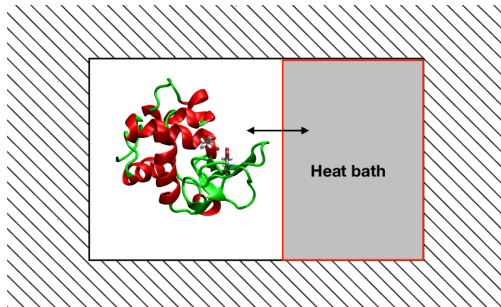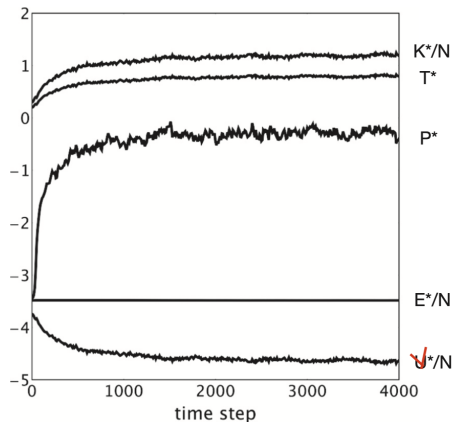# Molecular Modelling and Simulations

Heat bath

Shampa Raghunathan

Recap...

Theoretically, Newtonian dynamics conserves the total energy (isolated system)

LeSar, R. (2013). Introduction to Computational Materials Science: Fundamentals to Applications. Cambridge

University Press.

Velocity rescaling

In practice, constant energy dynamics often not used

▶ The constant energy dynamics (NVE) does rarely represents the experimental conditions for the system simulated.

● One easiest way to force the system to be in a specific temperature is velocity rescaling. If the desired temperature is T_s and the instantaneous temperature is $T(t) = 2K_{kinetic}(t)/3Nk_B$, the system can be forced to take the T_s by *rescaling* the velocities:

$$\mathrm{v}^{\mathrm{new}} = \sqrt{\frac{T_s}{T}}\mathrm{v}$$

T ∝ K ∝ <v²>, so T1/T2 ∝ K1/K2 ∝ <v²>₁/<v²>₂, or <v²>₂ ∝ <v²>₁ T2/T1

LeSar, R. (2013). Introduction to Computational Materials Science: Fundamentals to Applications. Cambridge University Press.
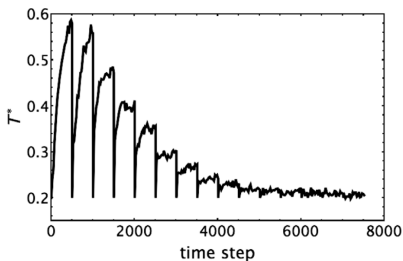
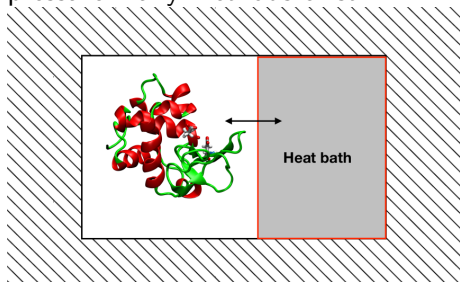## Maxwell-Boltzmann distribution

Temperature is related to the time average of the kinetic energy, K

$$<K> = \frac{3}{2}Nk_BT$$

$$\implies \frac{1}{2}\sum_{i=1}^{N} m_i \mathrm{v}_i^2 = \frac{3}{2}Nk_BT$$

$$\implies T = \frac{1}{3Nk_B}\sum_{i=1}^{N} m_i \mathrm{v}_i^2$$

Further...

- To extend molecular dynamics to constant temperature and pressure many methods exist

Outline

A macroscopic state is by described thermodynamic $constraints$ those operate on it:

N = Number of particles   E = K + U = internal energy
V = Volume   S = entropy
P = Pressure   H = E + PV = enthalpy
T = Temperature   A = E - TS = Helmholtz free energy
μ = Chemical potential   G = E - TS + PV = Gibbs free energy

> A thermodynamical ensemble is a collection of microscopic states those all realize an identical macroscopic state

A microscopic state of the system is given by a point $(\mathbf{r}, \mathbf{p})$ of the phase space of the system, where $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ and $\mathbf{p} = (\mathbf{p}_1, \mathbf{p}_2, \cdots, \mathbf{p}_N)$ are the positions and the momenta of the N atoms of the system.

Examples of thermodynamic ensembles:
- Microcanonical: fixed N, V, E
- Canonical: fixed N, V, T   often used in MD
- Constant P-T: fixed N, P, T   often used in MD
- Grand Canonical: fixed μ, P, T

Boltzmann (canonical) distribution

Boltzmann showed that the canonical probability of the microstate i is given by

$$P_i = \frac{1}{Q}e^{-\beta E_i} \qquad\qquad \beta = \frac{1}{k_B T}$$

Q is the partition function

$$Q = \sum e^{-\beta E_i}$$

k_B = Boltzmann constant such that:

$$\sum P_i = 1$$

Phase space

▶ A system containing N atoms has $6N$ coordinates defining
  the state of the system ($3N$ coordinates ($\mathbf{r}$), $3N$ momenta
  ($\mathbf{p}$)). The $6N$-dimensional space defined by these coordinates
  is called phase space of the system

▶ At any instant in time, the system occupies one point in phase
  space. Over time a dynamical system maps out a "trajectory"
  in phase space.

▶ Ensemble is a collection of phase space point Γ

Time average

▶ Now, for a given property A, the value on phase space point (Γ) can be written as $A(\Gamma)$

▶ As the system evolves in time, so does the Γ, therefore $A(\Gamma)$ will change. It is reasonable to assume that the experimentally observable "macroscopic" property A_{obs} is really the time average of $A(\Gamma)$ taken over a long time interval:

$$A_{\mathrm{obs}} = < A >_{\mathrm{time}} = < A(\Gamma(t)) >_{\mathrm{time}} = \lim_{t_{\mathrm{obs}} \to \infty} \frac{1}{t_{\mathrm{obs}}} \int_0^{t_{\mathrm{obs}}} A(\Gamma(t)) dt \tag{1}$$

▶ Truly macroscopic (e.g. 10^{23}) simulation not possible, therefore, the above Eq. 1 can be written for a long finite time

$$A_{\mathrm{obs}} = < A >_{\mathrm{time}} = \frac{1}{t_{\mathrm{obs}}} \sum_{t=1}^{t_{\mathrm{obs}}} A(\Gamma(t)) \tag{2}$$

Time average

- What is a sufficient time t_{obs} for a time average that corresponds to a macroscale observable?

  ▶ t_{obs} must be long enough so that the system can visit sufficient points in the parts of phase space accessible to it.

The ensemble average

The average could be determined by the value of, for example, E_α, at each distinct configuration (α) multiplied by the number of times (n_α) the system was in that configuration. The average is

$$< E >= \frac{1}{N_{\text{config}}} \sum_{\alpha=1}^{N_{\text{config}}} n_\alpha E_\alpha = \sum_{\alpha=1}^{N_{\text{config}}} P_\alpha E_\alpha$$

P_α probability density, *i.e.*, fraction of all possible states that are in configuration α, such that,

$$\sum_{\alpha=1}^{N_{\text{config}}} P_\alpha = 1$$

The ensemble average: An example

Now the probability on the energy associated can also be written as Boltzmann probability

$$P_\alpha = \frac{1}{Q}e^{-\beta E_\alpha}$$

Q is the system partition function

$$Q = \sum e^{-\beta E_\alpha}$$

$$E_{\text{obs}} = <E>_{\text{ens}} = \frac{1}{Q}\sum_\alpha E_\alpha e^{-\beta E_\alpha} \tag{3}$$

can be thought as the normalization constant for P

Ergodic hypothesis

The ergodic hypothesis is that the ensemble averages used to compute expectation values can be replaced by time averages over the simulation.

$$A_{\mathrm{obs}} = <A>_{ens} = <A>_{time} = \frac{1}{t_{\mathrm{obs}}} \sum_{t=1}^{t_{\mathrm{obs}}} A(\Gamma(t)) \qquad (4)$$

It assumes that Eq. 4 to be valid and independent of choice of t_{obs}.

Weighting function and probability

Introducing a "weighting function" w_α which basically specifies how thermodynamic quantities weight the probability of a state relative to other states; considering the probability P_α $(\propto w_\alpha)$ of a system being in state α

$$P_\alpha = \frac{1}{Q} w_\alpha \tag{5}$$

Q is the system partition function

$$Q = \sum_\alpha w_\alpha \tag{6}$$

Now, any average of a quantity A is written as

$$< A > = \frac{1}{Q} \sum_\alpha A_\alpha w_\alpha \tag{7}$$

Canonical ensemble

Systems with constraints (N, V, T) are referred to as being in the
canonical ensemble, which is sometimes referred to as the NVT
ensemble. The free energy associated with systems with constant
NVT is the Helmholtz free energy A. The partition function is

$$Q_{NVT} = \sum_{\alpha} e^{-\beta E_{\alpha}} \tag{8}$$

Now, the expectation value of energy in the canonical ensemble
takes the form,

$$<E> = \frac{1}{Q_{NVT}} \sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}} \tag{9}$$

The Helmholtz free energy, A, is related to the canonical partition
function by

$$A = -k_B T \ln Q_{NVT} \tag{10}$$

▶ Microcanonical ensemble (constant N, V, E); sampling obtained by simple integration of the Newtonian dynamics: Verlet, Velocity Verlet Thermodynamics: $S = -k_B \ln Q_{NVE}$

▶ Canonical ensemble (constant N, V, T); sampling obtained using thermostats: Berendsen, Nose-Hoover Thermodynamics: $A = -k_B T \ln Q_{NVT}$

▶ Isothermal-isobaric ensemble (constant N, P, T); thermostat, and volume of system is allowed to fluctuate, and is regulated by barostat algorithms Thermodynamics: $G = -k_B T \ln Q_{NPT}$