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

$$\begin{aligned}\mathsf{K}(\mathbf{x}_t \to \mathbf{x}_0) &= \int d(\mathcal{T}\mathbf{p}_0)d(\mathcal{T}\mathbf{p}_t)\,\Pi_m(\mathcal{T}\mathbf{p}_t)P_g((\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) \to (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)) \\ &\qquad \times \mathsf{A}((\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) \to (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)) \\ &= \int d\mathbf{p}_0 d\mathbf{p}_t\,\Pi_m(\mathbf{p}_t)\delta(g^t(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) - (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0))\mathsf{A}((\mathbf{x}_t, \mathbf{p}_t) \to (\mathbf{x}_0, \mathbf{p}_0))\end{aligned} \tag{5.4}$$

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

$$\begin{aligned}\int d\mathbf{x}_0\, P(\mathbf{x}_0)\mathsf{K}(\mathbf{x}_0 \to \mathbf{x}_t) &= \int d\mathbf{x}_0 d\mathbf{p}_0 d\mathbf{p}_t\, P(\mathbf{x}_0)\Pi_m(\mathbf{p}_0)\delta(g^t(\mathbf{x}_0, \mathbf{p}_0) - (\mathbf{x}_t, \mathbf{p}_t)) \\ &\qquad \times \min\left(1, \frac{\Pi(\mathbf{x}_t, \mathbf{p}_t)}{\Pi(\mathbf{x}_0, \mathbf{p}_0)}\right) \\ &= \int d\mathbf{x}_0 d\mathbf{p}_0 \min\left(\Pi(\mathbf{x}_0, \mathbf{p}_0), \Pi(g^t(\mathbf{x}_0, \mathbf{p}_0))\right),\end{aligned} \tag{5.5}$$

whereas

$$\begin{aligned}\int d\mathbf{x}_t\, P(\mathbf{x}_t)\mathsf{K}(\mathbf{x}_t \to \mathbf{x}_0) &= \int d\mathbf{x}_t d\mathbf{p}_0 d\mathbf{p}_t\, \Pi(\mathbf{x}_t, \mathbf{p}_t)\delta(g^t(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t) - (\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)) \\ &\qquad \times \min\left(1, \frac{\Pi(\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)}{\Pi(\mathbf{x}_t, \mathbf{p}_t)}\right) \\ &= \int d\mathbf{x}_t d\mathbf{p}_t \min\left(\Pi(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t), \Pi(g^t(\mathbf{x}_t, \mathcal{T}\mathbf{p}_t))\right)\end{aligned} \tag{5.6}$$

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

$$\begin{aligned} \int d\mathbf{x}_t \, P(\mathbf{x}_t) \, \mathsf{K}(\mathbf{x}_t \to \mathbf{x}_0) &= \int d\mathbf{x}_0 d\mathbf{p}_0 \, J((\mathbf{x}_t, \mathcal{T}\mathbf{p}_t); (\mathbf{x}_0, \mathbf{p}_0)) \min\left(\Pi(g^{-t}(\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)), \Pi(\mathbf{x}_0, \mathcal{T}\mathbf{p}_0)\right) \\ &= \int d\mathbf{x}_0 d\mathbf{p}_0 \min\left(\Pi(\mathcal{T} g^t(\mathbf{x}_0, \mathbf{p}_0)), \Pi(\mathbf{x}_0, \mathbf{p}_0), \right) \\ &= \int d\mathbf{x}_0 d\mathbf{p}_0 \min\left(\Pi(g^t(\mathbf{x}_0, \mathbf{p}_0)), \Pi(\mathbf{x}_0, \mathbf{p}_0)\right) \end{aligned} \tag{5.7}$$

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. □

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

$$U(\mathbf{r}^{(N)}) = \sum_{i=1}^{N} \sum_{j=i+4}^{N} V_{\rm nb}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=4}^{N} U_{\rm tor}(\phi_i) + \sum_{i=3}^{N} U_{\rm bend}(\theta_i) + \sum_{i=2}^{N} U_{\rm bond}(|\mathbf{r}_i - \mathbf{r}_{i-1}|).$$

In this potential, we have the following contributions:

1. A *bond-stretching potential* $U_{\rm bond}$ that typically is harmonic.

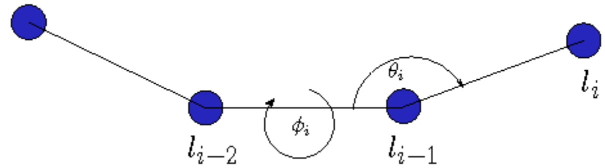
2. A *bond-angle potential* $U_{\rm bend}$, taken to be harmonic in $\cos\theta_i$, where θ_i is the bond angle defined by

   $$l_i l_{i-1} \cos\theta_i = (\mathbf{r}_i - \mathbf{r}_{i-1}) \cdot (\mathbf{r}_{i-2} - \mathbf{r}_{i-1}),$$

   where $l_i = |\mathbf{r}_i - \mathbf{r}_{i-1}|$ is the bond distance between monomers i and $i+1$.

3. A *torsional potential* $U_{\rm tor}$ 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* $U_{\rm nb}$ 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

$$\mathbf{r}_i = \mathbf{r}_1 + \mathsf{T}_2 \cdot \mathbf{l}_2 + \mathsf{T}_2 \cdot \mathsf{T}_3 \cdot \mathbf{l}_3 + \mathsf{T}_2 \cdot \mathsf{T}_3 \cdot \mathsf{T}_4 \cdot \mathbf{l}_4 + \cdots + \mathsf{T}_2 \cdot \mathsf{T}_3 \cdots \mathsf{T}_i \cdot \mathbf{l}_i, \qquad (5.8)$$

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 $\mathsf{T}_k^{\mathrm{lab}} = \mathsf{T}_2 \cdots \mathsf{T}_k$ transforms between the reference frame of bead k and the fixed lab frame and $\mathsf{T}_k^{\mathrm{lab}} \cdot \mathbf{l}_k$ 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

$$\begin{aligned} \frac{\partial c(\mathbf{r},t)}{\partial t} &= -\frac{\partial}{\partial \mathbf{r}}\cdot \mathbf{j}(\mathbf{r},t) \\ \frac{\partial c(\mathbf{r},t)}{\partial t} &= D\nabla^2 c(\mathbf{r},t). \end{aligned} \tag{5.9}$$

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 $c(r,t)$:

$$\langle r^2(t)\rangle = \int d\mathbf{r}\, r^2 c(r,t).$$

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

$$\langle AB(t)\rangle = \int d\mathbf{x}^{(N)}\, f(\mathbf{x}^{(N)})A(\mathbf{x}^{(N)})B(\mathbf{x}^{(N)}(t))$$

  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 $f(\mathbf{x}^{(N)})$. 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

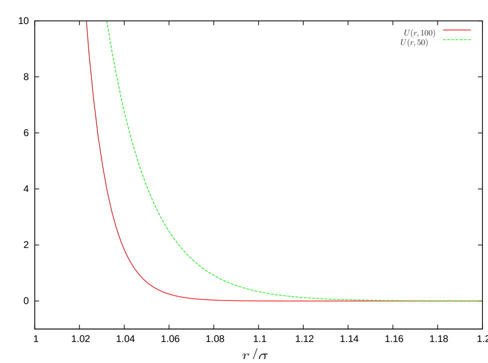
$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i,j} U(r_{ij}) = K + U = \begin{cases} K & \text{if no overlap} \\ \infty & \text{otherwise} \end{cases}.$$

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

$$\mathbf{r}_i(t_c) = \mathbf{r}_i(0) + \frac{\mathbf{p}_i}{m_i} t_c$$
$$\mathbf{r}_j(t_c) = \mathbf{r}_j(0) + \frac{\mathbf{p}_j}{m_j} t_c \qquad \mathbf{r}_{ij}(t_c) = \mathbf{r}_{ij}(0) + \mathbf{v}_{ij} t_c$$

– 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 $\Delta_{ij}^2 = (r_{ij}^2 - \sigma^2)v_{ij}^2$.

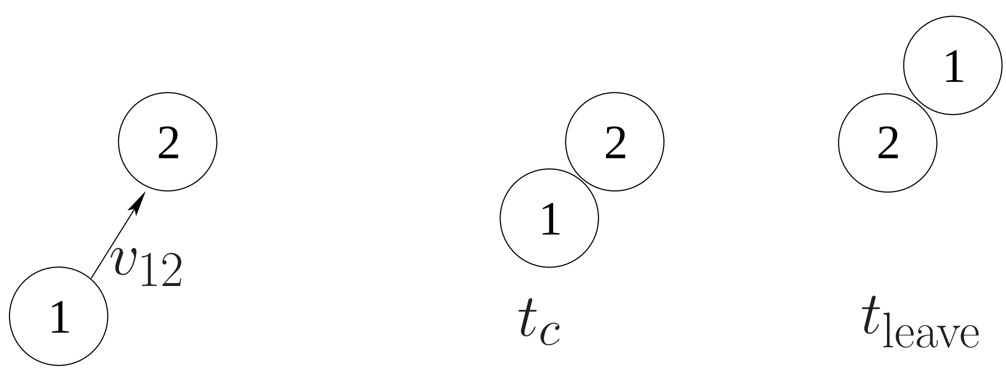
– Real solutions exist if $v_{ij}^2 \neq 0$ and $v_r^2 \geq \Delta_{ij}^2$.

– 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:

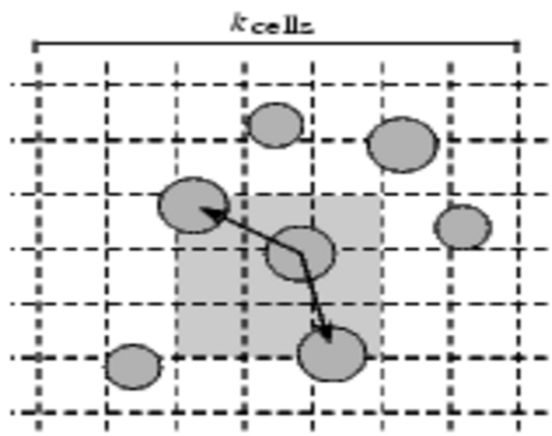
1. Initially calculate all collision events for system using Eq. (5.10).
   - Boundary conditions must be properly included: hard walls, periodic system, ...
2. Find first collision event and evolve system (with free evolution) up to that time.
3. For colliding pair, compute the consequences of the collision 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

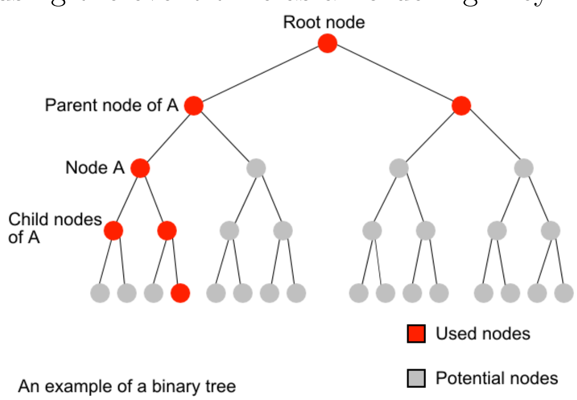
    - The position of any particle not involved in an event does not need to be updated since it will continue to move freely until it is specifically involved in a collision.
    - Time of last event for each particle can be stored and used to compute interaction times or updates of positions.
    - Global 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".



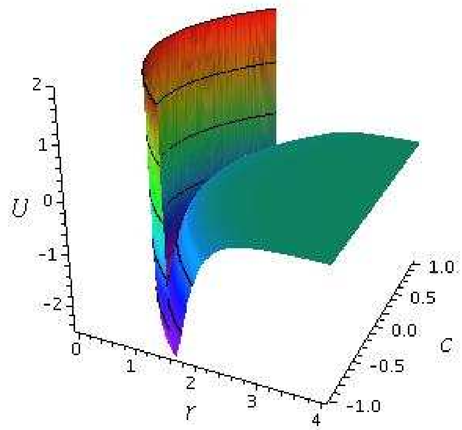
- Functions required to insert new events in tree and search for earliest times.
- Information for whether an event in the tree has been invalidated by an earlier event can be stored in each node of tree.
- Small hybrid tree structures that only insert valid events in the near future are an efficient 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.

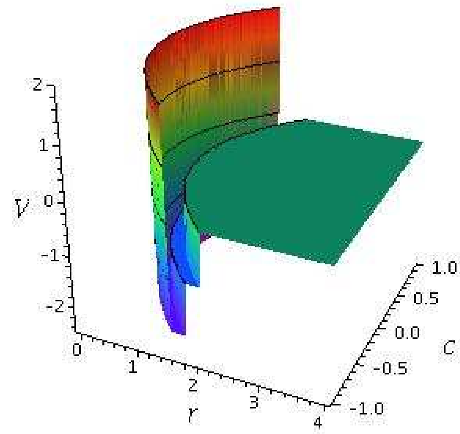
5.3.2 Generalization: Energy discretization

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 $U(r) = U_k$ ca 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

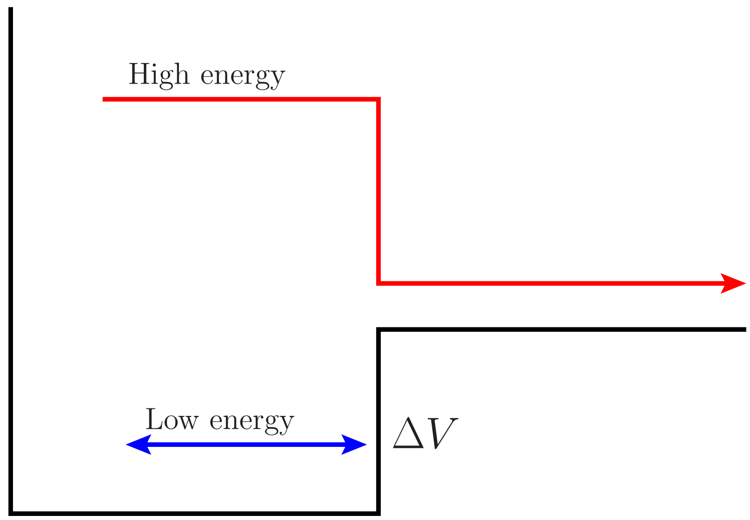
$$\begin{aligned} \mathbf{p}_i' &= \mathbf{p}_i + \Delta \mathbf{F}_{ij}(t_c) \\ \Delta \mathbf{F}_{ij}(t) &= S \mathbf{F}_{ij}(t_c) \delta(t - t_c), \end{aligned}$$

  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,

$$\begin{aligned}\langle A(\mathbf{r}^{(N)})\rangle &\approx \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\, P(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) A(\mathbf{r}^{(N)}) \delta(\boldsymbol{\sigma}) \Big/ \int d\mathbf{r}^{(N)}\, \rho(\mathbf{r}^{(N)}) \delta(\boldsymbol{\sigma}) \\ &= \int d\mathbf{r}^{(N)}\, \rho_{\text{con}}(\mathbf{r}^{(N)}, \sigma = 0) A(\mathbf{r}^{(N)}, \boldsymbol{\sigma} = 0) = \langle A(\mathbf{r}^{(N)})\rangle_c\end{aligned}$$

- How can the conditional ensemble average $\langle \dots \rangle_c$ be computed?
- This can be analyzed most easily by working in generalized coordinates rather than Cartesian coordinates.
- Define a coordinate transformation $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_N) \to \mathbf{u} = (\mathbf{u}_1, \dots, \mathbf{u}_N)$, 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 $\mathbf{p} = (\mathbf{p}_1, \dots, \mathbf{p}_n)$ 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 $\mathsf{m}^{-1}_{ij} = m_i^{-1} \delta_{i,j}$.

- Using $\mathbf{r}(\mathbf{u})$, 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

$$\mathbf{p}^u = \frac{\partial L}{\partial \dot{\mathbf{u}}} = \mathsf{G} \cdot \dot{\mathbf{u}} \qquad \text{so} \qquad \dot{\mathbf{u}} = \mathsf{G}^{-1} \cdot \mathbf{p}^u,$$

leading to the 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

$$\mathsf{G}^{-1}_{\alpha\beta} = \sum_i \frac{1}{m_i} \frac{\partial \mathbf{u}_\alpha}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathbf{u}_\beta}{\partial \mathbf{r}_i}.$$

– Note that 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

$$\rho_{\mathrm{con}}(\mathbf{q}, \boldsymbol{\sigma} = 0) = c\sqrt{\det\mathsf{G}}\, e^{-\beta V(\mathbf{q},\boldsymbol{\sigma}=0)}.$$

  – 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_c, 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

$$\begin{aligned}\rho(\mathbf{q})d\mathbf{q} &= d\mathbf{q}\int d\mathbf{p}^q\, e^{-\beta/2\,\mathbf{p}^q\cdot\mathsf{A}^{-1}\cdot\mathbf{p}^q} e^{-\beta V(\mathbf{q},\boldsymbol{\sigma}=0)} \\ &= c'\sqrt{\det\mathsf{A}}e^{-\beta V(\mathbf{q},\boldsymbol{\sigma}=0)}d\mathbf{q} \\ \rho(\mathbf{q}) &= \tilde{c}\frac{\sqrt{\det\mathsf{A}}}{\sqrt{\det\mathsf{G}}}\rho_{\mathrm{con}}(\mathbf{q},\boldsymbol{\sigma}=0).\end{aligned}$$

- Note that the probability density associated with the Hamiltonian dynamics of the constrained system is $\rho(\mathbf{q})$, while the targeted constrained density is $\rho_c(\mathbf{q},\boldsymbol{\sigma}=0)$.
  - 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:

$$\mathsf{G} = \begin{pmatrix}\mathsf{A} & \mathsf{B} \\ \mathsf{B}^T & \Gamma\end{pmatrix} \quad \mathsf{A} = \sum_i m_i\frac{\partial\mathbf{r}_i}{\partial\mathbf{q}}\cdot\frac{\partial\mathbf{r}_i}{\partial\mathbf{q}} \quad \mathsf{B} = \sum_i m_i\frac{\partial\mathbf{r}_i}{\partial\mathbf{q}}\cdot\frac{\partial\mathbf{r}_i}{\partial\boldsymbol{\sigma}} \quad \Gamma = \sum_i m_i\frac{\partial\mathbf{r}_i}{\partial\boldsymbol{\sigma}}\cdot\frac{\partial\mathbf{r}_i}{\partial\boldsymbol{\sigma}}$$

$$\mathsf{G}^{-1} = \begin{pmatrix}\Delta & \mathsf{E} \\ \mathsf{E}^T & \mathsf{Z}\end{pmatrix} \quad \Delta = \sum_i \frac{1}{m_i}\frac{\partial\mathbf{q}}{\partial\mathbf{r}_i}\cdot\frac{\partial\mathbf{q}}{\partial\mathbf{r}_i} \quad \mathsf{E} = \sum_i \frac{1}{m_i}\frac{\partial\boldsymbol{\sigma}}{\partial\mathbf{r}_i}\cdot\frac{\partial\mathbf{q}}{\partial\mathbf{r}_i} \quad \mathsf{Z} = \sum_i \frac{1}{m_i}\frac{\partial\boldsymbol{\sigma}}{\partial\mathbf{r}_i}\cdot\frac{\partial\boldsymbol{\sigma}}{\partial\mathbf{r}_i}$$

  - We now define a matrix X so that $\det\mathsf{X} = \det\mathsf{A}$:

$$\mathsf{X} = \begin{pmatrix}\mathsf{A} & 0 \\ \mathsf{B}^T & \mathsf{I}\end{pmatrix},$$

    where I is the identity matrix.
  - Writing $\mathsf{X} = \mathsf{G}\cdot\mathsf{G}^{-1}\cdot\mathsf{X}$, we get

$$\mathsf{X} = \mathsf{G}\cdot\begin{pmatrix}\Delta\cdot\mathsf{A}+\mathsf{E}\cdot\mathsf{B}^T & \mathsf{E} \\ \mathsf{E}^T\cdot\mathsf{A}+\mathsf{Z}\cdot\mathsf{B}^T & \mathsf{Z}\end{pmatrix} \qquad \mathsf{G}^{-1}\cdot\mathsf{G} = \begin{pmatrix}\Delta\cdot\mathsf{A}+\mathsf{E}\cdot\mathsf{B}^T & \Delta\cdot\mathsf{B}+\mathsf{E}\cdot\Gamma \\ \mathsf{E}^T\cdot\mathsf{A}+\mathsf{Z}\cdot\mathsf{B}^T & \mathsf{E}^T\cdot\mathsf{B}+\mathsf{Z}\cdot\Gamma\end{pmatrix}$$

    so $\Delta\cdot\mathsf{A}+\mathsf{E}\cdot\mathsf{B}^T = \mathsf{I}$ and $\mathsf{E}^T\cdot\mathsf{A}+\mathsf{Z}\cdot\mathsf{B}^T = 0$, and hence

$$\mathsf{X} = \mathsf{G}\cdot\begin{pmatrix}\mathsf{I} & \mathsf{E} \\ 0 & \mathsf{Z}\end{pmatrix}.$$

– Thus, $\det \mathsf{X} = \det \mathsf{A} = \det \mathsf{G} \det \mathsf{Z}$, from which we conclude

$$\frac{\det \mathsf{G}}{\det \mathsf{A}} = \frac{1}{\det \mathsf{Z}} \qquad \text{implying} \qquad \langle A(\mathbf{r}^{(N)})\rangle_c = \int d\mathbf{q}\, \det \mathsf{Z}^{-1/2} \rho(\mathbf{q}) A(\mathbf{q}, \boldsymbol{\sigma} = 0),$$

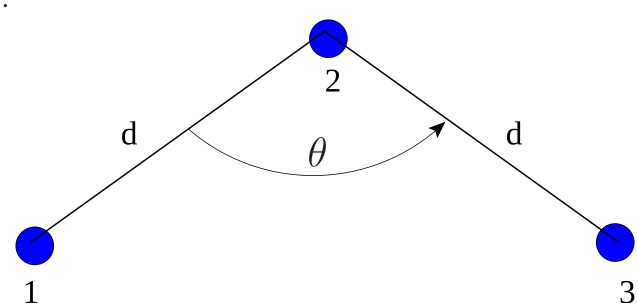
where

$$\mathsf{Z}_{\alpha\beta} = \sum_i \frac{1}{m_i} \frac{\partial \boldsymbol{\sigma}_\alpha}{\partial \mathbf{r}_i} \cdot \frac{\partial \boldsymbol{\sigma}_\beta}{\partial \mathbf{r}_i}$$

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

$$L' = L - \lambda_\alpha \sigma_\alpha \qquad L = \sum_i m_i/2\dot{r}_i^2 - V(\mathbf{r}^{(N)})$$

- Equation of motion from constrained Lagrangian:

$$\begin{aligned} \frac{\partial}{\partial t}\frac{\partial L'}{\partial \dot{\mathbf{r}}} &= \frac{\partial L'}{\partial \mathbf{r}} \\ m_i \ddot{\mathbf{r}}_i &= -\frac{\partial V}{\partial \mathbf{r}_i} - \lambda_\alpha \frac{\partial \boldsymbol{\sigma}_\alpha}{\partial \mathbf{r}_i}, \end{aligned}$$

  provide the constraints are *holonomic* (depend only on $\mathbf{r}$ and not on $\mathbf{p}$).

- 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 be 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

$$\lambda_\alpha \quad = \quad \mathsf{Z}^{-1}_{\alpha\beta}\left(\mathcal{F}_\beta + \mathcal{T}_\beta\right) \qquad \mathcal{F}_\beta = \sum_i \frac{\mathbf{F}_i}{m_i} \cdot \frac{\partial\sigma_\beta}{\partial\mathbf{r}_i} \qquad \mathcal{T}_\beta = \sum_{i,j} \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial^2\sigma_\alpha}{\partial\mathbf{r}_i\partial\mathbf{r}_j} \cdot \frac{\mathbf{p}_j}{m_j}.$$

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

$$\mathbf{r}(t+\Delta t) \;=\; 2\mathbf{r}(t) - \mathbf{r}(t-\Delta t) - \omega^2 \mathbf{r}(t)\Delta t^2.$$

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

$$\mathbf{r}(t+\Delta t) \;=\; \mathbf{r}_u(t+\Delta t) - \frac{\lambda}{m}\mathbf{r}(t),$$

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

$$d^2 \;=\; r^2(t+\Delta t) = r_u^2(t+\Delta t) - \frac{2\lambda}{m}\mathbf{r}(t)\cdot\mathbf{r}_u(t+\Delta t) + \left(\frac{\lambda}{m}r(t)\right)^2,$$

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:

$$\mathbf{r}_i(t+\Delta t) \;=\; \mathbf{r}_i^u(t+\Delta t) - \frac{\Delta t^2}{m_i}\lambda_\alpha \left(\frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i}\right)_{\mathbf{r}(t)},$$

   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 $\Delta_i^{(0)} = \mathbf{r}_i(t+\Delta t) - \mathbf{x}_i^{(0)}(t+\Delta t)$,

$$0 = \sigma_\alpha(t+\Delta t) \;=\; \sigma_\alpha(\mathbf{x}_i^{(0)}(t+\Delta t)) + \sum_i \left(\frac{\partial \sigma_\alpha}{\partial \mathbf{r}_i}\right)_{\mathbf{x}_i^{(0)}} \cdot \Delta_i^{(0)},$$

   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 $\mathsf{Z}^{(n+1)-1}$ 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}

$$\mathsf{G} = \left(\begin{array}{c|c} \mathsf{A} & \mathsf{B} \\ \hline \mathsf{B}^T & \Gamma \end{array}\right) \qquad \mathsf{G}^{-1} = \left(\begin{array}{c|c} \Delta & \mathsf{E} \\ \hline \mathsf{E}^T & \mathsf{Z} \end{array}\right),$$

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

$$\begin{pmatrix} \dot{\mathbf{q}} \\ \dot{\boldsymbol{\sigma}} \end{pmatrix} = \left(\begin{array}{c:c} \Delta & \mathsf{E} \\ \hdashline \mathsf{E}^T & \mathsf{Z} \end{array}\right) \cdot \begin{pmatrix} \mathbf{p}^q \\ \mathbf{p}^\sigma \end{pmatrix},$$

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 $\tilde{\mathsf{Z}}^{-1}(\mathbf{r})\dot{\boldsymbol{\sigma}}(\mathbf{r}, \mathbf{p})$ are 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.

$$\begin{aligned}\frac{d}{dt}\left(\rho_c(H_c)\, d\mathbf{q}d\mathbf{p}^q\delta(\boldsymbol{\sigma})\delta(\mathbf{p}^{\boldsymbol{\sigma}}-\tilde{\mathbf{p}}^{\boldsymbol{\sigma}})d\boldsymbol{\sigma}d\mathbf{p}^{\boldsymbol{\sigma}}\right) &= 0 \qquad \text{so}\\ \frac{d}{dt}\left(\rho_c(H(\mathbf{r},\mathbf{p}))\,\delta(\boldsymbol{\sigma})\,\delta(\dot{\boldsymbol{\sigma}})\,\det\mathsf{Z}\, d\mathbf{r}d\mathbf{p}\right) &= 0.\end{aligned}$$

- 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 $\mathbf{X}=(\mathbf{r},\mathbf{p})$,

$$\begin{aligned}\frac{d}{dt}\left(\det\mathsf{Z}\, d\mathbf{X}\right) &= 0\\ \det\mathsf{Z}(\mathbf{r}(t))\, d\mathbf{X}(t) &= \det\mathsf{Z}(\mathbf{r}(0))\, d\mathbf{X}(0).\end{aligned}$$

- 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 $\mathsf{D}_{ij}^n = \binom{n}{j}\lambda_i^{n-j}$ 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

$$\begin{aligned}
\frac{d \det \mathsf{J}}{dt} &= e^{\mathrm{Tr}\ln \mathsf{J}} \frac{d}{dt}(\mathrm{Tr}\ln \mathsf{J}) = \det \mathsf{J}\ \mathrm{Tr}\left(\frac{d\mathsf{J}}{dt} \cdot \mathsf{J}^{-1}\right) \\
&= \det \mathsf{J} \left(\sum_i \frac{\partial \dot{\mathbf{X}}_i(t)}{\partial \mathbf{X}(0)} \cdot \frac{\partial \mathbf{X}(0)}{\partial \mathbf{X}_i(t)} \right) = \det \mathsf{J} \sum_i \frac{\partial \dot{\mathbf{X}}_i(t)}{\partial \mathbf{X}_i(0)} \\
&= \det \mathsf{J} \left(\frac{\partial}{\partial \mathbf{X}(t)} \cdot \dot{\mathbf{X}}(t) \right) = \det \mathsf{J}\, \kappa(t),
\end{aligned}$$

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

$$\frac{d \det \mathsf{Z}}{dt} = -\kappa \det \mathsf{Z} \qquad \frac{d \ln \det \mathsf{Z}}{dt} = -\kappa.$$

– 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 $\dot{B}(\mathbf{x}) = \boldsymbol{\xi} \cdot \nabla_x B(\mathbf{x}) = \mathcal{L} B(\mathbf{x})$, where $\mathcal{L} = \boldsymbol{\xi} \cdot \nabla_x$.

- 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 $t = 0$.

- Noting 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

$$\begin{aligned}
\frac{d\ln\gamma(\mathbf{x},t)}{dt} &= -\kappa \\
\frac{df(\mathbf{x},t)}{dt} &= \frac{\partial f(\mathbf{x},t)}{\partial t} + \boldsymbol{\xi}(\mathbf{x})\cdot\nabla_x f(\mathbf{x},t) = \frac{\partial f(\mathbf{x},t)}{\partial t} + \mathcal{L}_0 f(\mathbf{x},t) = 0 \qquad (5.15)
\end{aligned}$$

  – 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. (5.15) 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, cince 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. (5.15), 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

$$\int d\mathbf{X} B(\mathbf{X})\mathcal{L}_0 A(\mathbf{X}) = \int d\mathbf{X}\Big[\Big(-\mathcal{L}_0 + \nabla_{\mathbf{X}}\cdot\dot{\mathbf{X}}\Big) B(\mathbf{X})\Big] A(\mathbf{X})$$
$$= -\int d\mathbf{X}\Big[(\mathcal{L}_0+\kappa) B(\mathbf{X})\Big] A(\mathbf{X})$$

by integration by parts. Now note that since $\mathcal{L}_0\gamma(\mathbf{X}) = -\kappa\gamma(\mathbf{X})$, it therefore follows that

$$\begin{aligned}
\int d\boldsymbol{\mu}(\mathbf{X})\, B(\mathbf{X})\mathcal{L}_0 A(\mathbf{X}) &= \int d\mathbf{X}\gamma(\mathbf{X})\, B(\mathbf{X})\mathcal{L}_0 A(\mathbf{X}) \\
&= -\int d\mathbf{X}\Big[(\mathcal{L}_0+\kappa)\,\gamma(\mathbf{X})B(\mathbf{X})\Big] A(\mathbf{X}) \\
&= -\int d\mathbf{X}\, A(\mathbf{X})\Big[\kappa\gamma(\mathbf{X})B(\mathbf{X}) + \gamma(\mathbf{X})\big(\mathcal{L}_0 B(\mathbf{X})\big) \\
&\qquad +\big(\mathcal{L}_0\gamma(\mathbf{X})\big)B(\mathbf{X})\Big] \\
&= -\int d\mathbf{X}\,\Big[\mathcal{L}_0 B(\mathbf{X})\Big]\gamma(\mathbf{X})A(\mathbf{X}) \\
&= -\int d\boldsymbol{\mu}(\mathbf{X})\Big[\mathcal{L}_0 B(\mathbf{X})\Big] A(\mathbf{X}).
\end{aligned}$$

– Using this result in the expansion of $e^{-\mathcal{L}_0 t}$, we see that

$$\int d\boldsymbol{\mu}(\mathbf{X})B(\mathbf{X})e^{-\mathcal{L}_0 t}A(\mathbf{X}) = \int d\boldsymbol{\mu}(\mathbf{X})\,\big(e^{\mathcal{L}_0 t}B(\mathbf{X})\big)\,A(\mathbf{X}) = \int d\boldsymbol{\mu}(\mathbf{X})\,B(\mathbf{X}(t))A(\mathbf{X}).$$

– 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

$$\begin{aligned}\dot{\mathbf{q}} &= \frac{\mathbf{p}}{m} \qquad \dot{\eta} = \alpha p_\eta \\ \dot{\mathbf{p}} &= \mathbf{F}(\mathbf{q}) - \alpha \mathbf{p} p_\eta - \eta K T'(\mathbf{q}) \qquad \dot{p}_\eta = \frac{\mathbf{p}\cdot\mathbf{p}}{m} - 3NkT(\mathbf{q}),\end{aligned} \tag{5.16}$$

  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

  $$3N\eta = \frac{1}{kT(\mathbf{q})}\left(E - \frac{\mathbf{p}\cdot\mathbf{p}}{2m} - \phi(\mathbf{q}) - \alpha\frac{p_\eta^2}{2}\right) = \frac{1}{kT(\mathbf{q})}\left(E - \tilde{H}\right). \tag{5.17}$$

    This allows the system of equations to be simplified by inserting relation (5.17) into Eq. (5.16).

- 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

$$\nabla_{\mathbf{x}} \cdot (\gamma(\mathbf{x})\dot{\mathbf{x}}) = 0, \tag{5.18}$$

  under the dynamical evolution determined by $\dot{\mathbf{x}}$.
- We'd like to find evolution operators $\mathcal{L}_\alpha$ that each satisfy Eq. (5.18) *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:

$$\begin{aligned}\mathcal{L}_1 &= F(q)\frac{\partial}{\partial p} \qquad \mathcal{L}_2 = \frac{p}{m}\left[\frac{\partial}{\partial q} + p\frac{\partial}{\partial p_\eta}\right] \\ \mathcal{L}_3 &= -kT\frac{\partial}{\partial p_\eta} \qquad \mathcal{L}_4 = \alpha p_\eta\left[-p\frac{\partial}{\partial p} + \frac{\partial}{\partial \eta}\right].\end{aligned} \tag{5.19}$$

* For $\mathcal{L}_1$, $\dot{\mathbf{x}} = (0, F(q), 0, 0)$ so $\nabla_{\mathbf{x}} \cdot (e^{\eta}\dot{\mathbf{x}}(1)) = \frac{\partial}{\partial p}(e^{\eta}F(q)) = 0$, 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 $\nabla_{\mathbf{x}}\cdot(e^{\eta}\dot{\mathbf{x}}(2)) = \frac{\partial}{\partial q}(e^{\eta}p/m) + \frac{\partial}{\partial p_\eta}(e^{\eta}p^2/m) = 0$.
* For $\mathcal{L}_3$, $\dot{\mathbf{x}} = (0, 0, 0, -kT)$ so $\nabla_{\mathbf{x}} \cdot (e^{\eta}\dot{\mathbf{x}}(3)) = \frac{\partial}{\partial p_\eta}(-e^{\eta}kT) = 0$.
* 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 $\nabla_{\mathbf{x}} \cdot (e^{\eta}\dot{\mathbf{x}}(4)) = \frac{\partial}{\partial p}(-e^{\eta}\alpha p p_\eta) + \frac{\partial}{\partial \eta}(e^{\eta}\alpha p_\eta) = -\alpha p_\eta e^{\eta} + \alpha p_\eta e^{\eta} = 0$.
* 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

$$\begin{aligned} e^{\mathcal{L}_1\Delta t}\mathbf{x} &= \begin{pmatrix} q \\ p + F\Delta t \\ \eta \\ p_\eta \end{pmatrix} \quad e^{\mathcal{L}_2\Delta t}\mathbf{x} = \begin{pmatrix} q + \frac{p}{m}\Delta t \\ p \\ \eta \\ p_\eta + \frac{p^2}{m}\Delta t \end{pmatrix} \\ e^{\mathcal{L}_3\Delta t}\mathbf{x} &= \begin{pmatrix} q \\ p \\ \eta \\ p_\eta - kT\Delta t \end{pmatrix} \quad e^{\mathcal{L}_4\Delta t}\mathbf{x} = \begin{pmatrix} q \\ p e^{-\alpha p_\eta \Delta t} \\ \eta + \alpha p_\eta \Delta t \\ p_\eta \end{pmatrix}, \end{aligned}$$

  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:

$$\dot{\mathbf{x}}_i = \mathsf{A}_{ij}(\mathbf{x})\frac{\partial H}{\partial \mathbf{x}_j} = \boldsymbol{\xi}_i(\mathbf{x}), \tag{5.20}$$

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. (5.19).