Q & A for MDMC

Spring 2025

Written Exam Details

Time/Date

Tuesday May 27th between 11h-13h

Location

Our lecture classroom BCH 1103

Content

5-6 questions and 1 bonus question.

Topics addressed in chapters 1-5 of script/lecture and theory topics from exercises.
This year, there is new content regarding force fields for chapter 5 (Slides and recording on Moodle).
Chapter 6 content will only be used for bonus questions.

Written Exam Details

Materials

- 1 page of summary notes will be permitted during the exam
  (1 A4 size paper, front and back)
- Calculators will be permitted during the exam, but not necessary
- No other electronic device allowed
- We will provide paper to write your answers

Mock Exam Solutions

1. What are some of the approximations made when moving from the time evolution of a quantum mechanical system to the one of a classical system? What do you gain and what do you lose?

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A:

- Adiabatic approximation: separation of electronic and nuclear wavefunctions, without considering possible couplings between different electronic states

$$\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(\{\mathbf{R}_I\}) + \mathcal{C}_{kk}(\{\mathbf{R}_I\})\right]\chi_k = i\hbar\frac{\partial}{\partial t}\chi_k$$

$$\mathcal{C}_{kk} = -\sum_I \frac{\hbar^2}{2M_I}\int \Psi_k^\star \ \nabla_I^2 \ \Psi_k \, d\mathbf{r}$$

dependence between electronic and nuclear wavefunction

- Born–Oppenheimer approximation: adiabatic approximation, where also the diagonal coupling term is neglected

$$\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(\{\mathbf{R}_I\})\right]\chi_k = i\hbar\frac{\partial}{\partial t}\chi_k$$

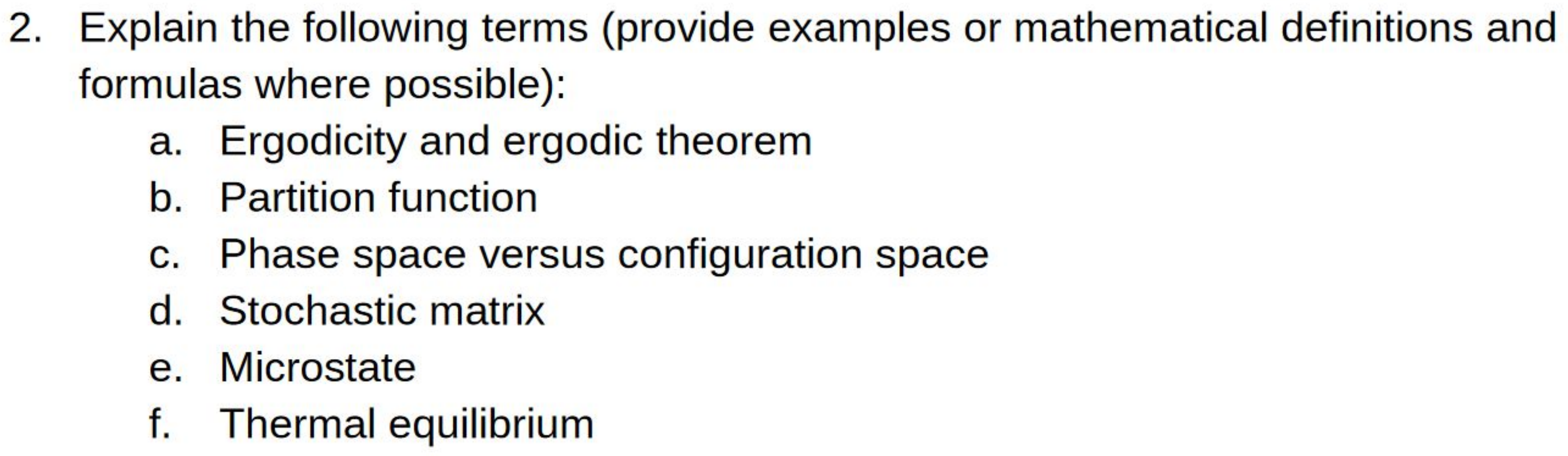
- Approximating the nuclei as classical point particles. Electronic problem solved at fixed nuclear positions
- No explicit treatment of electronic problem, included in pair atomic interactions (e.g. FFs)

1. What are some of the approximations made when moving from the time evolution of a quantum mechanical system to the one of a classical system? What do you gain and what do you lose?

A:

- Gain:
    - Classical problem becomes easy to solve and it is feasible to treat many thousands of atoms (while with full quantum treatment, only few atoms can be treated, order of hundreds with Born–Oppenheimer MD)
- Loose:
    - No reactions possible (bond break/formation)
    - Restricted to electronic ground state
    - No nuclear quantum effects

2. Explain the following terms (provide examples or mathematical definitions and formulas where possible):
    a. Ergodicity and ergodic theorem
    b. Partition function
    c. Phase space versus configuration space
    d. Stochastic matrix
    e. Microstate
    f. Thermal equilibrium



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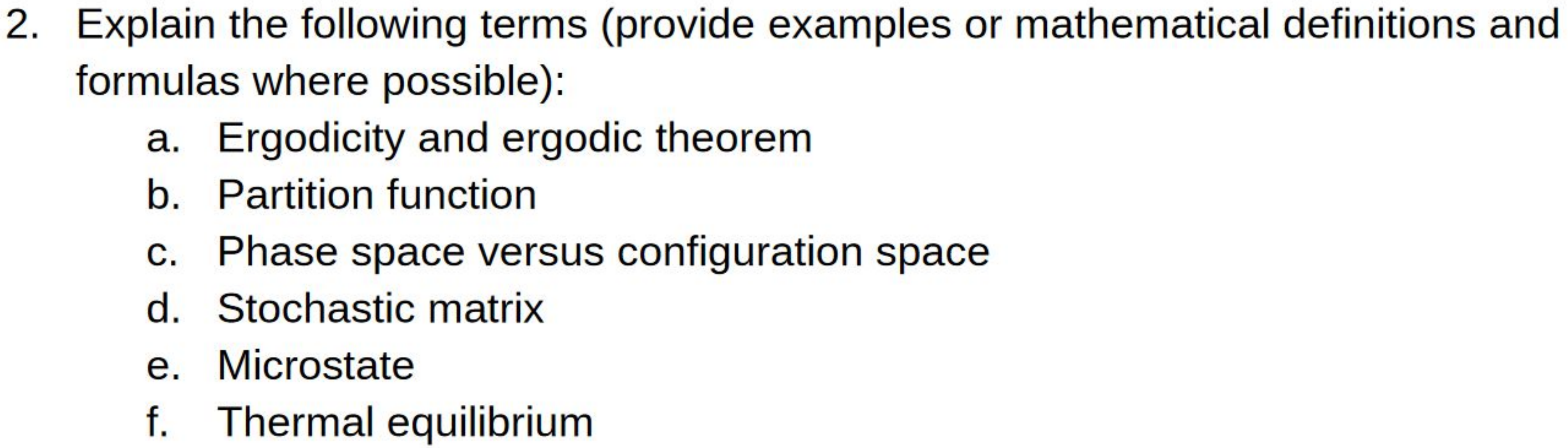
A:

a. Possibility to sample all regions of phase space in the limit of infinite sampling.
   Ensemble averages can be computed as time averages during a long-enough simulation.
b. Distribution of all states accessible to the the system. E.g. canonical partition function sums all Boltzmann’s factor for all energy levels at a given temperature.
c. Phase space = space of all positions and momenta (6N dimensional)
   Configuration space = space of all configurations (3N dimensional)
d. Matrix containing the probability for each move in MC, e.g. element (i,j) = P(i→j)



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   e. Microstate
   f. Thermal equilibrium

A:

e. One possible microscopic arrangement of all the particles in the system, i.e. a point in the phase space
f. Steady state, where on average macroscopic temperature remains constant - no net flow of thermal energy (microscopically system can switch between different accessible microstates, compatible with the given macrostate)

3. Describe differences between Monte Carlo and Molecular Dynamics sampling of an ensemble. Which advantages/disadvantages do you see for the two methods?

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A:

MC

- Stochastic
- Trial moves correspond to different configurations, that can be accepted or not based e.g. on Boltzmann's factor (Metropolis MC approach)
- Ensemble average calculated as average between all configurations
- Advantages: ?

MD

- Deterministic
- Atoms of the system evolve according to Newton's equation of motion
- Ensemble averages calculated as time averages along the MD
- Advantages: ?

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A:

MC

- Stochastic
- Trial moves correspond to different configurations, that can be accepted or not based e.g. on Boltzmann’s factor (Metropolis MC approach)
- Ensemble average calculated as average between all configurations
- Advantages: can be easy to implement for some systems,easy temperature control and can provide better sampling of different conformations at different energies

MD

- Deterministic
- Atoms of the system evolve according to Newton’s equation of motion
- Ensemble averages calculated as time averages along the MD
- Advantages: time information -> can access all dynamical properties, easier for e.g. dense system, biological systems

4. Consider a Metropolis Monte Carlo sampling procedure for a box of liquid water at room temperature. Which probability distribution would you use for accepting a trial move for this specific system? Suggest one trial move for this specific water system that obeys detailed balance and one that violates it. Are living systems obeying detailed balance? Why?

4. Consider a Metropolis Monte Carlo sampling procedure for a box of liquid water at room temperature. Which probability distribution would you use for accepting a trial move for this specific system? Suggest one trial move for this specific water system that obeys detailed balance and one that violates it. Are living systems obeying detailed balance? Why?

A: For accepting a trial move in the canonical ensemble we use a Boltzmann probability distribution:

$$\frac{P_{acc}(\text{old}\rightarrow\text{new})}{P_{acc}(\text{new}\rightarrow\text{old})} = \frac{N(\text{new})}{N(\text{old})} = e^{-\beta(V(\text{new})-V(\text{old}))}$$

Trial moves which might obey detailed balance:

- translational for single atom/molecule, many atoms/molecules
- rotational sometimes…unintended bias can occur more easily than with translational moves

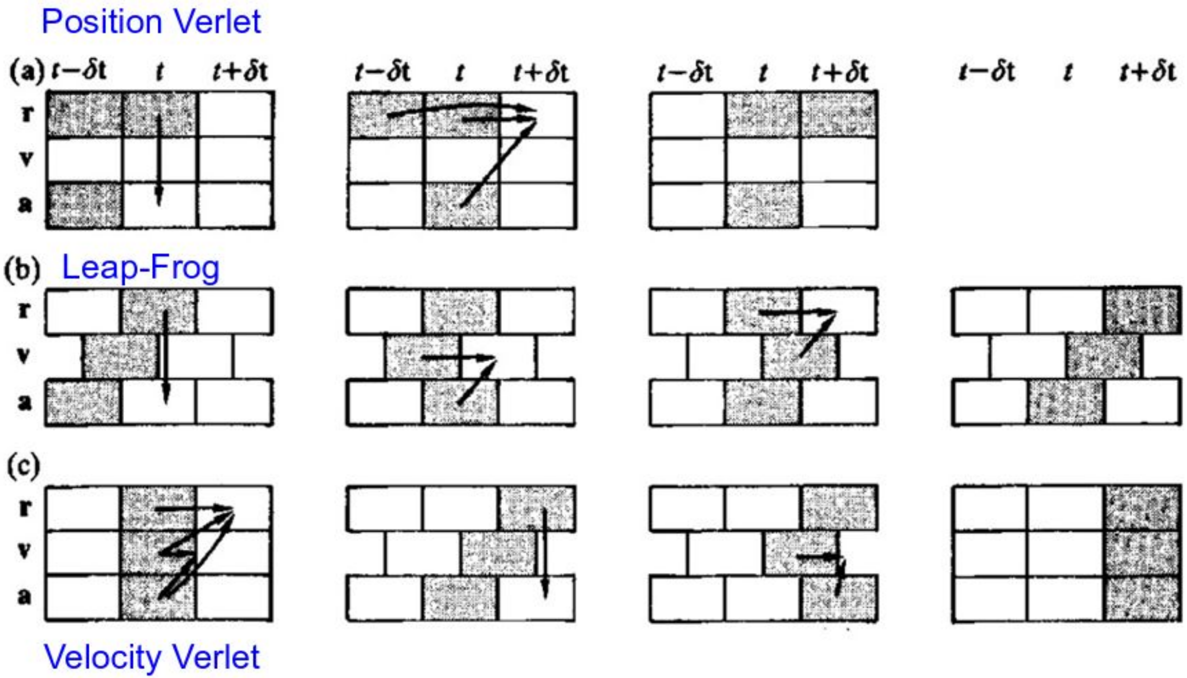
Trial move which might violate it:

- Any biased/forced move such as always moving in a specific direction which makes it such that the system can be driven from equilibrium state

Living systems exist outside of an equilibrium state in many ways. If our cells maintained equal probabilities to move certain ions inside and outside the cell, we'd be dead.

5. Which ones of the following equations and time integration algorithms are time-reversible, i.e. describe the same trajectory when reversing time from *t* to –*t* ? Why?
    a. Newton’s equation of motion
    b. Position Verlet
    c. Leap frog
    d. Gear predictor-corrector

Graphical Summary



© cartoon from Tildesley & Allen

$$
\begin{aligned}
\mathbf{r}^{\mathbf{p}}(t+\Delta t) &= \mathbf{r}(t) + \Delta t\mathbf{v}(t) + 1/2\Delta t^2\mathbf{a}(t) + 1/6\Delta t^3\mathbf{b}(t) + \ldots \\
\mathbf{v}^{\mathbf{p}}(t+\Delta t) &= \mathbf{v}(t) + \Delta t\mathbf{a}(t) + 1/2\Delta t^2\mathbf{b}(t) + \ldots \\
\mathbf{a}^{\mathbf{p}}(t+\Delta t) &= \mathbf{a}(t) + \Delta t\mathbf{b}(t) + \ldots \\
\mathbf{b}^{\mathbf{p}}(t+\Delta t) &= \mathbf{b}(t) + \ldots
\end{aligned}
\tag{4.8}
$$

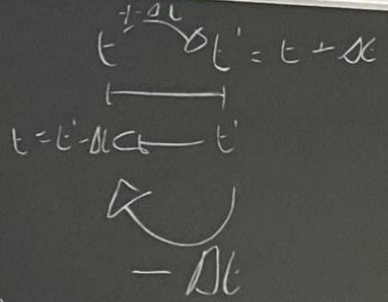
$$
\Delta\mathbf{a}(t+\Delta t) = \mathbf{a}^{\mathbf{c}}(t+\Delta t) - \mathbf{a}^{\mathbf{p}}(t+\Delta t) \tag{4.9}
$$

This error, and the results of the predictor step, are fed into the corrector step, which reads, typically,

$$
\begin{aligned}
\mathbf{r}^{\mathbf{c}}(t+\Delta t) &= \mathbf{r}^{\mathbf{p}}(t+\Delta t) + c_o\,\Delta a(t+\Delta t) \\
\mathbf{v}^{\mathbf{c}}(t+\Delta t) &= \mathbf{v}^{\mathbf{p}}(t+\Delta t) + c_1\,\Delta a(t+\Delta t) \\
\mathbf{a}^{\mathbf{c}}(t+\Delta t) &= \mathbf{a}^{\mathbf{p}}(t+\Delta t) + c_2\,\Delta a(t+\Delta t) \\
\mathbf{b}^{\mathbf{c}}(t+\Delta t) &= \mathbf{b}^{\mathbf{p}}(t+\Delta t) + c_3\,\Delta a(t+\Delta t)
\end{aligned}
\tag{4.10}
$$

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2$$

$$v(t+\Delta t) = v(t) + \frac{1}{2}a(t)\Delta t + \frac{1}{2}a(t+\Delta t)\Delta t$$



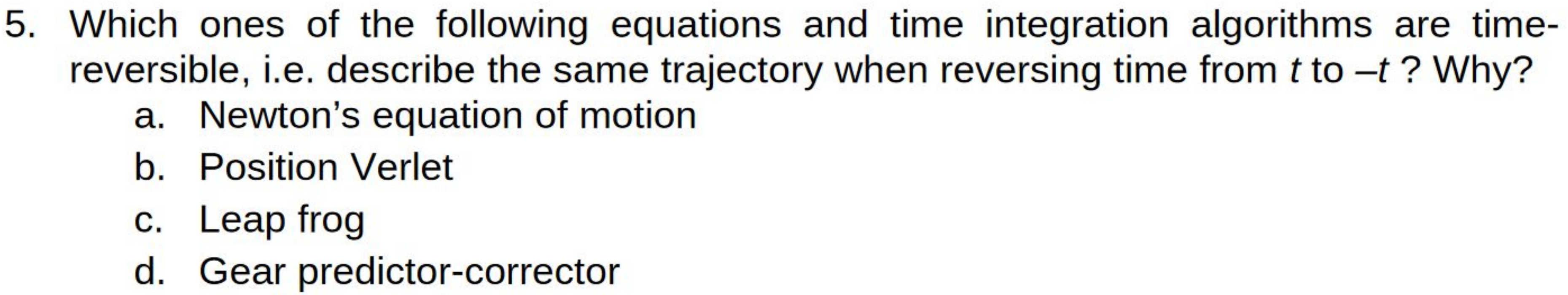
$$r(t'-\Delta t) = \underbrace{r(t')}_{} - v(t')\Delta t + \frac{1}{2}a(t')\Delta t^2 \quad \boxed{1}$$

$t' = t+\Delta t$

$$v(t'-\Delta t) = v(t') - \frac{1}{2}a(t')\Delta t - \frac{1}{2}a(t'-\Delta t)\Delta t$$

① $r(t) + \cancel{v(t)\Delta t} + \cancel{\frac{1}{2}a(t)\Delta t^2} - (\cancel{v(t)} + \cancel{\frac{1}{2}a(t)\Delta t} + \cancel{\frac{1}{2}a(t+\Delta t)\Delta t})\Delta t + \cancel{\frac{1}{2}a(t+\Delta t)\Delta t^2}$

$$= \underline{\underline{r(t)}}$$



5. Which ones of the following equations and time integration algorithms are time-reversible, i.e. describe the same trajectory when reversing time from *t* to –*t* ? Why?
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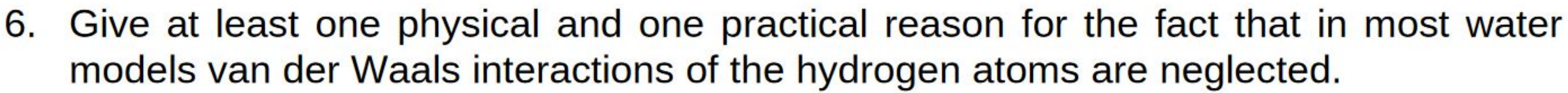
    b. Position Verlet
    c. Leap frog
    d. Gear predictor-corrector

A: All of time-reversible except for the Gear predictor-corrector algorithm.

When the Gear predictor-corrector algorithm is applied each MD step includes a different prediction meaning we cannot guarantee to follow the same set of predictions in both time directions.

All of the other algorithms are based on Newton’s equations of motion where each step depends on the information from the previous step(s) in both time directions.

6. Give at least one physical and one practical reason for the fact that in most water models van der Waals interactions of the hydrogen atoms are neglected.



6. Give at least one physical and one practical reason for the fact that in most water models van der Waals interactions of the hydrogen atoms are neglected.

A:

Physical reason:

- The polarity of water is conserved, but as hydrogen atoms contribute little to van der Waals forces their specific vdw parameters are not utilized in a simulation.

Practical reason(s):

- Computational cost to calculate forces for all hydrogen atoms present in solvent, especially considered that pairwise interactions scale as N^2
- Computational cost in terms of data storage. To calculate the forces for all of the hydrogen atoms present, the information about their positions and velocities must also be stored.

Bonus: a) What is the principal idea of the Car-Parrinello Method (in words)? b) Write down the extended Lagrangian.

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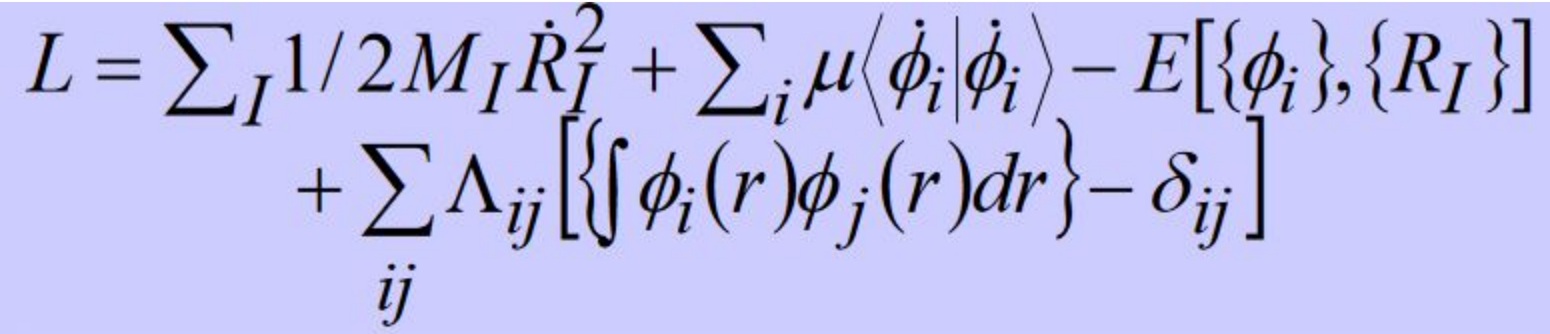
A:

In CP MD electrons have a fictitious mass and are treated as dynamical variables, which are propagated along the dynamics



$$L = \sum_I 1/2 M_I \dot{R}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle - E[\{\phi_i\},\{R_I\}] + \sum_{ij} \Lambda_{ij} \left[\left\{ \int \phi_i(r) \phi_j(r) dr \right\} - \delta_{ij} \right]$$

Topic Reviews

Major Topics from MDMC by “Chapter”

Chapter 1: From Quantum Mechanics to Classical Mechanics

- What assumptions made when we move from QM perspective to classical?
- What do the terms adiabatic and non-adiabatic mean?
- What cannot be described with classical models?
- What do we mean when we discuss “nuclear quantum dynamics”?

Chapter 2: Statistical Mechanics in a Nutshell

- Can you describe the different thermodynamic ensembles?
- What is the relationship between microstates, entropy, and energy?
- Can you recall the fundamental postulates of stat. mech.? How do the postulates relate to the canonical partition function?
- Could you explain what is the partition function? How is it useful? Can you recall the different forms of the partition function for different ensembles?
- What is phase space? Configurational space?
- What is an ensemble average? Under what conditions does the ensemble average equal the time average of a simulation?
- What is ergodicity?
- How do you compute an ensemble average for a general observable in statistical mechanics? What if the observable only depends on positions? And how do you do in practice, on a computer?

Chapter 3: Monte Carlo Simulations

- Why do we use a stochastic MC sampling scheme rather than sampling every point on a discretized grid?
- What is meant by “importance sampling” and “homogeneous sampling”?
- Can you describe the main steps of the Metropolis MC algorithm?
- What is a “Markov process” or “Markov” chain?
- What is a “stochastic matrix” and what properties must it possess for use in a simple Metropolis scheme which maintains detailed balance? Can you recall other names for this matrix?
- Can you describe “detailed balance” in words? With equations/math relationships?
- What kind of trial moves are permitted in a typical MC simulation? What are some of the considerations for designing possible trial moves?
- What is the default ensemble of Monte Carlo Simulations? How to switch to other ensembles?

Chapter 4: Molecular Dynamics Simulations

- Compare MD and MC
- How do we integrate Newton's equations of motion for time *t+dt*? What assumptions are made during each integration step?
- What information do we need in order update positions and velocities when using the velocity verlet algorithm?
- What are the main steps of an MD simulation?
- What are the common time propagators/numerical integrators for MD? What are the ideal properties we hope they achieve?
- What considerations should we make to select a time step?
- Why might we choose to use a constraint algorithm? Can you give an example of how to implement constraints?
- What is Noether's theorem and could you provide an example?
- Could you provide examples of thermostats and their limitations?

Chapters 5 & 6: Molecular Dynamics Simulations (2 & 3)

- What are different methods we use to determine the potential energy surface for a system? And what are the pros/cons of each?

- What do we mean by the term “force field?” What is needed to define one in practice? *What some improvements that can be made to point charge force fields?*

- What are the different terms included in a standard (bio)molecular force field?

- What do we mean by the term “water model” and why are there so many different ones?

- What are some limitations of empirical force fields?

Chapter 6 would only be used for bonus question if used at all on the exam:

- What do we mean when we say “first principles” MD?

- Compare BOMD and CPMD

- How is a QM/MM MD simulation designed?

Questions from Q&A 2022

Question 1

Explain following terms with mathematical definitions/equations where possible:

- Born-Oppenheimer approximation
- Microstate
- Maxwell-Boltzmann distribution
- Stochastic matrix
- Periodic boundary conditions
- Metropolis algorithm

Answer 1

Born-Oppenheimer Approximation (Chapter 1)
In essence, it allows for the separation of the electronic and nuclear degrees of freedom. More formally, it assumes a separable Ansatz for nuclear and electronic wavefunctions, and neglects coupling elements for electronic states. This approximation is valid when different electronic states are well separated in the energy scale and/or nuclear masses are large.

Microstate (Chapter 2)
Specific microscopic configuration of a system, defined by the momenta and coordinates of all its constituent particles. In contrast, the macrostate of a system refers to its macroscopic properties, such as its temperature, pressure, volume and density. Thus, microstates are different possible ways in which the system can achieve a particular macrostate.

Answer 1

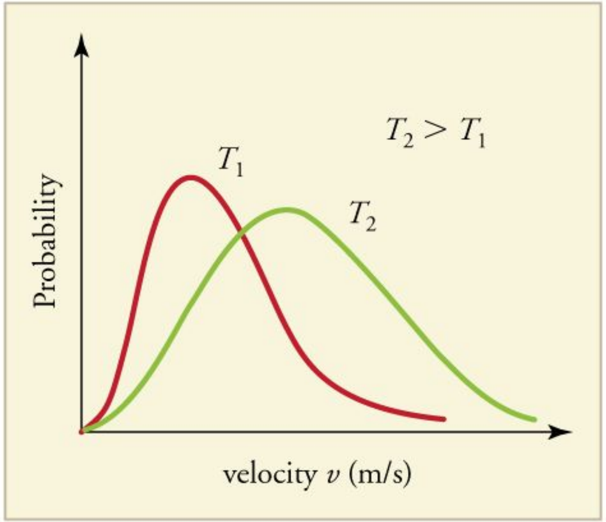


Image From: Chem LibreTexts

Maxwell-Boltzmann Distribution (Chapter 2-ish)

Probability distribution that describes the distribution of speeds among the particles in a sample of gas at a given temperature.

$$f(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 e^{-\frac{mv^2}{2kT}}$$

How does this compare to a Boltzmann distribution?

Stochastic/Transition Matrix (Chapter 3)

Matrix containing the probabilities of moving from one state i to another state j.

$$P = \begin{bmatrix} P_{1,1} & P_{1,2} & \dots & P_{1,j} & \dots & P_{1,\alpha} \\ P_{2,1} & P_{2,2} & \dots & P_{2,j} & \dots & P_{2,\alpha} \\ \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\ P_{i,1} & P_{i,2} & \dots & P_{i,j} & \dots & P_{i,\alpha} \\ \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\ P_{\alpha,1} & P_{\alpha,2} & \dots & P_{\alpha,j} & \dots & P_{\alpha,\alpha} \end{bmatrix}.$$

Image From: Wikipedia

Answer 1

Periodic Boundary Conditions (PBC) (Chapter 5)
Set of boundary conditions chosen to approximate/model a large (or infinite) system by using a small part called unit cell.

To implement PBC the unit cell is surrounded by translated copies in all directions to approximate an infinitely large system. When one molecule diffuses across the boundary of the simulation box it reappears on the opposite side. So each molecule always interacts with its neighbours even though they may be on opposite sides of the simulation box.

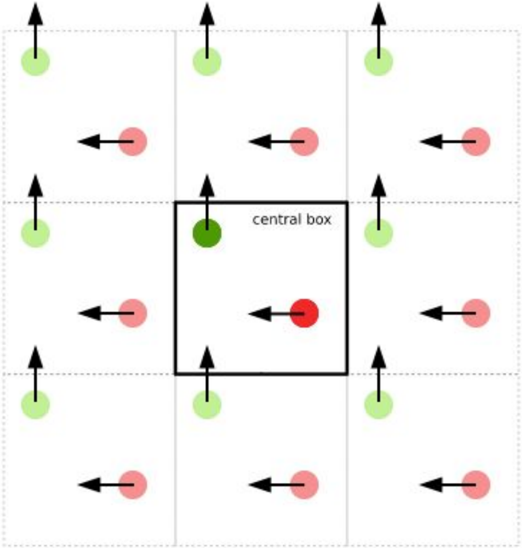


Image From: SA Grimlock

Answer 1

Metropolis Algorithm (Chapter 3)
Method for obtaining a sequence of random samples from a probability distribution from which direct sampling is difficult.

The algorithm works by generating a sequence of sample values in such a way that, as more and more sample values are produced, the distribution of values more closely approximates the desired distribution. These sample values are produced iteratively: at each iteration, the algorithm picks a candidate for the next sample value based on the current sample value.

Then, with some probability, the candidate is either accepted (in which case the candidate value is used in the next iteration) or rejected (in which case the candidate value is discarded, and current value is reused in the next iteration).

What is the difference between this and Monte Carlo Simulation?

Question 2

Why is it important to obey detailed balance in Monte Carlo simulations?

How does the stochastic matrix have to be chosen to fulfill detailed balance when using a Metropolis acceptance criterion?

Answer 2

Why is it important to obey detailed balance in MC? (Chapter 3)

It’s a way to ensure that once the simulation reaches equilibrium, the system remains in its equilibrium state (hence we are guaranteed to have a correct sampling scheme). Formally, we can write this as

$$N(\mathrm{old})P(\mathrm{old} \to \mathrm{new}) = N(\mathrm{new})P(\mathrm{new} \to \mathrm{old})$$

which means that, at equilibrium, every move is equilibrated by its reverse.

Stochastic matrix chosen to fulfill detailed balance? (Chapter 3)

The stochastic matrix is chosen to be symmetric: $P'(\mathrm{old} \to \mathrm{new}) = P'(\mathrm{new} \to \mathrm{old})$

By substituting this into the first equation, we see that a symmetric transition matrix leads to a very simple expression for the acceptance probability:

$$\boxed{\begin{aligned} &N(\mathrm{old})P'(\mathrm{old} \to \mathrm{new})P_{acc}(\mathrm{old} \to \mathrm{new}) = \\ &N(\mathrm{new})P'(\mathrm{new} \to \mathrm{old})P_{acc}(\mathrm{new} \to \mathrm{old}) \end{aligned}}$$

$$\boxed{\frac{P_{acc}(\mathrm{old} \to \mathrm{new})}{P_{acc}(\mathrm{new} \to \mathrm{old})} = \frac{N(\mathrm{new})}{N(\mathrm{old})} = e^{-\beta(V(\mathrm{new}) - V(\mathrm{old}))}}$$

Question 3

List at least 3 advantages and 3 disadvantages of Monte Carlo and molecular dynamics simulations.

Answer 3

Advantages/disadvantages of MC & MD (Chapters 3,4,5)

Monte Carlo (MC)		Molecular Dynamics (MD)	
+	-	+	-
Better at sampling. It doesn't follow trajectory of particle, it's less likely to get stuck in local minima (easy to cross barriers)	We lose information about the actual physical process (how the system goes from one state to another)	Information not only about the configurations, but also about how the system gets there. We can calculate time dependent quantities (e.g. transport coefficient)	Less efficient at sampling. It can get stuck in a potential energy well -> Not crossing the energy barriers sufficiently often
Easier to study systems in certain ensembles: keeping temperature or pressure constant is easy	Harder to sample complex molecules (e.g. hard to generate sensible moves for torsional rotations)	Easier to sample complex molecules than MC	Controlling pressure and temperature is harder with MD
Can be used for open systems where number of particles varies, which is not straightforward to model w/ MD	Harder to parallelize. Generally only moving one particle at a time, thus need to wait for previous move to generate next one	Easily to parallelize. For every step, the calculation of forces for each atom can be done in parallel	Harder to model open systems where the number of particles varies

MD and MC

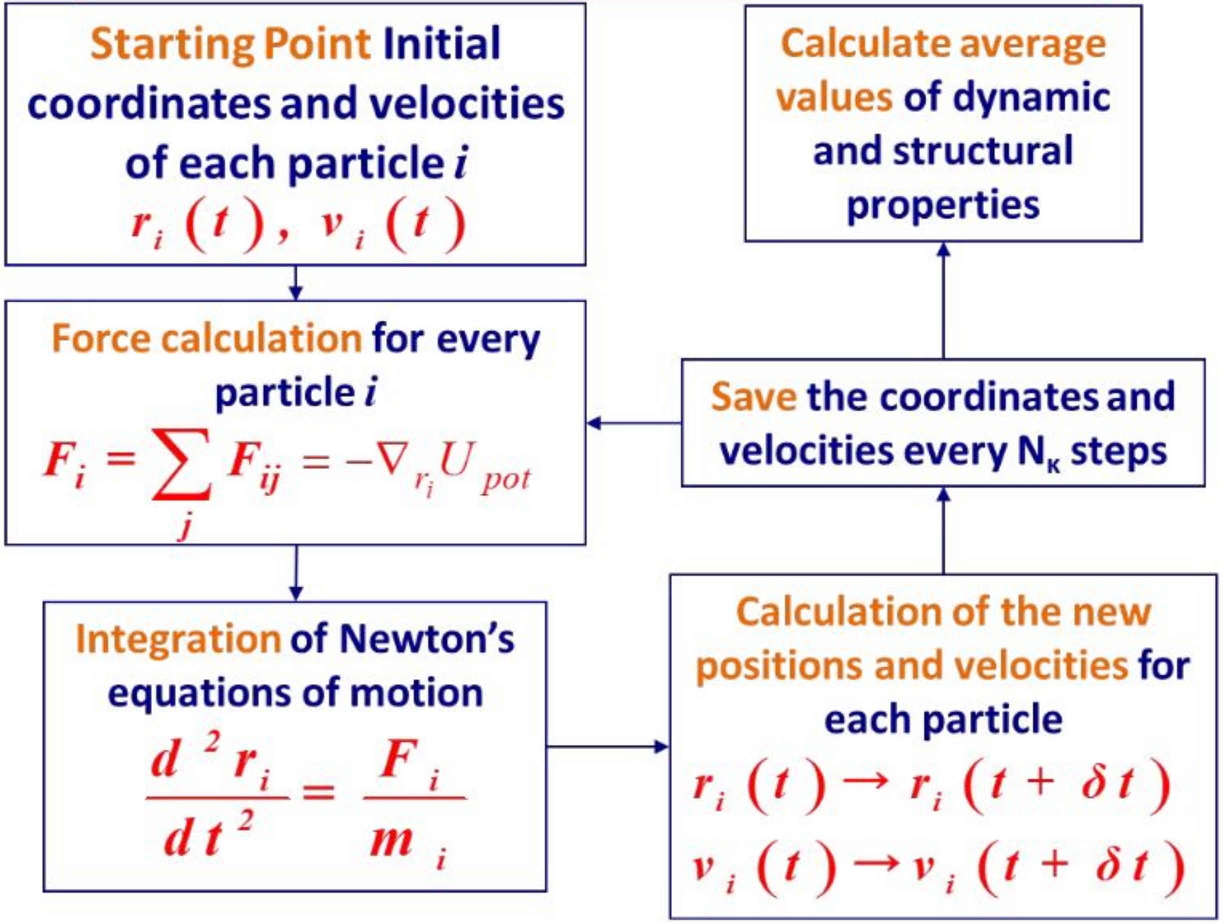
Slide from Nikolaos Lempesis, PhD.

Molecular Dynamics (MD) [Alder-Wainwright, JCP, 1957]	**Monte Carlo (MC)** [Metropolis et al., JCP, 1953]
• ***Classical Mechanics***	***Statistical Mechanics***
$\boxed{\mathbf{r}_i = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \mathbf{p}_i = -\frac{\partial H}{\partial \mathbf{r}_i}}$	$\boxed{\rho \sim \exp\left[-\frac{1}{k_B T}\left(\Delta U\left(\mathbf{r}^N\right) - \mu \Delta N + P \Delta V\right)\right]}$
• ***Phase space: {r*** $\{\mathbf{r}^N, \mathbf{p}^N\}$	***Configurational Space:*** $\{\mathbf{r}^N\}$
• ***Deterministic Method***	***Stochastic Method (Non-dynamic)***
• ***Realistic system evolution in time***	***No true time evolution (Unphysical Moves)***
• ***Average Physical Properties***	***Average Physical Properties***

$$\boxed{\left\langle A\left(\mathbf{r}^N, \mathbf{p}^N\right)\right\rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} A\left(\mathbf{r}^N, \mathbf{p}^N; t\right) dt} \xLeftrightarrow{\textit{Ergodic hypothesis}} \boxed{\left\langle A\left(\mathbf{r}^N\right)\right\rangle = \int \rho\left(\mathbf{r}^N\right) A\left(\mathbf{r}^N\right) \mathrm{d}\mathbf{r}^N}$$

Molecular Dynamics Flowchart

Slide from Nikolaos Lempesis, PhD.



Starting Point Initial coordinates and velocities of each particle i

$$r_i(t),\ v_i(t)$$

Force calculation for every particle i

$$F_i = \sum_j F_{ij} = -\nabla_{r_i} U_{pot}$$

Integration of Newton's equations of motion

$$\frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i}$$

Calculation of the new positions and velocities for each particle

$$r_i(t) \rightarrow r_i(t + \delta t)$$

$$v_i(t) \rightarrow v_i(t + \delta t)$$

Save the coordinates and velocities every N_K steps

Calculate average values of dynamic and structural properties

The Monte Carlo approach

Slide from Nikolaos Lempesis, PhD.

☐ Monte Carlo (MC):

- *Design and apply **artificial moves** – these can equilibrate the system in a new structure often unreachable or rarely occurring…*
- *The acceptance criterion is usually formulated in terms of the **potential energy** change between **trial** (new) and **existing** (old) states*

☐ A typical move:

$$\boxed{\rho_{acc} \sim \exp\left[-\frac{1}{k_B T}\left(\Delta U + \mu\Delta N + P\Delta V\right)\right]}$$

- *Instead of choosing configurations randomly, then weighting them with exp(-ΔE/kT), we choose configurations **with a probability exp(-ΔE/kT)** and weight them evenly (– Metropolis et al., JCP, 1953)*

☐ Restrictions:

- *Moves should not destroy the **molecular geometry** or **molecular architecture***
- *Moves should satisfy the criterion of **microscopic reversibility***
- *Moves should sample configuration space conserving **ergodicity***

Question 4

Which thermodynamic ensemble is sampled in a

a) typical Monte Carlo simulation
b) typical molecular dynamics simulation

Why?

Answer 4

Which thermodynamic ensemble is sampled in a

a) typical Monte Carlo simulation? Canonical ensemble (NVT)
b) typical molecular dynamics simulation? Microcanonical (NVE)

Why? (Chapter 3,4)

In a standard MC simulation, we often sample configurations according to the Boltzmann distribution, which gives the probability that a system will be in a certain microstate as a function of the state's energy and for a given temperature of the system (constant).

In MD, we solve Hamilton's equations of motion, which conserve the total energy during time evolution (hence we sample the NVE ensemble).

Question 5

If we want to perform molecular dynamics simulations in the canonical NVT ensemble, we have to make sure that

a) the average temperature of our system corresponds to T
    and that
b) all configurations are sampled according to their Boltzmann weights

How would you do impose condition a)? Condition b)?
Are both fulfilled at the same time?

Answer 5

How would you do impose condition a)? Condition b)? Are both fulfilled a the same time? (Chapter 5)

a) By coupling the system to a thermal bath (thermostat) (e.g. Andersen/ Langevin/Nose Hoover). All of these alter the particle velocities such that the trajectory samples the canonical NVT ensemble, but achieve this in different ways. Also, Andersen samples NVT, but affects dynamics. Whereas simple Nose Hoover may have issues with ergodicity, but represents dynamics well.

b) By performing MD simulation states already “automatically” populated according to Boltzmann population (e.g. higher energy states are less likely to be observed in MD simulations). Note: this is true when equilibrium is reached, i.e. over long simulation times (interesting discussion about this: chemistry.stackexchange)

Answer 5

How would you do impose condition a)? Condition b)? Are both fulfilled a the same time? (Chapter 5)

By coupling the system to a thermal bath (thermostat) (e.g. Andersen/Langevin/ Nose Hoover). We typically impose a thermostat with the following considerations:

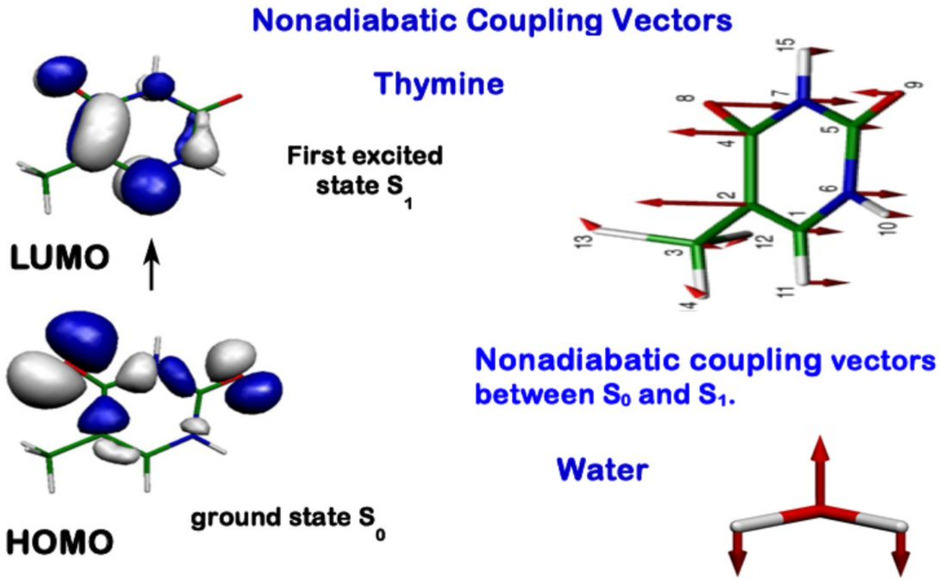
i) We initialize the particle velocities according to the Maxwell-Boltzmann distribution

ii) We run for enough time to ensure phase space is sufficiently explored -> we sample enough configurations -> time average approaches ensemble average (ergodicity)

iii) Constant volume simulation box

Questions from 2024

Q: From what I understood, the non-adiabatic coupling elements d_kl and D_kl are scalar values and represent the mixing of different electronic states which arises when trying to exactly describe the nuclear motion in molecules from QM. However,I am having trouble to see what this vector representation shows



A:

$$C_{kl} = -\sum_I \frac{\hbar^2}{2M_I} D^I_{kl}(R) + \sum_I \frac{\hbar^2}{M_I} \underline{d^I_{kl}(R)\nabla_I} \qquad (1.7a)$$

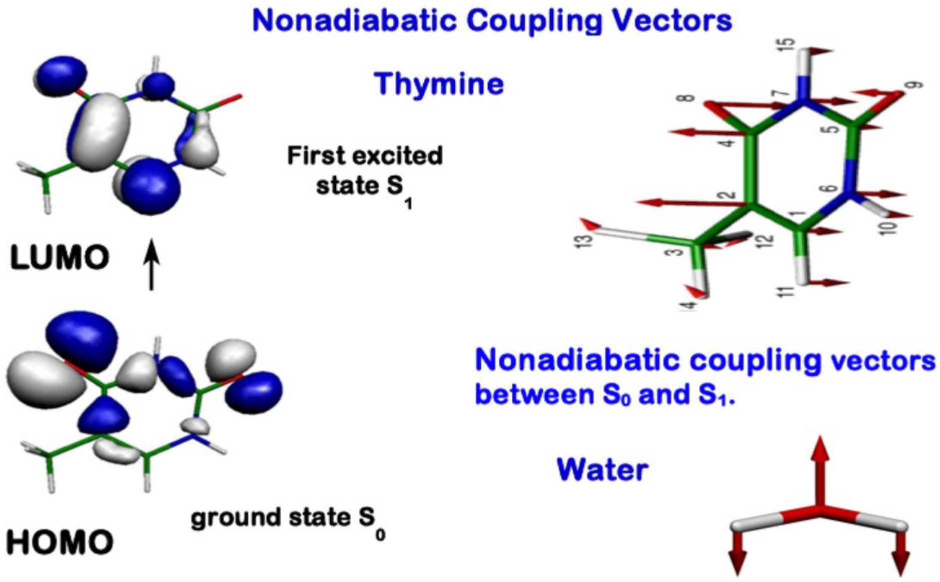
2nd order (scalar) nonadiabatic coupling elements

$$D^I_{kl}(R) = \int \psi_k^* \nabla_I^2 \psi_l \; dr \qquad (1.7b)$$

1st order nonadiabatic coupling vectors

$$d^I_{kl}(R) = \int \psi_k^* \nabla_I \; \psi_l \; dr \qquad (1.7c)$$

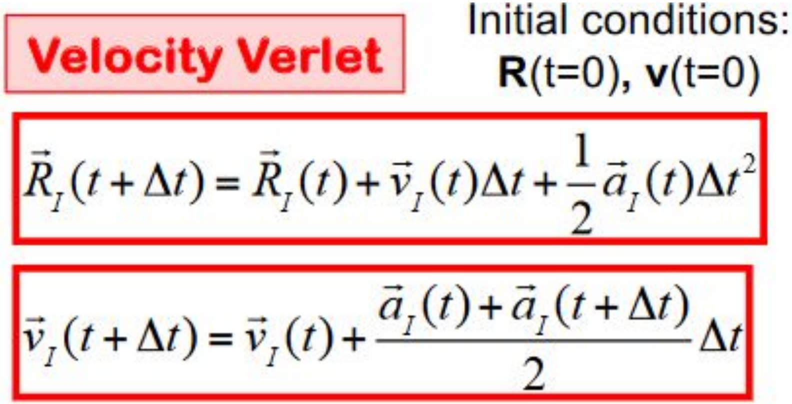
Non-adiabatic coupling vectors between two electronic states



Arrow direction shows how the nuclear motion of that particular atom influences the transition between the two states, while the length of the arrow indicates the magnitude of the non adiabatic coupling vector.

Note: exact interpretation (and non adiabatic dynamics more in general) are well beyond the scope of this course

Q: In the slides and in the exercise, why did we implement the Velocity Verlet algorithm with half-step propagation if the algorithm can be expressed for a full step?

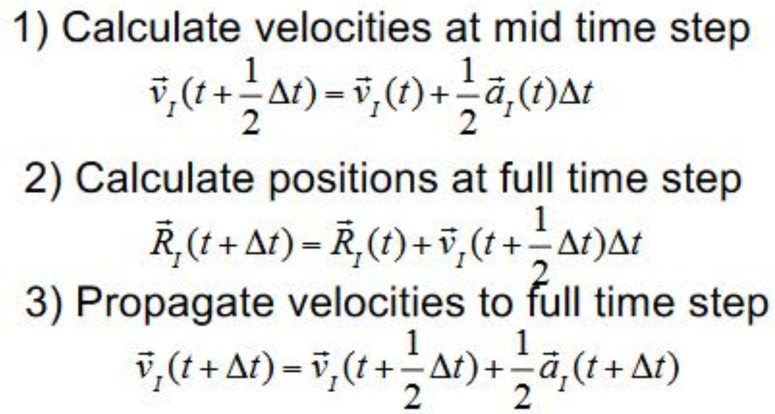


Velocity Verlet

Initial conditions:
R(t=0), **v**(t=0)

$$\vec{R}_I(t+\Delta t) = \vec{R}_I(t) + \vec{v}_I(t)\Delta t + \frac{1}{2}\vec{a}_I(t)\Delta t^2$$

$$\vec{v}_I(t+\Delta t) = \vec{v}_I(t) + \frac{\vec{a}_I(t) + \vec{a}_I(t+\Delta t)}{2}\Delta t$$



1) Calculate velocities at mid time step

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

2) Calculate positions at full time step

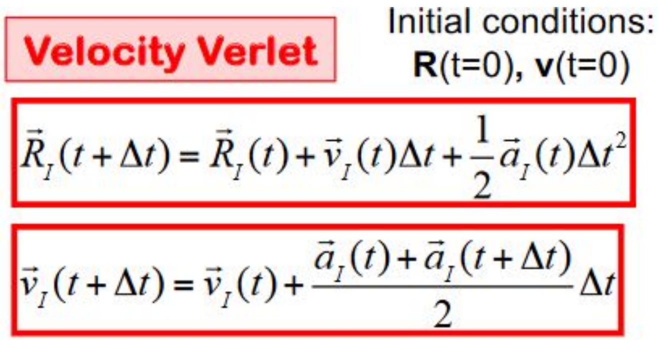
$$\vec{R}_I(t+\Delta t) = \vec{R}_I(t) + \vec{v}_I(t+\frac{1}{2}\Delta t)\Delta t$$

3) Propagate velocities to full time step

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

Q: In the slides and in the exercise, why did we implement the Velocity Verlet algorithm with half-step propagation if the algorithm can be expressed for a full step?

A: Both ways to solve for positions, velocities, and forces/accelerations are perfectly valid!
It comes down to a question of data storage. In the right-hand process, you avoid needing to store $a(t)$ and $a(t+\Delta t)$ simultaneously.



Velocity Verlet

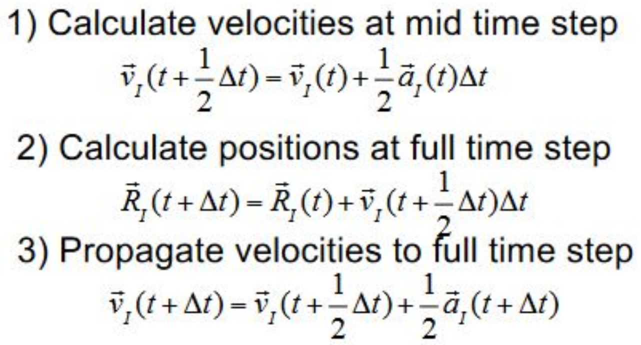
Initial conditions:
R(t=0), **v**(t=0)

$$\vec{R}_I(t+\Delta t)=\vec{R}_I(t)+\vec{v}_I(t)\Delta t+\frac{1}{2}\vec{a}_I(t)\Delta t^2$$

$$\vec{v}_I(t+\Delta t)=\vec{v}_I(t)+\frac{\vec{a}_I(t)+\vec{a}_I(t+\Delta t)}{2}\Delta t$$

For step one I need $R(t)$, $v(t)$, $a(t)$

For step two I need $R(t+\Delta t)$, $v(t)$, $a(t)$, and $a(t+\Delta t)$.



1) Calculate velocities at mid time step

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

2) Calculate positions at full time step

$$\vec{R}_I(t+\Delta t)=\vec{R}_I(t)+\vec{v}_I(t+\frac{1}{2}\Delta t)\Delta t$$

3) Propagate velocities to full time step

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

For step one I need $v(t)$, $a(t)$

For step two I need $R(t)$, $v(t+\Delta t/2)$

For step three I need $v(t+\Delta t/2)$ and $a(t+\Delta t)$

Q: In the derivation of classical statistical mechanics from quantum mechanics, we wrote

$$\mathrm{Tr}\exp(-\beta\mathcal{H}) \approx \mathrm{Tr}\exp(-\beta\mathcal{U})\exp(-\beta\mathcal{K}) \tag{2.19}$$

$$\mathrm{Tr}\exp(-\beta\mathcal{H}) = \sum_{\mathrm{r},\mathrm{k}} <\mathrm{r}|e^{-\beta\mathcal{U}}|\mathrm{r}><\mathrm{r}|\mathrm{k}><\mathrm{k}|e^{-\beta\mathcal{K}}|\mathrm{k}><\mathrm{k}|\mathrm{r}> \tag{2.20}$$

Leading to

$$\begin{aligned} \mathrm{Tr}\exp(-\beta\mathcal{H}) &\approx \frac{1}{h^{dN}N!}\int d\mathbf{p}^N d\mathbf{r}^N \exp\left\{-\beta\left[\sum_i p_i^2/(2m_i) + \mathcal{U}(\mathbf{r}^N)\right]\right\} \\ &\equiv Q_{\mathrm{classical}} \end{aligned} \tag{2.24}$$

How to get from **2.19** to **2.20**? And why $<\mathrm{r}|\mathrm{k}><\mathrm{k}|\mathrm{r}> = 1/V^N$?

A:

$$\mathrm{Tr}\ \exp\left(-\beta H\right) = \mathrm{Tr}\ \exp\left(-\beta\left(U+K\right)\right) = \mathrm{Tr}\ \left\{\exp\left(-\beta U\right)\exp\left(-\beta K\right) + O\left(\left[K,U\right]\right)\right\} \approx \mathrm{Tr}\ \left\{\exp\left(-\beta U\right)\exp\left(-\beta K\right)\right\}$$

$$= \sum_i \langle i|\exp\left(-\beta U\right)\exp\left(-\beta K\right)|i\rangle = \sum_i \langle i|\exp\left(-\beta U\right)\exp\left(-\beta K\right)\mathbb{I}|i\rangle = \sum_{i,j}\langle i|\exp\left(-\beta U\right)\exp\left(-\beta K\right)|j\rangle\langle j||i\rangle = \sum_{r,k}\langle r|\exp\left(-\beta U\right)\exp\left(-\beta K\right)|k\rangle\langle k||r$$

$$= \sum_{r,k}\langle r|\exp\left(-\beta U\right)\left(\langle k|\exp\left(-\beta K\right)|k\rangle\right)|k\rangle\langle k||r\rangle = \sum_{r,k}\langle r|\left(\langle r|\exp\left(-\beta U\right)|r\rangle\right)\langle k|\left(\langle k|\exp\left(-\beta K\right)|k\rangle\right)|k\rangle\langle k||r\rangle = 2.20$$

Q: In the derivation of classical statistical mechanics from quantum mechanics, we wrote

$$\mathrm{Tr}\exp(-\beta\mathcal{H}) \approx \mathrm{Tr}\exp(-\beta\mathcal{U})\exp(-\beta\mathcal{K}) \tag{2.19}$$

$$\mathrm{Tr}\exp(-\beta\mathcal{H}) = \sum_{r,k} < r|e^{-\beta\mathcal{U}}|r >< r|k >< k|e^{-\beta\mathcal{K}}|k >< k|r > \tag{2.20}$$

Leading to

$$\begin{aligned} \mathrm{Tr}\exp(-\beta\mathcal{H}) \quad &\approx \quad \frac{1}{h^{dN}N!}\int d\mathbf{p}^N d\mathbf{r}^N \exp\left\{-\beta\left[\sum_i p_i^2/(2m_i) + \mathcal{U}(\mathbf{r}^N)\right]\right\} \\ &\equiv \quad Q_{\mathrm{classical}} \end{aligned} \tag{2.24}$$

How to get from **2.19** to **2.20**? And why $< r|k >< k|r >= 1/V^N$?

A:

$$\langle r|k\rangle \langle k|r\rangle = |\langle r|k\rangle|^2 = \left|\frac{1}{h^{d/2}}e^{ikq/\hbar}\right|^2 = \frac{1}{h^d}$$

$$\sum_{r,k}\langle r|k\rangle \langle k|r\rangle = \sum_{r,k}\langle r|k\rangle \langle k|r\rangle \frac{1}{h^d} = \frac{1}{h^{dN}}$$