

Introduction to Molecular Dynamics Simulations

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Outline

- What is molecular Dynamics?
- Numerical solutions to equations of motion
- Ingredients of Molecular Dynamics Simulations
 - Constant energy molecular dynamics
 - Constant temperature molecular dynamics
- Other Considerations
- Summary

What is Molecular Dynamics?

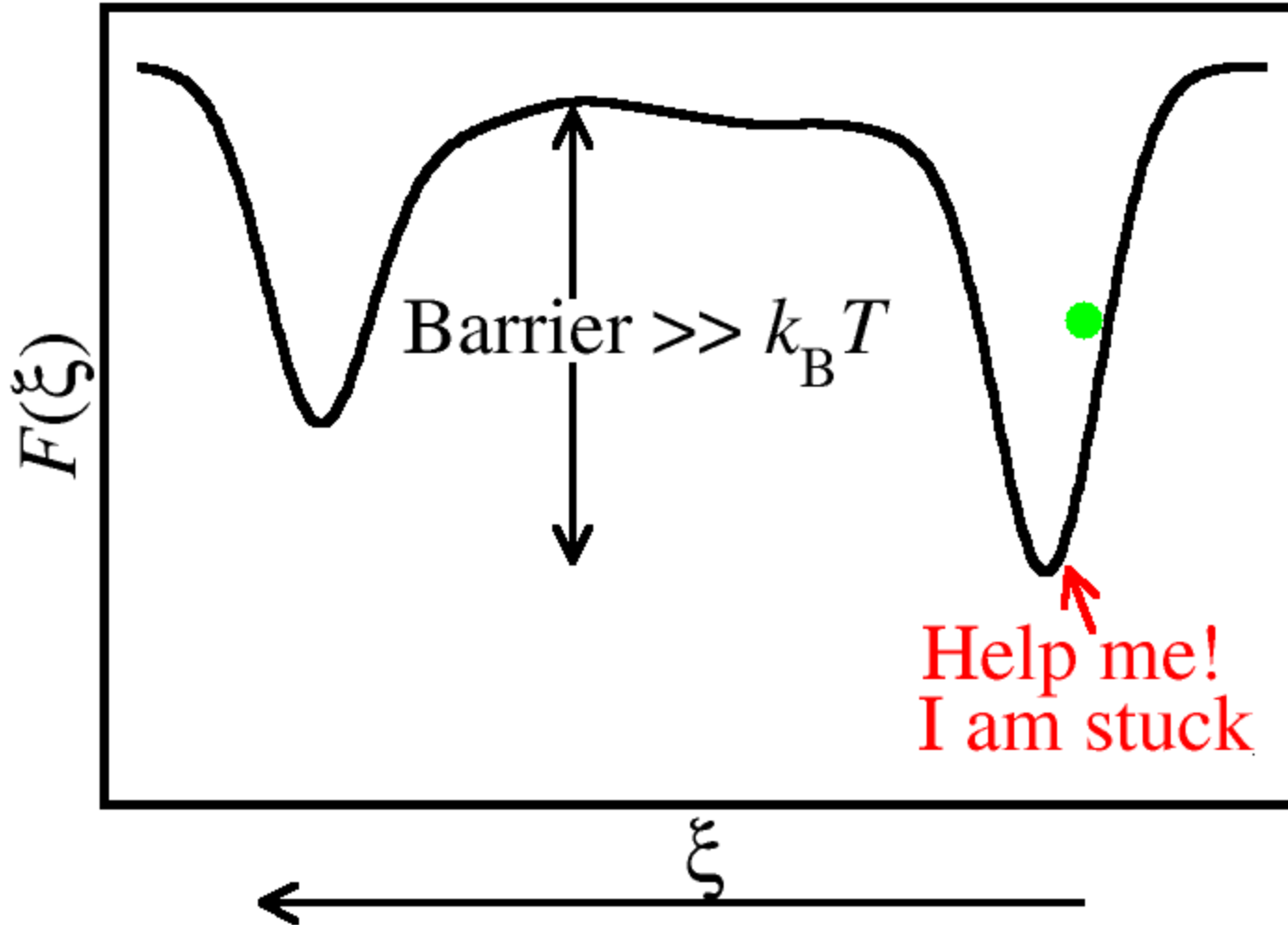
What is molecular dynamics?

Molecular dynamics is the time evolution of a system of atoms described by Newton's second law of motion under the influence of temperature (and pressure)

- Molecular dynamics provides a means for dynamical quantities [i.e. time-dependent quantities] and thermals quantities of a system to be readily computed.
- Examples of such properties are:
 - (i) the **rate of diffusion** (how fast or slow atoms move when subjected to thermal effects)
 - (ii) **thermal conductivity of a material** (how good or bad a material conducts heat)
 - (iii) **Phase transformations in materials** (how materials change, for example, their softness or hardness when subject to temperature and pressure)

What is Molecular Dynamics?

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Customized molecular dynamics simulations can be employed to access different energetic states of a system or material.

This applies to cases where the system can be trapped in one energy state for a long time [see cartoon; ξ denotes a state of the system and $F(\xi)$ denotes energy of that state]

What is Molecular Dynamics?

Newton's second law employed in molecular dynamics

- **Newton's second law of motion:** The net force \vec{F} acting on object of mass m is proportional to the object's acceleration \vec{a} :

$$\vec{F} \propto \vec{a} \Rightarrow \vec{F} = m\vec{a}$$

- Since \vec{a} is the rate of change of velocity \vec{v} with time t [that is, $\vec{a} = d\vec{v}/dt$] and \vec{v} is the rate of change of displacement \vec{r} with t [that is, $\vec{v} = d\vec{r}/dt$], Newton's second law can be restated at:

$$\vec{F} = m \frac{d\vec{v}}{dt} \text{ and } \vec{v} = \frac{d\vec{r}}{dt}$$

What is Molecular Dynamics?

- Consider a system of N atoms of masses $\{m_1, m_2, \dots, m_N\}$ with atomic positions $\{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\}$, velocities $\{\vec{v}_1, \vec{v}_2, \dots, \vec{v}_N\}$ under the action forces $\{\vec{F}_1, \vec{F}_2, \dots, \vec{F}_N\}$ at a given instant in time t .
- Per Newton's second law, the time evolution of the system is governed by the pair of coupled equations:

$$\begin{aligned}\frac{d\vec{v}_i(t)}{dt} &= \frac{\vec{F}_i}{m_i} \\ \frac{d\vec{r}_i(t)}{dt} &= \vec{v}_i\end{aligned}\quad [1]$$

where $i = 1, 2, \dots, N$ labels the atoms

- Let us examine a few standard **numerical algorithms** to solving the system of equations in [1] above.

What is Molecular Dynamics?

- Before we delve into widely employed numerical algorithms in molecular dynamics simulation, let us examine a few heuristics.

- First, we note following about **numerical approximation to first derivatives**:

$$d\vec{v}_i(t)/dt \approx [\vec{v}_i(t + \Delta t) - \vec{v}_i(t)]/\Delta t$$

$$d\vec{r}_i(t)/dt \approx [\vec{r}_i(t + \Delta t) - \vec{r}_i(t)]/\Delta t$$

where it is implicitly assumed that Δt is small enough.

- Per the above approximations, a simple solution to the pair of Newton's equations are:

$$\frac{d\vec{v}_i}{dt} = \frac{\vec{F}_i}{m_i} \Rightarrow \vec{v}_i(t + \Delta t) \approx \vec{v}_i(t) + \vec{a}_i(t)\Delta t \quad \left[\text{where } \vec{a}_i(t) = \frac{\vec{F}_i(t)}{m_i} \right]$$

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i \Rightarrow \vec{r}_i(t + \Delta t) \approx \vec{r}_i(t) + \vec{v}_i(t)\Delta t$$

where $i = 1, 2, \dots, N$ and Δt is known as the **time step**.

- Let us examine a few standard **numerical approaches**

Numerical solutions to equations of motion

Verlet method: The equations of motion are

$$\vec{r}_i(t + \Delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \Delta t) + \vec{a}_i(t)(\Delta t)^2 \text{ where } \vec{a}_i(t) = \frac{\vec{F}_i(t)}{m_i}$$

$$\vec{v}_i(t) = \frac{\vec{r}_i(t + \Delta t) - \vec{r}_i(t - \Delta t)}{2\Delta t}$$

- **Advantages of the Verlet method:** (i) Straightforward to implement; (ii) the propagation of the atomic positions does not explicitly require the atomic velocities [thus one can ignore the velocities unless they are really needed]
- **Disadvantages of the Verlet method:** (i) It is non-self starting; (ii) the velocities accumulate significant round-off errors (especially for dynamics spanning long time scales)

Numerical solutions to equations of motion

Leapfrog method: The equations of motion are

$$\vec{v}_i\left(t + \frac{\Delta t}{2}\right) = \vec{v}_i\left(t - \frac{\Delta t}{2}\right) + \vec{a}_i(t)\Delta t \quad \text{where } \vec{a}_i(t) = \frac{\vec{F}_i(t)}{m_i}$$

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i\left(t + \frac{\Delta t}{2}\right)\Delta t$$

The velocity at time t is given by

$$\vec{v}_i(t) = [\vec{v}_i(t - \Delta t/2) + \vec{v}_i(t + \Delta t/2)]/2$$

- **Advantages of the Leapfrog method:** (i) It is time reversible; (ii) it is symplectic (i.e. it conserves the energy of the system)
- **Disadvantage of the Leapfrog method:** The velocities and positions are computed at different times, that is, they leap frog each other by half a time step $[\Delta t/2]$

Numerical solutions to equations of motion

Velocity Verlet method: The equations of motion are

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{1}{2}\vec{a}_i(t)(\Delta t)^2 \quad \text{where } \vec{a}_i(t) = \frac{\vec{F}_i(t)}{m_i}$$

$$\vec{v}_i(t + \Delta t) = \vec{v}_i(t) + \frac{1}{2}[\vec{a}_i(t) + \vec{a}_i(t + \Delta t)]\Delta t$$

- **Advantages of the velocity Verlet method:** (i) It is time reversible; (ii) it is symplectic (i.e. it conserves the energy of the system)
- This algorithm is very popular; it is very reliable and accurate. **We will employ it in the Lab sessions.**

Ingredients of Molecular Dynamics Simulations

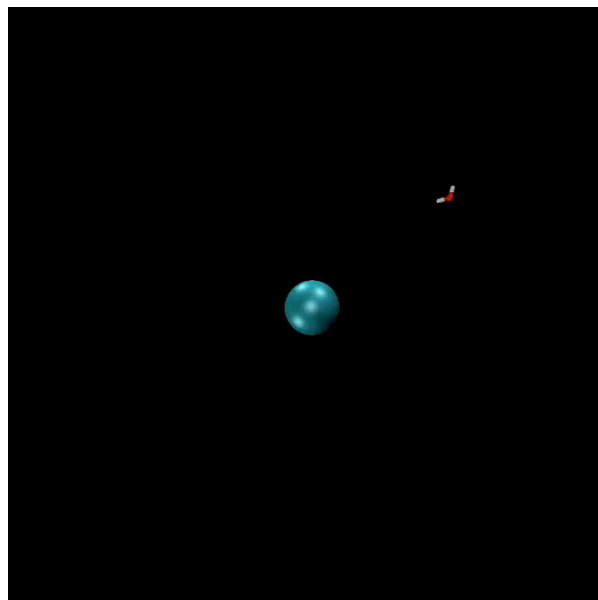
The following are the key ingredients required to successfully execute a molecular dynamics:

- (1) Atomistic model
- (2) Interaction potential (or potential energy)
- (3) Atomic forces
- (4) Basic molecular dynamics observables: kinetic energy, total energy, temperature, and pressure.
- (5) Thermodynamic ensembles: microcanonical and canonical ensembles
- (6) The ergodic hypothesis
- (7) Method for solving the equations of motion [**already discussed in three previous slides**]

Ingredients of Molecular Dynamics Simulations

Ingredient 1: Atomistic model:

- Comprises a set of atoms, which representative of the system of interest, with well-defined positions (or coordinates) $\{\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\}$.
- Normally, a random set of atomic positions are chosen subject to geometric constraints and other constraints such as the correct atomic density (i.e. the number of atoms per volume).



Atomistic model of a charged metal ion immersed in liquid water.

Ingredients of Molecular Dynamics Simulations

Ingredient 2: Potential energy (or interaction potential):

- The *potential energy* of a system of N atoms, denoted by U , tells us how the atoms interact with each other or position themselves relative to each other.
- The potential energy depends on the atomic positions: $U \equiv U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$.
- U usually has a well-defined analytic/mathematical representation.

Example: the potential energy due to the bond between two atoms i and j located at positions $\vec{r}_i = (x_i, y_i, z_i)$ and $\vec{r}_j = (x_j, y_j, z_j)$ respectively, may be represented as

$$U(\vec{r}_i, \vec{r}_j) = \frac{1}{2}k|\vec{r}_i - \vec{r}_j|^2 = \frac{1}{2}k[(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2]$$

where k is a constant.



Ingredients of Molecular Dynamics Simulations

Ingredient 3: **Atomic forces**:

- The *atomic forces* (needed to solve the equations of motion) are obtained from the potential energy $U \equiv U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$.
- The force \vec{F}_i acting on atom i is given by the *negative gradient of the potential energy U with respect to the atom's position \vec{r}_i* :

$$\vec{F}_i = -\nabla_i U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = -\frac{\partial U}{\partial \vec{r}_i} = \left(-\frac{\partial U}{\partial x_i}, -\frac{\partial U}{\partial y_i}, -\frac{\partial U}{\partial z_i} \right)$$

- **Example**: if the **potential energy** of a 2-atom system is given by

$$U(\vec{r}_i, \vec{r}_j) = \frac{1}{2}k|\vec{r}_i - \vec{r}_j|^2 = \frac{1}{2}k[(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2]$$

where k is a constant, then force \vec{F}_i on atom i is given by

$$\vec{F}_i = \left(-\frac{\partial U}{\partial x_i}, -\frac{\partial U}{\partial y_i}, -\frac{\partial U}{\partial z_i} \right) = (k(x_j - x_i), k(y_j - y_i), k(z_j - z_i))$$

Ingredients of Molecular Dynamics Simulations

(4) Basic molecular dynamics observables:

(a) The **total kinetic energy** (i.e. the energy due to atomic motion) is

$$KE = \frac{1}{2} \sum_{i=1}^N m_i v_i^2$$

where m_i and $v_i = |\vec{v}_i|$ are the mass and speed of atom i .

(b) The **total energy** E of a system at any instant is the **sum of the kinetic energy** KE and the **potential energy** U :

$$E = KE + U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 + U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Ingredients of Molecular Dynamics Simulations

Ingredient 4: Basic molecular dynamics observables:

(c) The *temperature* T of the system at any instant is given by the **equipartition theorem**:

$$\boxed{\frac{1}{2} N_f k_B T = KE} \Rightarrow T = \frac{2KE}{N_f k_B} = \frac{\sum_{i=1}^N m_i v_i^2}{N_f k_B T}$$

where N_f is the degrees of freedom (usually $N_f = 3N - 3$) and k_B is the **Boltzmann constant**.

(d) The *pressure* P of the system at any instant is given by virial equation

$$PV = Nk_B T - \frac{1}{3} \left\langle \sum_{i=1}^N \vec{F}_i \cdot \vec{r}_i \right\rangle \Rightarrow P = \frac{Nk_B T}{V} - \frac{1}{3V} \left\langle \sum_{i=1}^N \vec{F}_i \cdot \vec{r}_i \right\rangle$$

where $\langle \quad \rangle$ denotes **average over all atoms in the system**.

Ingredients of Molecular Dynamics Simulations

Ingredient 4: Basic molecular dynamics observables:

(c) The *temperature* T of the system at any instant is given by:

$$\frac{1}{2}N_f k_B T = KE \Rightarrow T = \frac{2KE}{N_f k_B} = \frac{\sum_{i=1}^N m_i v_i^2}{N_f k_B T}$$

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where $\langle \quad \rangle$ denotes average over all atoms in the system.

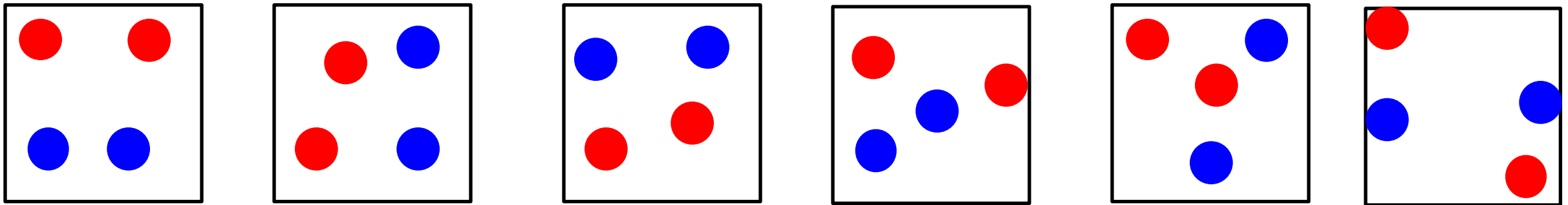
Ingredients of Molecular Dynamics Simulations

Ingredient 5: Thermodynamic ensembles:

An **ensemble**, within the context of **statistical thermodynamics**, denotes an **assembly of identical copies of a system in different states**. We will consider only two of such ensembles.

(a) Microcanonical or (N,V,E) ensemble: In this ensemble, copies of the system each have the same **number of particles N** , the same **volume V** , and the same **energy E** . But each copy can be in a **different state** characterized by **temperature T** and pressure **P** .

Example: an microcanonical ensemble comprising 6 copies; each copy has the same values of **N** , **V** , and **E** [note that **$N = 4$**]. However, each system can be in different **T** and **P** states.

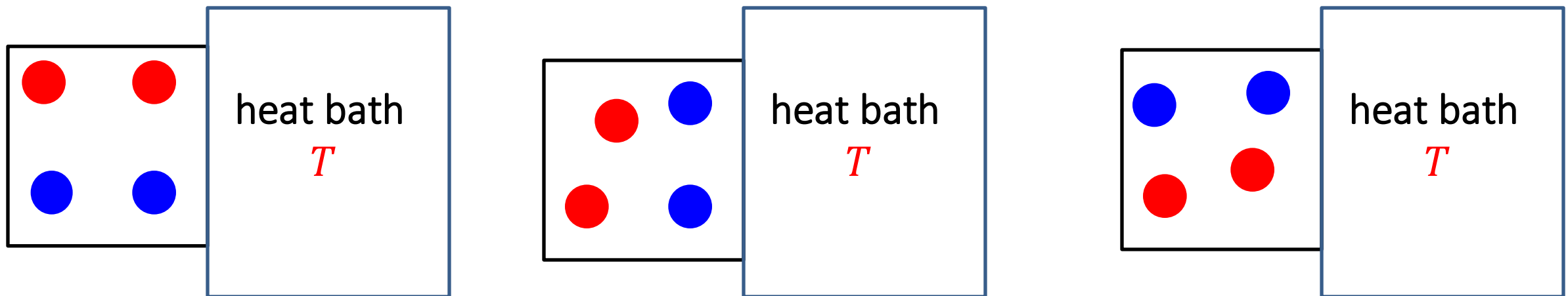


Ingredients of Molecular Dynamics Simulations

Ingredient 5: Thermodynamic ensembles:

(b) Canonical or (N,V,T) ensemble: In this ensemble, copies of the system each have the same number of particles N , the same volume V , and the system is connected to a heat bath (or thermostat) to keep temperature T constant. But each copy can be in a different state characterized by the energy E and pressure P .

Example: a canonical ensemble comprising 3 copies; each copy has the same values of N , V , and T [connected to heat bath]. However, each system can be in different E and P states.

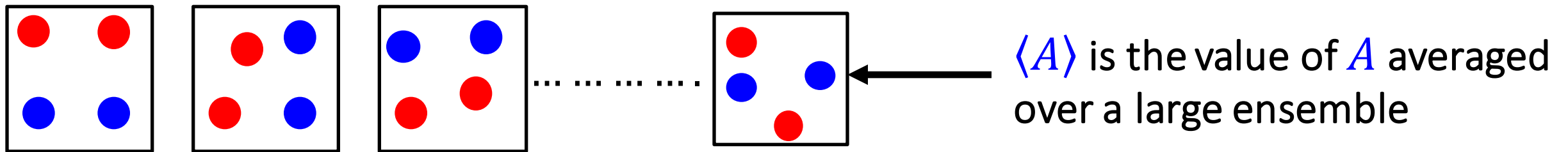


Ingredients of Molecular Dynamics Simulations

Ingredient 6: Ergodic Hypothesis:

Often in molecular dynamics simulations one is interested in some dynamical property A .

Per **statistical thermodynamics**, a representative value of the quantity A is the average value $\langle A \rangle$, obtained by averaging A is over a large ensemble (i.e. over several copies; see fig. below).



Practically, computing $\langle A \rangle$ is not feasible. Luckily, the **ergodic hypothesis** provides a solution.

Ergodic Hypothesis: the **time averaged value** of A over a long time span in only a **single copy** of the system, denoted by \bar{A} is equal to the ensemble average $\langle A \rangle$, that is,

$$\langle A \rangle = \bar{A}.$$

Other Considerations

Temperature Control in NVT simulation:

(i) Velocity scaling method

- Scale velocities to match the target temperature [easy to implement]
- Efficient, but does not correctly describe dynamics

(ii) Nose-Hoover thermostat

- Fictitious degree of freedom is added but correctly describes NVT dynamics
- Can cause temperature to fluctuate; not so easy to implement

(iii) Berendsen thermostat

- Scales velocities to match temperature
- Good compromise between the (i) and (ii); okay to use in simulations

Other Considerations

Initial velocities: Maxwell-Boltzmann velocity distribution

- The Maxwell-Boltzmann (MB) probability of finding a particle with speed v_x at a given temperature T

$$P(v_x) = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \exp\left(-\frac{1}{2} m v_x^2 / k_B T \right)$$

- Same for v_y and v_z
- Generate random initial atomic velocities using the
- Use the **equipartition theorem to scale each initial velocity** by a factor γ so that the kinetic energy matches the temperature T :

$$\gamma = \sqrt{\frac{3k_B T}{m(v_x^2 + v_y^2 + v_z^2)}}$$

Other Considerations

Choosing the time molecular dynamics step Δt

- Δt cannot be chosen to be too big other energy conservation will be destroyed
- Typically, $\Delta t \leq 4$ fs is employed [fs denotes “femto-seconds” i.e. $1 \text{ fs} = 10^{-15} \text{ f}$].
- It is fairly common to use $\Delta t = 1$ fs in practice
- If the computational cost is very cheap or if highly accurate dynamical results are required, then choose Δt as small as possible. E.g. $\Delta t = 0.1$ fs is considered small

Molecular Dynamics in Action

Molecular dynamics simulations of a charged metal ion interacting with water molecules at room temperature (300 K).

