       1. needs at least three cells in any direction to be of use.
       2. Still summing many pairs that do not interact (corners).

  2. Neighbour lists (also called Verlet lists or Verlet neighbour lists):

     - Make a list of pairs of particles that are closer than $r_c + \delta r$: these are 'neighbours'.
     - Sum over the list of pairs to compute the forces.
     - The neighbour list are to be used in subsequent force calculations as long as the list is still valid.
     - Invalidation criterion: a particle has moved more than $\delta r/2$.
     - Therefore, before a new force computation, check if any particle has moved more than $\delta r/2$ since the last list-building. If so, rebuild the Verlet list, otherwise use the old one.
     - Notes:
       1. δr needs to be chosen to balance the cost of rebuilding the list and considering non-interacting particles.
       2. The building of the list may be sped up by using cell divisions.

  For large systems, these methods of computing the interaction forces scale as N instead of as N^2, as the naive implementation of summing over all pairs would give.

Assessing the Euler scheme for the harmonic oscillator

- Consider the Euler scheme applied to $x = (r, p)$, and $f(x, t) = (p, -r)$. i.e., (cf. equation (4.1))

$$\dot{r} = p$$
$$\dot{p} = -r.$$

This is the simple one-dimensional harmonic oscillator with mass 1 and frequency 1, whose solutions are oscillatory

$$r(t) = r(0)\cos t + p(0)\sin t \tag{4.12}$$
$$p(t) = p(0)\cos t - r(0)\sin t. \tag{4.13}$$

The Euler scheme (4.3) gives for this system

$$\begin{pmatrix} r_{n+1} \\ p_{n+1} \end{pmatrix} = \begin{pmatrix} 1 & \Delta t \\ -\Delta t & 1 \end{pmatrix} \begin{pmatrix} r_n \\ p_n \end{pmatrix}. \tag{4.14}$$

- The eigenvalues of the matrix on the right hand side of equation (4.14) are given by $\lambda_\pm = 1 \pm \mathrm{i}\Delta t$, and the solution of equation (4.14) can be expressed as

$$\begin{pmatrix} r_n \\ p_n \end{pmatrix} = \begin{pmatrix} 1 & \Delta t \\ -\Delta t & 1 \end{pmatrix}^n \begin{pmatrix} r_0 \\ p_0 \end{pmatrix} \tag{4.15}$$
$$= \begin{pmatrix} \frac{1}{2}(\lambda_+^n + \lambda_-^n) & \frac{1}{2\mathrm{i}}(\lambda_+^n - \lambda_-^n) \\ \frac{-1}{2\mathrm{i}}(\lambda_+^n - \lambda_-^n) & \frac{1}{2}(\lambda_+^n + \lambda_-^n) \end{pmatrix} \begin{pmatrix} r_0 \\ p_0 \end{pmatrix} \tag{4.16}$$
$$= (\lambda_+\lambda_-)^{n/2} \begin{pmatrix} \frac{e^{i\omega'\Delta t n} + e^{-i\omega'\Delta t n}}{2} & \frac{e^{i\omega'\Delta t n} - e^{-i\omega'\Delta t n}}{2\mathrm{i}} \\ -\frac{e^{i\omega'\Delta t n} - e^{-i\omega'\Delta t n}}{2\mathrm{i}} & \frac{e^{i\omega'\Delta t n} + e^{-i\omega'\Delta t n}}{2} \end{pmatrix} \begin{pmatrix} r_0 \\ p_0 \end{pmatrix} \tag{4.17}$$
$$= (1 + \Delta t^2)^{\frac{t}{2\Delta t}} \begin{pmatrix} \cos(\omega' t) & \sin(\omega' t) \\ -\sin(\omega' t) & \cos(\omega' t) \end{pmatrix} \begin{pmatrix} r_0 \\ p_0 \end{pmatrix}, \tag{4.18}$$

where $e^{\mathrm{i}\omega'\Delta t} = (\lambda_+/\lambda_-)^{1/2}$. By comparing equations (4.13) and (4.18), we see that the behaviour of the numerical solution is similar to that of the real solution but with a different frequency, and with a prefactor which is larger than one and grows with time.

- Rather than performing a periodic, circular motion in phase space, the Euler scheme produces an outward spiral.

- *Accuracy*: $\omega' = \omega + \mathcal{O}(\Delta t)$ so this is only a first order integration scheme.

- *Time reversal invariant?* No.

- *Conserves energy?* No.
- *Conserves angular momentum?* No.
- *Conserves phase space?* No.
- *Stable?* No.

4.1.4 Verlet scheme

- If the system is governed by Newton's equations:

  $$\dot{R}^N = \frac{1}{m} P^N$$
  $$\dot{P}^N = F^N,$$

  then one can exploit the form of these equations to construct (better) integrators.

- The Verlet scheme is one of these schemes. It can be derived by Taylor expansion

  $$R^N_{n-1} = R^N(t-\Delta t) = R^N_n - P^N_n \frac{\Delta t}{m} + F^N_n \frac{\Delta t^2}{2m} - \dddot{R}^N(t)\frac{\Delta t^3}{6} + \mathcal{O}(\Delta t^4)$$
  $$R^N_{n+1} = R^N(t+\Delta t) = R^N_n + P^N_n \frac{\Delta t}{m} + F^N_n \frac{\Delta t^2}{2m} + \dddot{R}^N(t)\frac{\Delta t^3}{6} + \mathcal{O}(\Delta t^4).$$

  Adding these two equations leads to

  $$R^N_{n-1} + R^N_{n+1} = 2R^N_n + F^N_n \frac{\Delta t^2}{m} + \mathcal{O}(\Delta t^4) \Rightarrow$$
  $$\boxed{R^N_{n+1} = 2R^N_n - R^N_{n-1} + F^N_n \frac{\Delta t^2}{m}} \quad \underline{\textit{Position-only Verlet Integrator}} \tag{4.19}$$

- No momenta!
- Requires positions at the previous step!
- Simple algorithm (`r(i)` and `rprev(i)` are particle i's current and previous position)

```
VERLET ALGORITHM
SET time t to 0
WHILE t < tfinal
   COMPUTE the forces F(i) on all particles
   FOR each particle i
      COMPUTE new position rnew = 2*r(i)-rprev(i)+F(i)*dt*dt/m
```

```
        UPDATE previous position rprev(i) to r(i)
        UPDATE position r(i) to rnew
      END FOR
      UPDATE t to t+dt
    END WHILE
```

- Accuracy: This scheme is third order in the positions, so reasonably accurate.
- Respect physical laws?
  - Time reversal symmetry? Yes, since
$$R^N_{n-1} = 2R^N_n - R^N_{n+1} + F^N_n \frac{\Delta t^2}{m}.$$
  - Total energy conservation? No momenta, so energy conservation cannot be checked.
  - Linear momentum? Also not defined.
  - Angular momentum? Not defined.
  - Volume preserving? No phase space volume can be defined without momenta.
- Stability: very stable, no energy drift up to relatively large time steps. Why this is so will become clear later.

4.1.5 Leap Frog scheme

- Is a way to introduce momenta into the Verlet scheme.
- Define momenta at a 'half time step'
$$P^N_{n+1/2} = P^N(t + \Delta t/2) = m\frac{R^N_{n+1} - R^N_n}{\Delta t}. \tag{4.20}$$
- These momenta are correct up to $\mathcal{O}(\Delta t^2)$.
- If we get the positions from the Verlet scheme, then the errors in the momenta do not accumulate, so that the global order of the momenta in the Leap Frog method is also $\mathcal{O}(\Delta t^2)$.
- Given the half-step momenta, one may also perform the Leap Frog algorithm as follows:
$$R^N_{n+1} = R^N_n + P^N_{n+1/2}\frac{\Delta t}{m} \text{ (which follows from (4.20))},$$

where

$$\begin{aligned} P^N_{n+1/2} &= m\frac{R^N_{n+1} - R^N_n}{\Delta t} = m\frac{R^N_n - R^N_{n-1} + R^N_{n+1} + R^N_{n-1} - 2R^N_n}{\Delta t} \\ &= P^N_{n-1/2} + F^N_n \Delta t \text{ (as follows from (4.19)).} \end{aligned}$$

- The scheme is thus:

$$\boxed{\begin{aligned} P^N_{n+1/2} &= P^N_{n-1/2} + F^N_n \Delta t \\ R^N_{n+1} &= R^N_n + P^N_{n+1/2}\frac{\Delta t}{m} \end{aligned}} \quad \underline{\textit{Leap Frog integrator.}} \tag{4.21}$$

- Since the Leap Frog algorithm is derived from the Verlet scheme, it is equally stable.

- The Leap Frog algorithm has the appearance of a first order Taylor expansion, but because of the half-step momenta, it is third order in positions and second order in momenta.

- Since momenta are defined at different time points than positions, conservation laws (energy, momentum,...) can still not be checked.

- The Leap Frog scheme is easy to implement:

```
LEAP-FROG ALGORITHM
SET time t to 0
WHILE t < tfinal
   COMPUTE the forces F(i) on all particles
   FOR each particle i
      UPDATE momentum p(i) to p(i)+F(i)*dt
      UPDATE position r(i) to r(i)+p(i)*dt/m
   END FOR
   UPDATE t to t+dt
END WHILE
```

4.1.6 Momentum/Velocity Verlet scheme

- This scheme will integrate positions and momenta (or velocities) at the same time points, while keeping the position equivalence with the original Verlet scheme.

- We define the momenta at time $t = n\Delta t$ as

$$P^N_n = \frac{1}{2}\left(P^N_{n+1/2} + P^N_{n-1/2}\right).$$

- Using that the half step momenta are correct to $O(\Delta t^2)$, we see that this is also correct to that order, since

$$\begin{aligned}
&\frac{1}{2}\left[P^N\left(t+\frac{\Delta t}{2}\right)+P^N\left(t-\frac{\Delta t}{2}\right)\right] \\
&=\frac{1}{2}\left[P^N(t)+F_n^N\frac{\Delta t}{2}+P^N(t)-F_n^N\frac{\Delta t}{2}+\mathcal{O}(\Delta t^2)\right] \\
&=P^N(t)+\mathcal{O}(\Delta t^2).
\end{aligned}$$

- Using the momentum rule of the Leap Frog algorithm

$$P_{n+1/2}^N = P_{n-1/2}^N + F_n^N \Delta t,$$

and the definition of P_n^N, one gets

$$P_{n+1/2}^N = 2P_n^N - P_{n+1/2}^N + F_n^N \Delta t,$$

or

$$P_{n+1/2}^N = P_n^N + F_n^N \frac{\Delta t}{2}. \tag{4.22}$$

Substituting Eq. (4.22) into the position rule of the Leap Frog gives the position transformation in the momentum-Verlet scheme

$$R_{n+1}^N = R_n^N + P_n^N \frac{\Delta t}{m} + F_n^N \frac{\Delta t^2}{2m}.$$

- The corresponding momentum rule is found using the definition of the momentum and the momentum rule of the Leap Frog:

$$\begin{aligned}
P_{n+1}^N &= \frac{1}{2}[P_{n+3/2}^N + P_{n+1/2}^N] \\
&= \frac{1}{2}[P_{n+1/2}^N + F_{n+1}^N \Delta t + P_{n+1/2}^N] \\
&= P_{n+1/2}^N + F_{n+1}^N \frac{\Delta t}{2} \\
&= P_n^N + \frac{F_{n+1}^N + F_n^N}{2}\Delta t,
\end{aligned} \tag{4.23}$$

where (4.22) was used.

- This algorithm is usually called velocity Verlet, and is then expressed in terms of the velocities $V^N = P^N/m$.

- Summarizing:

$$\boxed{\begin{aligned} R^N_{n+1} &= R^N_n + \frac{P^N_n}{m}\Delta t + \frac{F^N_n}{2m}\Delta t^2 \\ P^N_{n+1} &= P^N_n + \frac{F^N_{n+1} + F^N_n}{2}\Delta t \end{aligned}}$$

<u>*Momentum Verlet Scheme (first version).*</u>

- The momentum rule appears to pose a problem since F^N_{n+1} is required. But to compute F^N_{n+1}, we need only R^N_{n+1}, which is computed in the integration step as well. That is, given that the forces are known at step n, the next step is can be taken by

```
STORE all the forces F(i) as Fprev(i)
FOR each particle i
   UPDATE position r(i) to r(i)+p(i)*dt/m+F(i)*dt*dt/(2*m)
END FOR
RECOMPUTE the forces F(i) using the updated positions
FOR each particle i
   UPDATE momentum p(i) to p(i)+(F(i)+Fprev(i))*dt/2
END FOR
```

- The extra storage step can be avoided by reintroducing the half step momenta as intermediates. From Eqs. (4.21) (first line), (4.23) and (4.22), one finds

$$\boxed{\begin{aligned} P^N_{n+1/2} &= P^N_n + \frac{1}{2}F^N_n\Delta t \\ R^N_{n+1} &= R^N_n + \frac{P^N_{n+1/2}}{m}\Delta t \\ P^N_{n+1} &= P^N_{n+1/2} + \frac{1}{2}F^N_{n+1}\Delta t \end{aligned}} \tag{4.24}$$

<u>*Momentum Verlet Scheme, second version.*</u>

- In pseudo-code:

```
MOMENTUM-VERLET ALGORITHM
SET time t to 0
COMPUTE the forces F(i)
WHILE t < tfinal
   FOR each particle i
      UPDATE momentum p(i) to p(i)+F(i)*dt/2
      UPDATE position r(i) to r(i)+p(i)*dt/m
   END FOR
   UPDATE t to t+dt
   RECOMPUTE the forces F(i)
   FOR each particle i
      UPDATE momentum p(i) to p(i)+F(i)*dt/2
   END FOR
END WHILE
```

4.2 Symplectic integrators from Hamiltonian splitting methods

- For sampling, one wants a long trajectory (formally $t_f \to \infty$).

- It is therefore important that an integration algorithm be stable.

- The instability of the Euler scheme is general, so generally, one would not use it.

- The momentum Verlet scheme, on the other hand, is much more stable.

- To see why, we will re-derive the momentum Verlet scheme from a completely different starting point, using a so-called *Hamiltonian splitting method* (also known as *Geometric integration*).

- We return to the formulation of the equations of motion using the Liouville operator:

$$\dot{X}^N = \mathcal{L}X^N, \tag{4.25}$$

where the Liouville operator $\mathcal{L}$ acting on a phase space function A was defined in terms of the Poison bracket as

$$\begin{aligned}\mathcal{L}A &= \{A, \mathcal{H}\} \\ &= \frac{\partial A}{\partial R^N} \cdot \frac{\partial H}{\partial P^N} - \frac{\partial H}{\partial R^N} \cdot \frac{\partial A}{\partial P^N} \\ &= \left(\frac{\partial \mathcal{H}}{\partial P^N} \cdot \frac{\partial}{\partial R^N} - \frac{\partial \mathcal{H}}{\partial R^N} \cdot \frac{\partial}{\partial P^N} \right) A = \left(\left[\mathsf{J} \cdot \frac{\partial \mathcal{H}}{\partial X^N} \right]^T \cdot \frac{\partial}{\partial X^N} \right) A,\end{aligned}$$

where J is the symplectic matrix

$$\mathsf{J} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}.$$

- Remembering that the Hamiltonian $\mathcal{H}$ was defined as

$$\mathcal{H} = \frac{P^N \cdot P^N}{2m} + U(R^N), \tag{4.26}$$

it is easy to show that (4.25) leads to

$$\boxed{\dot{X}^N = \mathsf{J} \cdot \frac{\partial H}{\partial X^N}} \tag{4.27}$$

which are just Newton's equation of motion

$$\dot{R}^N = P^N/m; \qquad \dot{P}^N = F^N = -\frac{\partial U}{\partial R^N}.$$

- Equations of motion of the form equation (4.27) are called symplectic.

- Symplecticity of the equations of motion has a number of important implications:

1. Symplecticity implies Liouville's theorem, i.e., conservation of phase space volume, because the rate by which phase space volume changes is given by the divergence of the flow in phase space, and

$$\frac{\partial}{\partial X^N} \cdot \dot{X}^N = \frac{\partial}{\partial X^N} \cdot \left[\mathsf{J} \cdot \frac{\partial \mathcal{H}}{\partial X^N} \right] = \mathsf{J} : \frac{\partial^2 \mathcal{H}}{\partial X^N X^N} = 0$$

since J is an antisymmetric matrix and $\frac{\partial^2 \mathcal{H}}{\partial X^N X^N}$ is symmetric.

2. If the Hamiltonian is independent of time, symplecticity implies conservation of energy $\mathcal{H}$, since

$$\frac{d\mathcal{H}}{dt} = \left[\frac{\partial \mathcal{H}}{\partial X^N} \right]^T \cdot \dot{X}^N = \left[\frac{\partial \mathcal{H}}{\partial X^N} \right]^T \cdot \mathsf{J} \cdot \frac{\partial \mathcal{H}}{\partial X^N} = 0,$$

again using the antisymmetry of J.

3. If the Hamiltonian is invariant under time reversal (i.e., even in momenta), then symplecticity implies time-reversibility.
   Time reversal means reversing the momenta, which will be denoted by an operator $\mathcal{T}$. Time reversal symmetry means that

   $$\mathcal{T}e^{\mathcal{L}t}\mathcal{T} = \left[e^{\mathcal{L}t}\right]^{-1} = e^{-\mathcal{L}t}.$$

   The infinitesimal-t version of this is

   $$\mathcal{T}\mathcal{L}\mathcal{T} = -\mathcal{L}$$

   When acting on a phase space point $X^N = (R^N, P^N)$, one may also write

   $$\mathcal{T}X^N = \mathsf{T} \cdot X^N,$$

   where the symmetric matrix

   $$\mathsf{T} = \begin{pmatrix} \mathbf{1} & \mathsf{0} \\ \mathsf{0} & -\mathsf{1} \end{pmatrix}.$$

   was defined. Similarly, for derivative one has

   $$\mathcal{T}\frac{\partial}{\partial X^N} = \mathsf{T} \cdot \frac{\partial}{\partial X^N},$$

   i.e.

   $$\mathcal{T}\frac{\partial}{\partial X^N}A = \mathsf{T} \cdot \frac{\partial}{\partial X^N}\mathcal{T}A,$$

   One easily shows that the T matrix and the symplectic matrix anti-commute

   $$\mathsf{T} \cdot \mathsf{J} = -\mathsf{J} \cdot \mathsf{T}.$$

   This property, when combined with a $\mathcal{T}$-invariant Hamiltonian, implies time-reversal, since

$$\begin{aligned}
\mathcal{TLT} &= \mathcal{T}\left(\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\frac{\partial}{\partial X^N}\mathcal{T}\\
&= \mathcal{T}\left(\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathcal{T}\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= \mathcal{T}\mathcal{T}\left(\mathsf{J}\cdot\mathsf{T}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= \left(\mathsf{J}\cdot\mathsf{T}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= -\left(\mathsf{T}\cdot\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= -\left(\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathsf{T}^T\cdot\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= -\left(\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\frac{\partial}{\partial X^N}\\
&= -\mathcal{L} \qquad\qquad\qquad\qquad\qquad\qquad \text{q.e.d.}
\end{aligned}$$

- The idea is now to construct symplectic integrators, such that (by construction), they conserve phase space volume, conserve momentum and linear momentum when applicable and are time-reversible.

- Remember that the formal solution of the equations of motions in equation (4.25) is

  $$X^N(t) = e^{\mathcal{L}t}X^N(0),$$

  but this exponent can only be evaluated explicitly for exceptional forms of $\mathcal{L}$, such as for

  - free particles (e.g. an ideal gas),
  - systems with harmonic forces (e.g. particles harmonically bound on a lattice), and
  - free rigid bodies.

- Thus, for a Hamiltonian without the potential in (4.26), which is just the kinetic energy

  $$K = \frac{P^N\cdot P^N}{2m},$$

one has

$$\mathcal{L}_K = \left(\mathsf{J}\cdot\frac{\partial K}{\partial X^N}\right)^T\cdot\frac{\partial}{\partial X^N} \quad = \frac{P^N}{m}\cdot\frac{\partial}{\partial R^N},$$

the exponentiated Liouville operator $e^{\mathcal{L}_K t}$ corresponds to free motion:

$$e^{\mathcal{L}_K t}A(R^N,P^N) = A\left(R^N + \frac{P^N}{m}t,\ P^N\right).$$

We call this a free propagation over a time t.

- For a Liouville operator composed of just the potential energy,

$$\mathcal{L}_U = \left(\mathsf{J}\cdot\frac{\partial U}{\partial X^N}\right)^T\cdot\frac{\partial}{\partial X^N} \quad = F^N\cdot\frac{\partial}{\partial P^N}$$

one can also evaluate the exponential

$$e^{\mathcal{L}_U t}A(R^N,P^N) = A\left(R^N, P^N + F^N t\right).$$

We will call this a force propagation over a time t.

- For the composition of the two "propagators", we operate from the left side towards the right. For a one-dimensional system this looks like

$$\begin{aligned}
e^{t_1\mathcal{L}_K}e^{t_2\mathcal{L}_U}A(r,p) &= e^{t_1\frac{p}{m}\partial_r}e^{t_2F(r)\partial_p}A(r,p)\\
&= e^{t_2F(r+pt_1/m)\partial_p)}A(r+t_1p/m,p)\\
&= A\big(r+t_1p/m+t_1t_2F(r+t_1p/m)/m, p+t_2F(r+t_1p/m)\big)
\end{aligned}$$

This can be viewed as a two-step process where first the position is evolved forward in time to a new position $r(t_1) = r + t_1p/m$ using the current momentum. The force $F(t_1) = F(r(t_1))$ is evaluated at that new position at $r(t_1)$, and this force then propagates the momentum p forward to time t_2. Notice that it also updates the position $r(t_1)$ to $r(t_1) + t_1t_2F(t_1)/m$ since $r(t_1)$ also depends on p. We will see how this type of concatention of propagators can lead to the velocity (or momentum) Verlet scheme.

- Although we can solve the exponent of the operators $\mathcal{L}_K$ and $\mathcal{L}_U$ separately, we cannot exponentiate their sum, because

$$e^{X+Y} \neq e^X e^Y$$

when X and Y are non-commuting operators. The operators $\mathcal{L}_K$ and $\mathcal{L}_U$ do not commute since

$$\begin{aligned}
[\mathcal{L}_K, \mathcal{L}_U] &= \mathcal{L}_K \mathcal{L}_U - \mathcal{L}_U \mathcal{L}_K \\
&= P^N \cdot \frac{\partial}{\partial R^N} F^N \cdot \frac{\partial}{\partial P^N} - F^N \cdot \frac{\partial}{\partial P^N} P^N \cdot \frac{\partial}{\partial R^N} \\
&= P^N \cdot \left(\frac{\partial F^N}{\partial R^N} \right) \cdot \frac{\partial}{\partial P^N} - F^N \cdot \frac{\partial}{\partial R^N} \\
&\neq 0.
\end{aligned}$$

4.2.1 The Baker-Campbell Hausdorff (BCH) formula

The BCH formula for non-commuting operators X and Y is:

$$e^{sX} e^{sY} = e^{sX + sY + \frac{s^2}{2}[X,Y] + \frac{s^3}{12}([X,[X,Y]] + [Y,[Y,X]]) + \text{further repeated commutators of } X \text{ and } Y}. \tag{4.28}$$

We will see that the BCH formula can be used to systematically derive integrators of arbitrary order. The proof of the BCH formula is an interesting exercise in operator algebra that can be done in a number of different ways, including using Lie algebra. We will show one conceptually simple though fairly tedious approach to establishing this relation.

To start, we wish to find an operator $G(s) = sG_1 + s^2 G_2 + s^3 G_3 + \ldots$ that obeys the relation for non-commuting operators X and Y,

$$e^{sX} e^{sY} = e^{G(s)} = e^{sG_1 + s^2 G_2 + s^3 G_3 + \ldots}. \tag{4.29}$$

We will evaluate what the relation must be between the G_i and the X and Y operators if Eq. (4.29) is to hold by expanding the exponential operators in a power series in s and comparing terms of the same order in s.

- Note that the inverse of the operators $\exp\{sX\} \exp\{sY\}$ is $\exp\{-sY\} \exp\{-sX\}$ so that

$$\left(e^{-sY} e^{-sX}\right) e^{sX} e^{sY} = e^{-sY} e^{sY} = 1.$$

- Now consider

$$\begin{aligned}
\left(e^{-sY} e^{-sX}\right) \frac{d}{ds} \left(e^{sX} e^{sY}\right) &= e^{-G(s)} \frac{d}{ds} e^{G(s)} \\
&= e^{-sY} e^{-sX} X e^{sX} e^{sY} + e^{-sY} e^{-sX} e^{sX} Y e^{sY} \\
&= e^{-sY} X e^{sY} + Y = F(s) + Y.
\end{aligned} \tag{4.30}$$

- By writing $F(s) = \exp\{-sY\}X\exp\{sY\} = \sum_{n=0}^{\infty}\frac{s^n}{n!}F_n$ and taking the derivative with respect to s, we obtain

$$\begin{aligned}\frac{dF(s)}{ds} &= F(s)Y - YF(s) = [F(s), Y] = \sum_{n=0}^{\infty}\frac{s^{n-1}}{(n-1)!}F_n \\ &= \sum_{n=0}^{\infty}\frac{s^n}{n!}[F_n, Y] = \sum_{n=0}^{\infty}\frac{s^n}{n!}F_{n+1},\end{aligned}$$

and hence $F_0 = X$ and $F_1 = [X, Y]$, $F_2 = [[X, Y], Y]$ and $F_{n+1} = [F_n, Y]$ which has $n + 1$ commutators.

- Note that this established the useful relation

$$e^{-sB}Ae^{sB} = A + s[A, B] + \frac{s^2}{2!}[[A, B], B] + \ldots \tag{4.31}$$

It follows that Eq. (4.30) can be written as the power series,

$$e^{-G(s)}\frac{d}{ds}e^{G(s)} = X + Y + s[X, Y] + \frac{s^2}{2!}[[X, Y], Y] + \ldots \tag{4.32}$$

- Consider now the derivative of $\exp\{G(s)\}$ with respect to s:

$$\begin{aligned}\frac{d}{ds}e^{G(s)} &= \frac{d}{ds}\sum_{\ell=0}^{\infty}\frac{1}{\ell!}G(s)^\ell \\ &= G' + \frac{GG' + G'G}{2!} + \frac{G'G^2 + GG'G + G^2G'}{3!} + \ldots \\ &= \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\frac{1}{(n+m+1)!}G^nG'G^m,\end{aligned}$$

where we have suppressed the s-dependence of $G(s)$ for notational convenience.

- A nice trick is to notice that

$$\int_0^1 dy\ (1-y)^n y^m = \frac{n!m!}{(n+m+1)!},$$

so that

$$\begin{aligned}\frac{d}{ds}e^{G(s)} &= \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\frac{1}{n!m!}\int_0^1 dy\ (1-y)^nG^nG'G^my^m \\ &= \int_0^1 dy\ e^{(1-y)G}G'e^{yG} = e^G\int_0^1 dy\ e^{-yG}G'e^{yG},\end{aligned} \tag{4.33}$$

a perhaps not so obvious identity.

- We now multiply the relation by $\exp\{-G\}$ and expand the integrand using the relation Eq. (4.31) with $B = G$ and $A = G'$ to get

$$\begin{aligned} e^{-G}\frac{d}{ds}e^{G} &= \int_0^1 dy\,\left(G' + y[G', G] + \frac{y^2}{2!}[[G', G]G] + \dots\right) \\ &= G' + \frac{1}{2!}[G', G] + \frac{1}{3!}[[G', G], G] + \dots \end{aligned} \tag{4.34}$$

This must be equal to Eq. (4.32), which is a power series in s. Inserting the expansions of $G(s)$ and $G'(s)$, and using the equality of the expressions in Eqs. (4.29) and (4.34),

$$\begin{aligned} G(s) &= sG_1 + s^2G_2 + s^3G_3 + \dots \\ G'(s) &= G_1 + 2sG_2 + 3s^2G_3 \dots \end{aligned}$$

we find that

$$X + Y + s[X, Y] + \frac{s^2}{2!}[[X, Y], Y] + \dots = G_1 + 2sG_2 + s^2\left(3G_3 - \frac{1}{2}[G_1, G_2]\right) + \dots \tag{4.35}$$

Equating like powers of s gives

$$\begin{aligned} G_1 &= X + Y \\ G_2 &= \frac{1}{2}[X, Y] \qquad (4.36) \\ G_3 &= \frac{1}{6}[G_1, G_2] + \frac{1}{6}[[X, Y], Y] = \frac{1}{12}\left([X, [X, Y]] + [Y, [Y, X]]\right) \\ &\vdots \qquad (4.37) \end{aligned}$$

This completes the derivation.

4.2.2 Derivation of symplectic integration schemes

We now use the BCH formula to derive integrators. Recall the formula is:

$$e^X e^Y = e^{X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\text{further repeated commutators of } X \text{ and } Y}. \tag{4.38}$$

In the current context this is useful if X and Y are small, so that repeated commutators become successively smaller. This smallness can be achieved by taking $M = t/\Delta t$ small time steps, as follows:

$$e^{\mathcal{L}t} = e^{\mathcal{L}\Delta t(t/\Delta t)} = \left[e^{\mathcal{L}\Delta t}\right]^{t/\Delta t} = \left[e^{\mathcal{L}_K\Delta t+\mathcal{L}_U\Delta t}\right]^{M}. \tag{4.39}$$

- Now let $X = \mathcal{L}_U\Delta t$ and $Y = \mathcal{L}_K\Delta t$, then $[X,Y] = \mathcal{O}(\Delta t^2)$, $[X,[X,Y]] = \mathcal{O}(\Delta t^3)$ etc.
- Denote any repeated commutators by $\ldots$, then the BCH formula gives

$$\begin{aligned}
e^X e^Y e^{-\frac{1}{2}[X,Y]} &= e^{X+Y+\frac{1}{2}[X,Y]+\ldots} e^{-\frac{1}{2}[X,Y]} \\
&= e^{X+Y+\frac{1}{2}[X,Y]-\frac{1}{2}[X,Y]+\frac{1}{2}[X+Y+\frac{1}{2}[X,Y],-\frac{1}{2}[X,Y]]+\ldots} \\
&= e^{X+Y+\frac{1}{2}[X+Y+\frac{1}{2}[X,Y],-\frac{1}{2}[X,Y]]+\ldots} \\
&= e^{X+Y+\ldots}
\end{aligned}$$

- Since $\ldots = \mathcal{O}(\Delta t^3)$ and $[X,Y] = \mathcal{O}(\Delta t^2)$, we see that

$$e^{\mathcal{L}\Delta t} = e^{\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t} + \mathcal{O}(\Delta t^2) \tag{4.40}$$

- Using this in Eq. (4.39) would give a scheme in which alternating force and free propagation is performed over small time steps Δt.
- The accumulated error of this scheme is $\mathcal{O}(\Delta t)$, but the Verlet scheme was $\mathcal{O}(\Delta t^2)$.
- The missing ingredient is time reversal. Note that while the true propagation satisfies time reversal invariance:

$$\mathcal{T} e^{\mathcal{L}_U\Delta t+\mathcal{L}_K\Delta t}\mathcal{T} = \left[e^{\mathcal{L}_U\Delta t+\mathcal{L}_K\Delta t}\right]^{-1}.$$

  Due to the symplecticity of the $\mathcal{L}_U\Delta t$ and $\mathcal{L}_K\Delta t$ operators separately, the approximate evolution has

$$\mathcal{T} e^{\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t}\mathcal{T} = \mathcal{T} e^{\mathcal{L}_U\Delta t}\mathcal{T}\mathcal{T} e^{\mathcal{L}_K\Delta t}\mathcal{T} = e^{-\mathcal{L}_U\Delta t} e^{-\mathcal{L}_K\Delta t},$$

  which is *not* equal to the inverse

$$\left[e^{\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t}\right]^{-1} = e^{-\mathcal{L}_K\Delta t} e^{-\mathcal{L}_U\Delta t}.$$

- Time reversal can be restored by taking

$$e^{\mathcal{L}_U\Delta t+\mathcal{L}_K\Delta t} = e^{\mathcal{L}_U\Delta t/2} e^{\mathcal{L}_K\Delta t} e^{\mathcal{L}_U\Delta t/2} + \ldots, \tag{4.41}$$

  since

$$\begin{aligned}
\mathcal{T} e^{\mathcal{L}_U\Delta t/2} e^{\mathcal{L}_K\Delta t} e^{\mathcal{L}_U\Delta t/2}\mathcal{T} &= \mathcal{T} e^{\mathcal{L}_U\Delta t/2}\mathcal{T}\mathcal{T} e^{\mathcal{L}_K\Delta t}\mathcal{T}\mathcal{T} e^{\mathcal{L}_U\Delta t/2}\mathcal{T} \\
&= e^{-\mathcal{L}_U\Delta t/2} e^{-\mathcal{L}_K\Delta t} e^{-\mathcal{L}_U\Delta t/2} \\
&= \left[e^{\mathcal{L}_U\Delta t/2} e^{\mathcal{L}_K\Delta t} e^{\mathcal{L}_U\Delta t/2}\right]^{-1}
\end{aligned}$$

- Equation (4.41) is actually of higher order than equation (4.40), as one sees from applying the BCH formula

$$
\begin{aligned}
e^{\mathcal{L}_U \Delta t + \mathcal{L}_K \Delta t} &= e^{\mathcal{L}_U \Delta t/2 + \mathcal{L}_K \Delta t + \mathcal{L}_U \Delta t/2} \\
&= e^{\mathcal{L}_U \Delta t/2 + \mathcal{L}_K \Delta t} e^{-\frac{1}{2}[\mathcal{L}_U \Delta t/2 + \mathcal{L}_K \Delta t, \mathcal{L}_U \Delta t/2] + \cdots} e^{\mathcal{L}_U \Delta t/2} \\
&= e^{\mathcal{L}_U \Delta t/2 + \mathcal{L}_K \Delta t} e^{-\frac{1}{4}[\mathcal{L}_K \Delta t, \mathcal{L}_U \Delta t] + \cdots} e^{\mathcal{L}_U \Delta t/2} \\
&= e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{-\frac{1}{2}[\mathcal{L}_U \Delta t/2, \mathcal{L}_K \Delta t] + \cdots} e^{-\frac{1}{4}[\mathcal{L}_K \Delta t, \mathcal{L}_U \Delta t] + \cdots} e^{\mathcal{L}_U \Delta t/2} \\
&= e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{-\frac{1}{4}[\mathcal{L}_U \Delta t, \mathcal{L}_K \Delta t] + \cdots} e^{-\frac{1}{4}[\mathcal{L}_K \Delta t, \mathcal{L}_U \Delta t] + \cdots} e^{\mathcal{L}_U \Delta t/2} \\
&= e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\cdots} e^{\mathcal{L}_U \Delta t/2}
\end{aligned}
$$

  Remember that $\ldots$ was $\mathcal{O}(\Delta t^3)$, so this scheme has a third order local error and consequently a second order global error.

- The scheme in equation (4.41) is our momentum Verlet scheme that was obtained in equation (4.24). It first performs a half force propagation, a whole free propagation and then another half force propagation. To see this, consider the operation

$$
\begin{aligned}
e^{\Delta t/2\, F \partial_p}\, e^{\Delta t\, p/m \partial_r}\, e^{\Delta t/2\, F(r) \partial_p} \begin{pmatrix} r \\ p \end{pmatrix} &= e^{\Delta t\, p(\Delta t/2)/m\, \partial_r}\, e^{\Delta t/2\, F \partial_{p(\Delta t/2)}} \begin{pmatrix} r \\ p(\Delta t/2) \end{pmatrix} \\
&= e^{\Delta t/2\, F(\Delta t) \partial_{p(\Delta t/2)}} \begin{pmatrix} r(\Delta t) \\ p(\Delta t/2) \end{pmatrix} \\
&= \begin{pmatrix} r(\Delta t) \\ p(\Delta t) \end{pmatrix},
\end{aligned}
$$

  where $F = F(r) = F(0)$ is the force evaluated at position $r(0) = r$,

$$
\begin{aligned}
p(\Delta t/2) &= p + F(0)\Delta t/2 \\
r(\Delta t) &= r + \Delta t/m\; p(\Delta t/2) = r + \Delta t\; p/m + \Delta t^2/2\; F(0)/m \\
p(\Delta t) &= p(\Delta t/2) + \Delta t/2\; F(\Delta t) \\
&= p + \Delta t/2\; (F(0) + F(\Delta t))
\end{aligned}
$$

  and $F(\Delta t) = F(r(\Delta t))$ is the force evaluation at the position $r(\Delta t)$ as in the momentum Verlet [see Eqs. (4.24)].

- The splitting method is more general than what we have just derived. One does not *have* to split up the Hamiltonian into the kinetic and potential part. All that is required is that the separate sub-Hamiltonian can be explicitly exponentiated.

- The following general construction of a splitting scheme is as follows

1. Split the Hamiltonian H up into n partial Hamiltonians $\mathcal{H}_1$, $\mathcal{H}_2$, $\ldots \mathcal{H}_n$:

$$\mathcal{H} = \sum_{j=1}^{n} \mathcal{H}_j.$$

In more advanced splitting schemes, one may in addition define auxiliary Hamiltonians $\mathcal{H}_{j>n}$ which do not enter in $\mathcal{H}$.

2. Associate with each partial Hamiltonian $\mathcal{H}_j$ a partial Liouville operator

$$\mathcal{L}_j = \mathcal{L}_{\mathcal{H}_j} = \left[\mathsf{J} \cdot \frac{\partial \mathcal{H}_j}{\partial X^N}\right]^T \cdot \frac{\partial}{\partial X^N}$$

such that the full Liouvillean is given by

$$\mathcal{L} = \sum_{j=1}^{n} \mathcal{L}_j.$$

3. One splits up the exponentiated Liouvillean in S factors

$$e^{\mathcal{L}\Delta t} = e^{\sum_{j=1}^{n} \mathcal{L}_j \Delta t} \approx \prod_{s=1}^{S} e^{\mathcal{L}_{j_s} \Delta t_s}, \tag{4.42}$$

where the product is taken left-to-right, such that the first factor on the left is $s = 1$ while the last on the right is $s = S$.

4. Since each Liouvillean is multiplied by a total time interval Δt in the original exponent, the separate time intervals for each Liouvillean $\mathcal{L}_{j'}$ have to add up to Δt as well, at least up to the order of the scheme

$$\sum_{\substack{s=1 \\ \text{with } j_s = j'}}^{S} \Delta t_s = \Delta t + \mathcal{O}(\Delta t^{k+1}).$$

for each $j' = 1 \ldots n$.
For auxiliary Hamiltonians $\mathcal{H}_{j>n}$, their combined time steps should be zero up to the order of the scheme:

$$\sum_{\substack{s=1 \\ \text{with } j_s = j'}}^{S} \Delta t_s = 0 + \mathcal{O}(\Delta t^{k+1}).$$

for $j' > n$.

5. One should take $t_{S+1-s} = t_s$ and $j_{S+1-s} = t_s$ in order to have time reversal invariance (we will assume that the $\mathcal{H}_j$ are invariant under time reversal).
6. One uses the BCH formula to adjust the Δt_s further, such that

$$e^{\mathcal{L}\Delta t} = \prod_{s=1}^{P} e^{\mathcal{L}_{j_s}\Delta t_s} + \mathcal{O}(\Delta t^{k+1}) \tag{4.43}$$

which would make this scheme of order k.

- Properties:
  - Symplectic $\Rightarrow$ phase space volume preserving.
  - Given 4., also time reversible. Proof:

$$\begin{aligned}\mathcal{T}\left[\prod_{s=1}^{S} e^{\mathcal{L}_{j_s}\Delta t_s}\right]\mathcal{T} &= \prod_{s=1}^{S}\left[\mathcal{T}e^{\mathcal{L}_{j_s}\Delta t_s}\mathcal{T}\right] = \prod_{s=1}^{S} e^{-\mathcal{L}_{j_s}\Delta t_s} \\ &= \prod_{s=1}^{S}\left[e^{\mathcal{L}_{j_s}\Delta t_s}\right]^{-1} = \left[\prod_{s=S}^{1} e^{\mathcal{L}_{j_s}\Delta t_s}\right]^{-1} = \left[\prod_{s=1}^{S} e^{\mathcal{L}_{j_s}\Delta t_s}\right]^{-1}\end{aligned}$$

  - The scheme is of even order: Reason: the scheme is time reversible, so each error found by applying the BCH formula must also be time-reversible, i.e., each term X in the exponent satisfies $\mathcal{T}X\mathcal{T} = -X$. Thus, the error terms are odd in the partial Liouvilleans. Since each Liouvillean comes with a factor of Δt, the local error terms are odd in Δt.
    The resulting global error is then even in Δt.
  - If the full Hamiltonian conserves a quantity Q, i.e. $\{\mathcal{H}, Q\} = 0$, and if also each partial Hamiltonian $\mathcal{H}_j$ also satisfies $\{\mathcal{H}_j, Q\} = 0$, then the quantity Q is conserved in each step in equation (4.42), and thus exactly conserved in the integration scheme.

4.3 The shadow or pseudo-Hamiltonian

- Energy $\mathcal{H}$ is rarely conserved in integration schemes, even symplectic ones.
- Nonetheless, the energy is almost conserved. We will now see in what sense.
- In the derivation of the splitting schemes, we used that repeated commutators of small-time step Liouvilleans are higher order corrections, so that they may be omitted.

- In fact, one can show that the commutator of two Liouvilleans $\mathcal{L}_{\mathcal{H}_1}$ and $\mathcal{L}_{\mathcal{H}_2}$ associated with two Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$ is again a Liouvillean of another Hamiltonian:

$$\begin{aligned}[\mathcal{L}_{\mathcal{H}_1}, \mathcal{L}_{\mathcal{H}_2}]A &= \mathcal{L}_{\mathcal{H}_1}\mathcal{L}_{\mathcal{H}_2}A - \mathcal{L}_{\mathcal{H}_2}\mathcal{L}_{\mathcal{H}_1}A \\ &= \mathcal{L}_{\mathcal{H}_1}\{A, \mathcal{H}_2\} - \mathcal{L}_{\mathcal{H}_2}\{A, \mathcal{H}_1\} \\ &= \{\{A, \mathcal{H}_2\}, \mathcal{H}_1\} - \{\{A, \mathcal{H}_1\}, \mathcal{H}_2\} \\ &= \{\{A, \mathcal{H}_2\}, \mathcal{H}_1\} + \{\{\mathcal{H}_1, A\}, \mathcal{H}_2\}.\end{aligned}$$

Using the Jacobi identity for Poisson brackets

$$\{\{A, B\}, C\} + \{\{B, C\}, A\} + \{\{C, A\}, B\} = 0,$$

we find

$$[\mathcal{L}_{\mathcal{H}_1}, \mathcal{L}_{\mathcal{H}_2}]A = -\{\{\mathcal{H}_2, \mathcal{H}_1\}, A\} = \{A, \{H_2, H_1\}\}$$

so that

$$[\mathcal{L}_{\mathcal{H}_1}, \mathcal{L}_{\mathcal{H}_2}] = \mathcal{L}_{\{\mathcal{H}_2, \mathcal{H}_1\}}.$$

- Consider now the Verlet splitting scheme, writing for brevity $X = \mathcal{L}_U \Delta t/2$ and $Y = \mathcal{L}_K \Delta t$ and using the BCH formula to one order further than before:

$$\begin{aligned}e^X e^Y e^X &= e^{X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\dots} e^X \\ &= e^{X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+X+\frac{1}{2}[X+Y+\frac{1}{2}[X,Y],X]+\frac{1}{12}[X+Y,[X+Y,X]]+\frac{1}{12}[X,[X,X+Y]]+\dots} \\ &= e^{2X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{2}[Y+\frac{1}{2}[X,Y],X]+\frac{1}{12}[X+Y,[Y,X]]+\frac{1}{12}[X,[X,Y]]+\dots} \\ &= e^{2X+Y+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{2}[\frac{1}{2}[X,Y],X]+\frac{1}{12}[X+Y,[Y,X]]+\frac{1}{12}[X,[X,Y]]+\dots} \\ &= e^{2X+Y+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{4}[[X,Y],X]+\frac{1}{12}[X,[Y,X]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{12}[X,[X,Y]]+\dots} \\ &= e^{2X+Y+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]-\frac{1}{4}[X,[X,Y]]-\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{12}[X,[X,Y]]+\dots} \\ &= e^{2X+Y+\frac{1}{12}[X,[X,Y]]-\frac{1}{4}[X,[X,Y]]+\frac{1}{12}[X,[X,Y]]-\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{12}[Y,[Y,X]]+\dots} \\ &= e^{2X+Y-\frac{1}{6}[X,[X,Y]]+\frac{1}{6}[Y,[Y,X]]+\dots} \end{aligned} \tag{4.44}$$

Re-substituting X and Y, we get

$$\begin{aligned}e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\mathcal{L}_U \Delta t/2} &= e^{\mathcal{L}_{\mathcal{H}}\Delta t-\frac{1}{24}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]\Delta t^3+\frac{1}{12}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]\Delta t^3+\mathcal{O}(\Delta t^5)} \\ &= e^{\left\{\mathcal{L}_{\mathcal{H}}-\frac{1}{24}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]\Delta t^2+\frac{1}{12}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]\Delta t^2+\mathcal{O}(\Delta t^4)\right\}\Delta t}\end{aligned}$$

This is the evolution belonging to the following operator

$$
\begin{aligned}
\mathcal{L}_{\text{shadow}} &= \mathcal{L}_{\mathcal{H}} - \frac{1}{24}[\mathcal{L}_U, [\mathcal{L}_U, \mathcal{L}_K]]\Delta t^2 + \frac{1}{12}[\mathcal{L}_K, [\mathcal{L}_K, \mathcal{L}_U]]\Delta t^2 + \mathcal{O}(\Delta t^4) \\
&= \mathcal{L}_{\mathcal{H}} - \frac{1}{24}[\mathcal{L}_U, \mathcal{L}_{\{K,U\}}]\Delta t^2 + \frac{1}{12}[\mathcal{L}_K, \mathcal{L}_{\{U,K\}}]\Delta t^2 + \mathcal{O}(\Delta t^4) \\
&= \mathcal{L}_{\mathcal{H}} - \frac{1}{24}\mathcal{L}_{\{\{K,U\},U\}}\Delta t^2 + \frac{1}{12}\mathcal{L}_{\{\{U,K\},K\}}\Delta t^2 + \mathcal{O}(\Delta t^4) \\
&= \mathcal{L}_{\mathcal{H}_{\text{pseudo}}},
\end{aligned}
$$

where the pseudo-Hamiltonian or shadow Hamiltonian is

$$
\mathcal{H}_{\text{pseudo}} = \mathcal{H} - \frac{1}{24}\{\{K,U\},U\}\Delta t^2 + \frac{1}{12}\{\{U,K\},K\}\Delta t^2 + \mathcal{O}(\Delta t^4).
$$

If $\mathcal{H}$ is of the form $|P^N|^2/(2m) + U(R^N)$, one has

$$
\{\{K,U\},U\} = \frac{\partial U}{\partial R^N} \cdot \frac{\partial^2 K}{\partial P^N \partial P^N} \cdot \frac{\partial U}{\partial R^N} = \frac{1}{m}\left|\frac{\partial U}{\partial R^N}\right|^2 = \frac{1}{m}|F^N|^2 \tag{4.45}
$$

$$
\{\{U,K\},K\} = \frac{\partial K}{\partial P^N} \cdot \frac{\partial^2 U}{\partial R^N \partial R^N} \cdot \frac{\partial K}{\partial P^N} = \frac{1}{m^2}P^N \cdot \frac{\partial^2 U}{\partial R^N \partial R^N} \cdot P^N, \tag{4.46}
$$

so that

$$
\mathcal{H}_{\text{pseudo}} = \mathcal{H} - \frac{\Delta t^2}{24m}\frac{\partial U}{\partial R^N} \cdot \frac{\partial U}{\partial R^N} + \frac{\Delta t^2}{12m^2}P^N \cdot \frac{\partial^2 U}{\partial R^N \partial R^N} \cdot P^N + \mathcal{O}(\Delta t^4). \tag{4.47}
$$

$\Rightarrow$ <u>*The leading correction to the scheme is of Hamiltonian form.*</u>

- This could be worked out to any order in Δt, and because commutators of Liouvilleans are Liouvilleans themselves, one would always find that the correction terms to the integration scheme can in principle be taken together into a pseudo-Hamiltonian:

$$
e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t/2} e^{\mathcal{L}_U \Delta t/2} = e^{\mathcal{L}_{\mathcal{H}_{\text{pseudo}}} \Delta t}
$$

where

$$
\mathcal{H}_{\text{pseudo}} = \sum_{h=0}^{\infty} \mathcal{H}_h \Delta t^h, \tag{4.48}
$$

with all odd $\mathcal{H}_h$ zero and

$$
\begin{aligned}
\mathcal{H}_0 &= K + U = \mathcal{H} \\
\mathcal{H}_2 &= -\frac{1}{24}\{\{K,U\},U\} + \frac{1}{12}\{\{U,K\},K\}.
\end{aligned}
$$

- For a general splitting scheme (4.43), there is also a pseudo-Hamiltonian, although the expressions for the $\mathcal{H}_h$ differ (except for $\mathcal{H}_0$ which is always $\mathcal{H}$).
  If the scheme is of order k, all $\mathcal{H}_h$ with $0 < h < k$ vanish.
- We conclude that for schemes derived from Hamiltonian splitting schemes, the dynamics in the simulation is that corresponding to the pseudo-Hamiltonian rather than the real Hamiltonian.
- Since the dynamics generated by the splitting scheme is that of the pseudo-Hamiltonian, the value of the pseudo-Hamiltonian is conserved in the dynamics.
- Because the real Hamiltonian and the pseudo-Hamiltonian differ by an amount $\mathcal{O}(\Delta t^k)$, the value of the real Hamiltonian varies in the simulation only up to that order. $\Rightarrow$No energy drift.

4.4 Stability limit of the Verlet scheme for harmonic oscillators

- Despite the theoretical prediction that splitting schemes should be stable, one sees in practice that large time steps still lead to instabilities.
- To understand that, we will apply the splitting method to a harmonic oscillator.
- Hamiltonian of the harmonic oscillator:
  $$\mathcal{H} = \frac{1}{2}p^2 + \frac{1}{2}r^2$$
- Note: mass and frequency have been set to 1.
- Split the Hamiltonian in a kinetic part $K = \frac{1}{2}p^2$ and a potential part $U = \frac{1}{2}r^2$
- Use the Verlet scheme
  $$e^{\mathcal{L}_{\mathcal{H}}\Delta t} = e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\mathcal{L}_U \Delta t/2} + \mathcal{O}(\Delta t^3)$$
- Since $\mathcal{L}_K = (\mathsf{J} \cdot \frac{\partial K}{\partial \Gamma})^T \cdot \frac{\partial}{\partial \Gamma}$, one has
  $$e^{\mathcal{L}_K \Delta t}\mathbf{x} = \begin{pmatrix} r + p\Delta t \\ p \end{pmatrix} = \begin{pmatrix} 1 & \Delta t \\ 0 & 1 \end{pmatrix} \cdot \mathbf{x},$$
  where
  $$\mathbf{x} = \begin{pmatrix} r \\ p \end{pmatrix},$$
  so the operator $e^{\mathcal{L}_K \Delta t}$ acts as a linear operator.

- Similarly, $\mathcal{L}_U = (\mathsf{J}\cdot\frac{\partial U}{\partial\Gamma})^T\cdot\frac{\partial}{\partial\Gamma}$, and

$$e^{\frac{1}{2}\mathcal{L}_U\Delta t}\mathbf{x} = \begin{pmatrix} r \\ p-\frac{1}{2}r\Delta t\end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -\frac{1}{2}\Delta t & 1\end{pmatrix}\cdot\mathbf{x}.$$

- Combining these linear operators in a single Verlet step gives

$$e^{\mathcal{L}_U\Delta t/2}e^{\mathcal{L}_K\Delta t}e^{\mathcal{L}_U\Delta t/2}\mathbf{x} = \begin{pmatrix} 1-\frac{1}{2}\Delta t^2 & \Delta t \\ -\Delta t(1-\frac{1}{4}\Delta t^2) & 1-\frac{1}{2}\Delta t^2\end{pmatrix}\cdot\mathbf{x}. \tag{4.49}$$

- We saw above that a splitting method conserves a pseudo-Hamiltonian, which is composed of the original Hamiltonian plus repeated Poisson brackets of the partial Hamiltonians.

- To leading order, we had

$$\mathcal{H}_{\text{pseudo}} = \mathcal{H} - \frac{1}{24}\{\{K,U\},U\}\Delta t^2 + \frac{1}{12}\{\{U,K\},K\}\Delta t^2 + \dots$$

- Since $\{K,U\} = -pr$, one finds

$$\{\{K,U\},U\} = r^2$$
$$\{\{U,K\},K\} = p^2$$

- Thus, the first additional terms in the pseudo-Hamiltonian are of the same form as those in the Hamiltonian itself.

- Since higher order terms are repeated Poisson brackets, these too are of the same forms, so the full pseudo-Hamiltonian can be written as a renormalized harmonic oscillator Hamiltonian:

$$\mathcal{H}_{\text{pseudo}} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2,$$

  where m and ω are a renormalized mass and a renormalized frequency.

- From the leading order terms in the pseudo Hamiltonian, we find

$$\omega = 1 + \frac{\Delta t^2}{24} + \mathcal{O}(\Delta t^4)$$
$$m = 1 - \frac{\Delta t^2}{6} + \mathcal{O}(\Delta t^4)$$

- As long as m and ω^2 are positive quantities, the scheme is stable, since a harmonic oscillator is stable.

- To test whether this is the case, we need to know all the correction terms.
- In this harmonic case, this can be done, as follows:
- We know the general form $\frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2$ of the Hamiltonian, which we write in matrix form

  $$\mathcal{H}_{\text{pseudo}} = \mathbf{x}^T \cdot \mathsf{H} \cdot \mathbf{x}$$

  where

  $$\mathsf{H} = \begin{pmatrix} \frac{1}{2m} & 0 \\ 0 & \frac{1}{2}m\omega^2 \end{pmatrix}.$$

- The resulting Liouvillean is then

  $$\mathcal{L}_{\mathcal{H}_{\text{pseudo}}}\mathbf{x} = \left[\mathsf{J} \cdot \frac{\partial \mathcal{H}_{\text{pseudo}}}{\partial \mathbf{x}}\right]^T \frac{\partial}{\partial \mathbf{x}}\mathbf{x} = \mathsf{J} \cdot \frac{\partial \mathcal{H}_{\text{pseudo}}}{\partial \mathbf{x}} = \underbrace{2\mathsf{J} \cdot \mathsf{H}}_{\equiv \mathsf{L}} \cdot \mathbf{x},$$

  so the linear matrix corresponding to the Liouvillian is given by

  $$\mathsf{L} = \begin{pmatrix} 0 & m\omega^2 \\ -\frac{1}{m} & 0 \end{pmatrix}$$

- The solutions of the equations of motion are determined by $e^{\mathsf{L}\Delta t}$, which is found to be

  $$e^{\mathsf{L}\Delta t} = \begin{pmatrix} \cos(\omega\Delta t) & m\omega \sin(\omega\Delta t) \\ -\frac{1}{m\omega}\sin(\omega\Delta t) & \cos(\omega\Delta t) \end{pmatrix}$$

  This is not a surprising result, since it is just the solution of the classical harmonic oscillator.

- This result should coincide with the form on the right-hand side of equation (4.49).
- We can therefore identify the renormalized frequency and mass in the splitting scheme:

  $$\omega = \frac{1}{\Delta t}\arccos(1 - \frac{1}{2}\Delta t^2) \tag{4.50}$$

  $$m = \frac{\Delta t}{\omega \sin(\omega\Delta t)} \tag{4.51}$$

- Note that the arccos gives a real result for $\Delta t \leq 2$.
- For larger Δt, the arccos becomes imaginary, indicating that the scheme has become unstable.

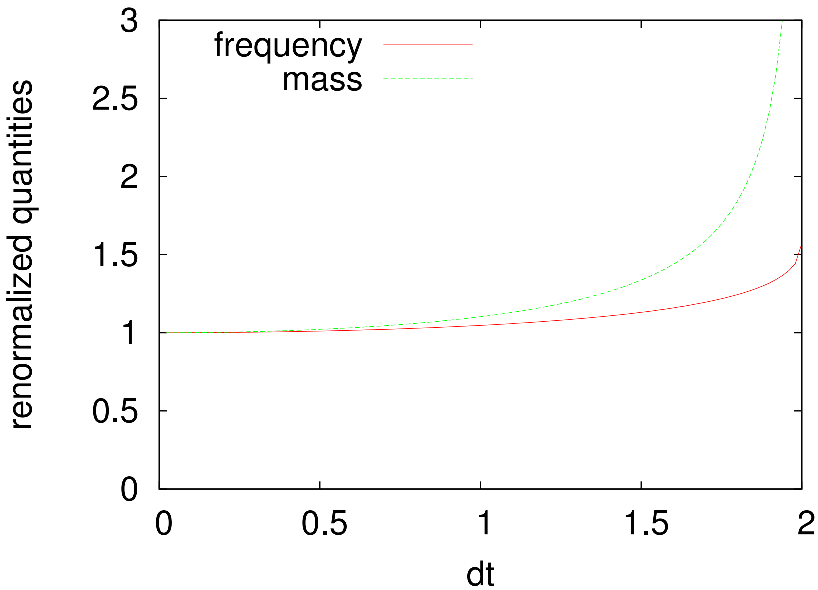


Figure 4.1: The way the instability limit is approached when using the Verlet splitting scheme on the harmonic oscillator. Plotted are the renormalized frequency ω and mass m as a function of Δt. The unnormalized values were 1.

- The way the instability limit is approached is illustrated in figure 4.1, where ω and m are plotted as a function of Δt.
- We see that while the renormalized frequency remains finite up to the limit $\Delta t = 2$, the renormalized mass goes to infinity.
- This divergence shows that the pseudo Hamiltonian is not bounded.
- Only a bounded pseudo-Hamiltonian guarantees a stable algorithm.
- So an instability for large time steps arises even for the simple case of an harmonic oscillator
- The instability arises from an unbounded, diverging pseudo-Hamiltonian.
- Why could the pseudo-Hamiltonian diverge in the first place?
- Consider equation (4.48) again, which gives the pseudo-Hamiltonian as a power series in Δt.
- Generally, power series converge only if $\Delta t < \Delta t^*$, where Δt^* is the radius of convergence.

- For the harmonic oscillator, the radius of convergence was clearly $\Delta t^* = 2$.
- Also for general system, one expects a radius of convergence, i.e., a time step beyond which the pseudo-Hamiltonian becomes unbounded and the simulation becomes unstable.

4.5 More accurate splitting schemes

- Higher order schemes give better accuracy, but at the price of performing more force computations.
- Higher order schemes are very important in contexts such as astrophysics, where accurate trajectories matter.
- For MD, depending on the level of accuracy required, higher order schemes can also be advantageous.
- Higher order schemes may be devised by
  - taking time points which are not evenly spaced,
  - incorporating leading order correction terms in the pseudo-Hamiltonian
  - incorporating more time points,
  - or a combination of the above.

  All but the first option lead to more force computations per unit of physical time, which decreases the efficiency.
- We will restrict ourselves to symmetric splitting schemes, to ensure time-reversibility.
- To facilitate many of the derivations, we restate the symmetrized BCH formula of equation (4.44)

$$e^X e^Y e^X = e^{2X+Y-\frac{1}{6}[X,[X,Y]]+\frac{1}{6}[Y,[Y,X]]+\text{fifth repeated } X,Y \text{ commutators}}. \tag{4.52}$$

4.5.1 Optimized schemes

- Given the same Hamiltonian split-up

$$\mathcal{H} = K + U,$$
$$\mathcal{L} = \mathcal{L}_K + \mathcal{L}_U,$$

  let us now explore a five-fold split up

$$e^{\mathcal{L}\Delta t} \approx e^{\eta\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t/2} e^{(1-2\eta)\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t/2} e^{\eta\mathcal{L}_U\Delta t}. \tag{4.53}$$

- Note that this is a case of uneven time-intervals.
- Work out the inner three exponentials using equation (4.52)

$$
\begin{aligned}
& e^{\eta\mathcal{L}_U\Delta t}e^{\mathcal{L}_K\Delta t/2}e^{(1-2\eta)\mathcal{L}_U\Delta t}e^{\mathcal{L}_K\Delta t/2}e^{\eta\mathcal{L}_U\Delta t} \\
&= e^{\eta\mathcal{L}_U\Delta t}e^{\mathcal{L}_K\Delta t+(1-2\eta)\mathcal{L}_U\Delta t-\frac{(1-2\eta)\Delta t^3}{24}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\frac{(1-2\eta)^2\Delta t^3}{12}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]+\mathcal{O}(\Delta t^5)}e^{\eta\mathcal{L}_U\Delta t} \\
&= \exp\Bigg\{\mathcal{L}_K\Delta t+\mathcal{L}_U\Delta t-\frac{(1-2\eta)\Delta t^3}{24}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\frac{(1-2\eta)^2\Delta t^3}{12}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]] \\
&\qquad -\frac{\eta^2\Delta t^3}{6}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]+\frac{\eta\Delta t^3}{6}[\mathcal{L}_K+(1-2\eta)\mathcal{L}_U,[\mathcal{L}_K,\mathcal{L}_U]]+\mathcal{O}(\Delta t^5)\Bigg\} \\
&= e^{\mathcal{L}_\mathcal{H}\Delta t+\Delta t^3\left(\frac{6\eta-1}{24}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\frac{1-6\eta+6\eta^2}{12}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]\right)+\mathcal{O}(\Delta t^5)} \\
&= e^{\mathcal{L}_\mathcal{H}\Delta t+\Delta t^3(\nu_1[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\nu_2[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]])+\mathcal{O}(\Delta t^5)}
\end{aligned}
$$

  where

$$
\begin{aligned}
\nu_1 &= \frac{6\eta-1}{24} \\
\nu_2 &= \frac{1-6\eta+6\eta^2}{12}
\end{aligned}
$$

- If both ν_1 and ν_2 were zero, this would give a fourth order scheme.
  However, this is not possible here: we have one parameter and two prefactors to set to zero.
- Alternatively, one could make the error "as small as possible", e.g. by minimizing $\nu_1^2+\nu_2^2$. This gives

$$
\eta = 0.1931833275037836\ldots \tag{4.54}
$$

- The scheme in equation (4.53) that uses this value of η is called the Higher-order Optimized Advanced scheme of second order, or HOA2 for short.
- In general, optimized schemes are based on minimizing the formal error, but this cannot guarantee that the actual error is small: Numerical tests are necessary.
- The HOA2 scheme requires two force computations:

$$
\underbrace{e^{\eta\mathcal{L}_U\Delta t}}_{\text{from previous step}}\quad e^{\mathcal{L}_K\Delta t/2}\quad \underbrace{e^{(1-2\eta)\mathcal{L}_U\Delta t}}_{\text{1st force computation}}\quad e^{\mathcal{L}_K\Delta t/2}\quad \underbrace{e^{\eta\mathcal{L}_U\Delta t}}_{\text{2nd force computation,}} \tag{4.55}
$$

  whereas the Verlet scheme requires just one.

- Thus, to compare accuracies at fixed numerical cost, the time step should be taken twice as large in the HOA2 scheme as in the Verlet scheme.

- The HOA2 scheme was tested on a model of water (TIP4P) [Van Zon, Omelyan and Schofield, J. Chem. Phys **128**, 136102 (2008)], with the following results:

  - As long as it is stable, the HOA2 scheme leads to smaller fluctuations in the total energy than the Verlet scheme at the same computational cost.
  - In the water simulation, the HOA2 scheme becomes unstable for smaller time steps than the Verlet scheme.
  - The superior stability of the Verlet scheme means that it is the method of choice for quick and dirty simulations of water with an accuracy less than approximately 1.5% (as measured by the energy fluctuations).
  - For more accurate simulations, the HOA2 is more efficient, by about 50%, until the HOA2 scheme becomes unstable.

- The higher instability of HOA2 at large time steps, is due to the uneven time-steps that are taken.

- The average time step determines the computational cost, but the largest of the time steps determines the stability.

- Using uneven time steps instead of even time steps (at fixed computational cost) therefore increases some of the time intervals and decreases other.

- $\Rightarrow$ uneven time steps become unstable for smaller time steps than even time step variants.

4.5.2 Higher order schemes from more elaborate splittings

- While using the HOA2 scheme is beneficial, this can only be assessed after numerical tests.

- True higher-order schemes are a bit better in that respect: one knows that at least for small enough Δt, they are more efficient.

- The simplest way to get a higher order scheme is to concatenate lower order schemes.

- To understand this, note that if we have a k-th order scheme $S_k(\Delta t)$ approximating $S(\Delta t) = e^{\mathcal{L}\Delta}$ up to $\mathcal{O}(\Delta t^{k+1})$, i.e., if

$$S_k(\Delta t) = S(\Delta t) + \Delta t^{k+1}\delta S + \mathcal{O}(\Delta t^{k+3})$$

then

$$S_k(\Delta s)S_k(\Delta t - 2\Delta s)S_k(\Delta s) \tag{4.56}$$

$$= S(\Delta t) + \left[2\Delta s^{k+1} + (\Delta t - 2\Delta s)^{k+1}\right]\delta S + \mathcal{O}(\Delta t^{k+3}) \tag{4.57}$$

The leading order term can be eliminated by choosing

$$2\Delta s^{k+1} = -(\Delta t - 2\Delta s)^{k+1}, \tag{4.58}$$

which, if k is even, can be solved and gives

$$\Delta s = \frac{\Delta t}{2 - 2^{1/(k+1)}}. \tag{4.59}$$

- When $S_k = S_2$ is given by the second Verlet scheme, the corresponding fourth order scheme becomes

$$e^{\mathcal{L}\Delta t} \approx e^{\mathcal{L}_U \Delta s/2} e^{\mathcal{L}_K \Delta s} e^{\mathcal{L}_U \Delta s/2} e^{\mathcal{L}_U (\Delta t/2 - \Delta s)} e^{\mathcal{L}_K (\Delta t - 2\Delta s)} e^{\mathcal{L}_U (\Delta t/2 - \Delta s)} e^{\mathcal{L}_U \Delta s/2} e^{\mathcal{L}_K \Delta s} e^{\mathcal{L}_U \Delta s/2}$$
$$= e^{\mathcal{L}_U \Delta s/2} e^{\mathcal{L}_K \Delta s} e^{\mathcal{L}_U (\Delta t - \Delta s)/2} e^{\mathcal{L}_K (\Delta t - 2\Delta s)} e^{\mathcal{L}_U (\Delta t - \Delta s)/2} e^{\mathcal{L}_K \Delta s} e^{\mathcal{L}_U \Delta s/2} \tag{4.60}$$

  This is called the fourth order Forest-Ruth integration scheme (FR4). Note that it has seven parts and requires three force evaluations per time step.

- Note that $\Delta s > \Delta t/2$, so that $\Delta t - 2\Delta s < 0$.

- It therefore requires to take a negative time step:
  This tends to lead to instabilities.

- One can prove that order k splitting schemes using a two-operator split up (such as $\mathcal{L}_U$ and $\mathcal{L}_K$) must have at least one negative time step if $k > 2$.

- The negative steps thus seem unavoidable.

- One can minimize these however, by allowing more general splitting schemes than those constructed from equation (4.56), i.e., using the general form in equation (4.42).

- This gives more parameters, allowing one to combine this with the higher-order nature with optimization, i.e. minimizing the leading error terms (cf. the HOA2 scheme).

- A good fourth order scheme of this type is called EFRL4 (Extended Forest-Ruth-like Fourth order scheme) and looks like this:

$$e^{\mathcal{L}\Delta t} = e^{\mathcal{L}_U \xi \Delta t} e^{\mathcal{L}_K (\frac{1}{2} - \lambda)\Delta t} e^{\mathcal{L}_U \chi \Delta t} e^{\mathcal{L}_K \lambda \Delta t} e^{\mathcal{L}_U (1 - 2\chi - 2\xi)\Delta t} e^{\mathcal{L}_K \lambda \Delta t} e^{\mathcal{L}_U \chi \Delta t} e^{\mathcal{L}_K (\frac{1}{2} - \lambda)\Delta t} e^{\mathcal{L}_U \xi \Delta t} \tag{4.61}$$
$$+ \mathcal{O}(\Delta t^5),$$

where

$$\xi = 0.3281827559886160$$
$$\lambda = 0.6563655119772320$$
$$\chi = -0.09372690852966102$$

Even though this requires four force evaluations for each time step, it is more efficient than the FR4 scheme due to a much smaller leading order error.

4.5.3 Higher order schemes using gradients

- Gradients are, in this context, derivatives and higher-order derivatives of the potential.
- Using gradients as auxiliary Hamiltonians, one can reduce the order of a scheme
- The simplest can be derived by considering once more the five-fold splitting scheme, before optimization:

$$\begin{aligned}
e^{\eta\mathcal{L}_U\Delta t}e^{\mathcal{L}_K\Delta t/2}e^{(1-2\eta)\mathcal{L}_U\Delta t}e^{\mathcal{L}_K\Delta t/2}e^{\eta\mathcal{L}_U\Delta t} &= e^{\mathcal{L}_\mathcal{H}\Delta t+\Delta t^3(\nu_1[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\nu_2[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]])+\mathcal{O}(\Delta t^5)} \\
&= e^{\mathcal{L}_\mathcal{H}\Delta t+\Delta t^3\left(\nu_1\mathcal{L}_{\{\{U,K\},K\}}+\nu_2\mathcal{L}_{\{\{K,U\},U\}}\right)+\mathcal{O}(\Delta t^5)}
\end{aligned}$$

where

$$\nu_1 = \frac{6\eta-1}{24}$$
$$\nu_2 = \frac{1-6\eta+6\eta^2}{12}$$

and let K and U be of the usual form such that (cf. equations (4.45) and (4.46))

$$\begin{aligned}
\{\{K,U\},U\} &= \frac{\partial U}{\partial R^N}\cdot\frac{\partial^2 K}{\partial P^N\partial P^N}\cdot\frac{\partial U}{\partial R^N} = \frac{1}{m}\left|\frac{\partial U}{\partial R^N}\right|^2 = \frac{1}{m}|F^N|^2 \\
\{\{U,K\},K\} &= \frac{\partial K}{\partial P^N}\cdot\frac{\partial^2 U}{\partial R^N\partial R^N}\cdot\frac{\partial K}{\partial P^N} = \frac{1}{m^2}P^N\cdot\frac{\partial^2 U}{\partial R^N\partial R^N}\cdot P^N.
\end{aligned}$$

- The former depends only on R^N, but the latter is more complicated and depends on both R^N and P^N.
- We can eliminate the more complicated term by setting $\nu_1 = 0 \Rightarrow \eta = 1/6$, leaving us with

$$\begin{aligned}
e^{\frac{1}{6}\mathcal{L}_U\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{2}{3}\mathcal{L}_U\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{1}{6}\mathcal{L}_U\Delta t} &= e^{\mathcal{L}_\mathcal{H}\Delta t+\Delta t^3\frac{1}{72m}\mathcal{L}_{|F^N|^2}+\mathcal{O}(\Delta t^5)} \\
&= e^{\left[\mathcal{L}_K+\mathcal{L}_{U+\frac{\Delta t^2}{72m}|F^N|^2}\right]\Delta t+\mathcal{O}(\Delta t^5)}
\end{aligned}$$

- This equation holds for any form of U!
- Thus we may substitute for U the expression

$$\tilde{U} = U - \frac{\Delta t^2}{72m} \left| F^N \right|^2 , \tag{4.62}$$

giving

$$e^{\frac{1}{6}\mathcal{L}_{\tilde{U}}\Delta t} e^{\frac{1}{2}\mathcal{L}_K\Delta t} e^{\frac{2}{3}\mathcal{L}_{\tilde{U}}\Delta t} e^{\frac{1}{2}\mathcal{L}_K\Delta t} e^{\frac{1}{6}\mathcal{L}_{\tilde{U}}\Delta t} = e^{\left[\mathcal{L}_K + \mathcal{L}_{\tilde{U}+\frac{\Delta t^2}{72m}|F^N|^2}\right]\Delta t + \mathcal{O}(\Delta t^5)}$$
$$= e^{[\mathcal{L}_K + \mathcal{L}_U]\Delta t + \mathcal{O}(\Delta t^5)} = e^{\mathcal{L}_{\mathcal{H}}\Delta t + \mathcal{O}(\Delta t^5)}$$

A fourth order integration scheme!

- Note that no negative time steps were needed.
- The scheme in the current form uses an effective potential $\tilde{U}$, which differs from the real potential U by an additional term $\delta U = -\frac{\Delta t^2}{72m} \left| F^N \right|^2$ of order $\mathcal{O}(\Delta t^2)$. To leading order, this term commutes with all factors, so one may also write

$$\begin{aligned} e^{\mathcal{L}_{\mathcal{H}}\Delta t + \mathcal{O}(\Delta t^5)} &= e^{\frac{1}{6}\mathcal{L}_U\Delta t} e^{\frac{1}{2}\mathcal{L}_K\Delta t} e^{\frac{2}{3}\mathcal{L}_U\Delta t + \delta U \Delta t} e^{\frac{1}{2}\mathcal{L}_K\Delta t} e^{\frac{1}{6}\mathcal{L}_U\Delta t} \\ &= e^{\frac{1}{6}\mathcal{L}_U\Delta t} e^{\frac{1}{2}\mathcal{L}_K\Delta t} e^{\frac{2}{3}[\mathcal{L}_U + \frac{3}{2}\delta U]\Delta t} e^{\frac{1}{2}\mathcal{L}_K\Delta t} e^{\frac{1}{6}\mathcal{L}_U\Delta t} \\ &= e^{\frac{1}{6}\mathcal{L}_U\Delta t} e^{\frac{1}{2}\mathcal{L}_K\Delta t} e^{\frac{2}{3}[\mathcal{L}_{\tilde{\tilde{U}}}]\Delta t} e^{\frac{1}{2}\mathcal{L}_K\Delta t} e^{\frac{1}{6}\mathcal{L}_U\Delta t} \end{aligned} \tag{4.63}$$

where the modified potential in the middle step is

$$\tilde{\tilde{U}} = U + \frac{3}{2}\delta U = U - \frac{\Delta t^2}{48m} \left| F^N \right|^2 . \tag{4.64}$$

- Scheme (4.63) is due to Suzuki.
- To summarize: by taking uneven intervals and incorporating the correction terms (using gradients of the potentials), we get a fourth order scheme which does not require negative partial steps and only needs two force evaluations per step.
- Note that to be able to use the modified potentials, the forces have to be well defined, i.e., any cut-off has to be smooth enough.

4.5.4 Multiple time-step algorithms

- Decompose the potential and the corresponding Liouville operator into two parts: one for fast varying forces and the other for the slow varying forces:

$$U = U_{\mathrm{f}} + U_{\mathrm{s}} \tag{4.65}$$

- The fast motion could represent e.g. , intermolecular vibrations while the slowly varying forces might be intermolecular forces.

- The simplest multiple time-step algorithm is then

$$e^{\frac{1}{2}\mathcal{L}_{U_\mathrm{s}}\Delta t}\left(e^{\frac{1}{2}\mathcal{L}_{U_\mathrm{f}}\Delta t/M}e^{\mathcal{L}_K\Delta t/M}e^{\frac{1}{2}\mathcal{L}_{U_\mathrm{f}}\Delta t/M}\right)^M e^{\frac{1}{2}\mathcal{L}_{U_\mathrm{s}}\Delta t} = e^{\mathcal{L}\Delta t+\mathcal{O}(\Delta t^3)}. \tag{4.66}$$

- While this is of second order, like the Verlet scheme, the time step for the fast part of the motion if M times smaller than that of the slow motion.

5

Advanced topics

5.1 Hybrid Monte Carlo

5.1.1 The Method

One drawback of traditional Monte-Carlo simulation methods is that typically the method of generating trial configurations based on a probability $\mathsf{T}(x \to y)$ results in trial configurations y that are highly correlated with the initial configuration x, with only small differences between the configurations.

- As an example, consider a dense liquid system where one could generate trial configurations by randomly selecting one of the particles in the fluid and giving the particle a random displacement.
  - Very inefficient since particles are close to one another on average in a dense fluid, so the trial configuration has a high probability of either overlapping with another particle (hard spheres) or being in the strongly repulsive region of the interaction potential of another particle, resulting in a configuration of high potential energy.
  - Molecular dynamics, in contrast, moves *all* particles in a cooperative fashion, so that the potential energy undergoes only small fluctuations.
  - It is possible to try to move a group or cluster of particles cooperatively using tricks, but this requires some cleverness.
- Can we devise a dynamical procedure of generating a trial configuration in which a large number of degrees of freedom are moved cooperatively in a energetically reasonable fashion?

Suppose we use a dynamical procedure to change a set of coordinates for use as a trial configuration in a Monte-Carlo procedure. See S. Duane, A.D. Kennedy, B.J. Pendleton and D. Roweth, *Phys. Lett. B* **45**, 216 (1987).

- We require a momentum coordinate $\mathbf{p}$ conjugate to each spatial degree of freedom $\mathbf{x}$ we wish to evolve dynamically.

- Suppose the evolution is a one-to-one mapping (i.e. deterministic evolution) of the initial phase point $(\mathbf{x}_0, \mathbf{p}_0)$ to another phase point $(\mathbf{x}_t, \mathbf{p}_t)$

$$g^t(\mathbf{x}_0, \mathbf{p}_0) = (\mathbf{x}_0(t), \mathbf{p}_0(t)) = (\mathbf{x}_t, \mathbf{p}_t). \tag{5.1}$$

- The inverse of this mapping is well-defined, so that

$$g^{-t}(\mathbf{x}_t, \mathbf{p}_t) = (\mathbf{x}_0, \mathbf{p}_0).$$

- Consider using this mapping to define a transition matrix in a Markov process somehow so that the transition matrix is defined using the dynamics, $\mathsf{K}(\mathbf{x}_0 \to \mathbf{x}_t)$.

- We want our transition matrix to be stationary with respect to the target distribution $P(\mathbf{x})$, which requires:

$$\int d\mathbf{x}_0 \, P(\mathbf{x}_0)\mathsf{K}(\mathbf{x}_0 \to \mathbf{x}_t) - \int d\mathbf{x}_t \, P(\mathbf{x}_t)\mathsf{K}(\mathbf{x}_t \to \mathbf{x}_0) = 0. \tag{5.2}$$

- How can we define K? Suppose we draw the conjugate momenta $\mathbf{p}_0$ randomly from a density $\Pi_m(\mathbf{p}_0)$ and then generate the phase point $(\mathbf{x}_t, \mathbf{p}_t)$ according to our mapping Eq. (5.1). Starting from the initial phase point $(\mathbf{x}_0, \mathbf{p}_0)$, the probability of generating the phase point $(\mathbf{x}_t, \mathbf{p}_t)$ by evolving the system using the deterministic dynamics over a time interval t is therefore

$$P_g((\mathbf{x}_0, \mathbf{p}_0) \to (\mathbf{x}_t, \mathbf{p}_t)) = \delta((\mathbf{x}_0(t), \mathbf{p}_0(t)) - (\mathbf{x}_t, \mathbf{p}_t)) = \delta(g^t(\mathbf{x}_0, \mathbf{p}_0) - (\mathbf{x}_t, \mathbf{p}_t)).$$

- The transition probability $\mathsf{K}(\mathbf{x}_0 \to \mathbf{x}_t)$ is therefore

$$\mathsf{K}(\mathbf{x}_0 \to \mathbf{x}_t) = \int d\mathbf{p}_0 d\mathbf{p}_t \, \Pi_m(\mathbf{p}_0) P_g((\mathbf{x}_0, \mathbf{p}_0) \to (\mathbf{x}_t, \mathbf{p}_t)) \, \mathsf{A}((\mathbf{x}_0, \mathbf{p}_0) \to (\mathbf{x}_t, \mathbf{p}_t)), \tag{5.3}$$

  where $\mathsf{A}((\mathbf{x}_0, \mathbf{p}_0) \to (\mathbf{x}_t, \mathbf{p}_t))$ is the acceptance probability for the phase point $(\mathbf{x}_t, \mathbf{p}_t)$ if the initial configuration was $(\mathbf{x}_0, \mathbf{p}_0)$.

- To define this acceptance probability, let $\Pi(\mathbf{x}, \mathbf{p}) = P(\mathbf{x})\Pi_m(\mathbf{p})$ be the probability density for the augmented coordinate $(\mathbf{x}, \mathbf{p})$.

- We then define the acceptance probability to be

$$\mathsf{A}((\mathbf{x}_0, \mathbf{p}_0) \to (\mathbf{x}_t, \mathbf{p}_t)) = \min\left(1, \frac{\Pi(\mathbf{x}_t, \mathbf{p}_t)}{\Pi(\mathbf{x}_0, \mathbf{p}_0)}\right)$$

- Claim: The transition probability Eq. (5.3) satisfies the stationarity condition Eq. (5.2) provided

  1. The dynamics is symplectic, so that the mapping is volume-preserving and time-reversible.
  2. The probability density for the conjugate momenta satisfies $\Pi_m(-\mathbf{p}) = \Pi_m(\mathcal{T}\mathbf{p}) = \Pi_m(\mathbf{p})$, where $\mathcal{T}$ is the momentum inversion operator $\mathcal{T}f(\mathbf{p}) = f(-\mathbf{p})$.

Proof. To show Eq. (5.2) is satisfied, we must compute $\mathsf{K}(\mathbf{x}_t \to \mathbf{x}_0)$ under the dynamical procedure. Suppose the dynamical mapping is symplectic and hence reversible. The mapping g^t therefore satisfies $g^{-t} = \mathcal{T}g^t\mathcal{T}$ and hence if $g^t(\mathbf{x}_0, \mathbf{p}_0) = (x_0(t), \mathbf{p}_0(t)) = (\mathbf{x}_t, \mathbf{p}_t)$, we have $\mathcal{T}g^t\mathcal{T}(\mathbf{x}_t, \mathbf{p}_t) = (\mathbf{x}_0, \mathbf{p}_0)$ and hence $g^t(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) = (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)$. From the definition of the transition probability, we have

$$\begin{aligned}
\mathsf{K}(\mathbf{x}_t \to \mathbf{x}_0) &= \int d(\mathcal{T}\mathbf{p}_0)d(\mathcal{T}\mathbf{p}_t)\,\Pi_m(\mathcal{T}\mathbf{p}_t)P_g((\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) \to (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)) \\
&\qquad \times \mathsf{A}((\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) \to (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)) \qquad (5.4)\\
&= \int d\mathbf{p}_0 d\mathbf{p}_t\,\Pi_m(\mathbf{p}_t)\delta(g^t(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) - (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0))\mathsf{A}((\mathbf{x}_t, \mathbf{p}_t) \to (\mathbf{x}_0, \mathbf{p}_0))
\end{aligned}$$

since $\Pi_m(\mathcal{T}\mathbf{p}_t) = \Pi_m(\mathbf{p}_t)$, $\Pi(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) = \Pi(\mathbf{x}_t, \mathbf{p}_t)$ and $\Pi(\mathbf{x}_0, \mathcal{T}\mathbf{p}_0) = \Pi(\mathbf{x}_0, \mathbf{p}_0)$ by assumption. Now

$$\begin{aligned}
\int d\mathbf{x}_0\, P(\mathbf{x}_0)\mathsf{K}(\mathbf{x}_0 \to \mathbf{x}_t) &= \int d\mathbf{x}_0 d\mathbf{p}_0 d\mathbf{p}_t\, P(\mathbf{x}_0)\Pi_m(\mathbf{p}_0)\delta(g^t(\mathbf{x}_0, \mathbf{p}_0) - (\mathbf{x}_t, \mathbf{p}_t)) \\
&\qquad \times \min\left(1, \frac{\Pi(\mathbf{x}_t, \mathbf{p}_t)}{\Pi(\mathbf{x}_0, \mathbf{p}_0)}\right) \\
&= \int d\mathbf{x}_0 d\mathbf{p}_0 \min\left(\Pi(\mathbf{x}_0, \mathbf{p}_0), \Pi(g^t(\mathbf{x}_0, \mathbf{p}_0))\right), \qquad (5.5)
\end{aligned}$$

whereas

$$\begin{aligned}
\int d\mathbf{x}_t\, P(\mathbf{x}_t)\mathsf{K}(\mathbf{x}_t \to \mathbf{x}_0) &= \int d\mathbf{x}_t d\mathbf{p}_0 d\mathbf{p}_t\, \Pi(\mathbf{x}_t, \mathbf{p}_t)\delta(g^t(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) - (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)) \\
&\qquad \times \min\left(1, \frac{\Pi(\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)}{\Pi(\mathbf{x}_t, \mathbf{p}_t)}\right) \\
&= \int d\mathbf{x}_t d\mathbf{p}_t \min\left(\Pi(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t), \Pi(g^t(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t))\right) \qquad (5.6)
\end{aligned}$$

Changing the variables of integration from $(\mathbf{x}_t, \mathbf{p}_t)$ to $(\mathbf{x}_0, \mathbf{p}_0) = \mathcal{T} g^t(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t)$ gives

$$\begin{aligned}
\int d\mathbf{x}_t \, P(\mathbf{x}_t)\, \mathsf{K}(\mathbf{x}_t \to \mathbf{x}_0) &= \int d\mathbf{x}_0 d\mathbf{p}_0 \, J((\mathbf{x}_t, \mathcal{T}\mathbf{p}_t); (\mathbf{x}_0, \mathbf{p}_0)) \min\left(\Pi(g^{-t}(\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)), \Pi(\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)\right) \\
&= \int d\mathbf{x}_0 d\mathbf{p}_0 \min\left(\Pi(\mathcal{T} g^t(\mathbf{x}_0, \mathbf{p}_0)), \Pi(\mathbf{x}_0, \mathcal{T}\mathbf{p}_0), \right) \\
&= \int d\mathbf{x}_0 d\mathbf{p}_0 \min\left(\Pi(g^t(\mathbf{x}_0, \mathbf{p}_0)), \Pi(\mathbf{x}_0, \mathbf{p}_0)\right) \qquad (5.7)
\end{aligned}$$

since the Jacobian $J((\mathbf{x}_t, \mathcal{T}\mathbf{p}_t); (\mathbf{x}_0, \mathbf{p}_0))$ of the transformation is unity due to the volume-preserving property of the dynamical evolution. Since Eq. (5.5) and Eq. (5.7) are equal, the equilibrium distribution is stationary under the transition matrix K. $\square$

5.1.2 Application of Hybrid Monte-Carlo

As an example of a useful application of hybrid Monte-Carlo, consider a bead polymer system where the interaction between monomers is determined by a potential of the form

$$U(\mathbf{r}^{(N)}) = \sum_{i=1}^{N} \sum_{j=i+4}^{N} V_{\text{nb}}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=4}^{N} U_{\text{tor}}(\phi_i) + \sum_{i=3}^{N} U_{\text{bend}}(\theta_i) + \sum_{i=2}^{N} U_{\text{bond}}(|\mathbf{r}_i - \mathbf{r}_{i-1}|).$$

In this potential, we have the following contributions:

1. A *bond-stretching potential* U_{bond} that typically is harmonic.

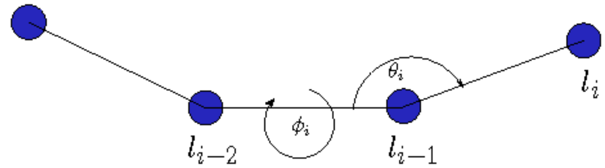
2. A *bond-angle potential* U_{bend}, taken to be harmonic in $\cos\theta_i$, where θ_i is the bond angle defined by

$$l_i l_{i-1} \cos\theta_i = (\mathbf{r}_i - \mathbf{r}_{i-1}) \cdot (\mathbf{r}_{i-2} - \mathbf{r}_{i-1}),$$

   where $l_i = |\mathbf{r}_i - \mathbf{r}_{i-1}|$ is the bond distance between monomers i and $i+1$.

3. A *torsional potential* U_{tor} that depends on the torsional angle ϕ_i, defined to be the angle between the normal vectors to the planes formed by monomers $(i-3, i-2, i-1)$ and $(i-2, i-1, i)$. The torsional angle can be computed readily from the Cartesian positions of monomers $i-4$ through i.

4. A *non-bonded potential* U_{nb} that describes interactions between monomers separated from one another by at least 4 other monomers. This potential typically is of Lennard-Jones form, and can also include electrostatic interactions.



The configuration of the polymer can be specified by either the Cartesian coordinates of all the monomers, $(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, or by a set of *generalized coordinates* $(\mathbf{r}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)$ where $\mathbf{q}_i = (l_i, \theta_i, \phi_i)$.

- The coordinates θ_2, ϕ_3 and ϕ_4 can be defined with respect to fictitious fixed Cartesian coordinates $\mathbf{r}_0$ and $\mathbf{r}_{-1}$ that do not change.

- Cartesian positions can be calculated from the generalized coordinates via a set of locally-defined spherical polar reference frames in which the monomer i is placed along the x-axis at a distance l_i from the origin, chosen to be the Cartesian position of bead $i-1$. Then the Cartesian position of bead i can be written in the lab frame (defined to be the frame of bead 1) as

$$\mathbf{r}_i = \mathbf{r}_1 + \mathsf{T}_2 \cdot \mathbf{l}_2 + \mathsf{T}_2 \cdot \mathsf{T}_3 \cdot \mathbf{l}_3 + \mathsf{T}_2 \cdot \mathsf{T}_3 \cdot \mathsf{T}_4 \cdot \mathbf{l}_4 + \cdots + \mathsf{T}_2 \cdot \mathsf{T}_3 \cdots \mathsf{T}_i \cdot \mathbf{l}_i, \tag{5.8}$$

  where $\mathbf{l}_i = (l_i, 0, 0)$ is the vector position of bead i in the local reference frame for bead i with monomer $i-1$ as an origin. In Eq. (5.8), the matrix $\mathsf{T}_i(\theta_i, \phi_i)$ is the transformation (a rotation) matrix between the reference frames of bead i and bead $i-1$, and is given by

$$\mathsf{T}_i = \begin{pmatrix} \cos\theta_i & \sin\theta_i & 0 \\ -\sin\theta_i\cos\phi_i & \cos\theta_i\cos\phi_i & \sin\phi_i \\ \sin\theta_i\sin\phi_i & -\cos\theta_i\sin\phi_i & \cos\phi_i \end{pmatrix}.$$

  Note that $\mathsf{T}_k^{\text{lab}} = \mathsf{T}_2 \cdots \mathsf{T}_k$ transforms between the reference frame of bead k and the fixed lab frame and $\mathsf{T}_k^{\text{lab}} \cdot \mathbf{l}_k$ is the lab frame representation of the relative vector $\mathbf{r}_k - \mathbf{r}_{k-1}$ connecting monomers k and $k-1$.

- Ensemble averages $\langle A \rangle$ of a variable A can be written as integrals over Cartesian or generalized coordinates using

$$\begin{aligned} \langle A \rangle &= \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \, P(\mathbf{r}_1, \ldots, \mathbf{r}_N) A(\mathbf{r}_1, \ldots, \mathbf{r}_N) \\ &= \int d\mathbf{r}_1 d\mathbf{q}_2 \ldots d\mathbf{q}_N \, J(\mathbf{q}_2, \ldots, \mathbf{q}_M) P(\mathbf{r}_1, \ldots \mathbf{q}_N) A(\mathbf{r}_1, \ldots \mathbf{q}_N), \end{aligned}$$

where $J(\mathbf{q}_2, \ldots, \mathbf{q}_N)$ is the Jacobian of the transformation between Cartesian and generalized coordinates. It can be shown that

$$J(\mathbf{q}_2, \ldots, \mathbf{q}_N) = \prod_{i=2}^{N} l_i^2 \cos\theta_i.$$

- We could construct a Monte-Carlo procedure to generate equilibrium configurations of the polymer either
  - Randomly displacing Cartesian positions of the monomers and accepting/rejecting trial configurations based on energy differences. This typically is very inefficient since the bond-stretching potential greatly restricts the range of displacements allowed that are accepted.
  - Randomly displacing the generalized coordinates $\mathbf{q}_i = (l_i, \theta_i, \phi_i)$. This can result in large conformational changes as small rotations around one of the torsional angles rotates all the subsequent monomers. In some situations, the drastic change in conformation caused by changing a single dihedral angle can lead to leads to trial configurations with large energies, and hence poor acceptance.
  - General problem is we'd like to move the generalized coordinates $\mathbf{q}$ together in a cooperative fashion to change the configuration of the polymer in a reasonable way. Ideally, we'd like to keep some degrees of freedom, such as bond lengths, fixed during the generation of a trial configuration. This can be accomplished by using a dynamical updating scheme on a *restricted* set of coordinates ($\{\theta_i, \phi_i\}$).
- Implementation: use hybrid Monte-Carlo with *fictitious* momenta P_{θ_i} and P_{ϕ_i} conjugate to each of the selected coordinates θ_i and ϕ_i.
  - Draw momenta for degrees of freedom of monomer i from Boltzmann weights

    $$\Pi_m(\theta_i, \phi_i) \sim e^{-\beta \frac{P_{\theta_i}^2}{2m_\theta}} e^{-\beta \frac{P_{\phi_i}^2}{2m_\phi}},$$

    where the effective "masses" m_θ and m_ϕ are arbitrary.
  - Evolve the configuration $(\theta_i, \phi_i, P_{\theta_i}, P_{\phi_i})$ for a fixed amount of time τ using a symplectic integrator, preferably with a large time step to change the configuration rapidly. The equations to integrate are

    $$\begin{aligned} \dot{\theta}_i &= \frac{P_{\theta_i}}{m_\theta} \qquad \dot{\phi}_i = \frac{P_{\phi_i}}{m_\phi} \\ \dot{P}_{\theta_i} &= -\frac{\partial U}{\partial \theta_i} \qquad \dot{P}_{\phi_i} = -\frac{\partial U}{\partial \phi_i}. \end{aligned}$$

  * A symplectic integrator is easy to construct based on the usual Hamiltonian splitting scheme of separating the kinetic and potential energy terms and defining Liouville operators for each of the terms.
  * The effective forces in the evolution of momenta require evaluation of derivatives $\partial \mathbf{r}_j/\partial\theta_i$ and $\partial \mathbf{r}_j/\partial\phi_i$.
- Track the effective Hamiltonian

$$H_e = \sum_i \left(\frac{P_{\theta_i}^2}{m_\theta} + \frac{P_{\phi_i}^2}{m_\phi} \right) + U(\mathbf{r}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N).$$

- The stationary distribution Π for the phase point in the Monte-Carlo process is proportional to $e^{-\beta H_e}$, due to the form of the densities of the momenta.
- If the current configuration at the start of the dynamical update is $\mathbf{X}$, accept the trial configuration $\mathbf{Y}$ generated by the trajectory with probability

$$\min\left(1, \frac{J(\mathbf{Y})}{J(\mathbf{X})} e^{-\beta\Delta H_e}\right),$$

  where $\Delta H_e = H_e(\mathbf{Y}) - H_e(\mathbf{X})$.
  * Note that if the dynamics was integrated perfectly, $\Delta H_e = 0$ since the effective Hamiltonian is conserved by the dynamics.

- Comments:

1. The smaller the time step, the smaller the average ΔH_e and the greater the acceptance probability.
2. The smaller the time step, the smaller the overall change in configuration of the system for a fixed number of molecular dynamics steps.
3. The dynamics is fictitious, as the equations of motion are *not* the Hamiltonian equations for the generalized coordinates. In particular, the kinetic energy in the Hamiltonian has a different form.
4. The Jacobian factor is important in the acceptance probability. However, if the l_i and θ_i are held fixed and only the torsional angles evolve, the Jacobian factor is constant.
5. Any subset of coordinates can be selected for updating for any trial move. It may be advantageous to select different groups of coordinates for updating at different times.

5.2 Time-dependent correlations

We have considered primarily averages of static properties that are constructed out ensemble averages involving a single phase point at a time. We have seen that these averages may be computed by either:

1. A monte-carlo algorithm that generates ensemble averages by sampling phase points from the phase space density for the ensemble. Different ensemble averages can be computed by altering the transition matrix. Within this class of algorithms, we include the hybrid monte-carlo scheme, which uses a dynamical procedure to generate trial configurational coordinates.

2. A molecular dynamics procedure that uses the real Hamiltonian dynamics of the system to compute the time average of a dynamical variable. By hypothesis, the time average is equal to the micro-canonical ensemble average. In the dynamical evolution, the micro-canonical phase space density and phase space volume are conserved, which reflects the conservation of probability.

In many physical situations, we are interested in computing quantities that obey some physical law, and which may involve the real dynamics of the system. For example, suppose one is interested in computing how an initially nonuniform concentration profile (say a drop of dye in water) is smoothed in the absence of flow or stirring. Such a process is described phenomenologically by the law of diffusion (Fick's law), which states that the flux $\mathbf{j}$ of the diffusing species is proportional to the negative gradient in the concentration of the species:

$$\mathbf{j} = -D\frac{\partial c(\mathbf{r},t)}{\partial \mathbf{r}},$$

where $c(\mathbf{r},t)$ is the local concentration of the species and D is a constant known as the *diffusion coefficient*. Under Fick's law, the concentration obeys the equation

$$\begin{aligned}\frac{\partial c(\mathbf{r},t)}{\partial t} &= -\frac{\partial}{\partial \mathbf{r}}\cdot \mathbf{j}(\mathbf{r},t)\\ \frac{\partial c(\mathbf{r},t)}{\partial t} &= D\nabla^2 c(\mathbf{r},t). \qquad (5.9)\end{aligned}$$

If the initial dye is concentrated in a small region $c(\mathbf{r},0) = \delta(\mathbf{r})$, then the concentration profile is

$$c(r,t) = \frac{1}{(4\pi Dt)^{3/2}}e^{-r^2/(4Dt)}.$$

Note that the concentration profile is normalized, $\int d\mathbf{r}\, c(r,t) = 1$. This is of the form of a Gaussian distribution with a time-dependent width $2Dt$. Hence the diffusion coefficient is related to the second moment of $c(r,t)$:

$$\left\langle r^2(t)\right\rangle = \int d\mathbf{r}\, r^2 c(r,t).$$

The second moment can be interpreted to mean the average distance squared that a particle moves away from the origin in a time interval t. To see how one might compute the coefficient D, we multiply Eq. (5.9) by r^2 to compute the second moment to get

$$\frac{\partial \langle r^2(t)\rangle}{\partial t} = D\int d\mathbf{r}\, r^2\nabla^2 c(r,t) = 6D\int d\mathbf{r}\, c(r,t) = 6D,$$

after the angular integrals have been carried out using the spherical symmetry of $c(r,t)$. This equation suggests that $\langle r^2(t)\rangle = 6Dt$, so that a plot of the average squared distance versus time should be linear with slope $6D$. To compute diffusion coefficient from the *time-dependent* correlation function $\langle r^2(t)\rangle$, we must:

1. Draw an initial configuration according to the correct phase space density (i.e. micro-canonical, canonical, etc..).

2. Propagate the system using the correct dynamics and measure the displacement vector $\Delta\mathbf{r}_i(t) = \mathbf{r}_i(t) - \mathbf{r}_i(0)$ of each particle for a set of different times t.

3. If we ignore any cross-correlation between the motion of particles, we can measure the *self-diffusion coefficient* D_s by calculating

$$D_s = \frac{\langle r^2(t)\rangle}{6t} = \frac{1}{N}\sum_{i=1}^{N}\frac{\Delta\mathbf{r}_i(t)\cdot\Delta\mathbf{r}_i(t)}{6t}.$$

   From the equations of motion, $\Delta\mathbf{r}_i(t) = \int_0^t d\tau\, \mathbf{v}_i(\tau)$, and hence the average can be written as

$$\langle r^2(t)\rangle = \frac{1}{N}\sum_{i=1}^{N}\int_0^t d\tau \int_0^t d\tau'\, \mathbf{v}_i(\tau)\cdot\mathbf{v}_i(\tau').$$

- Note that the procedure consists of two different steps, the drawing of the initial phase points and then the propagation of the system.

- General time-dependent correlation functions of the form

$$\langle AB(t)\rangle = \int d\boldsymbol{x}^{(N)}\, f(\boldsymbol{x}^{(N)})A(\boldsymbol{x}^{(N)})B(\boldsymbol{x}^{(N)}(t))$$

  can be computed analogously.

  - If the ensemble is not microcanonical, the initial points must be drawn using a Monte-Carlo algorithm (or with a special dynamical procedure) that generates phase points according to $f(\boldsymbol{x}^{(N)})$. Then the system must be evolved using the real dynamics of the system, preferably with a symplectic integrator. This evolution therefore evolves the system with *constant energy*.

5.3 Event-driven simulations

Consider a system of N impenetrable hard spheres that interact via the potential

$$U(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases} ,$$

where r is the distance between the centres of two hard spheres and σ is the diameter of the spheres.

- The probability of finding the system in a configuration in which spheres overlap is zero.

- The energy of the system is given by the Hamiltonian

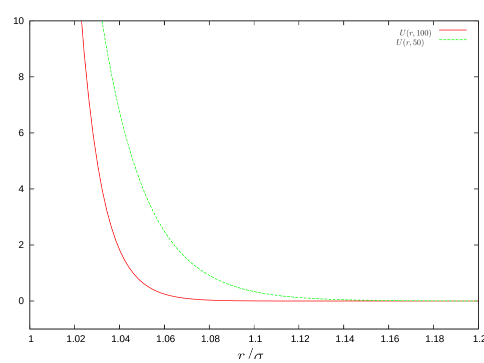
$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i,j} U(r_{ij}) = K + U = \begin{cases} K & \text{if no overlap} \\ \infty & \text{otherwise} \end{cases} .$$

How can dynamics of this system be performed on a computer?

- Particles coming together should bounce off one another, but preserve the total energy H.

To examine the complications of systems with discontinuous potentials, consider a system interacting with the short-ranged potential

$$\begin{aligned} U(r,\alpha) &= \alpha e^{-\alpha(r-\sigma)} \\ f(r,\alpha) &= \alpha^2 e^{-\alpha(r-\sigma)} \end{aligned}$$



- As $\alpha \to \infty$, the potential approaches the hard sphere potential.

- Note that the force on sphere i due to sphere j is given by $\mathbf{F}_{ij} = f(r_{ij})\hat{\mathbf{r}}_{ij}$, where $\hat{\mathbf{r}}_{ij}$ is the unit vector along the relative vector $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. This force becomes infinite in magnitude and infinitely short-ranged around σ as $\alpha \to \infty$.

- If integrated by Verlet-scheme, the shadow Hamiltonian H_s to leading order in Δt is

$$H_s = H + \frac{\Delta t^2}{12m^2}\sum_{i,j}\mathbf{p}_i \cdot \frac{\partial^2 U}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \cdot \mathbf{p}_j - \frac{\Delta t^2}{24m}\sum_i \mathbf{F}_i \cdot \mathbf{F}_i + O(\Delta t^4).$$

- From form of the potential, we see that the correction term is proportional to $(\alpha^2\Delta t)^2$, and hence the radius of convergence of the shadow Hamiltonian shrinks to zero as $\alpha \to \infty$.
  - The integrator is unstable for *any* choice of Δt.
  - In impulsive limit $\alpha \to \infty$, force acts discontinuously at a time t_c where $r_{ij}(t_c) = \sigma$.
- How can we integrate equations of motion with "impulsive" forces that act at only one time? Consider the integral form of the equation of motion for the momentum

$$\mathbf{p}_i(t + \Delta t) = \mathbf{p}_i(t - \Delta t) + \int_{t-\Delta t}^{t+\Delta t} d\tau\, \mathbf{F}_i(\tau).$$

- In impulsive limit, the force takes the form

$$\begin{aligned}\mathbf{F}_{ij} &= \tilde{S}\hat{\mathbf{r}}_{ij}\delta(r_{ij} - \sigma)\\ &= S\hat{\mathbf{r}}_{ij}\delta(t - t_c),\end{aligned}$$

  where the second equality is obtained by solving the equation $r_{ij}(t_c) = \sigma$ and rewriting the delta function in terms of time.
  - S is a constant dependent on the configuration at the moment of collision, to be determined.
  - Note that the direction of the force is along the relative vector $\hat{\mathbf{r}}_{ij}$ for a "central potential" that depends only on the magnitude $|\mathbf{r}_{ij}|$ of the relative vector $\mathbf{r}_{ij}$.
- Inserting the impulsive force into the momentum equation gives

$$\Delta \mathbf{p}_i = \mathbf{p}_i(t + \Delta t) - \mathbf{p}_i(t - \Delta t) = \begin{cases} S\hat{\mathbf{r}}_{ij} & \text{if } tc \in [t - \Delta t, t + \Delta t] \\ 0 & \text{otherwise.}\end{cases}$$

  - In impulsive limit, only one collision at most can occur as $\Delta t \to 0$.
- How is the collision time determined? Solve for the collision time by considering when $r_{ij}(t_c) = \sigma$ or $\mathbf{r}_{ij}(t_c) \cdot \mathbf{r}_{ij}(t_c) = \sigma^2$.

– Up to the moment of collision, the pair of spheres i and j move freely with constant momentum, so

$$\begin{aligned}\mathbf{r}_i(t_c) &= \mathbf{r}_i(0) + \frac{\mathbf{p}_i}{m_i}t_c \\ \mathbf{r}_j(t_c) &= \mathbf{r}_j(0) + \frac{\mathbf{p}_j}{m_j}t_c\end{aligned} \qquad \mathbf{r}_{ij}(t_c) = \mathbf{r}_{ij}(0) + \mathbf{v}_{ij}t_c$$

– The collision time is therefore determined from

$$r_{ij}(t_c)^2 = \sigma^2 = \mathbf{r}_{ij}(0)^2 + 2v_r t_c + v_{ij}^2 t_c^2$$

$$t_c^2 + \frac{2v_r t_c}{v_{ij}^2} + \frac{r_{ij}^2 - \sigma^2}{v_{ij}^2} = 0$$

$$t_c = -\frac{v_r}{v_{ij}^2} \pm \frac{1}{v_{ij}^2}\left(v_r^2 - \Delta_{ij}^2\right)^{1/2},$$

if $v_{ij}^2 \neq 0$, where $v_r = \hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}$ is the projection of the relative along the relative vector $\hat{\mathbf{r}}_{ij}$ and $\Delta_{ij}^2 = (r_{ij}^2 - \sigma^2)v_{ij}^2$.

– Real solutions exist if $v_{ij}^2 \neq 0$ and $v_r^2 \geq \Delta_{ij}^2$.

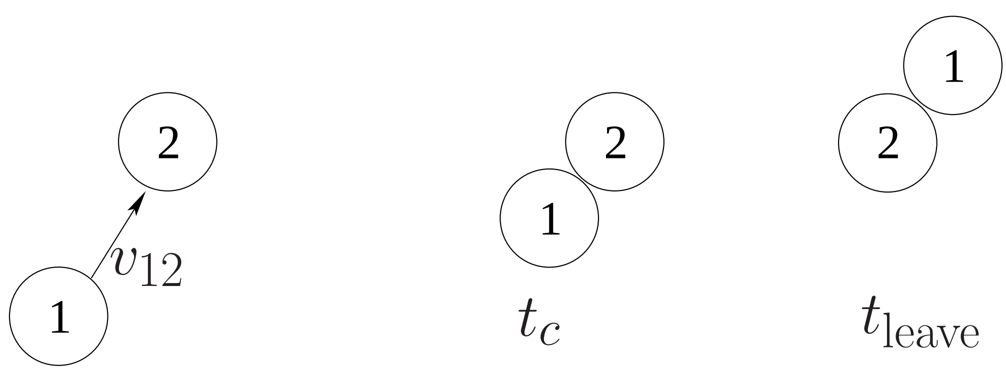
– If no initial overlap, then $r_{ij}^2 > \sigma^2$ and hence $\Delta_{ij}^2 > 0$.

– If $\Delta_{ij}^2 > 0$, then $|v_r| > \left(v_r^2 - \Delta_{ij}^2\right)^{1/2}$.

1. If $v_r > 0$, then $t_c < 0$. Particles are moving *away* from one another and will not collide (in a non-periodic system).
2. If $v_r < 0$, the particles moving towards one another and 2 positive roots are found:

$$t_c = \frac{-v_r - \sqrt{v_r^2 - \Delta_{ij}^2}}{v_i j^2} = \text{time of initial contact} \tag{5.10}$$

$$t_{\text{leave}} = \frac{-v_r + \sqrt{v_r^2 - \Delta_{ij}^2}}{v_{ij}^2} = \text{time particles pass through one another}$$



- Determination of magnitude of impulse S is based on conservation principles. If the potential depends only on the magnitude of the relative vector r_{ij} and the Hamiltonian does not depend explicitly on time, then linear momentum as well as total energy must be conserved once the collision has occurred.

- Conservation of linear momentum implies:

$$\begin{aligned}\mathbf{p}_i' + \mathbf{p}_j' &= \mathbf{p}_i + \mathbf{p}_j, \\ \mathbf{p}_i' &= \mathbf{p}_i + \Delta\mathbf{p}_i = \mathbf{p}_i + S\hat{\mathbf{r}}_{ij} \\ \mathbf{p}_j' &= \mathbf{p}_j + \Delta\mathbf{p}_j = \mathbf{p}_j - S\hat{\mathbf{r}}_{ij}\end{aligned} \tag{5.11}$$

  where $\mathbf{p}_i'$ is the momentum of particle i after the collision with particle j.

- Conservation of energy implies that the post-collisional energy H' is equal to the pre-collisional energy H, or

$$\frac{\mathbf{p}_i' \cdot \mathbf{p}_i'}{2m_i} + \frac{\mathbf{p}_j' \cdot \mathbf{p}_j'}{2m_j} = \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} + \frac{\mathbf{p}_j \cdot \mathbf{p}_j}{2m_j},$$

  which, using Eq. (5.11), gives a condition on the impulse S

$$\frac{S^2}{2\mu} - Sv_r = 0 \qquad \rightarrow \qquad S = 2\mu v_r,$$

  where $\mu = m_i m_j/(m_i + m_j)$ is the reduced mass.

- After a collision, the momentum are therefore given by

$$\begin{aligned}\mathbf{p}_i' &= \mathbf{p}_i + 2\mu v_r\,\hat{\mathbf{r}}_{ij} \\ \mathbf{p}_j' &= \mathbf{p}_j - 2\mu v_r\,\hat{\mathbf{r}}_{ij}.\end{aligned} \tag{5.12}$$

5.3.1 Implementation of event-driven dynamics

For the hard sphere system, the dynamics can be executed by:

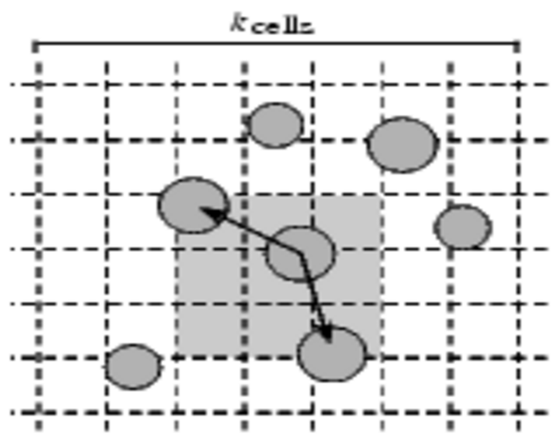
1. Initially calculate all collision events for system using Eq. (5.10).
   - Boundary conditions must be properly included: hard walls, periodic system, ...
2. Find first collision event and evolve system (with free evolution) up to that time.
3. For colliding pair, compute the consequences of the collision using Eq. (5.12).

4. Compute the new first collision time for system after the momentum adjustments and repeat steps 2 to 4.

Tricks of the Trade: A number of standard techniques have been developed to improve the efficiency of event-driven simulations. These include:

1. Cell division and crossing events

    - If cubic cells of length σ are used to partition the system, collisions of a given particle in a cell can occur only with particles in the same or neighboring cells before the particle moves out of a cell.



    - If a particle moves out of a cell (i.e. a cell-crossing event), the new neighboring cells must be check for a collision.
    - Cell-crossing time is analytically computable.
    - Can treat cell-crossing as an event to be processed like a collision, with the processing of the event defined to mean the computation of new collision times with particles in the new neighboring cells.

2. Local clocks

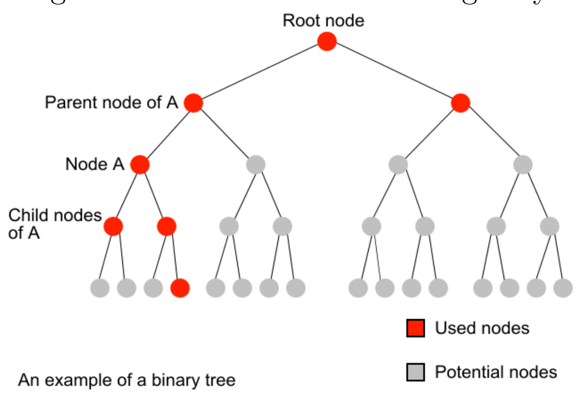
    - The position of any particle not involved in an event does not need to be updated since it will continue to move freely until it is specifically involved in a collision.
    - Time of last event for each particle can be stored and used to compute interaction times or updates of positions.
    - Global updates of the positions of all particles must be performed before any measurement of the system takes place.

3. Elimination of redundant calculation of event times

- If a collision occurs between a pair of particles $i - j$, new event times result only for particles that have an collision event involving particle i or j as a partner.
- Most event times unaffected in large system, and need not be recomputed.
- Can devise routines that only compute new possible events following a collision.

4. Usage of data structures to manage event times

- Search for first event time in system can be facilitated by use of binary tree data structures, using the event time as an ordering "key".



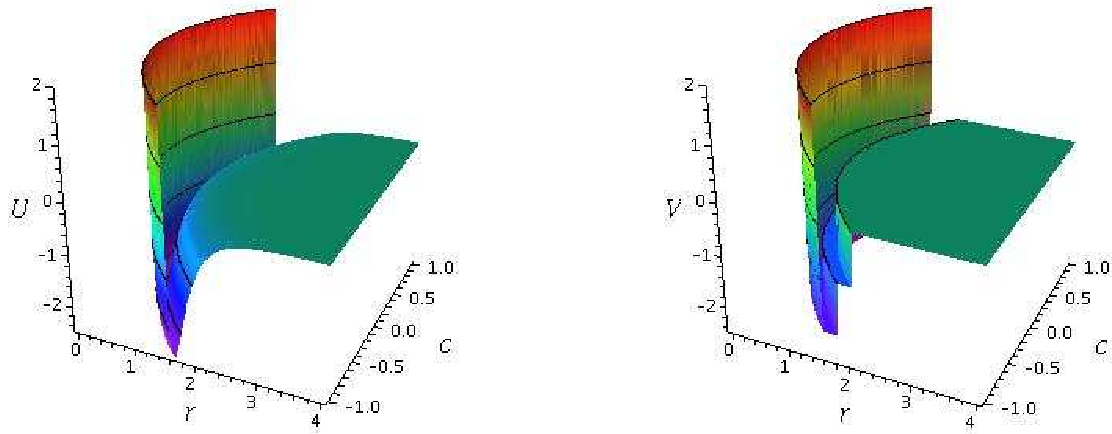
- Functions required to insert new events in tree and search for earliest times.
- Information for whether an event in the tree has been invalidated by an earlier event can be stored in each node of tree.
- Small hybrid tree structures that only insert valid events in the near future are an efficient means of managing events in the system. These data structures typically use linked lists of events in specific time intervals that are periodically used to populate the binary tree.

5.3.2 Generalization: Energy discretization

To mimic systems interacting by a continuous potential $U(r)$, one can construct a discontinuous potential $V(r)$ with discrete energies [see van Zon and Schofield, *J. Chem. Phys.* **128**, 154119 (2008)]:

$$V(r) = U_{\min} + \sum_{k=1}^{K} \Theta(U(r) - U_k)\Delta V_k,$$

where Θ is the Heaviside function and ΔV_k is the change in potential when $U(r) = U_k$.



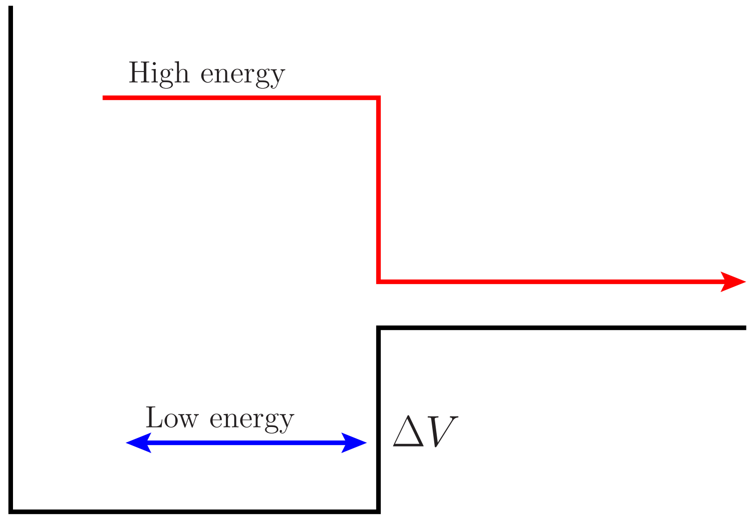
- If pair of particles has a potential energy $U(r)$ under the continuous potential, where $U_k < U(r) < U_{k+1}$, then the interaction is assigned potential energy $V(r) = U_{\min} + \sum_{i=1}^{k} \Delta V_i$.
- Collision times at which $U(r) = U_k$ can be solved analytically for simple potentials.
- By examining representations of the Heaviside function, one can derive that the impulse on body i due to an interaction with another body j can be written as

$$\begin{aligned} \mathbf{p}_i' &= \mathbf{p}_i + \Delta \mathbf{F}_{ij}(t_c) \\ \Delta \mathbf{F}_{ij}(t) &= S\mathbf{F}_{ij}(t_c)\delta(t - t_c), \end{aligned}$$

  where $\mathbf{F}_{ij}(t)$ is the force on i due to j arising from the continuous potential $U(r_{ij})$.
- At discontinuity at U_k, the impulse S satisfies

$$S^2 \frac{\mathbf{F}_{ij} \cdot \mathbf{F}_{ij}}{m} + S\mathbf{v}_{ij} \cdot \mathbf{F}_{ij} + \Delta V_k = 0.$$

  - If real roots of quadratic exist, the physical solution is given by
    1. Positive branch of root if $\mathbf{v}_{ij} \cdot \mathbf{F}_{ij} > 0$.
    2. Negative branch of root if $\mathbf{v}_{ij} \cdot \mathbf{F}_{ij} < 0$.
  - If roots are complex, the collision is a reflection (bounce back) due to inadequate total energy to overcome the discontinuity. In this case, $S = -m\mathbf{v}_{ij} \cdot \mathbf{F}_{ij}/F_{ij}^2$.



- The level of discretization $\Delta V_k/(kT)$ relative to kT is an adjustable parameter.
  - For small values $\Delta V_k/(kT) \ll 1$, the dynamics is effectively equivalent to that in the continuous potential system.
- Method is ideally suited for low density systems where free motion dominates.
  - First event corresponds to time at which two particles enter a range of the potential, which can be quite rare.
  - In ordinary molecular dynamics, the integration time step is restricted by the curvature of the potential in the repulsive region. This can be extremely small if the potential is short-ranged.
  - Event driven dynamics is like an *adaptable* time step integrator, where large time steps are used in between interactions while small time steps are used in the interaction region.
- Method can be implemented for rigid body systems [de la Pena *et al.*, *J. Chem. Phys.* **126**, 074106 (2007)].
  - Requires the solution of free motion [van Zon and Schofield, *J. Comput. Phys.* **225**, 145 (2007)].
  - Torques, angular velocities and orientational matrices necessary.
  - Need to use numerical methods to find event times.

5.4 Constraints and Constrained Dynamics

Typical time scales of most intramolecular motions are 10 to 50 times shorter than the translational time scale of a molecule.

- Time step of an integrator determined by shortest relevant time scale.
- Multiple time step methods can be used to deal with differing time scales in dynamical simulations.
- Many observables are independent or insensitive to intramolecular motion.
  - Molecular conformation is usually only weakly dependent on bond lengths. Bond vibrations are typically restricted to small motions on rapid time scales.
  - Some bond angles remain relatively constant, aside from high frequency oscillations.

5.4.1 Constrained Averages

- Suppose a set of ℓ variables, such as bond lengths, are effectively constant during a simulation.
- We will assume that the constraints are only functions of the positions, and independent of momenta. Such constraints are called *holonomic*.
- Can specify these constraints by

$$\begin{aligned} &\sigma_1(\mathbf{r}^{(N)}) = 0 \qquad \text{such as} \qquad \sigma_1(r_{12}) = r_{12}^2 - d^2 \\ &\sigma_2(\mathbf{r}^{(N)}) = 0 \\ &\qquad \vdots \end{aligned}$$

- We write the condition that the set of all constraints $\boldsymbol{\sigma} = (\sigma_1, \ldots, \sigma_\ell)$ are satisfied in the compact notation

$$\prod_{i=1}^{\ell} \delta(\sigma_i(\mathbf{r}^{(N)})) = \delta(\boldsymbol{\sigma}).$$

- An ensemble average of an observable $A(\mathbf{r}^{(N)})$ that depends only on the configuration of the system can be written as

$$\langle A(\mathbf{r}^{(N)})\rangle = \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\, P(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) A(\mathbf{r}^{(N)}) = \int d\mathbf{r}^{(N)}\, \rho(\mathbf{r}^{(N)}) A(\mathbf{r}^{(N)}),$$

where $P(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$ is the full phase space density and $\rho(\mathbf{r}^{(N)}) = \int d\mathbf{p}^{(N)}\, P(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$ is the configurational phase space density.

- If $A(\mathbf{r}^{(N)})$ depends only weakly on the constraints,

$$\begin{aligned}
\langle A(\mathbf{r}^{(N)})\rangle &\approx \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\, P(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) A(\mathbf{r}^{(N)}) \delta(\boldsymbol{\sigma}) \Big/ \int d\mathbf{r}^{(N)}\, \rho(\mathbf{r}^{(N)}) \delta(\boldsymbol{\sigma}) \\
&= \int d\mathbf{r}^{(N)}\, \rho_{\rm con}(\mathbf{r}^{(N)}, \sigma = 0) A(\mathbf{r}^{(N)}, \boldsymbol{\sigma} = 0) = \langle A(\mathbf{r}^{(N)})\rangle_c
\end{aligned}$$

- How can the conditional ensemble average $\langle \ldots \rangle_c$ be computed?
- This can be analyzed most easily by working in generalized coordinates rather than Cartesian coordinates.
- Define a coordinate transformation $\mathbf{r} = (\mathbf{r}_1, \ldots, \mathbf{r}_N) \to \mathbf{u} = (\mathbf{u}_1, \ldots, \mathbf{u}_N)$, where the last ℓ coordinates are the ℓ constraint conditions σ_α. We can represent $\mathbf{u} = (\mathbf{q}_i, \boldsymbol{\sigma})$, where the dimension of the $\mathbf{q}_i$ is $3N - \ell$ and the dimension of $\boldsymbol{\sigma}$ is ℓ.
- If $\mathbf{p} = (\mathbf{p}_1, \ldots, \mathbf{p}_n)$ and the potential of the system is $V(\mathbf{r})$, then the Lagrangian and the Hamiltonian in the Cartesian coordinates are

$$L(\mathbf{r}, \dot{\mathbf{r}}) = \frac{1}{2}\dot{\mathbf{r}} \cdot \mathsf{m} \cdot \dot{\mathbf{r}} - V(\mathbf{r}) \qquad H(\mathbf{r}, \mathbf{p}) = \frac{1}{2}\mathbf{p} \cdot \mathsf{m}^{-1} \cdot \mathbf{p} + V(\mathbf{r}),$$

where $\mathsf{m}_{ij} = m_i \delta_{i,j}$ and $\mathsf{m}^{-1}_{ij} = m_i^{-1}\delta_{i,j}$.

- Hamilton's principle of minimizing the action with respect to trajectories that start and end at fixed points gives the equation of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{r}}}\right) = -\frac{dV(\mathbf{r})}{dt} = \frac{d}{dt}\left(\mathsf{m} \cdot \dot{\mathbf{r}}\right).$$

which can be written in term of the Poisson bracket of the Hamiltonian $H(\mathbf{r}, \mathbf{p})$ when the momentum is defined to be $\mathbf{p} = \frac{\partial L}{\partial \dot{\mathbf{r}}} = \mathsf{m} \cdot \dot{\mathbf{r}}$.

- Using $\mathbf{r}(\mathbf{u})$, we note that $\dot{\mathbf{r}} = \frac{\partial \mathbf{r}}{\partial \mathbf{u}} \cdot \dot{\mathbf{u}}$.
- the Lagrangian in the generalized coordinates can be written as

$$\begin{aligned}
L(\mathbf{u}, \dot{\mathbf{u}}) &= \frac{1}{2}\sum_i m_i \dot{\mathbf{u}}_\alpha \frac{\partial \mathbf{r}_i}{\partial \mathbf{u}_\alpha} \cdot \frac{\partial \mathbf{r}_i}{\partial \mathbf{u}_\beta} \dot{\mathbf{u}}_\beta - V(\mathbf{u}) = \frac{1}{2}\dot{\mathbf{u}} \cdot \mathsf{G} \cdot \dot{\mathbf{u}} - V(\mathbf{u}) \\
\mathsf{G}_{\alpha\beta} &= \sum_i m_i \frac{\partial \mathbf{r}_i}{\partial \mathbf{u}_\alpha} \cdot \frac{\partial \mathbf{r}_i}{\partial \mathbf{u}_\beta}
\end{aligned}$$

where we have used a notation that repeated Greek indices are summed over. The conjugate momenta $\mathbf{p}^u$ to the generalize coordinates are therefore

$$\mathbf{p}^u = \frac{\partial L}{\partial \dot{\mathbf{u}}} = \mathsf{G} \cdot \dot{\mathbf{u}} \qquad \text{so} \qquad \dot{\mathbf{u}} = \mathsf{G}^{-1} \cdot \mathbf{p}^u,$$

and the equations of motion

$$\frac{d}{dt}\left(\mathsf{G} \cdot \dot{\mathbf{u}}\right) = \frac{d\mathbf{p}^u}{dt} = -\frac{\partial V(\mathbf{u})}{\partial \mathbf{u}}$$

and the corresponding Hamiltonian

$$H = \mathbf{p}^u \cdot \dot{\mathbf{q}} - L = \frac{1}{2}\mathbf{p}^u \cdot \mathsf{G}^{-1} \cdot \mathbf{p}^u + U(\mathbf{u}).$$

– Note from the definition of the matrix G, we have

$$\mathsf{G}^{-1}_{\alpha\beta} = \sum_i \frac{1}{m_i} \frac{\partial \mathbf{u}_\alpha}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathbf{u}_\beta}{\partial \mathbf{r}_i}.$$

– The equations of motion in the Cartesian phase space coordinates $\boldsymbol{\eta} = (\mathbf{r}, \mathbf{p})$ and in the generalized phase space coordinates $\boldsymbol{\zeta} = (\mathbf{u}, \mathbf{p}^u)$ are in symplectic form

$$\dot{\boldsymbol{\eta}} = \mathcal{J} \cdot \frac{\partial H}{\partial \boldsymbol{\eta}} \qquad \dot{\boldsymbol{\zeta}} = \mathcal{J} \cdot \frac{\partial H(\boldsymbol{\zeta})}{\partial \boldsymbol{\zeta}}.$$

Transformations $\boldsymbol{\eta} \to \boldsymbol{\zeta}$ that preserve the symplectic form are called *canonical*.

- Claim: The phase space probability satisfies $P(\boldsymbol{\eta})d\boldsymbol{\eta} = P(\boldsymbol{\eta}(\boldsymbol{\zeta}))d\boldsymbol{\zeta}$.

Proof. Consider the transformation of phase space coordinates $\boldsymbol{\zeta} = \boldsymbol{\zeta}(\boldsymbol{\eta})$. The time derivative of this relation gives

$$\dot{\boldsymbol{\zeta}} = \frac{\partial \boldsymbol{\zeta}}{\partial \boldsymbol{\eta}} \cdot \dot{\boldsymbol{\eta}} = \mathsf{M} \cdot \dot{\boldsymbol{\eta}} \qquad \mathsf{M}_{\alpha\beta} = \frac{\partial \boldsymbol{\zeta}_\alpha}{\partial \boldsymbol{\eta}_\beta}.$$

From the symplectic form of the equation of motion for $\boldsymbol{\eta}$, we see that

$$\dot{\boldsymbol{\zeta}} = \mathsf{M} \cdot \mathcal{J} \cdot \frac{\partial H}{\partial \boldsymbol{\eta}}.$$

Considering the inverse of the transformation, $\boldsymbol{\eta} = \boldsymbol{\eta}(\boldsymbol{\zeta})$, we find that

$$\frac{\partial H}{\partial \boldsymbol{\eta}_\beta} = \frac{\partial H}{\partial \boldsymbol{\zeta}_\alpha} \frac{\partial \boldsymbol{\zeta}_\alpha}{\partial \boldsymbol{\eta}_\beta} = \frac{\partial H}{\partial \boldsymbol{\zeta}_\alpha} \mathsf{M}_{\alpha\beta} \quad \text{so} \quad \frac{\partial H}{\partial \boldsymbol{\eta}} = \mathsf{M}^T \cdot \frac{\partial H}{\partial \boldsymbol{\zeta}}.$$

Thus we find the equation of motion for the transformed phase space coordinates obeys

$$\dot{\boldsymbol{\zeta}} = \left(\mathsf{M} \cdot \mathcal{J} \cdot \mathsf{M}^T\right) \cdot \frac{\partial H}{\partial \boldsymbol{\zeta}}.$$

This equation maintains symplectic form if $\mathsf{M} \cdot \mathcal{J} \cdot \mathsf{M} = \mathcal{J}$. Now consider the transformation of the volume element $d\boldsymbol{\eta} = |\det \mathsf{M}| d\boldsymbol{\zeta}$. If the transformed coordinates preserve the symplectic form, then $\det\left(\mathsf{M} \cdot \mathcal{J} \cdot \mathsf{M}^T\right) = \det(\mathcal{J}) = \det^2(\mathsf{M}) \det(\mathcal{J})$, and hence $\det(\mathsf{M}) = \pm 1$, and so $d\boldsymbol{\eta} = d\boldsymbol{\zeta}$. If the phase space probability is $P(\boldsymbol{\eta})d\boldsymbol{\eta}$, it therefore follows that $P(\boldsymbol{\eta})d\boldsymbol{\eta} = P(\boldsymbol{\eta}(\boldsymbol{\zeta}))d\boldsymbol{\zeta}$. □

- From this equality, the canonical configurational density can be expressed as

$$\begin{aligned}
\rho(\mathbf{r})d\mathbf{r} &= \frac{d\mathbf{r}}{Z} \int d\mathbf{p} e^{-\beta H} = \frac{d\mathbf{u}}{Z} \int d\mathbf{p}^u \, e^{-\beta/2\, \mathbf{p}^u \cdot \mathsf{G}^{-1} \cdot \mathbf{p}^u} e^{-\beta V(\mathbf{u})} \\
&= c\sqrt{\det \mathsf{G}}\, e^{-\beta V(\mathbf{u})} d\mathbf{u} = \rho(\mathbf{u})d\mathbf{u},
\end{aligned}$$

  where c is a normalization constant.

- From our transformation where $\mathbf{u} = (\mathbf{q}, \boldsymbol{\sigma})$, the conditional density is therefore

$$\rho_{\text{con}}(\mathbf{q}, \boldsymbol{\sigma} = 0) = c\sqrt{\det \mathsf{G}}\, e^{-\beta V(\mathbf{q}, \boldsymbol{\sigma}=0)}.$$

  - Note that the factor $\sqrt{\det \mathsf{G}}$ is related to the Jacobian of the transform from Cartesian spatial coordinates $\mathbf{r}$ to generalized spatial coordinates $\mathbf{u}$.

- Conditional averages can be computed by either

  1. Devising a Monte-Carlo procedure that works in the $\mathbf{q}$ generalized coordinates. Note trial moves must not violate the constraints $\boldsymbol{\sigma} = 0$, which is easy to implement if generalized spatial coordinates are used. The transition matrix should have limit density of ρ_{con}, and therefore the Jacobian factor must be used in the final acceptance criterion of the Monte-Carlo procedure.
  2. Carrying out *constrained dynamics*, which effectively correspond to Hamiltonian dynamics in a lower-dimensional sub-space of the full phase space $(\mathbf{r}, \mathbf{p})$ or $(\mathbf{u}, \mathbf{p}^u)$.

5.4.2 Constrained Dynamics

To construct the equations of motion for a constrained system, consider the Lagrangian written in the generalized coordinates $\mathbf{u}$ while the ℓ constraints $\boldsymbol{\sigma} = 0$ are maintained:

$$
\begin{aligned}
L(\mathbf{u}, \dot{\mathbf{u}}) &= \frac{1}{2}\dot{\mathbf{u}} \cdot \mathsf{G} \cdot \dot{\mathbf{u}} - V(\mathbf{u}) \\
&= \frac{1}{2}\dot{\mathbf{q}} \cdot \mathsf{A} \cdot \dot{\mathbf{q}} - V(\mathbf{q}, \boldsymbol{\sigma} = 0),
\end{aligned}
$$

since $\dot{\boldsymbol{\sigma}} = 0$ under the constraint. In this equation, the matrix A is a sub-matrix of G given by

$$
\mathsf{A}_{\alpha\beta} = \sum_i m_i \frac{\partial \mathbf{r}_i}{\partial \mathbf{q}_\alpha} \cdot \frac{\partial \mathbf{r}_i}{\partial \mathbf{q}_\beta},
$$

which is of dimension $(N-\ell) \times (N-\ell)$. From the Lagrangian, we construct the Hamiltonian in generalized coordinates

$$
H_c = \frac{1}{2}\mathbf{p}^q \cdot \mathsf{A}^{-1} \cdot \mathbf{p}^q + V(\mathbf{q}, \boldsymbol{\sigma} = 0) \qquad \mathbf{p}^q = \frac{\partial L}{\partial \mathbf{q}} = \mathsf{A} \cdot \dot{\mathbf{q}}.
$$

- Note that there is no momentum conjugate to the fixed coordinates $\boldsymbol{\sigma}$.
- The canonical probability density for this Hamiltonian system is obtained from

$$
\begin{aligned}
\rho(\mathbf{q})d\mathbf{q} &= d\mathbf{q} \int d\mathbf{p}^q \, e^{-\beta/2\, \mathbf{p}^q \cdot \mathsf{A}^{-1} \cdot \mathbf{p}^q} e^{-\beta V(\mathbf{q}, \boldsymbol{\sigma}=0)} \\
&= c' \sqrt{\det \mathsf{A}} e^{-\beta V(\mathbf{q}, \boldsymbol{\sigma}=0)} d\mathbf{q} \\
\rho(\mathbf{q}) &= \tilde{c} \frac{\sqrt{\det \mathsf{A}}}{\sqrt{\det \mathsf{G}}} \rho_{\text{con}}(\mathbf{q}, \boldsymbol{\sigma} = 0).
\end{aligned}
$$

- Note that the probability density associated with the Hamiltonian dynamics of the constrained system is $\rho(\mathbf{q})$, while the targeted constrained density is $\rho_{\text{con}}(\mathbf{q}, \boldsymbol{\sigma} = 0)$.
  - Each configuration generated by constrained dynamics must be weighted by ratio of Jacobian factors $\sqrt{\det \mathsf{G} / \det \mathsf{A}}$.
- How can this weight factor be evaluated?
  - We write G and its inverse G^{-1} in block form:

$$
\mathsf{G} = \left(\begin{array}{c:c} \mathsf{A} & \mathsf{B} \\ \hdashline \mathsf{B}^T & \Gamma \end{array}\right) \quad \mathsf{A} = \sum_i m_i \frac{\partial \mathbf{r}_i}{\partial \mathbf{q}} \cdot \frac{\partial \mathbf{r}_i}{\partial \mathbf{q}} \quad \mathsf{B} = \sum_i m_i \frac{\partial \mathbf{r}_i}{\partial \mathbf{q}} \cdot \frac{\partial \mathbf{r}_i}{\partial \boldsymbol{\sigma}} \quad \Gamma = \sum_i m_i \frac{\partial \mathbf{r}_i}{\partial \boldsymbol{\sigma}} \cdot \frac{\partial \mathbf{r}_i}{\partial \boldsymbol{\sigma}}
$$

$$
\mathsf{G}^{-1} = \left(\begin{array}{c:c} \Delta & \mathsf{E} \\ \hdashline \mathsf{E}^T & \mathsf{Z} \end{array}\right) \quad \Delta = \sum_i \frac{1}{m_i} \frac{\partial \mathbf{q}}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathbf{q}}{\partial \mathbf{r}_i} \quad \mathsf{E} = \sum_i \frac{1}{m_i} \frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathbf{q}}{\partial \mathbf{r}_i} \quad \mathsf{Z} = \sum_i \frac{1}{m_i} \frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{r}_i} \cdot \frac{\partial \boldsymbol{\sigma}}{\partial \mathbf{r}_i}
$$

– We now define a matrix X so that $\det\mathsf{X} = \det\mathsf{A}$:

$$\mathsf{X} = \left(\begin{array}{c:c} \mathsf{A} & \mathsf{0} \\ \hdashline \mathsf{B}^T & \mathsf{I} \end{array}\right),$$

where I is the identity matrix.

– Writing $\mathsf{X} = \mathsf{G}\cdot\mathsf{G}^{-1}\cdot\mathsf{X}$, we get

$$\mathsf{X} = \mathsf{G}\cdot\left(\begin{array}{c:c} \Delta\cdot\mathsf{A}+\mathsf{E}\cdot\mathsf{B}^T & \mathsf{E} \\ \hdashline \mathsf{E}^T\cdot\mathsf{A}+\mathsf{Z}\cdot\mathsf{B}^T & \mathsf{Z} \end{array}\right) \qquad \mathsf{G}^{-1}\cdot\mathsf{G} = \left(\begin{array}{c:c} \Delta\cdot\mathsf{A}+\mathsf{E}\cdot\mathsf{B}^T & \Delta\cdot\mathsf{B}+\mathsf{E}\cdot\Gamma \\ \hdashline \mathsf{E}^T\cdot\mathsf{A}+\mathsf{Z}\cdot\mathsf{B}^T & \mathsf{E}^T\cdot\mathsf{B}+\mathsf{Z}\cdot\Gamma \end{array}\right)$$

so $\Delta\cdot\mathsf{A}+\mathsf{E}\cdot\mathsf{B}^T = \mathsf{I}$ and $\mathsf{E}^T\cdot\mathsf{A}+\mathsf{Z}\cdot\mathsf{B}^T = \mathsf{0}$, and hence

$$\mathsf{X} = \mathsf{G}\cdot\left(\begin{array}{c:c} \mathsf{I} & \mathsf{E} \\ \hdashline \mathsf{0} & \mathsf{Z} \end{array}\right).$$

– Thus, $\det\mathsf{X} = \det\mathsf{A} = \det\mathsf{G}\det\mathsf{Z}$, from which we conclude

$$\frac{\det\mathsf{G}}{\det\mathsf{A}} = \frac{1}{\det\mathsf{Z}} \qquad \text{implying} \qquad \langle A(\mathbf{r}^{(N)})\rangle_c = \int d\mathbf{q}\,\det\mathsf{Z}^{-1/2}\rho(\mathbf{q})A(\mathbf{q},\boldsymbol{\sigma}=0),$$

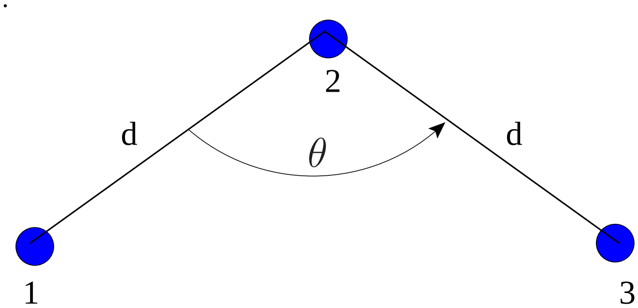
where

$$\mathsf{Z}_{\alpha\beta} = \sum_i \frac{1}{m_i}\frac{\partial\boldsymbol{\sigma}_\alpha}{\partial\mathbf{r}_i}\cdot\frac{\partial\boldsymbol{\sigma}_\beta}{\partial\mathbf{r}_i}$$

is a simple matrix to calculate from the constraint conditions $\boldsymbol{\sigma}(\mathbf{r}^{(N)})$.

Specific example

Consider a molecular trimer like water with bond constraints $\sigma_1(r_{12}) = r_{12}^2 - d^2 = 0$ and $\sigma_2(r_{23}) = r_{23}^2 - d^2 = 0$.



- If all atoms in the trimer have equal masses, then

$$\mathsf{Z} = \frac{1}{m}\begin{pmatrix} \sum_{i=1}^{3} \frac{\partial \sigma_1}{\partial \mathbf{r}_i}\cdot\frac{\partial \sigma_1}{\partial \mathbf{r}_i} & \sum_{i=1}^{3} \frac{\partial \sigma_1}{\partial \mathbf{r}_i}\cdot\frac{\partial \sigma_2}{\partial \mathbf{r}_i} \\ \sum_{i=1}^{3} \frac{\partial \sigma_2}{\partial \mathbf{r}_i}\cdot\frac{\partial \sigma_1}{\partial \mathbf{r}_i} & \sum_{i=1}^{3} \frac{\partial \sigma_2}{\partial \mathbf{r}_i}\cdot\frac{\partial \sigma_2}{\partial \mathbf{r}_i} \end{pmatrix} = \frac{1}{m}\begin{pmatrix} 4r_{12}^2 & -2\mathbf{r}_{12}\cdot\mathbf{r}_{23} \\ -2\mathbf{r}_{12}\cdot\mathbf{r}_{23} & 4r_{23}^2 \end{pmatrix},$$

but $|\mathbf{r}_{12}| = |\mathbf{r}_{23}| = d$, so

$$\det\mathsf{Z} = \frac{8d^4}{m}\left(1 - 1/4\left(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{23}\right)^2\right) = \frac{8d^4}{m}\left(1-\cos^2\theta/4\right).$$

Procedure

- Generate dynamics and then calculate constrained averages properly weighted by factor $\det\mathsf{Z}^{-1/2}$.
- Constrained dynamics may be done in two different ways:
  1. Re-writing Hamiltonian in generalized coordinates and using symplectic integrator with Hamiltonian system.
     - Typically, Hamiltonian has complicated form as A^{-1} is not diagonal.
  2. Lagrange multiplier approach: Define Lagrangian with constraints $\lambda_\alpha(\mathbf{r},\dot{\mathbf{r}})$

$$L' = L - \lambda_\alpha\sigma_\alpha \qquad L = \sum_i \frac{m_i\dot{r}_i^2}{2} - V(\mathbf{r}^{(N)})$$

- Hamilton's principle is again applied to minimize the constrained action

$$S'(t_2,t_1) = \int_{t_1}^{t_2} dt L'(\mathbf{r},\dot{\mathbf{r}})$$

for variations $\delta\mathbf{r}(t)$ and $\delta\dot{\mathbf{r}}(t)$ that satisfy $\delta\mathbf{r}(t_1) = \delta\mathbf{r}(t_2) = 0$.

- Computing the variation of L', we find

$$\begin{aligned} \delta S' &= \int_{t_1}^{t_2} dt\left(\frac{\partial L'}{\partial\dot{\mathbf{r}}}\frac{d\delta\mathbf{r}}{dt} + \frac{\partial L'}{\partial\mathbf{r}}\delta\mathbf{r}\right) \\ &= \left.\frac{\partial L'}{\partial\dot{\mathbf{r}}}\delta\mathbf{r}\right|_{t_1}^{t_2} + \int_{t_1}^{t_2} dt\left(\frac{\partial L'}{\partial\mathbf{r}} - \frac{d}{dt}\frac{\partial L'}{\partial\dot{\mathbf{r}}}\right)\delta\mathbf{r} = 0 \end{aligned}$$

so that for arbitrary variations in trajectory

$$\begin{aligned}
\frac{d}{dt}\frac{\partial L'}{\partial \dot{\mathbf{r}}} - \frac{\partial L'}{\partial \mathbf{r}} &= 0 \\
\frac{d}{dt}\frac{\partial L}{\partial \dot{\mathbf{r}}} - \frac{\partial L}{\partial \mathbf{r}} &= \left(\frac{d}{dt}\frac{\partial \lambda_\alpha}{\partial \dot{\mathbf{r}}} - \frac{\partial \lambda_\alpha}{\partial \mathbf{r}}\right)\sigma_\alpha + \frac{\partial \lambda_\alpha}{\partial \dot{\mathbf{r}}}\frac{d\sigma_\alpha}{dt} - \lambda_\alpha \frac{\partial \sigma_\alpha}{\partial \mathbf{r}} \\
&= -\lambda_\alpha \frac{\partial \sigma_\alpha}{\partial \mathbf{r}}
\end{aligned}$$

since $\sigma_\alpha = 0$ and $d\sigma_\alpha/dt = 0$.

- The equation of motion from the constrained Lagrangian is:

$$\begin{aligned}
\frac{\partial}{\partial t}\frac{\partial L'}{\partial \dot{\mathbf{r}}} &= \frac{\partial L'}{\partial \mathbf{r}} \\
m_i \ddot{\mathbf{r}}_i &= -\frac{\partial V}{\partial \mathbf{r}_i} - \lambda_\alpha \frac{\partial \boldsymbol{\sigma}_\alpha}{\partial \mathbf{r}_i},
\end{aligned}$$

provided the constraints are *holonomic* (depend only on $\mathbf{r}$ and not on $\dot{\mathbf{r}}$ or $\mathbf{p}$).

- The dynamics in the full phase $\mathbf{X} = (\mathbf{r}, \mathbf{p})$ is generated by the linear operator $\mathcal{L}_0$

$$\begin{aligned}
\mathcal{L}_0 &= \dot{\mathbf{X}} \cdot \frac{\partial}{\partial \mathbf{X}} = \sum_i \left(\frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} - \lambda_\alpha \left(\frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i}\right) \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) \\
\frac{dA(\mathbf{X}(t))}{dt} &= \mathcal{L}_0 A(\mathbf{X}(t))
\end{aligned}$$

with formal solution $A(\mathbf{X}(t)) = \exp\{\mathcal{L}_0 t\} A(\mathbf{X}(0))$.

  - The effective forces have been re-defined to include a *constraint force* $\mathbf{G}_i = -\lambda_\alpha \partial\sigma_\alpha/\partial \mathbf{r}_i$.
  - The Lagrange multipliers λ_α typically depend on *both* $\mathbf{r}$ and $\mathbf{p}$, and so the system is *non-Hamiltonian*, as the generalized forces depend on $\mathbf{p}$.
  - The operator $\mathcal{L}_0$ is *not* obtained from the Poisson bracket of a Hamiltonian.
  - Even though the dynamics is not Hamiltonian in the *full* phase space $\mathbf{X}$, we saw earlier that it **is** Hamiltonian in a sub-space of the phase space $\mathbf{X}$.

- To solve for the Lagrange multipliers, note that the time-derivatives of the constraint condition $\boldsymbol{\sigma}_\alpha = 0$ must vanish, so

$$\begin{aligned}
\dot{\sigma}_\alpha &= 0 \qquad \text{so} \qquad \sum_i \dot{\mathbf{r}}_i \cdot \frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i} = 0 \\
\ddot{\sigma}_\alpha &= 0 \qquad \text{so} \qquad \sum_i \left(\ddot{\mathbf{r}}_i \cdot \frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i} + \dot{\mathbf{r}}_i \cdot \frac{\partial}{\partial \mathbf{r}_i}\dot{\sigma}_\alpha \right) = 0.
\end{aligned}$$

The equation of motion $m_i\ddot{\mathbf{r}}_i = \mathbf{F}_i - \lambda_\alpha \partial\sigma_\alpha/\partial\mathbf{r}_i$ therefore gives a linear equation for the Lagrange multipliers

$$\sum_i \left(\frac{\mathbf{F}_i}{m_i} - \frac{1}{m_i}\frac{\partial\sigma_\beta}{\partial\mathbf{r}_i}\lambda_\beta\right)\cdot\frac{\partial\sigma_\alpha}{\partial\mathbf{r}_i} + \sum_{i,j}\dot{\mathbf{r}}_i\cdot\frac{\partial^2\sigma_\alpha}{\partial\mathbf{r}_i\partial\mathbf{r}_j}\cdot\dot{\mathbf{r}}_j = 0$$

or

$$\lambda_\alpha \;=\; \mathsf{Z}^{-1}_{\alpha\beta}\left(\mathcal{F}_\beta + \mathcal{T}_\beta\right) \qquad \mathcal{F}_\beta = \sum_i \frac{\mathbf{F}_i}{m_i}\cdot\frac{\partial\sigma_\beta}{\partial\mathbf{r}_i} \qquad \mathcal{T}_\beta = \sum_{i,j}\frac{\mathbf{p}_i}{m_i}\cdot\frac{\partial^2\sigma_\alpha}{\partial\mathbf{r}_i\partial\mathbf{r}_j}\cdot\frac{\mathbf{p}_j}{m_j}.$$

and Z is the matrix defined earlier.

- From this expression, one sees an explicit dependence of the Lagrange multipliers λ_α on the momenta through the $\mathcal{T}$ term.
- The equations of motion

$$\mathcal{L}_0\mathbf{X} = \begin{pmatrix}\dot{\mathbf{r}}_i\\ \dot{\mathbf{p}}_i\end{pmatrix} = \begin{pmatrix}\dfrac{\mathbf{p}_i}{m_i}\\ \mathbf{F}_i - \dfrac{\partial\sigma_\alpha}{\partial\mathbf{r}_i}\cdot\mathsf{Z}^{-1}_{\alpha\beta}\left(\mathcal{F}_\beta+\mathcal{T}_\beta\right)\end{pmatrix}$$

  is difficult to solve in the full phase space. One can construct a symplectic integrator in a lower dimensional phase space, or resort to an iterative solution method known as *SHAKE*.

Example:

Consider the example of a particle moving on a sphere of radius d centered at the origin. The constraint condition on the position vector $\mathbf{r}$ can be written as $\sigma = (r^2 - d^2)/2 = 0$. For this system, the constraint force $\mathbf{G} = -\lambda\mathbf{r}$ and $\mathsf{Z} = r^2/m$ and hence $\mathsf{Z}^{-1} = m/r^2$. We also find

$$\mathcal{F} = \frac{\mathbf{F}}{m}\cdot\frac{\partial\sigma}{\partial\mathbf{r}} = \frac{\mathbf{F}\cdot\mathbf{r}}{m} \qquad \mathcal{T} = \dot{\mathbf{r}}\cdot\frac{\partial^2\sigma}{\partial\mathbf{r}^2}\cdot\dot{\mathbf{r}} = \dot{r}^2.$$

leading to

$$\lambda = \frac{m}{r^2}\left(\frac{\mathbf{F}\cdot\mathbf{r}}{m} + \dot{r}^2\right).$$

If there is no potential, $\mathbf{F} = 0$, and $\lambda = m\dot{r}^2/r^2$. Noting that the angular velocity of a particle on a sphere is $\omega = \dot{r}/r$, we can write the constraint force as $\mathbf{G} = -m\omega^2\mathbf{r}$, which is known as the *centripetal force*, and the equation of motion can be written as

$$m\ddot{\mathbf{r}} = -\lambda\mathbf{r} = -m\omega^2\mathbf{r}.$$

In finite difference form, this may be written as

$$\mathbf{r}(t+\Delta t) \quad = \quad 2\mathbf{r}(t) - \mathbf{r}(t-\Delta t) - \omega^2 \mathbf{r}(t)\Delta t^2.$$

How well would the constraint be satisfied at time $t + \Delta t$ in this updating scheme if it is satisfied exactly at time t, $r^2(t) = d^2$, as well as at time $t - \Delta t$? Squaring the left hand side of the equation above, we get

$$\begin{aligned} r^2(t+\Delta t) &= d^2 \left(5 + (\omega\Delta t)^4 - 4(\omega\Delta t)^2 + \cos(\omega\Delta t)(2(\omega\Delta t)^2 - 4)\right) \\ &= d^2 \left(1 - \frac{(\omega\Delta t)^4}{6} + O(\Delta t^6)\right), \end{aligned}$$

where we have used the exact solution $\mathbf{r}(t) = \mathbf{r}(0)\cos(\omega t) + \dot{\mathbf{r}}(0)\sin \omega t/\omega$. Although the error in the constraint may appear small, *it will build* over the course of the simulation and will eventually result in serious violations of the constraint condition. When working with the difference equations, it turns out to be better to solve the Lagrange multiplier by requiring that the constraint condition itself is satisfied exactly at each time step (rather than using the second derivative condition). Consider the difference equation with an undetermined Lagrange multiplier λ

$$\mathbf{r}(t+\Delta t) \quad = \quad \mathbf{r}_u(t+\Delta t) - \frac{\lambda}{m}\mathbf{r}(t),$$

where $\mathbf{r}_u(t+\Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}(t)\Delta t + \ldots$ would be the position of the particle at time $t + \Delta t$ in the absence of the constraint. Imposing the constraint condition results in a quadratic equation for λ

$$d^2 \quad = \quad r^2(t+\Delta t) = r_u^2(t+\Delta t) - \frac{2\lambda}{m}\mathbf{r}(t)\cdot\mathbf{r}_u(t+\Delta t) + \left(\frac{\lambda}{m}r(t)\right)^2,$$

whose solution is

$$\lambda = \frac{m}{d}\left(r_p(t+\Delta t) - \sqrt{r_p^2(t+\Delta t) - (r_u^2(t+\Delta t) - d^2)}\right),$$

where $r_p(t+\Delta t) = \hat{\mathbf{r}}(t)\cdot\mathbf{r}_u(t+\Delta t)$ is the projection of the new unconstrained position $\mathbf{r}_u(t+\Delta t)$ along the direction $\hat{\mathbf{r}}(t)$.

- Cannot always solve for the exact λ that satisfies the constraint condition analytically if multiple constraints are applied.

- Iterative and efficient numerical solutions of the Lagrange multiplier exist, called *SHAKE*.

Basis of SHAKE algorithm

In situations where an analytical solution of the Lagrange multipliers is not possible, a numerical solution can be found by the following procedure:

1. The equation of motion is written as a difference equation to some order in the time step:

$$\mathbf{r}_i(t+\Delta t) \quad = \quad \mathbf{r}_i^u(t+\Delta t) - \frac{\Delta t^2}{m_i}\lambda_\alpha \left(\frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i}\right)_{\mathbf{r}(t)},$$

   where $\mathbf{r}_i^u(t+\Delta t)$ is the solution of the *unconstrained* position of component i at time $t+\Delta t$.

2. We require that all constraints are satisfied at the new time step, $\sigma_\alpha(t+\Delta t) = \sigma_\alpha(\mathbf{r}(t+\Delta t)) = 0$. To enforce this, we use an iterative procedure starting with a guess of $\lambda_\alpha^{(0)} = 0$ and taking the positions $\mathbf{x}_i^{(0)}(t+\Delta t) = \mathbf{r}_i^u(t+\Delta t)$. We then Taylor expand the constraint condition at the estimated coordinates $\mathbf{x}_i^{(0)}$ around the difference $\Delta_i^{(0)} = \mathbf{r}_i(t+\Delta t) - \mathbf{x}_i^{(0)}(t+\Delta t)$,

$$0 = \sigma_\alpha(t+\Delta t) \quad = \quad \sigma_\alpha(\mathbf{x}_i^{(0)}(t+\Delta t)) + \sum_i \left(\frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i}\right)_{\mathbf{x}_i^{(0)}} \cdot \Delta_i^{(0)},$$

   but from the difference equation, we have

$$\Delta_i^{(0)} = \frac{-\Delta t^2}{m_i}\lambda_\beta^{(1)} \left(\frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i}\right)_{\mathbf{r}_i(t)} + O(\Delta t^4),$$

   and hence we need

$$\sigma_\alpha(\mathbf{x}_i^{(0)}) = \sum_i \frac{\Delta t^2}{m_i}\lambda_\beta^{(1)} \left(\frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i}\right)_{\mathbf{x}_i^{(0)}} \cdot \left(\frac{\partial \sigma_\beta}{\partial \mathbf{r}_i}\right)_{\mathbf{r}_i(t)} = \Delta t^2 \mathsf{Z}_{\alpha\beta}^{(0)}\lambda_\beta^{(1)}.$$

   Solving this equation for the new estimate of the Lagrange multipliers $\lambda^{(1)}$ corresponds to the matrix form

$$\Delta t^2 \lambda_\alpha^{(1)} = \mathsf{Z}_{\alpha\beta}^{(0)-1}\sigma_\beta(\mathbf{x}_i^{(0)}(t+\Delta t)).$$

3. Armed with this Lagrange multiplier, we form a new estimate of the constrained position at time $t+\Delta t$ using

$$\mathbf{x}_i^{(1)}(t+\Delta t) = \mathbf{x}_i^{(0)}(t+\Delta t) - \frac{\Delta t^2 \lambda_\alpha^{(1)}}{m_i}\left(\frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i}\right)_{\mathbf{r}_i(t)}$$

4. We repeat the previous steps to get $\lambda^{(n+1)}$ by forming $\mathsf{Z}^{(n)-1}$ and $\sigma(\mathbf{x}_i^{(n)})$ until the $\mathbf{x}_i^{(n)}(t+\Delta t)$ converge, at which point $\mathbf{r}_i(t+\Delta t) = \mathbf{x}_i^{(n)}(t+\Delta t)$ satisfy all the constraints to some specified precision.

- It is possible to avoid the matrix inversion step by modifying the algorithm to evaluate the λ_α *sequentially*. In practice, this is carried out by taking only the diagonal terms of the matrix Z^{-1}. This effectively amounts to using the iteration

$$\Delta t^2 \lambda_\alpha^{(n+1)} = \frac{\sigma_\alpha(\mathbf{x}^{(n)}(t+\Delta t))}{\mathsf{Z}_{\alpha\alpha}^{(n)}}$$

for each constraint in succession.

5.5 Statistical Mechanics of Non-Hamiltonian Systems

In the previous section, we saw that the constrained dynamics generated configurational states with a probability density ρ which differs from the constrained probability density ρ_{con}. What ensemble does the constrained dynamics generate?

- Consider the unconstrained Hamiltonian written in the generalized coordinates $(\mathbf{u}, \mathbf{p}^u) = (\mathbf{q}, \boldsymbol{\sigma}, \mathbf{p}^q, \mathbf{p}^\sigma)$,

$$H(\mathbf{u}, \mathbf{p}^u) = \frac{1}{2}\mathbf{p}^{uT} \cdot \mathsf{G}^{-1} \cdot \mathbf{p}^u - V(\mathbf{u}),$$

where we recall the block form of the matrices G and G^{-1}

$$\mathsf{G} = \left(\begin{array}{c:c} \mathsf{A} & \mathsf{B} \\ \hdashline \mathsf{B}^T & \Gamma \end{array}\right) \qquad \mathsf{G}^{-1} = \left(\begin{array}{c:c} \Delta & \mathsf{E} \\ \hdashline \mathsf{E}^T & \mathsf{Z} \end{array}\right),$$

and from $\mathbf{p}^u = \mathsf{G} \cdot \dot{\mathbf{u}}$, we see

$$\mathbf{p}^q = \mathsf{A} \cdot \dot{\mathbf{q}} + \mathsf{B} \cdot \dot{\sigma} \qquad \mathbf{p}^\sigma = \mathsf{B}^T \cdot \dot{\mathbf{q}} + \Gamma \cdot \dot{\boldsymbol{\sigma}}$$

In the *constrained* system, we have $\boldsymbol{\sigma} = 0$ and $\dot{\boldsymbol{\sigma}} = 0$, and hence the momenta $\mathbf{p}^\sigma$ are no longer independent variables and must be constrained to a specific value that depends on $(\mathbf{q}, \mathbf{p}^q)$. In particular, we now have

$$\mathbf{p}^q = \tilde{\mathsf{A}} \cdot \dot{\mathbf{q}} \qquad \mathbf{p}^\sigma = \tilde{\mathsf{B}}^T \cdot \dot{\mathbf{q}} = \tilde{\mathsf{B}}^T \tilde{\mathsf{A}}^{-1} \mathbf{p}^q = \tilde{\mathbf{p}}^\sigma,$$

where $\tilde{\mathsf{A}} = \mathsf{A}(\mathbf{q}, \boldsymbol{\sigma} = 0)$ and $\tilde{\mathsf{B}} = \mathsf{B}(\mathbf{q}, \boldsymbol{\sigma} = 0)$.

- Recall that before, the constrained Hamiltonian was written as

$$H_c = \frac{1}{2}\mathbf{p}^q \cdot \tilde{\mathsf{A}}^{-1} \cdot \mathbf{p}^q + V(\mathbf{q}, \boldsymbol{\sigma} = 0),$$

and the equations of motion in the phase space $(\mathbf{q}, \mathbf{p}^q)$ was of symplectic form (canonical). The probability to find the system in a volume $d\mathbf{q}d\mathbf{p}^q$ around $(\mathbf{q}, \mathbf{p}^q)$ for this Hamiltonian system is

$$\rho_c(\mathbf{q}, \mathbf{p}^q)\, d\mathbf{q}d\mathbf{p}^q = \rho_c\big(H(\mathbf{q}, \boldsymbol{\sigma} = 0, \mathbf{p}^q, \mathbf{p}^{\boldsymbol{\sigma}} \;=\; \tilde{\mathbf{p}}^{\boldsymbol{\sigma}})\big)\, d\mathbf{q}d\mathbf{p}^q.$$

- In the extended phase space $(\mathbf{q}, \boldsymbol{\sigma}, \mathbf{p}^q, \mathbf{p}^{\boldsymbol{\sigma}})$, the probability is therefore

$$\begin{aligned}\rho_c(\mathbf{q}, \mathbf{p}^q)d\mathbf{q}d\mathbf{p}^q\, \delta(\boldsymbol{\sigma})\delta(\mathbf{p}^{\boldsymbol{\sigma}} - \tilde{\mathbf{p}}^{\boldsymbol{\sigma}})d\boldsymbol{\sigma}d\mathbf{p}^{\boldsymbol{\sigma}} &= \rho_c\big(H(\mathbf{u}, \mathbf{p}^u)\big)\delta(\boldsymbol{\sigma})\delta(\mathbf{p}^{\boldsymbol{\sigma}} - \tilde{\mathbf{p}}^{\boldsymbol{\sigma}})\, d\mathbf{u}d\mathbf{p}^u \\ &= \rho_c\big(H(\mathbf{r}, \mathbf{p})\big)\delta(\boldsymbol{\sigma}(\mathbf{r}))\delta(\mathbf{p}^{\boldsymbol{\sigma}}(\mathbf{r}, \mathbf{p}) - \tilde{\mathbf{p}}^{\boldsymbol{\sigma}}(\mathbf{r}, \mathbf{p}))\, d\mathbf{r}d\mathbf{p},\end{aligned}$$

where we have used the fact that the Jacobian for the *canonical* transformation between coordinates $(\mathbf{u}, \mathbf{p}^u)$ and $(\mathbf{r}, \mathbf{p})$ is unity.

- To re-write the condition $\mathbf{p}^{\boldsymbol{\sigma}} = \tilde{\mathbf{p}}^{\boldsymbol{\sigma}}$ in terms of the coordinates $(\mathbf{r}, \mathbf{p})$, note that

$$\begin{pmatrix} \dot{\mathbf{q}} \\ \dot{\boldsymbol{\sigma}} \end{pmatrix} = \left(\begin{array}{c:c} \Delta & \mathsf{E} \\ \hdashline \mathsf{E}^T & \mathsf{Z} \end{array}\right) \cdot \begin{pmatrix} \mathbf{p}^q \\ \mathbf{p}^\sigma \end{pmatrix}, \qquad \text{from} \qquad \mathsf{G}^{-1} \cdot \mathbf{p}^u = \dot{\mathbf{u}},$$

and hence $\dot{\boldsymbol{\sigma}} = \tilde{\mathsf{E}}^T \cdot \mathbf{p}^q + \tilde{\mathsf{Z}} \cdot \mathbf{p}^\sigma$, where $\tilde{\mathsf{A}}$ indicates a matrix A evaluated when $\boldsymbol{\sigma} = 0$. Multiplying this equality by the matrix $\tilde{\mathsf{Z}}^{-1}$ gives

$$\tilde{\mathsf{Z}}^{-1}(\mathbf{r}) \cdot \dot{\boldsymbol{\sigma}}(\mathbf{r}) = \mathbf{p}^{\boldsymbol{\sigma}} + \tilde{\mathsf{Z}}^{-1} \cdot \tilde{\mathsf{E}}^T \cdot \mathbf{p}^q.$$

From the block forms of G and G^{-1}, we have $\mathsf{A}\cdot\mathsf{E} + \mathsf{B}\cdot\mathsf{Z} = 0$, and hence $\mathsf{E}^T\cdot\mathsf{A}^T + \mathsf{Z}^T\cdot\mathsf{B}^T = 0$. From the definitions of the symmetric matrices A and Z, we see that $\mathsf{A}^T = \mathsf{A}$ and $\mathsf{Z}^T = \mathsf{Z}$, so $\mathsf{E}^T \cdot \mathsf{A} = -\mathsf{Z} \cdot \mathsf{B}^T$, which implies $\mathsf{Z}^{-1} \cdot \mathsf{E}^T = -\mathsf{B}^T \cdot \mathsf{A}^{-1}$. Finally, when $\boldsymbol{\sigma} = 0$, we have

$$\tilde{\mathsf{Z}}^{-1}\dot{\boldsymbol{\sigma}} = \mathbf{p}^\sigma - \tilde{\mathsf{B}} \cdot \tilde{\mathsf{A}}^{-1} \cdot \mathbf{p}^q = \mathbf{p}^{\boldsymbol{\sigma}} - \tilde{\mathbf{p}}^{\boldsymbol{\sigma}},$$

and so $\delta(\mathbf{p}^{\boldsymbol{\sigma}} - \tilde{\mathbf{p}}^{\boldsymbol{\sigma}}) = \delta(\tilde{\mathsf{Z}}^{-1} \cdot \dot{\boldsymbol{\sigma}})$. Note that $\tilde{\mathsf{Z}}^{-1}(\mathbf{r})\dot{\boldsymbol{\sigma}}(\mathbf{r}, \mathbf{p})$ is easily expressed in the original phase space coordinates $(\mathbf{r}, \mathbf{p})$.

- The probability therefore obeys

$$\begin{aligned}
\rho_c(H_c)\, d\mathbf{q}d\mathbf{p}^q \delta(\boldsymbol{\sigma})\delta(\mathbf{p}^{\boldsymbol{\sigma}} - \tilde{\mathbf{p}}^{\boldsymbol{\sigma}})d\boldsymbol{\sigma}d\mathbf{p}^{\boldsymbol{\sigma}} &= \rho_c(H(\mathbf{r},\mathbf{p}))\delta(\boldsymbol{\sigma})\delta(\tilde{\mathsf{Z}}^{-1}\cdot\dot{\boldsymbol{\sigma}})\, d\mathbf{r}d\mathbf{p} \quad (5.13)\\
&= \rho_c(H(\mathbf{r},\mathbf{p}))\delta(\boldsymbol{\sigma}) \det \mathsf{Z}\, \delta(\dot{\boldsymbol{\sigma}})\, d\mathbf{r}d\mathbf{p} \quad (5.14)
\end{aligned}$$

  using the fact that $\delta(\mathsf{Z}^{-1}\cdot\dot{\boldsymbol{\sigma}}) = \det\mathsf{Z}\,\delta(\dot{\boldsymbol{\sigma}})$.

- In the constrained Hamiltonian system in canonical coordinates $(\mathbf{q},\mathbf{p}^q)$, the probability $P(\mathbf{q},\mathbf{p}^q) = \rho_c d\mathbf{q}d\mathbf{p}^q$ is conserved under the evolution of the system by Liouville's theorem, so that $P(\mathbf{q}(t),\mathbf{p}^q(t)) = P(\mathbf{q}(0),\mathbf{p}^q(0))$. In addition, it is found that the phase space volume $d\mathbf{X}_q(t) = d\mathbf{X}_q(0)$ is also conserved under the flow.

$$\begin{aligned}
\frac{d}{dt}\Bigg(\rho_c(H_c)\, d\mathbf{q}d\mathbf{p}^q\delta(\boldsymbol{\sigma})\delta(\mathbf{p}^{\boldsymbol{\sigma}} - \tilde{\mathbf{p}}^{\boldsymbol{\sigma}})d\boldsymbol{\sigma}d\mathbf{p}^{\boldsymbol{\sigma}}\Bigg) &= 0 \qquad \text{so}\\
\frac{d}{dt}\Bigg(\rho_c(H(\mathbf{r},\mathbf{p}))\,\delta(\boldsymbol{\sigma})\,\delta(\dot{\boldsymbol{\sigma}})\,\det\mathsf{Z}\, d\mathbf{r}d\mathbf{p}\Bigg) &= 0.
\end{aligned}$$

- The constrained dynamics conserves $H(\mathbf{r},\mathbf{p}) = H_c(\mathbf{q},\mathbf{p}^q)$ and satisfies the constraint conditions $\boldsymbol{\sigma} = 0$ and $\dot{\boldsymbol{\sigma}} = 0$ at all times. Hence, for the full phase space $\mathbf{X} = (\mathbf{r},\mathbf{p})$,

$$\begin{aligned}
\frac{d}{dt}\Bigg(\det\mathsf{Z}\, d\mathbf{X}\Bigg) &= 0\\
\det\mathsf{Z}(\mathbf{r}(t))\, d\mathbf{X}(t) &= \det\mathsf{Z}(\mathbf{r}(0))\, d\mathbf{X}(0).
\end{aligned}$$

- Once can therefore interpret $d\boldsymbol{\mu}(\mathbf{X}) = \det\mathsf{Z}\, d\mathbf{X}$ as the *invariant measure* for the phase space flow.

- To see the connection between the dynamics of the system and the $\det\mathsf{Z}$ factor, consider the flow of the standard volume element $d\mathbf{X}_0$ under the dynamics to a time t at which the volume is $d\mathbf{X}_t = \det\mathsf{J}(\mathbf{X}_t;\mathbf{X}_0)\, d\mathbf{X}_0$, where the matrix J has elements $\mathsf{J}_{ij} = \partial\mathbf{X}_i(t)/\partial\mathbf{X}_j(0)$. To find the evolution of the Jacobian determinant, we use the fact that $\det\mathsf{J} = e^{\mathrm{Tr}\ln\mathsf{J}}$, which follows from the general property of a square matrix, $\det\mathsf{A} = e^{\mathrm{Tr}\,\mathsf{A}}$, with $\mathsf{J} = e^{\mathsf{A}}$.

  Proof. To establish this fact, note that any square matrix can be written in Jordan normal form as $\mathsf{A} = \mathsf{P}^{-1}\cdot\mathsf{D}\cdot\mathsf{P}$, where D is in Jordan form. Recall that the Jordan form consists of an upper-triangular matrix with the eigenvalues of A along the diagonal, and that the determinant of a triangular matrix is the product of the diagonal elements. The exponential of the matrix A can be written as $e^{\mathsf{A}} = \mathsf{P}^{-1}\cdot e^{\mathsf{D}}\cdot\mathsf{P}$, and the determinant of this exponential is $\det e^{\mathsf{A}} = \det\mathsf{P}^{-1}\det e^{\mathsf{D}}\det\mathsf{P}$. Since $\det\mathsf{P}^{-1} = 1/\det\mathsf{P}$, we see that $\det e^{\mathsf{A}} = \det e^{\mathsf{D}}$. Since D is in Jordan form, e^{D} is a triangular matrix with diagonal elements $1 + \lambda_i + \lambda_i^2/2 + \cdots = e^{\lambda_i}$, where $\lambda_i = \mathsf{D}_{ii}$ is an eigenvalue of A, where we have used the fact that $\mathsf{D}^n_{ij} = \binom{n}{j}\lambda_i^{n-j}$ for $j \geq i$. Since the determinant of e^{D} is the product of its diagaonal elements $\prod_i e^{\lambda_i} = e^{\sum_i \lambda_i}$, we see that $\det e^{\mathsf{A}} = e^{\mathrm{Tr}\,\mathsf{A}}$ since $\mathrm{Tr}\,\mathsf{A} = \sum_i \lambda_i$. □

From this property, we have

$$\begin{aligned}
\frac{d \det \mathsf{J}}{dt} &= e^{\mathrm{Tr}\ln\mathsf{J}} \frac{d}{dt}\left(\mathrm{Tr}\ln\mathsf{J}\right) = \det\mathsf{J}\ \mathrm{Tr}\left(\frac{d\mathsf{J}}{dt}\cdot\mathsf{J}^{-1}\right) \\
&= \det\mathsf{J}\left(\sum_i \frac{\partial\dot{\mathbf{X}}_i(t)}{\partial\mathbf{X}(0)}\cdot\frac{\partial\mathbf{X}(0)}{\partial\mathbf{X}_i(t)}\right) = \det\mathsf{J}\sum_i\frac{\partial\dot{\mathbf{X}}_i(t)}{\partial\mathbf{X}_i(t)} \\
&= \det\mathsf{J}\left(\frac{\partial}{\partial\mathbf{X}(t)}\cdot\dot{\mathbf{X}}(t)\right) = \det\mathsf{J}\,\kappa(t),
\end{aligned}$$

where $\kappa(t) = \partial/\partial\mathbf{X}(t)\cdot\dot{\mathbf{X}}(t)$ is called the *phase space compressibility.*

– For a Hamiltonian system, phase space volume is conserved and $\kappa = 0$ at all times (incompressible phase space).

- The relation between the Jacobian and the compressibility can be written

$$\begin{aligned}
\frac{d\ln\det\mathsf{J}}{dt} &= \kappa(t) \\
\det\mathsf{J}(t) &= \det\mathsf{J}\,e^{\int_0^t d\tau\,\kappa(\tau)} = e^{\int_0^t d\tau\,\kappa(\tau)}.
\end{aligned}$$

- From the form of the invariant measure for which $d\boldsymbol{\mu}(t) = d\boldsymbol{\mu}(0)$, it therefore follows that

$$\begin{aligned}
\frac{d}{dt}\big(\det\mathsf{Z}\det\mathsf{J}\big) &= \left[\frac{d\det\mathsf{Z}}{dt}\det\mathsf{J}\right] + \det\mathsf{Z}\frac{d\det\mathsf{J}}{dt} = 0 \\
\kappa\,\det\mathsf{Z}\det\mathsf{J} + \det\mathsf{J}\frac{d\det\mathsf{Z}}{dt} &= 0,
\end{aligned}$$

which implies that

$$\frac{d\det\mathsf{Z}}{dt} = -\kappa\det\mathsf{Z} \qquad \frac{d\ln\det\mathsf{Z}}{dt} = -\kappa. \tag{5.15}$$

– This relation can be verified explicitly by evaluating $\kappa = \nabla_{\mathbf{X}} \cdot \dot{\mathbf{X}}$ from the equations of motion

$$\kappa = \nabla_{\mathbf{X}} \cdot \dot{\mathbf{X}} = -\sum_i \frac{\partial \lambda_\alpha(\mathbf{X})}{\partial \mathbf{p}_i} \cdot \frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i} = -\frac{d}{dt} \ln \det \mathsf{Z}.$$

– For the holonomically constrained system, we note that κ is the total time derivative of a function of the phase space variable $\mathbf{X}$, $-\ln \det \mathsf{Z} = \omega(\mathbf{X})$. Thus the integral $\int_0^t d\tau\, \kappa(\tau) = \omega(\mathbf{X}(t)) - \omega(\mathbf{X}(0))$ and

$$\det \mathsf{J}(t) e^{-\omega(X(t))} = \det \mathsf{J}(0) e^{-\omega(\mathbf{X}(0))} = e^{-\omega(\mathbf{X}(0))}.$$

– Noting that $d\mathbf{X}(t) = \det \mathsf{J}(\mathbf{X}(t); \mathbf{X}(0))\, d\mathbf{X}(0)$, we see that the invariant volume element can be written as $e^{-\omega(\mathbf{X}(t))}\, d\mathbf{X}(t) = e^{-\omega(\mathbf{X}(0))}\, d\mathbf{X}(0)$, and $e^{-\omega(\mathbf{X}(0))} = \det \mathsf{Z}(\mathbf{X}(0))$.

5.5.1 Non-Hamiltonian Dynamics and the Canonical Ensemble

Consider a system with phase space coordinate $\mathbf{x}$ that obeys the evolution equation

$$\dot{\mathbf{x}}(t; \mathbf{x}_0) = \frac{d\mathbf{x}}{dt} = \boldsymbol{\xi}\big(\mathbf{x}(t; \mathbf{x}_0)\big)$$

and suppose the solution of this equation is $\mathbf{x}(t; \mathbf{x}_0)$ subject to the boundary condition $\mathbf{x}(0; \mathbf{x}_0) = \mathbf{x}_0$.

- The time derivative of a dynamical variable B is given by $\dot{B}(\mathbf{x}) = \boldsymbol{\xi} \cdot \nabla_x B(\mathbf{x}) = \mathcal{L}_0 B(\mathbf{x})$, where $\mathcal{L}_0 = \boldsymbol{\xi} \cdot \nabla_x$.

- We assume the dynamics is ergodic so that the time average is equal to an ensemble average according to

$$\overline{A}(t) = \lim_{T\to\infty} \frac{1}{T} \int_0^T d\tau A(\mathbf{x}(t+\tau)) = \langle A \rangle_t = \int d\mathbf{x}_0\, \rho(\mathbf{x}_0) A(\mathbf{x}(t; \mathbf{x}_0)),$$

  where $\rho(\mathbf{x}_0)$ is the density at the phase point $\mathbf{x}_0$ at time $t = 0$.

- Note that

$$\begin{aligned}\langle A \rangle_t &= \int d\mathbf{x} d\mathbf{x}_0\, \delta(\mathbf{x} - \mathbf{x}(t; \mathbf{x}_0))\, \rho(\mathbf{x}_0) A(\mathbf{x}) = \int d\mathbf{x}\, \langle \delta(\mathbf{x} - \mathbf{x}(t; \mathbf{x}_0)) \rangle_0 A(\mathbf{x}) \\ &= \int d\mathbf{x}\, \rho(\mathbf{x}, t) A(\mathbf{x}),\end{aligned}$$

  where $\rho(\mathbf{x}, t) = \langle \delta(\mathbf{x} - \mathbf{x}(t; \mathbf{x}_0)) \rangle_0 = \int d\mathbf{x}_0\, \rho(\mathbf{x}_0) \delta(\mathbf{x} - \mathbf{x}(t; \mathbf{x}_0))$.

- The equation of motion for $\rho(\mathbf{x},t)$, the Liouville equation, follows from

$$\begin{aligned}
\frac{\partial\rho(\mathbf{x},t)}{\partial t} &= \frac{d}{dt}\langle\delta(\mathbf{x}-\mathbf{x}(t;\mathbf{x}_0))\rangle_0 = \big\langle\dot{\mathbf{x}}(t;\mathbf{x}_0)\cdot\nabla_{\mathbf{x}(t)}\delta(\mathbf{x}-\mathbf{x}(t;\mathbf{x}_0))\big\rangle_0 \\
&= -\nabla_x\cdot\langle\dot{\mathbf{x}}(t;\mathbf{x}_0)\delta(\mathbf{x}-\mathbf{x}(t;\mathbf{x}_0))\rangle_0 = -\nabla_x\cdot\langle\boldsymbol{\xi}(\mathbf{x}(t;\mathbf{x}_0))\delta(\mathbf{x}-\mathbf{x}(t;\mathbf{x}_0))\rangle_0 \\
&= -\nabla_x\cdot\big(\boldsymbol{\xi}(\mathbf{x})\langle\delta(\mathbf{x}-\mathbf{x}(t;\mathbf{x}_0))\rangle_0\big) = -\nabla_x\cdot\big(\boldsymbol{\xi}(\mathbf{x})\rho(\mathbf{x},t)\big).
\end{aligned}$$

- We have seen that many dynamics $\boldsymbol{\xi}$ have non-zero phase space compressibilities $\kappa = \nabla_x\cdot\boldsymbol{\xi}(\mathbf{x})$, so that the invariant measure, if it exists, assumes the general form $d\boldsymbol{\mu}(\mathbf{x}) = \gamma(\mathbf{x})d\mathbf{x}$. We therefore define a density with respect to this measure $f(\mathbf{x})$ by the relation $\rho(\mathbf{x}) = \gamma(\mathbf{x})f(\mathbf{x})$, where $\gamma(\mathbf{x})$ is a positive function of the phase point $\mathbf{x}$.

  – Inserting this definition in the Liouville equation, we find

$$\begin{aligned}
\frac{\partial f(\mathbf{x},t)}{\partial t} + \boldsymbol{\xi}(\mathbf{x})\cdot\nabla_x f(\mathbf{x},t) &= -\omega(\mathbf{x},t)f(\mathbf{x},t) \\
\omega(\mathbf{x},t) &= \frac{1}{\gamma(\mathbf{x},t)}\left(\frac{\partial\gamma(\mathbf{x},t)}{\partial t} + \nabla_x\cdot(\boldsymbol{\xi}(\mathbf{x})\gamma(\mathbf{x},t))\right).
\end{aligned}$$

  – If we *choose* $\gamma(\mathbf{x},t)$ to satisfy $\omega(\mathbf{x},t) = 0$, then we find it must satisfy Liouville's equation,

$$\begin{aligned}
\frac{\partial\gamma}{\partial t} + \nabla_x\cdot(\boldsymbol{\xi}\gamma) &= 0 \\
\frac{\partial\gamma}{\partial t} + \boldsymbol{\xi}\cdot\nabla_x\gamma &= -\gamma\nabla_x\cdot\boldsymbol{\xi} = -\gamma\kappa
\end{aligned}$$

  then

$$\begin{aligned}
\frac{d\ln\gamma(\mathbf{x},t)}{dt} &= -\kappa \\
\frac{df(\mathbf{x},t)}{dt} &= \frac{\partial f(\mathbf{x},t)}{\partial t} + \boldsymbol{\xi}(\mathbf{x})\cdot\nabla_x f(\mathbf{x},t) \\
&= \frac{\partial f(\mathbf{x},t)}{\partial t} + \mathcal{L}_0 f(\mathbf{x},t) = 0.
\end{aligned} \tag{5.16}$$

  – If a function $w(\mathbf{x})$ exists that satisfies

$$\kappa(\mathbf{x}) = \frac{dw(\mathbf{x})}{dt} = \boldsymbol{\xi}(\mathbf{x})\cdot\nabla_x w(\mathbf{x}),$$

  then $\ln(\gamma(\mathbf{x},t)/\gamma(\mathbf{x},0)) = w(\mathbf{x}(t;\mathbf{x}_0)) - w(\mathbf{x}_0)$, and one can define the invariant measure to be

$$d\boldsymbol{\mu}(\mathbf{x}) = e^{-w(\mathbf{x})}d\mathbf{x}.$$

- If $\kappa(\mathbf{x})$ cannot be written as the total time derivative, then

$$\gamma(\mathbf{x}(t;\mathbf{x}_0)) = \gamma(\mathbf{x}_0)e^{-\int_0^t d\tau\,\kappa(\mathbf{x}(\tau,\mathbf{x}_0))}$$

which is equivalent to solving the full equation for the density $\rho(\mathbf{x},t)$. There is no clear way to define an invariant measure for this type of dynamics.

  * Note that if we have periodic orbits in the dynamics (only possible in non-Hamiltonian systems) so that $\mathbf{x}(T) = \mathbf{x}(0)$, then we must have

$$w(\mathbf{x}(T)) = w(\mathbf{x}(0)) \quad \text{or} \quad e^{-\int_0^T d\tau\kappa(\tau)} = 1.$$

  * If the periodic orbit is net contracting or expanding, then we either have that κ cannot be written as a total time derivative of $w(\mathbf{x})$ *or* that $w(\mathbf{x})$ is not well-behaved (singular).

- The formal solution of Eq. (5.16) is

$$f(\mathbf{X},t) = e^{-\mathcal{L}_0 t} f(\mathbf{X},0),$$

as in the normal situation.

- For the special case of a constrained system, since the equations of motion have $H(\mathbf{X})$, $\boldsymbol{\sigma}$ and $\dot{\boldsymbol{\sigma}}$ as constants of motion, we can write the equilibrium phase space distribution function, which is a stationary solution of Eq. (5.16), as

$$f_{eq}(\mathbf{X}) = \Omega(E)^{-1}\delta(H(\mathbf{X}) - E)\delta(\boldsymbol{\sigma})\delta(\dot{\boldsymbol{\sigma}}),$$

where $\Omega(E)$ is a normalizing factor. Note that this result is suggested by Eq. (5.14).

- In non-equilibrium systems, the density $f(\mathbf{X},t)$ has an explicit time dependence, and non-equilibrium averages can be written as

$$\overline{B}(t) = \int d\boldsymbol{\mu}(\mathbf{X})\, B(\mathbf{X}) f(\mathbf{X},t) = \int d\boldsymbol{\mu}(\mathbf{X})\, B(\mathbf{X}) e^{-\mathcal{L}_0 t} f(\mathbf{X},0),$$

where $f(\mathbf{X},0)$ is the initial non-equilibrium density.

  - For a canonical Hamiltonian system, the Liouville operator $\mathcal{L}_0$ is self-adjoint in the sense that

$$\int d\mathbf{X}\, B(\mathbf{X}) e^{-\mathcal{L}_0 t} A(\mathbf{X}) = \int d\mathbf{X}\, \left(e^{\mathcal{L}_0 t} B(\mathbf{X})\right) A(\mathbf{X}).$$

– To examine whether this still holds, consider

$$\begin{aligned}\int d\mathbf{X} B(\mathbf{X})\mathcal{L}_0 A(\mathbf{X}) &= \int d\mathbf{X}\left[\left(-\mathcal{L}_0 + \nabla_{\mathbf{X}}\cdot\dot{\mathbf{X}}\right)B(\mathbf{X})\right]A(\mathbf{X})\\ &= -\int d\mathbf{X}\left[(\mathcal{L}_0+\kappa)\,B(\mathbf{X})\right]A(\mathbf{X})\end{aligned}$$

by integration by parts. Now note that since $\mathcal{L}_0\gamma(\mathbf{X}) = -\kappa\gamma(\mathbf{X})$, it therefore follows that

$$\begin{aligned}\int d\boldsymbol{\mu}(\mathbf{X})\,B(\mathbf{X})\mathcal{L}_0 A(\mathbf{X}) &= \int d\mathbf{X}\gamma(\mathbf{X})\,B(\mathbf{X})\mathcal{L}_0 A(\mathbf{X})\\ &= -\int d\mathbf{X}\left[(\mathcal{L}_0+\kappa)\,\gamma(\mathbf{X})B(\mathbf{X})\right]A(\mathbf{X})\\ &= -\int d\mathbf{X}\,A(\mathbf{X})\Big[\kappa\gamma(\mathbf{X})B(\mathbf{X}) + \gamma(\mathbf{X})\big(\mathcal{L}_0 B(\mathbf{X})\big)\\ &\qquad +\big(\mathcal{L}_0\gamma(\mathbf{X})\big)B(\mathbf{X})\Big]\\ &= -\int d\mathbf{X}\,\left[\mathcal{L}_0 B(\mathbf{X})\right]\gamma(\mathbf{X})A(\mathbf{X})\\ &= -\int d\boldsymbol{\mu}(\mathbf{X})\left[\mathcal{L}_0 B(\mathbf{X})\right]A(\mathbf{X}).\end{aligned}$$

– Using this result in the expansion of $e^{-\mathcal{L}_0 t}$, we see that

$$\int d\boldsymbol{\mu}(\mathbf{X})B(\mathbf{X})e^{-\mathcal{L}_0 t}A(\mathbf{X}) = \int d\boldsymbol{\mu}(\mathbf{X})\left(e^{\mathcal{L}_0 t}B(\mathbf{X})\right)A(\mathbf{X}) = \int d\boldsymbol{\mu}(\mathbf{X})\,B(\mathbf{X}(t))A(\mathbf{X}).$$

– Note that this result also applies for $A(\mathbf{X}) = f(\mathbf{X})$, so that the operator $\mathcal{L}_0$ is *self-adjoint* when the invariant measure $d\boldsymbol{\mu}(\mathbf{X})$ is used to define the innner-product. This is not the case when the inner product does not include the factor of $\gamma(\mathbf{X})$ in the measure.

– For Hamiltonian systems, we have $\gamma(\mathbf{X}) = 1$, and the Liouville operator $\mathcal{L}_0$ is self-adjoint with respect to the simple measure $d\mathbf{X}$.

– Note that for the special case of holonomically-constrained systems, we have $\gamma(\mathbf{X}) = \det \mathsf{Z}(\mathbf{X})$ as the term in the invariant measure.

Canonical Dynamics

- Now consider a system with $3N$ coordinates $\mathbf{q}$ and η with corresponding momenta $\mathbf{p}$ and p_η whose evolution is governed by the equations

$$\begin{aligned} \dot{\mathbf{q}} &= \frac{\mathbf{p}}{m} \qquad \dot{\eta} = \alpha p_\eta \\ \dot{\mathbf{p}} &= \mathbf{F}(\mathbf{q}) - \alpha \mathbf{p} p_\eta - \eta K T'(\mathbf{q}) \qquad \dot{p}_\eta = \frac{\mathbf{p}\cdot\mathbf{p}}{m} - 3NkT(\mathbf{q}), \end{aligned} \tag{5.17}$$

  where $T(\mathbf{q})$ is a locally-defined temperature and $T'(\mathbf{q}) = dT/d\mathbf{q}$.

  - From these equations of motion, we find that

    $$H(\mathbf{q}, \eta, \mathbf{p}, p^\eta) = \frac{\mathbf{p}\cdot\mathbf{p}}{2m} + \phi(\mathbf{q}) + \alpha\frac{p_\eta^2}{2} + 3N\eta kT(\mathbf{q}) = \tilde{H}(\mathbf{q}, \mathbf{p}, p_\eta) + 3N\eta kT(\mathbf{q})$$

    is conserved by the dynamics if $\mathbf{F}(\mathbf{q}) = -d\phi(\mathbf{q})/d\mathbf{q}$.
  - Suppose the initial conditions set $H = E$, so that

    $$3N\eta = \frac{1}{kT(\mathbf{q})}\left(E - \frac{\mathbf{p}\cdot\mathbf{p}}{2m} - \phi(\mathbf{q}) - \alpha\frac{p_\eta^2}{2}\right) = \frac{1}{kT(\mathbf{q})}\left(E - \tilde{H}\right). \tag{5.18}$$

    This allows the system of equations to be simplified by inserting relation (5.18) into Eq. (5.17).

- These dynamics give rise to a phase space compressibility

$$\begin{aligned} \kappa &= \nabla_x \cdot \boldsymbol{\xi}(\mathbf{x}) = \sum_{i=1}^{N}\left[\frac{\partial}{\partial \mathbf{q}_i}\cdot\dot{\mathbf{q}}_i + \frac{\partial}{\partial \mathbf{p}_i}\cdot\dot{\mathbf{p}}_i\right] + \frac{\partial \dot{p}_\eta}{\partial p_\eta} + \frac{\partial \dot{\eta}}{\partial \eta} = -3N\alpha p_\eta = -3N\dot{\eta} \\ &= -\frac{d}{dt}\left[\frac{E - \tilde{H}}{kT(\mathbf{q})}\right] \end{aligned}$$

  - In this case, the compressiblity *is* equal to a total time derivative, and hence the invariant measure is

    $$\gamma(\mathbf{q}, \mathbf{p}, p_\eta) = e^{(E - \tilde{H}(\mathbf{q},\mathbf{p},p_\eta))/(kT(\mathbf{q}))},$$

    and the dynamics generates an ensemble with probability density

    $$\rho(\mathbf{q}, \eta, \mathbf{p}, p_\eta) = \delta(E - H(\mathbf{q}, \eta, \mathbf{p}, p_\eta))\, e^{E/(kT(\mathbf{q}))} e^{-\alpha p_\eta^2/(2kT(\mathbf{q}))}\, e^{-H_0(\mathbf{q},\mathbf{p})/(kT(\mathbf{q}))}/Z,$$

    where $H_0 = \mathbf{p}\cdot\mathbf{p}/(2m) + \phi(\mathbf{q})$ and Z is a normalization constant

$$
\begin{aligned}
Z &= \int d\mathbf{q}d\mathbf{p}\, d\eta dp_\eta\, \delta(E-H)e^{E/(kT(\mathbf{q}))}e^{-\alpha p_\eta^2/(2kT(\mathbf{q}))}\, e^{-H_0(\mathbf{q},\mathbf{p})/(kT(\mathbf{q}))} \\
&= \int d\mathbf{q}d\mathbf{p}\, d\eta dp_\eta\, \frac{1}{3NkT(\mathbf{q})}\delta(E/(3NkT(\mathbf{q}))-\eta)e^{E/(kT(\mathbf{q}))}e^{-\alpha p_\eta^2/(2kT(\mathbf{q}))}\, e^{-H_0(\mathbf{q},\mathbf{p})/(kT(\mathbf{q}))} \\
&= \int d\mathbf{q}d\mathbf{p}\, \frac{1}{3N}\sqrt{\frac{2\pi\alpha}{kT(\mathbf{q})}}e^{-H_0/(kT(\mathbf{q}))}.
\end{aligned}
$$

- The reduced density $\rho_r(\mathbf{q},\mathbf{p}) = \int d\eta dp_\eta \rho(\mathbf{q},\eta,\mathbf{p},p_\eta)$ is therefore

$$
\begin{aligned}
\rho_r(\mathbf{q},\mathbf{p}) &= \frac{1}{\sqrt{kT(\mathbf{q})}}e^{-H_0(\mathbf{q},\mathbf{p})/(kT(\mathbf{q}))}/Z_r \\
Z_r &= \int d\mathbf{q}d\mathbf{p}\, \frac{1}{\sqrt{kT(\mathbf{q})}}e^{-H_0(\mathbf{q},\mathbf{p})/(kT(\mathbf{q}))}.
\end{aligned}
$$

- Note that when $T = T(\mathbf{q})$ is uniform, the $\rho_r(\mathbf{q},\mathbf{p})$ is the canonical density for an ensemble with temperature T.
- If the system is *ergodic*, then the dynamics will generate the canonical density, so that a time average of a quantity will correspond to the canonical ensemble average.
- This approach can be extended to include a system with better mixing properties by using a chain of "thermostat" variables η_i.
- The isobaric-isothermal ensemble can also be sampled using molecular dynamics schemes using the volume V as a dynamical coordinate with conjugate moment P_V.

Systems with no invariant measure

- A different type of system can be defined by the set of equations

$$
\dot{q} = \frac{p}{m} \qquad \dot{p} = F(q) - \alpha p p_\eta \qquad \dot{p}_\eta = \frac{p^2}{m} - kT(q),
$$

  - This system does not have an invariant measure as $\kappa = -\alpha p_\eta$ is *not* equal to a total time derivative.
  - It has been shown that this system has a fractal steady state and attracting periodic orbits. [Posch and Hoover, Phys. Rev. E **55**, 6803 (1997)]

- Another type of system that has a *singular* invariant measure is

$$
\dot{x} = -\alpha x \qquad \dot{y} = \beta y \qquad \alpha > \beta > 0
$$

- System has a fixed point at the origin $(0,0)$ that is net attractive.
- Compressibility is $\kappa = -(\alpha - \beta) = d/dt\,(\ln|x| + \ln|y|)$, and hence invariant measure $\gamma = 1/(|x||y|)$ is singular along the x-axis, y-axis and at the origin.

5.5.2 Volume-preserving integrators for non-Hamiltonian systems

We'd like to develop good integration schemes for non-Hamiltonian systems along the lines used for Hamiltonian systems. Using splitting methods, it turns out that we can sometimes develop integrators that

1. are time reversible,
2. preserve the invariant volume (should it exist).

In particular, the preservation of phase space volume is an important property in determining the stability of an integrator.

- The idea is to break up the evolution equations $\dot{\mathbf{x}} = \sum_\alpha \dot{\mathbf{x}}(\alpha)$ by splitting up the Liouville operator $\mathcal{L} = \dot{\mathbf{x}} \cdot \nabla_{\mathbf{x}}$ into parts $\mathcal{L} = \sum_\alpha \mathcal{L}_\alpha$ so that $\dot{\mathbf{x}}(\alpha) = \mathcal{L}_\alpha \mathbf{x}$.
- We have seen that if it exists, the invariant measure $d\boldsymbol{\mu}(\mathbf{x}) = \gamma(\mathbf{x})d\mathbf{x}$ satisfies the divergence equation
$$\nabla_{\mathbf{x}} \cdot (\gamma(\mathbf{x})\dot{\mathbf{x}}) = 0, \tag{5.19}$$
under the dynamical evolution determined by $\dot{\mathbf{x}}$.
- We'd like to find evolution operators $\mathcal{L}_\alpha$ that each satisfy Eq. (5.19) *and* lead to dynamics that is exactly solvable.
- To see how this can be accomplished, consider the Nosé-Hoover system with phase space $\mathbf{x} = (q, p, \eta, p_\eta)$ and equations of motion
$$\dot{q} = \frac{p}{m} \qquad \dot{\eta} = \alpha p_\eta \qquad \dot{p} = F(q) - \alpha p p_\eta \qquad \dot{p}_\eta = \frac{p^2}{m} - kT,$$
where m, α and kT are constants.
  - The full Liouville operator for this system is
$$\mathcal{L} = \frac{p}{m}\frac{\partial}{\partial q} + F(q)\frac{\partial}{\partial p} - \alpha p p_\eta \frac{\partial}{\partial p} + \left(\frac{p^2}{m} - kT\right)\frac{\partial}{\partial p_\eta}.$$
  - We now examine a decomposition $\mathcal{L} = \sum_\alpha \mathcal{L}_\alpha$ that satisfies $\nabla_{\mathbf{x}} \cdot (\gamma(\mathbf{x})\dot{\mathbf{x}}(\alpha)) = 0$, where $\mathcal{L}_\alpha \mathbf{x} = \dot{\mathbf{x}}(\alpha)$.

– For the Nosé-Hoover dynamics, the invariant measure corresponds to a choice $\gamma(\mathbf{x}) = e^{\eta}$.

– There are a number of decompositions that work:

1. The choice:

$$\begin{aligned}
\mathcal{L}_1 &= F(q)\frac{\partial}{\partial p} \qquad \mathcal{L}_2 = \frac{p}{m}\left[\frac{\partial}{\partial q} + p\frac{\partial}{\partial p_\eta}\right] \\
\mathcal{L}_3 &= -kT\frac{\partial}{\partial p_\eta} \qquad \mathcal{L}_4 = \alpha p_\eta\left[-p\frac{\partial}{\partial p} + \frac{\partial}{\partial \eta}\right].
\end{aligned} \tag{5.20}$$

∗ For $\mathcal{L}_1$, $\dot{\mathbf{x}} = (0, F(q), 0, 0)$ so $\nabla_{\mathbf{x}} \cdot (e^{\eta}\dot{\mathbf{x}}(1)) = \frac{\partial}{\partial p}\left(e^{\eta}F(q)\right) = 0$, and hence $\mathcal{L}_1$ preserves the volume element $d\boldsymbol{\mu} = \gamma d\mathbf{x}$.

∗ For $\mathcal{L}_2$, $\dot{\mathbf{x}} = (p/m, 0, 0, p^2/m)$ so $\nabla_{\mathbf{x}} \cdot (e^{\eta}\dot{\mathbf{x}}(2)) = \frac{\partial}{\partial q}\left(e^{\eta}p/m\right) + \frac{\partial}{\partial p_\eta}\left(e^{\eta}p^2/m\right) = 0$.

∗ For $\mathcal{L}_3$, $\dot{\mathbf{x}} = (0, 0, 0, -kT)$ so $\nabla_{\mathbf{x}} \cdot (e^{\eta}\dot{\mathbf{x}}(3)) = \frac{\partial}{\partial p_\eta}\left(-e^{\eta}kT\right) = 0$.

∗ Finally, for $\mathcal{L}_4$ the time derivative of γ is non-zero and $\dot{\mathbf{x}} = (0, -\alpha p p_\eta, \alpha p_\eta, 0)$ and $\nabla_{\mathbf{x}} \cdot (e^{\eta}\dot{\mathbf{x}}(4)) = \frac{\partial}{\partial p}\left(-e^{\eta}\alpha p p_\eta\right) + \frac{\partial}{\partial \eta}\left(e^{\eta}\alpha p_\eta\right) = -\alpha p_\eta e^{\eta} + \alpha p_\eta e^{\eta} = 0$.

∗ Note that each of the effect of each of the propagators $e^{\mathcal{L}_\alpha \Delta t}$ on the phase point $\mathbf{x}$ is exactly computable since

$$\begin{aligned}
e^{\mathcal{L}_1\Delta t}\mathbf{x} &= \begin{pmatrix} q \\ p + F\Delta t \\ \eta \\ p_\eta \end{pmatrix} \qquad e^{\mathcal{L}_2\Delta t}\mathbf{x} = \begin{pmatrix} q + \frac{p}{m}\Delta t \\ p \\ \eta \\ p_\eta + \frac{p^2}{m}\Delta t \end{pmatrix} \\
e^{\mathcal{L}_3\Delta t}\mathbf{x} &= \begin{pmatrix} q \\ p \\ \eta \\ p_\eta - kT\Delta t \end{pmatrix} \qquad e^{\mathcal{L}_4\Delta t}\mathbf{x} = \begin{pmatrix} q \\ p e^{-\alpha p_\eta \Delta t} \\ \eta + \alpha p_\eta \Delta t \\ p_\eta \end{pmatrix},
\end{aligned}$$

where we have used the fact that $\exp\{cxd/dx\}x = xe^{c}$.

∗ This splitting can then be used in a symmetric sequence of $\exp\{\mathcal{L}_i \Delta t_k\}$ with $\sum_k \Delta t_k = \Delta t$.

2. The choice:

$$\begin{aligned}
\mathcal{L}_1 &= F(q)\frac{\partial}{\partial p} \qquad \mathcal{L}_2 = \frac{p}{m}\frac{\partial}{\partial q} \\
\mathcal{L}_3 &= \left(\frac{p^2}{m} - kT\right)\frac{\partial}{\partial p_\eta} \qquad \mathcal{L}_4 = \alpha p_\eta\left[-p\frac{\partial}{\partial p} + \frac{\partial}{\partial \eta}\right].
\end{aligned}$$

∗ The difference from the first scheme is in the combination of operators in the definitions of $\mathcal{L}_2$ and $\mathcal{L}_3$. This are trivial re-arrangements that still satisfy the conservation of the invariant phase space volume, but now

$$e^{\mathcal{L}_2 \Delta t}\mathbf{x} = \begin{pmatrix} q + \frac{p}{m}\Delta t \\ p \\ \eta \\ p_\eta \end{pmatrix} \quad e^{\mathcal{L}_3 \Delta t}\mathbf{x} = \begin{pmatrix} q \\ p \\ \eta \\ p_\eta \left(\frac{p^2}{m} - kT\right)\Delta t \end{pmatrix}.$$

3. The choice

$$\begin{aligned} \mathcal{L}_1 &= \frac{p}{m}\frac{\partial}{\partial q} + \frac{p^2}{m}\frac{\partial}{\partial p_\eta} \qquad \mathcal{L}_2 = F(q)\frac{\partial}{\partial p} - kT\frac{\partial}{\partial p_\eta} \\ \mathcal{L}_4 &= \alpha p_\eta \left[-p\frac{\partial}{\partial p} + \frac{\partial}{\partial \eta}\right]. \end{aligned}$$

   * Note that this choice is superior since it involves fewer Liouville operators.

– Note that all these schemes use the same $\mathcal{L}_4$, since this form is the one which preserves the volume when the compressibility is non-zero.

General splitting procedure

- Suppose we can write the dynamics in a form that is a generalization of the symplectic form:

$$\dot{\mathbf{x}}_i = \mathsf{A}_{ij}(\mathbf{x})\frac{\partial H}{\partial \mathbf{x}_j} = \boldsymbol{\xi}_i(\mathbf{x}), \tag{5.21}$$

where H is the Hamiltonian function that is conserved in the dynamics and $\mathsf{A}_{ij}(\mathbf{x})$ is an anti-symmetric matrix, satisfying $\mathsf{A}_{ij}(\mathbf{x}) = -\mathsf{A}_{ji}(\mathbf{x})$, that generalizes the symplectic matrix J.

- Since A is anti-symmetric, we can write $\mathsf{A}_{ij} = \frac{1}{2}(\mathsf{A}_{ij} - \mathsf{A}_{ji})$, which implies

$$\begin{aligned} \dot{H} &= \boldsymbol{\xi} \cdot \frac{\partial H}{\partial \mathbf{x}} = \boldsymbol{\xi}_i \frac{\partial H}{\partial \mathbf{x}_i} = \frac{\partial H}{\partial x_i}\mathsf{A}_{ij}\frac{\partial H}{\partial x_j} \\ &= \frac{1}{2}\left(\frac{\partial H}{\partial x_i}\mathsf{A}_{ij}\frac{\partial H}{\partial x_j} - \frac{\partial H}{\partial x_i}\mathsf{A}_{ji}\frac{\partial H}{\partial x_j}\right) = 0, \end{aligned}$$

where we have used the convention that repeated indices are summed over.

- If $d\boldsymbol{\mu}(\mathbf{x}) = \gamma(\mathbf{x})d\mathbf{x}$ is the invariant volume element under the dynamics, then $\gamma(\mathbf{x})$ obeys

$$\nabla_{\mathbf{x}} \cdot (\gamma\dot{\mathbf{x}}) = 0 = \frac{\partial}{\partial x_i}(\gamma \dot{x}_i) = \frac{\partial}{\partial x_i}\left(\gamma \mathsf{A}_{ij}\frac{\partial H}{\partial x_j}\right).$$

– Defining the anti-symmetric matrix $\mathsf{B} = \gamma\mathsf{A}$, we have $\partial\mathsf{B}_{ij}/\partial x_i = 0$, because

$$\begin{aligned}\frac{\partial}{\partial x_i}\left(\mathsf{B}_{ij}\frac{\partial H}{\partial x_j}\right) &= 0 \\ &= \frac{\partial \mathsf{B}_{ij}}{\partial x_i} + \mathsf{B}_{ij}\frac{\partial^2 H}{\partial x_i \partial x_j} = \frac{\partial \mathsf{B}_{ij}}{\partial x_i},\end{aligned}$$

since

$$\mathsf{B}_{ij}\frac{\partial^2 H}{\partial x_i \partial x_j} = 0$$

as $\partial^2 H/\partial x_i \partial x_j = \partial^2 H/\partial x_j \partial x_i$.

- Separating the Hamiltonian H into several different terms, $H = \sum_\alpha H(\alpha)$, we can write the flow equation as $\boldsymbol{\xi} = \sum_\alpha \boldsymbol{\xi}(\alpha)$, where $\boldsymbol{\xi}_i(\alpha) = \mathsf{A}_{ij}\partial H(\alpha)/\partial x_j$ and define the Liouville operators

$$\mathcal{L}_\alpha = \boldsymbol{\xi}_i(\alpha)\frac{\partial}{\partial x_i} = \mathsf{A}_{ij}\frac{\partial H(\alpha)}{\partial x_j}\frac{\partial}{\partial x_i}.$$

- The action of each of the Liouville operators on the invariant measure is therefore

$$\frac{\partial}{\partial x_i}\left(\gamma(\mathbf{x})\mathsf{A}_{ij}\frac{\partial H(\alpha)}{\partial x_j}\right) = \frac{\partial \mathsf{B}_{ij}}{\partial x_i}\frac{\partial H(\alpha)}{\partial x_j} + \mathsf{B}_{ij}\frac{\partial^2 H(\alpha)}{\partial x_i \partial x_j} = 0,$$

since B_{ij} is anti-symmetric and obeys $\partial\mathsf{B}_{ij}/\partial x_i = 0$.

– The invariant volume (and also $H(\alpha)$) preserved under the flow generated by $\mathcal{L}_\alpha$, for *any* $H(\alpha)$.

Nosé-Hoover system

We now show that the Nosé-Hoover dynamical system that generates the canonical ensemble (provided the dynamics is ergodic) can be written using the generalized symplectic matrix form. Consider the phase space variables (q, p, η, p_η) with Hamiltonian $H = p^2/2m + \phi(q) + kT\eta + \alpha p_\eta^2/2$. From the equations of motion,

$$\dot{q} = \frac{p}{m} \qquad \dot{\eta} = \alpha p_\eta \qquad \dot{p} = F(q) - \alpha p p_\eta \qquad \dot{p}_\eta = \frac{p^2}{m} - kT,$$

and the Hamiltonian H, we will deduce the form of the asymmetric matrix A as follows:

- Note that

$$\frac{\partial H}{\partial x_1} = \phi'(q) \qquad \frac{\partial H}{\partial x_2} = \frac{p}{m} \qquad \frac{\partial H}{\partial x_3} = kT \qquad \frac{\partial H}{\partial x_4} = \alpha p_\eta.$$

- Since A is anti-symmetric, all diagonal elements are zero.

- Since $\dot{q} = p/m = \mathsf{A}_{ij}\partial H/\partial x_j = \partial H/\partial x_2$, we see we must have $\mathsf{A}_{1j} = \delta_{j,2} = -\mathsf{A}_{j1}$.

- From the second equation $\dot{p} = F(q) - \alpha p p_\eta = \mathsf{A}_{2j}\partial H/\partial x_j$ and noting that $\mathsf{A}_{21} = -1$, we have $\dot{p} = -\phi'(q) + \mathsf{A}_{23}kT + \mathsf{A}_{24}\alpha p_\eta$, hence $\mathsf{A}_{23} = 0 = \mathsf{A}_{32}$ and $\mathsf{A}_{24} = -p = -\mathsf{A}_{42}$.

- The only remaining element to determine is A_{34}, which we get from $\dot{\eta} = \alpha p_\eta = \mathsf{A}_{34}\alpha p_\eta$, so $\mathsf{A}_{34} = 1$ and $\mathsf{A}_{43} = -1$, giving the final matrix,

$$\mathsf{A} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & -p \\ 0 & 0 & 0 & 1 \\ 0 & p & -1 & 0 \end{pmatrix}.$$

- From this matrix, one can easily verify that $\mathsf{B}_{ij} = e^\eta \mathsf{A}_{ij}$ satisfies $\partial \mathsf{B}_{ij}/\partial i = 0$ for all j. For example, consider $j = 4$:

$$\frac{\partial \mathsf{B}_{i4}}{\partial x_i} = \frac{\partial}{\partial p}\left(e^\eta p\right) + \frac{\partial}{\partial \eta}\left(e^\eta\right) = 0.$$

- The first integration scheme is obtained by choosing

$$H(1) = \phi(q) \qquad H(2) = \frac{p^2}{2m} \qquad H(3) = kT\eta \qquad H(4) = \alpha\frac{p_\eta^2}{2}$$

leading to the Liouville operators of Eq. (5.20).

Appendix A

Math Appendices

A.1 Taylor expansion

- Expand function $f(x+a)$ from small a around $a=0$.

$$
\begin{aligned}
f(x+a) &= f(x) + f'(x)a + \frac{1}{2}f''(x)a^2 + \cdots \\
&= \sum_{j=0}^{\infty} \frac{a^j}{j!}\frac{d^j}{dx^j} f(x).
\end{aligned}
$$

- Since

$$
\begin{aligned}
e^{\lambda x} &= \exp(\lambda x) = \sum_{j=0}^{\infty} x^j \frac{\lambda^j}{j!}, \\
f(x+a) &= \exp\left(a\frac{d}{dx}\right) f(x).
\end{aligned}
$$

A.2 Series expansions

For $|x| < 1$,

$$
\begin{aligned}
\frac{1}{1+x} &= 1 - x + x^2 - x^3 + \cdots \\
\frac{1}{1-x} &= 1 + x + x^2 + \cdots \\
\sin(x) &= x - \frac{x^3}{3!} + \frac{x^5}{5!} + \cdots \\
\cos(x) &= 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots \\
\ln(1+x) &= x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots
\end{aligned}
$$

A.3 Probability theory:

A.3.1 Discrete systems

Suppose have measurable E with n discrete values $E_1, E_2, \ldots, E_n$. Let

$$
\begin{aligned}
N &= \text{number of measurements} \\
N_i &= \text{number of measurements of } E_i.
\end{aligned}
$$

Then

$$
P_i = \text{Probability that } E_i \text{ is measured} = \lim_{N\to\infty} \frac{N_i}{N} \equiv P(E_i)
$$

Properties:

1. $0 \le P_i \le 1$
2. $\sum_{i=1}^{n} P_i = 1$

Averages:

$$
\begin{aligned}
\overline{E} &= \sum_{i=1}^{n} E_i P_i \\
\overline{E^2} &= \sum_{i=1}^{n} E_i^2 P_i \\
\overline{H(E)} &= \sum_{i=1}^{n} H(E_i) P_i
\end{aligned}
$$

Variance of E:

$$\begin{aligned}\sigma_E^2 &\equiv \overline{E^2} - \left(\overline{E}\right)^2 \\ &= \overline{\left(E_i - \overline{E}\right)^2}\end{aligned}$$

- σ_E^2 measures the dispersion of the probability distribution: how spread out values are.
- In general, $\sigma_E^2 \neq 0$ unless $P_i = \delta_{ij}$ for some j. This notation means:

$$P_i = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases} \qquad \text{which implies } \overline{E} = E_i.$$

- Tchebycheff Inequality:

$$Prob\left(\left|E - \overline{E}\right| \geq \lambda\overline{E}\right) \leq \frac{\sigma_E^2}{\lambda^2\overline{E}^2}.$$

- Joint probability: Suppose N measurements of two properties E and G.

$$\begin{aligned}n_{ij} &= \text{number of measurements of } E_i \text{ and } G_j \\ P_{ij} &= \lim_{N\to\infty}\frac{n_{ij}}{N} \equiv P(E_i, G_j) \equiv \text{joint probability.}\end{aligned}$$

Properties:

1. $\sum_{i.j} P(E_i, G_j) = 1$.
2. $\sum_i P(E_i, G_j) = P(G_j)$.
3. $\sum_j P(E_i, G_j) = P(E_i)$.
4. If E_i and G_j are independent, then $P(E_i, G_j) = P(E_i)P(G_j)$.

A.3.2 Continuous Systems

- Probability of measure an observable X with values between $x, x + dx$ is $p(x)dx$. $p(x)$ is called the "probability density".
  Properties:
  1. Positive definite: $p(x) \geq 0$.
  2. Normalized: $\int_{-\infty}^{\infty} dxp(x) = 1$
- Averages:

$$\begin{aligned}\overline{x} &= \int_{-\infty}^{\infty} dx\, xp(x) \qquad \overline{f(x)} = \int_{-\infty}^{\infty} dx\, f(x)p(x) \\ \sigma_x^2 &= \overline{x^2} - \overline{x}^2 = \int_{-\infty}^{\infty} dx\, \left(x^2 - \overline{x}^2\right) p(x)\end{aligned}$$

A.3.3 Gaussian distributions

1. Distribution specified by first + second moments:

$$P(x) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \mathrm{e}^{-\frac{(x-\langle x\rangle)^2}{2\sigma^2}} \qquad \begin{aligned}\langle x\rangle &= \text{average of x}\\ \langle (x-\langle x\rangle)^2\rangle &= \sigma^2\end{aligned}$$

2. Important properties (assuming $\langle x\rangle = 0$): $\langle x^{2n+1}\rangle = 0$ and $\langle x^{2n}\rangle = f(\sigma^2)$.

3. If $P(x_1,\ldots,x_n) = \left(\frac{1}{2\pi\langle x_1^2\rangle}\right)^{1/2} \ldots \left(\frac{1}{2\pi\langle x_n^2\rangle}\right)^{1/2} \exp\left\{-\left(\frac{x_1^2}{2\langle x_1^2\rangle}, \ldots + \frac{x_n^2}{2\langle x_n^2\rangle}\right)\right\}$

   Then

$$\begin{aligned}\langle x_i\rangle &= 0\\ \langle x_i x_j\rangle &= \sigma_i^2\delta_{i,j}\end{aligned}$$

- What happens when $\sigma_x^2 \to 0$? Infinitely narrow distribution, called a *dirac delta function*. Probability density has all the weight on one value.
- There are other representations of the dirac delta function: basically defined in such a way that *one* value receives all the weight.
- Delta functions: defined in a limiting sense.

$$\delta^{(\epsilon)}(x) = \left\{\begin{array}{ll}\frac{1}{\epsilon} & -\frac{\epsilon}{2} \le x \le \frac{\epsilon}{2}\\ 0 & |x| > \frac{\epsilon}{2}\end{array}\right. \qquad \int_{-\infty}^{\infty} dx\ \delta^{(\epsilon)}(x) = \int_{-\epsilon/2}^{\epsilon/2} dx\frac{1}{\epsilon} = 1.$$

$$\int_{-\infty}^{\infty} dx\ \delta^{(\epsilon)}(x) f(x) \approx f(0)\int_{-\infty}^{\infty} dx\ \delta^{(\epsilon)}(x) = f(0) \qquad \text{if } \epsilon \ll 1.$$

  - Function $f(x)$ essentially constant over infinitesimal interval.
  - Definition of delta function: $\delta(x) = \lim_{\epsilon\to 0}\delta^{(\epsilon)}(x)$.
- Representations of delta function in limit $\epsilon \to 0$:
  1. $\frac{1}{2\epsilon}e^{-|x|/\epsilon}$
  2. $\frac{1}{\pi}\frac{\epsilon}{x^2+\epsilon^2}$
  3. $\frac{1}{\epsilon\sqrt{\pi}}e^{-x^2/\epsilon^2}$

4. $\frac{1}{\pi}\frac{\sin x/\epsilon}{x}$

– For any continuous function f of x, for all forms above we get

$$\lim_{\epsilon\to 0}\int_{-\infty}^{\infty} dx\ \delta^{(\epsilon)}(x-x_0)f(x) = f(x_0).$$

Some properties of the delta function

1. $\delta(-x) = \delta(x)$
2. $\delta(cx) = \frac{1}{|c|}\delta(x)$
3. $\delta[g(x)] = \sum_j \frac{\delta(x-x_j)}{|g'(x_j)|}$ where $g(x_j) = 0$ and $g'(x_j) \neq 0$.
4. $g(x)\delta(x-x_0) = g(x_0)\delta(x-x_0)$
5. $\int_{-\infty}^{\infty} dx\ \delta(x-y)\delta(x-z) = \delta(y-z)$
6. $\int_{-\infty}^{\infty} dx\ \frac{d\delta(x-x_0)}{dx} f(x) = -\int_{-\infty}^{\infty} dx\ \delta(x-x_0)f'(x) = -f'(x_0)$

A.4 Fourier and Laplace Transforms

- *Fourier Transform:*

$$\begin{aligned}\tilde{f}(k) &= \int_{-\infty}^{\infty} e^{ikx} f(x)\ dx \\ f(x) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}\tilde{f}(k)\ dk\end{aligned}$$

– Properties:

$$\begin{aligned}\int_{-\infty}^{\infty} e^{-ix(k-k_0)}dx &= 2\pi\delta(k-k_0). \\ \int_{-\infty}^{\infty} f(x-y)g(y)\ dy &= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx}\tilde{f}(k)\tilde{g}(k)\ dk. \\ f(x) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} e^{-x^2/2\sigma^2} &\longrightarrow \tilde{f}(k) = \left(\frac{\sigma^2}{2\pi}\right)^{1/2} e^{-\sigma^2k^2/2} \\ f(x) = \frac{e^{-\lambda x}}{x} &\longrightarrow \tilde{f}(k) = \frac{4\pi}{k^2+\lambda^2} \\ f(x) = \frac{1}{x} &\longrightarrow \tilde{f}(k) = \frac{4\pi}{k^2}\end{aligned}$$

- *Laplace Transform:*

$$\tilde{f}(z) = \int_0^{-\infty} e^{-zt} f(t)\, dt$$

  - Useful properties and transforms:

$$\begin{aligned}
\int_0^t f(t-\tau)g(\tau) &= \tilde{f}(z)\tilde{g}(z) \\
f(t) = e^{-at} \;\rightarrow\; & \tilde{f}(z) = \frac{1}{z+a} \\
f(t) = \frac{1}{t^n} \;\rightarrow\; & \tilde{f}(z) = \frac{t^{n-1}}{(n-1)!}.
\end{aligned}$$

A.5 Calculus

A.5.1 Integration by parts

$$\int u dv = uv - \int v du$$

- Example:

$$\int_a^b dx\ f'(x)g(x) = f(x)g(x)\Big|_a^b - \int_a^b dx\ f(x)g'(x)$$

A.5.2 Change of Variable and Jacobians

Let $I = \int_{R_{xy}} dxdy\ f(x,y)$ be the integral over a connected region $R_{x,y}$. Change variables to u, v via the transform $g(u,v) = x$ and $h(u,v) = y$. It follows that:

$$I = \int_{R_{uv}} dudv\ f(g(u,v), h(u,v)) \left| \frac{\partial(g,h)}{\partial(u,v)} \right|.$$

where the *Jacobian* $\frac{\partial(g,h)}{\partial(u,v)}$ is

$$\frac{\partial(g,h)}{\partial(u,v)} \equiv \begin{vmatrix} \frac{\partial g}{\partial u} & \frac{\partial g}{\partial v} \\ \frac{\partial h}{\partial u} & \frac{\partial h}{\partial v} \end{vmatrix}$$

- Example: Suppose

$$I = \int_{-\infty}^{\infty} dxdy\ f(x)g(x-y).$$

Let $u = x$ and $v = x - y$. Under this transformation, range of v is $(-\infty, \infty)$ at a fixed value of u (or x). The Jacobian J is

$$J = \left| \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right| = -1$$

Thus,

$$I = \int_{-\infty}^{\infty} dudv\ f(u)g(v)|-1| = \int_{-\infty}^{\infty} duf(u)\ \int_{-\infty}^{\infty} dvg(v).$$