Time averages

What one typically would like to do in a molecular dynamics simulation is to compute the time average of some observable A that is a function of all classical phase space variables $\mathbf{R}$ and $\mathbf{p}$.

$$A(t) = A(\mathbf{R}(t), \mathbf{p}(t))$$

The phase space variables change in time, that is, along the MD trajectory, and so does A. Moreover, the time evolution of $A(t)$ will be different for different trajectories, i.e. for different initial values of the phase space variables $(\mathbf{R}(0), \mathbf{p}(0))$

The time average of A over a continuous trajectory $\mathbf{R}(t)$ of finite length Δt is given by

$$\bar{A}_{\Delta t} = \frac{1}{\Delta t} \int_0^{\Delta t} dt A(t).$$

In practical calculations the trajectories are discrete and the continuous time average   is approximated by the discrete time average,

$$\bar{A}_{\Delta t} \approx \frac{1}{M} \sum_{m=1}^{M} A(t_m)$$

where $\Delta t = M\delta t$ and δt is the time step.

Microcanonical (NVE) Ensemble

Consider a large number of copies of an isolated system that all have the same constant particle number N, constant volume V and constant total energy E. The collection of states in phase space $(\mathbf{R}, \mathbf{p})$ that have the same total energy E is called the microcanonical or NVE ensemble. One of the fundamental assumptions of statistical mechanics is that the probability of a state, $\rho_{\mathrm{NVE}}(\mathbf{R}, \mathbf{p})\, d\mathbf{R} d\mathbf{p}$, is the same for all states of the NVE ensemble. The condition that only states of energy E are occupied and that all of them have the same probabilty can be expressed in terms of a delta function δ, which restricts the manifold of accessible phase space points to a hypersurface of constant E only.

$$\rho_{\mathrm{NVE}}(\mathbf{R}, \mathbf{p}) = \frac{(h^{3N} N!)^{-1}}{\Omega_{\mathrm{NVE}}} \delta\left[\mathbf{H}(\mathbf{R}, \mathbf{p}) - E\right]$$

$$\Omega_{\mathrm{NVE}} = (h^{3N} N!)^{-1} \int d\mathbf{R}\, d\mathbf{p}\, \delta\left[\mathbf{H}(\mathbf{R}, \mathbf{p}) - E\right]$$

Here ρ_{NVE} is the probability density, $\mathbf{H} = \sum_{I=1}^{N} \mathbf{p}_I^2/(2M_I) + E_{\mathbf{R}}$ is the Hamiltonian, $E_{\mathbf{R}}$ is the potential energy, h is Planck's constant, and Ω_{NVE} is the microcanonical partition function. The denominator of the probability density contains the partition function which normalizes the probability to unity, $\int d\mathbf{R}\, d\mathbf{p}\, \rho_{\mathrm{NVE}} = 1$. It also contains the unit volume in phase space, $h^{3N} N!$, which makes the probability dimensionless.
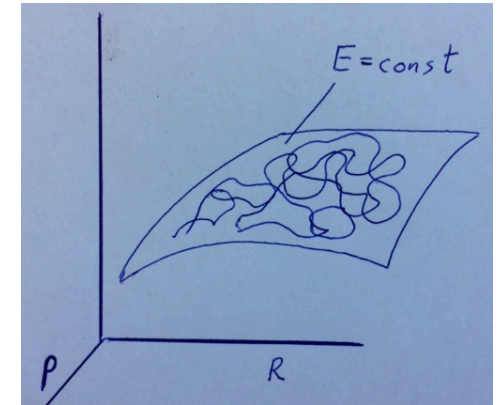
Ergodic Hypothesis

In order to obtain the average or the expectation value of an observable $A(\mathbf{R}, \mathbf{p})$ in the NVE ensemble, $\langle A \rangle_{\mathrm{NVE}}$, one has to integrate A over the phase space variables, where each point in phase space is weighted with the probability density ρ_{NVE}.

$$\langle A \rangle_{\mathrm{NVE}} = \int d\mathbf{R}\, d\mathbf{p}\, \rho_{\mathrm{NVE}}(\mathbf{R}, \mathbf{p}) A(\mathbf{R}, \mathbf{p})$$

The ergodic hypothesis establishes a connection between the time averages obtained from molecular dynamics and the ensemble averages used in statistical mechanics. It states that for ergodic systems, the time average of an observable A is equal to the ensemble average in the limit of an infinitely long trajectory.

$$\lim_{\Delta t \to \infty} \bar{A}_{\Delta t} = \langle A \rangle_{\mathrm{NVE}}$$

This means that the number of times a point in phase space is visited along an (infinitely long) MD trajectory is proportional to its statistical weight in the NVE ensemble. The equivalence of time and and ensemble averages is an assumption valid for stable many-body systems. However, there are systems for which this condition is not satisfied, such as glasses.

Schematic of constant (total) energy surface in phase space with chaotic trajectory. At long times, each point will be visited an equal number of times, according to the ergodic hypothesis.

Canonical (NVT) Ensemble

Consider a large number of copies of a system that is connected to a heat bath at temperature T. All copies have the same constant particle number N, constant volume V, but they can exchange heat with the bath and thus can have a different total system energy E. The collection of these states is called the canonical or NVT ensemble. From arguments based on the maximization of possibilities to realize a given total energy $E_{\text{tot}} = E + E_{\text{bath}}$, one can derive that each state in the canonical ensemble has a probability density

$$\rho_{\text{NVT}}(\mathbf{R}, \mathbf{p}) = \frac{(h^{3N} N!)^{-1}}{\Omega_{\text{NVT}}} \exp\left[-\beta \mathbf{H}(\mathbf{R}, \mathbf{p})\right]$$

$$\Omega_{\text{NVT}} = (h^{3N} N!)^{-1} \int d\mathbf{R} \, d\mathbf{p} \, \exp\left[-\beta \mathbf{H}(\mathbf{R}, \mathbf{p})\right]$$

where $\beta = 1/(k_{\text{B}} T)$ and k_{B} is the Boltzmann constant. The distribution is also called Boltzmann distribution, and Ω_{NVT} is the canonical partition function.

The expectation value for an observable A in the NVT ensemble is calculated similarly as for the NVE ensemble replacing ρ_{NVE} by the probability density ρ_{NVT}

$$\langle A \rangle_{\text{NVT}} = \int d\mathbf{R} \, d\mathbf{p} \, \rho_{\text{NVT}}(\mathbf{R}, \mathbf{p}) A(\mathbf{R}, \mathbf{p})$$

There exists an ergodic hypothesis also for NVT ensembles. However, before we state this explicitly we have to define temperature in molecular dynamics simulation.

Temperature and kinetic energy

Temperature was introduced previously as a parameter in the exponent of the canonical ensemble distribution function. Comparison of the expressions of state functions in statistical mechanics and classical thermodynamics shows that the statistical temperature is indeed equivalent with the empirical temperature measured in experiments.

One can easily show that in the canonical ensemble temperature is proportional to the expectation value of the total kinetic energy. Insertion of $A = \sum_{I=1}^{N} \frac{\mathbf{p}_I^2}{2\,M_I}$ we obtain

$$\left\langle \sum_{I=1}^{N} \frac{\mathbf{p}_I^2}{2\,M_I} \right\rangle_{\text{NVT}} = \frac{(h^{3N}N!)^{-1} \int d\mathbf{R}\, d\mathbf{p}\, \left(\sum_{I=1}^{N} \frac{\mathbf{p}_I^2}{2\,M_I}\right) \exp\left[-\beta \sum_{J=1}^{N} \frac{\mathbf{p}_J^2}{2\,M_J} + E_{\mathbf{R}}\right]}{(h^{3N}N!)^{-1} \int d\mathbf{R}\, d\mathbf{p}\, \exp\left[-\beta \sum_{I=1}^{N} \frac{\mathbf{p}_I^2}{2\,M_I} + E_{\mathbf{R}}\right]}$$

$$= \frac{3N}{2} k_{\mathrm{B}} T,$$

where we have used $\int_{-\infty}^{\infty} dx\, x^2 \exp(-ax^2) = \frac{1}{2a}\sqrt{\pi/a}$. Thus, temperature can be defined by the average kinetic energy, which is perhaps a more intuitive quantity than the ensemble distribution function.

Nose thermostat

The MD algorithms presented in the first lecture are numerical schemes that solve Newton's equation of motion. As the total energy is conserved during the motion, Newton Dynamics samples the NVE ensemble (assuming ergodicity). On the other hand, experiments are usually carried out at constant temperature. Thus, in order to allow for a consistent comparison between simulation and experiment, it would be desirable to carry out MD simulations in the NVT ensemble. The famous Nosé constant temperature MD algorithm has been developed for this purpose. In this method Newton's equations are extended by a friction term, i.e. a term proportional to the velocity, $\zeta \dot{\mathbf{R}}_I$,

$$\ddot{\mathbf{R}}_I = \frac{\mathbf{f}_I}{M_I} - \zeta \dot{\mathbf{R}}_I$$

$$\dot{\zeta} = \frac{1}{Q} \left(\sum_{I=1}^{N} \frac{M_I \dot{\mathbf{R}}_I^2}{2} - 3N k_{\mathrm{B}} T \right),$$

where ζ is the friction constant, Q is the fictitious mass and T is the target temperature.

Nose thermostat (contd.)

During the dynamics defined in previous slide the total energy is not conserved any more due to the dissipation of heat caused by the friction term. This can be shown by taking the time derivative of the Hamiltonian $\mathbf{H} = \sum_{I=1}^{N} \frac{\mathbf{p}_I^2}{2M_I} + E_{\mathbf{R}}$ using the chain rule as before, and substituting $\dot{\mathbf{p}} = M_I \ddot{\mathbf{R}}$ The result is

$$\frac{d\mathbf{H}}{dt} = -\zeta \sum_{I=1}^{N} M_I \dot{\mathbf{R}}_I^2.$$

The dissipation by the friction term can be positive or negative, thus leading either to an accelaration or deccelaration of the particles in addition to the accelaration or deccelaration due to the atomistic potential energy $E_{\mathbf{R}}$.

One can show that for $\zeta > 0$ the total energy (potential + kinetic) decreases = **COOLING** and that for $\zeta < 0$ the total energy decreases = **HEATING**

Assuming that the Nose dynamics is ergodic, one can show that each point in phase space is sampled according to the canonical probability distribution, that is, **Nose dynamics samples the NVT ensemble.**
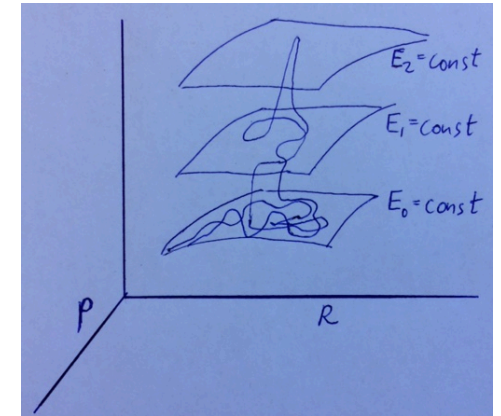
Schematic of constant (total) energy surfaces in phase space with chaotic trajectory. At long times, each surface will be visited proportional to its Boltzmann weight, $\exp(-E_i/k_B T)$.