Density-Functional Theory for Practitioners - Tutorial 4

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(Developed by Patrick Rinke and Milica Todorović)

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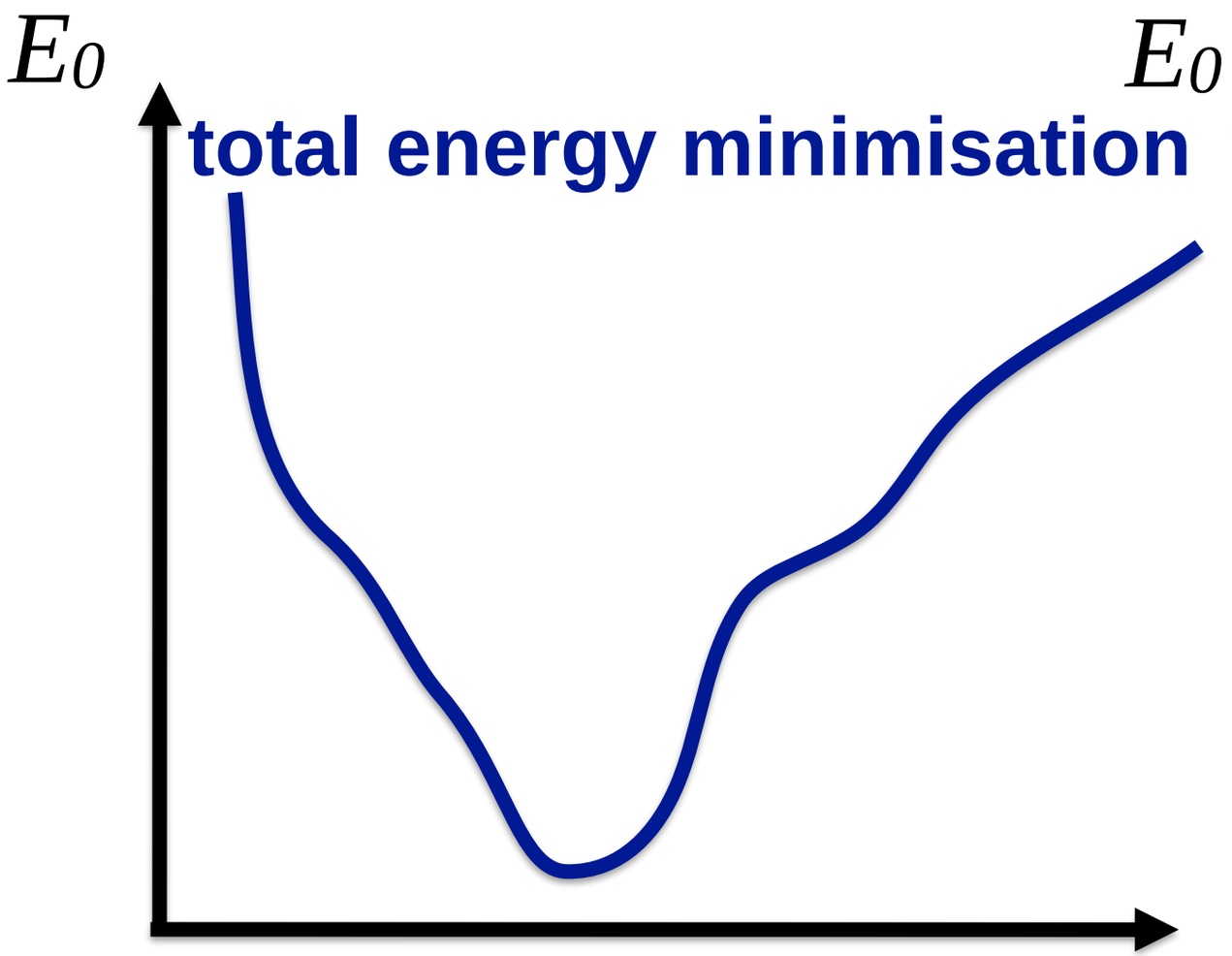
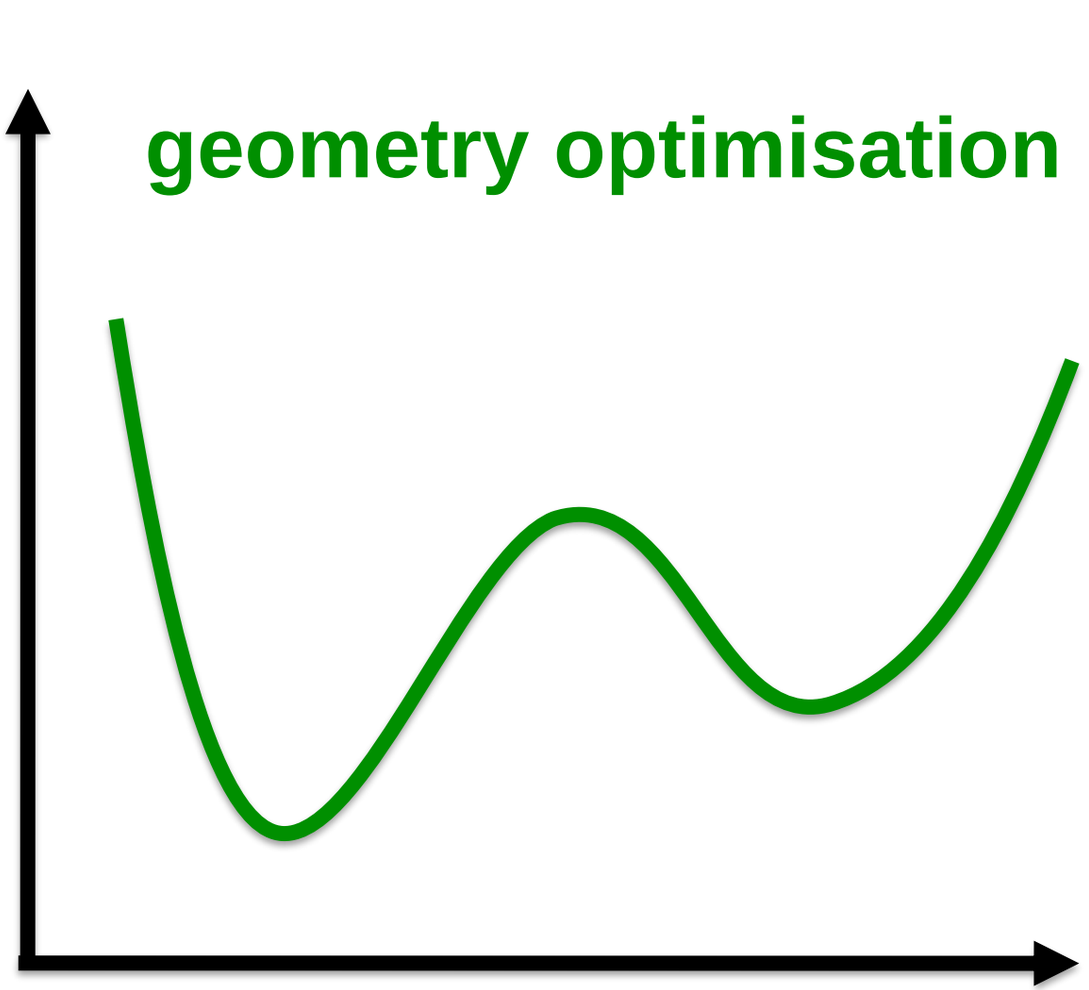
School of Science

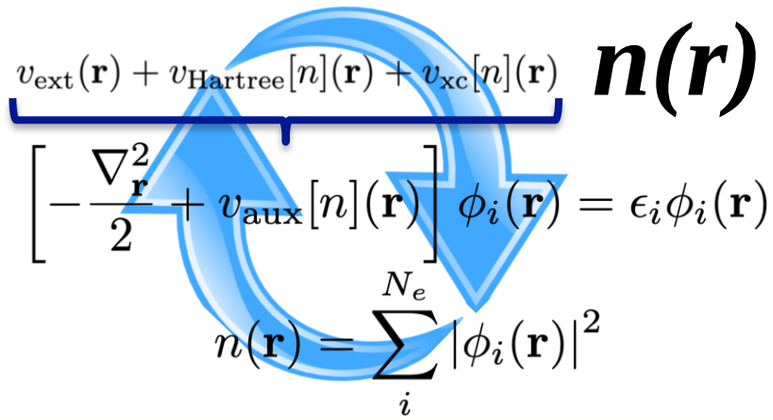
Recap - two minimisations in DFT structure search

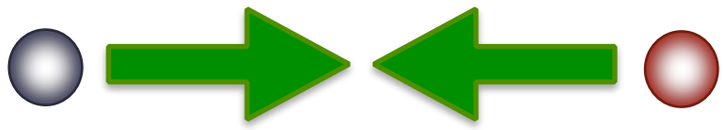




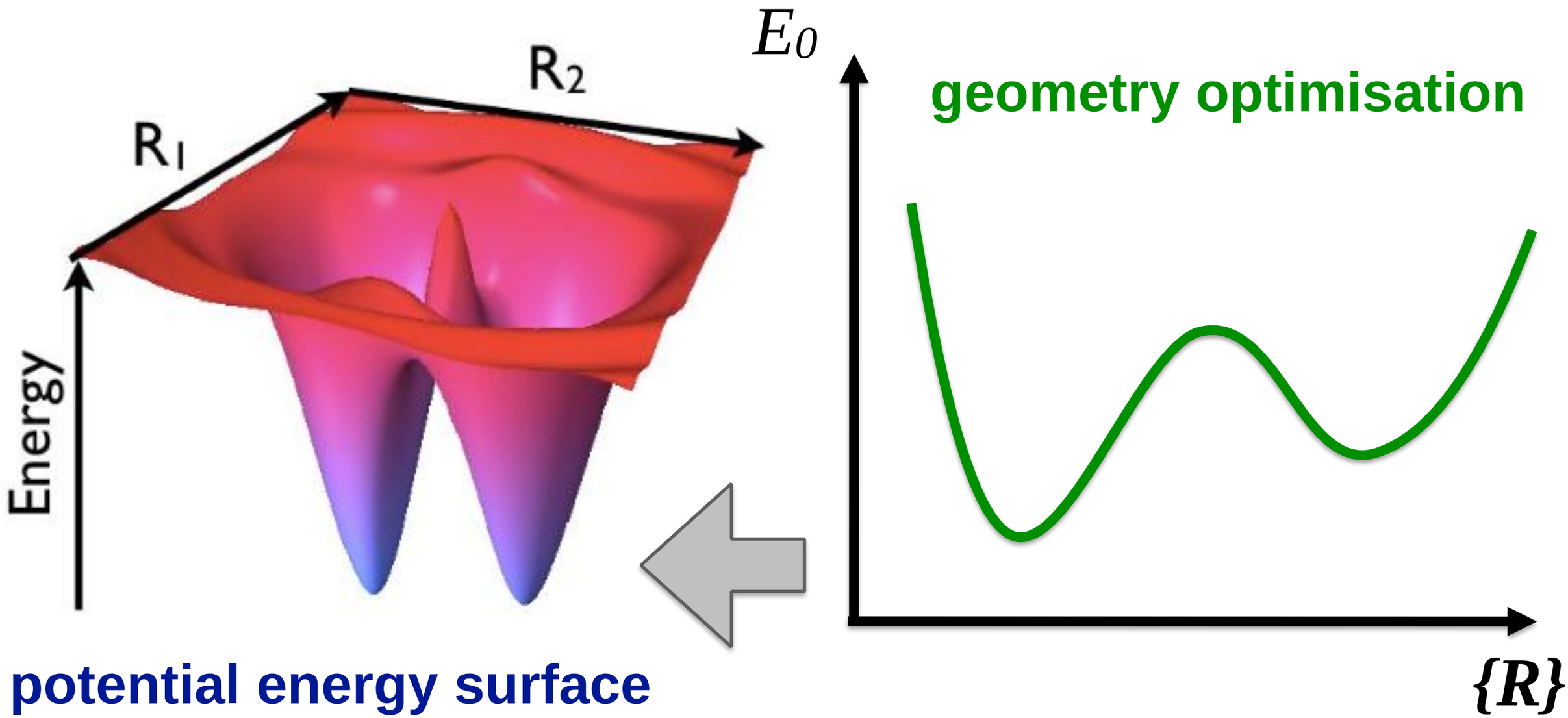
In practice:

1. **start with trial density**
2. **iterate to self-consistency**



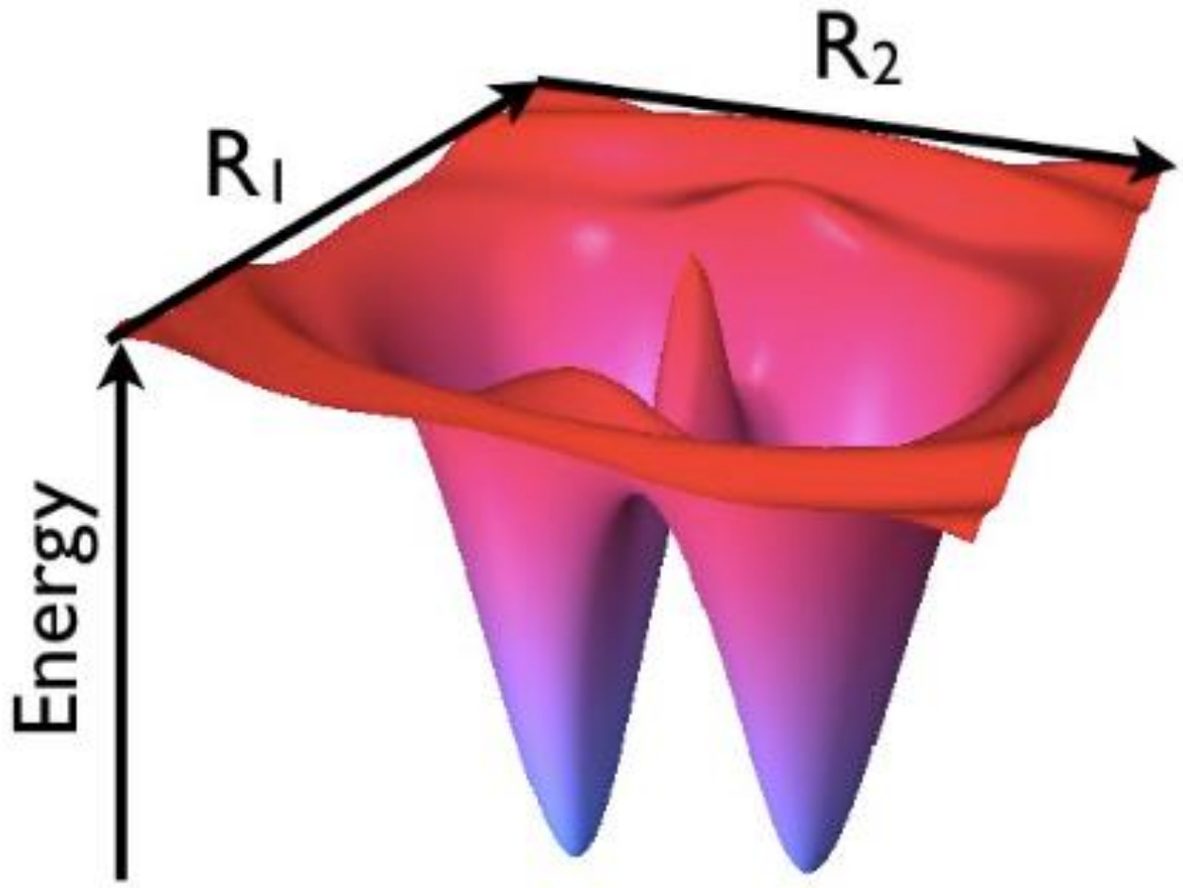


DFT potential energy surface



potential energy surface

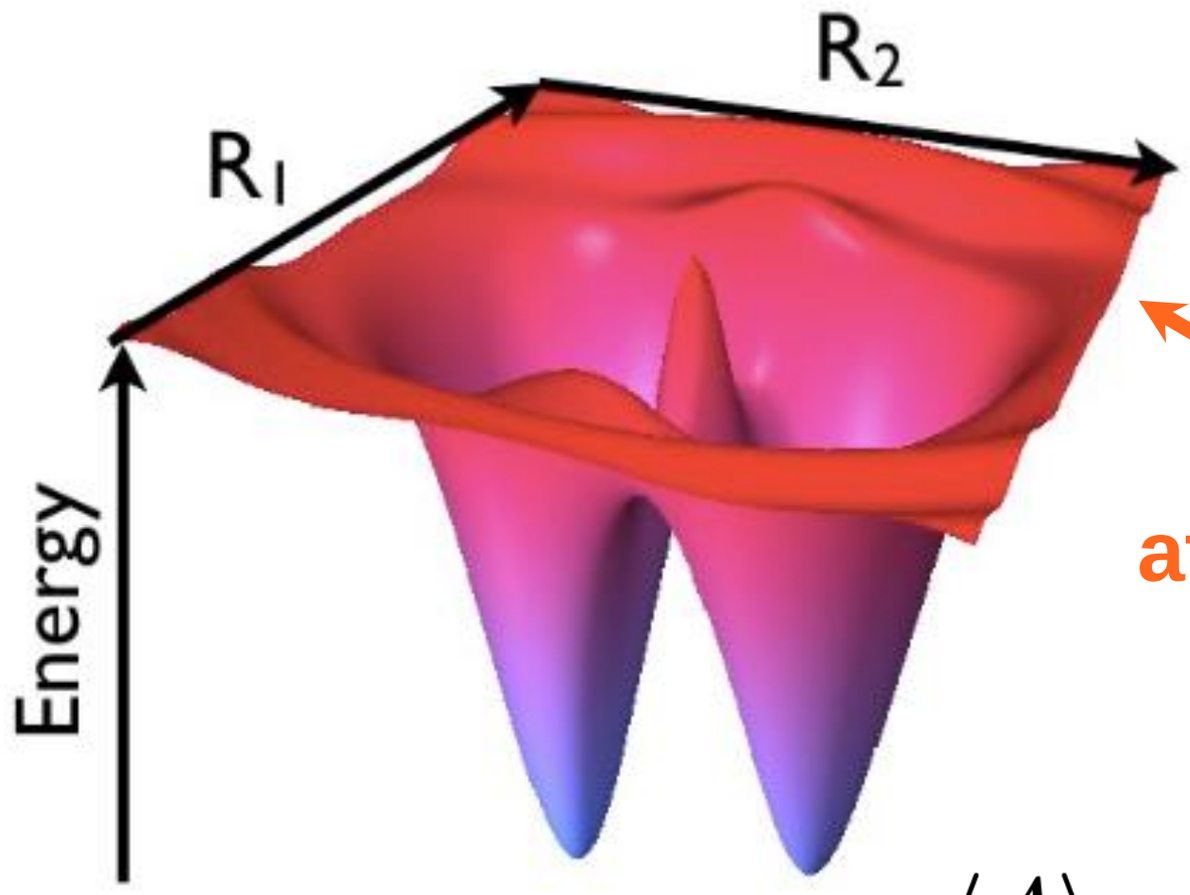
DFT molecular dynamics (MD)



potential energy surface

Molecular dynamics **or how to move on a potential energy surface.**

Statistical sampling



Ensemble averages

sampling points {*R*,*p*}

atomic positions

atomic momenta

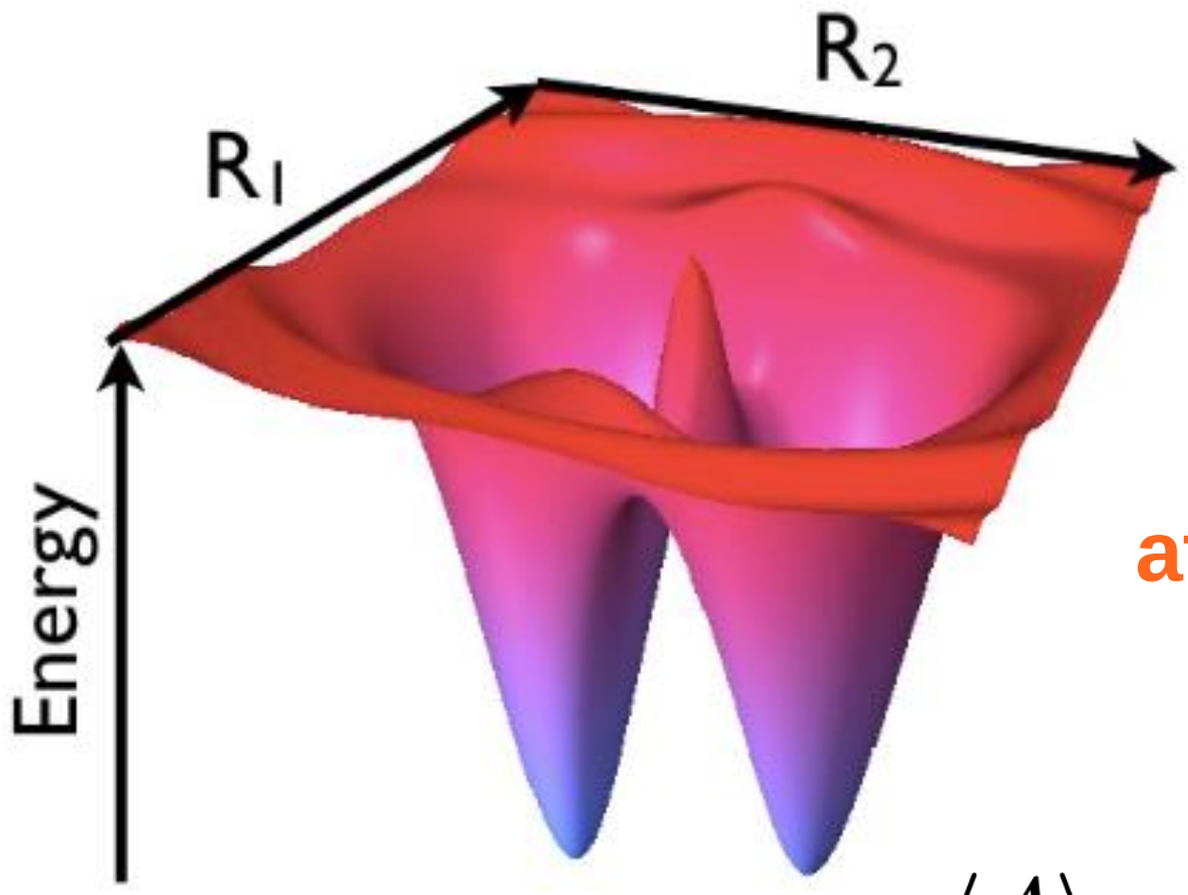
$$\langle A \rangle = \frac{1}{Z} \int d\mathbf{R} \int d\mathbf{p}\, e^{-\frac{H}{k_B T}} A(\mathbf{p}, \mathbf{R})$$

ensemble average

partition function

Hamiltonian

Statistical sampling



Ensemble averages

atomic positions

atomic momenta

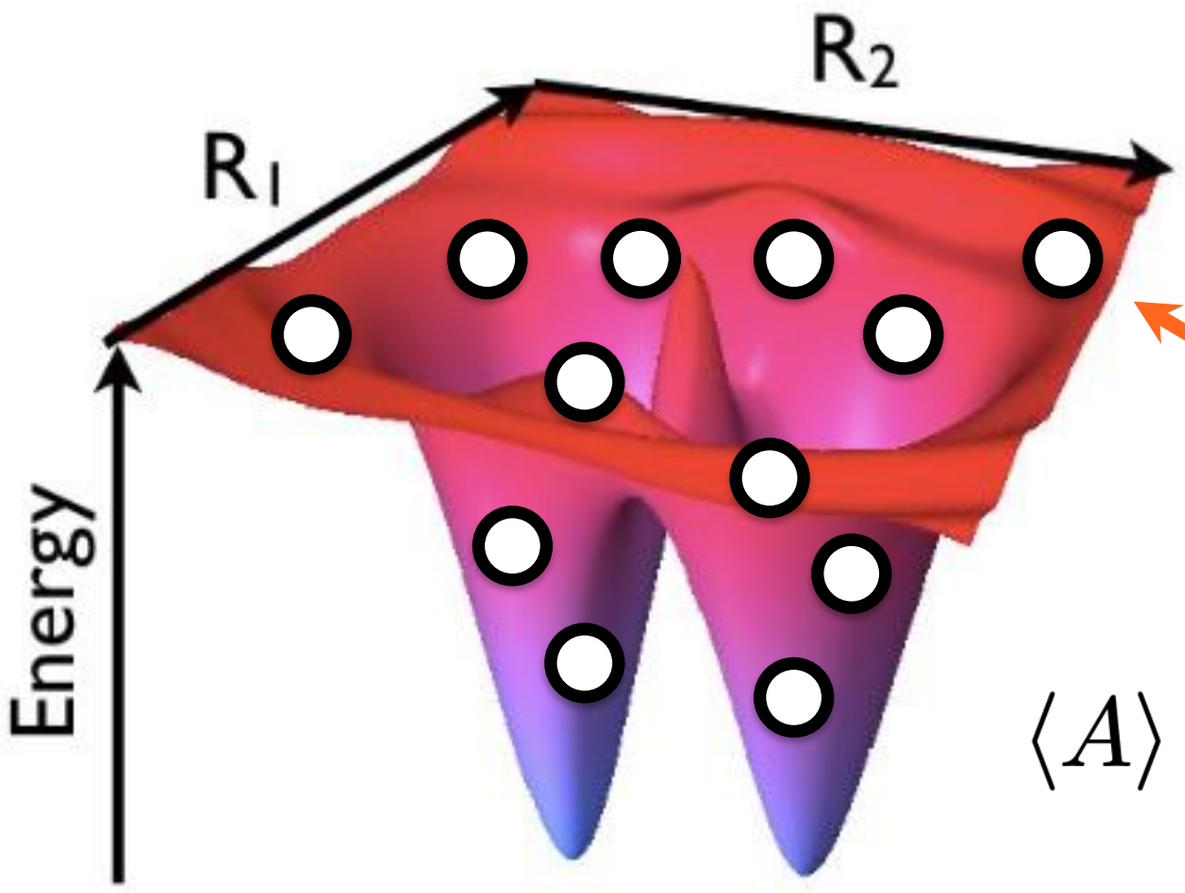
ensemble average

$$\langle A \rangle = \frac{1}{Z} \int d\mathbf{R} \int d\mathbf{p}\, e^{-\frac{H}{k_B T}} A(\mathbf{p}, \mathbf{R})$$

partition function

$$Z = \int d\mathbf{R} \int d\mathbf{p}\, e^{-\frac{H}{k_B T}}$$

Statistical sampling



Ensemble averages

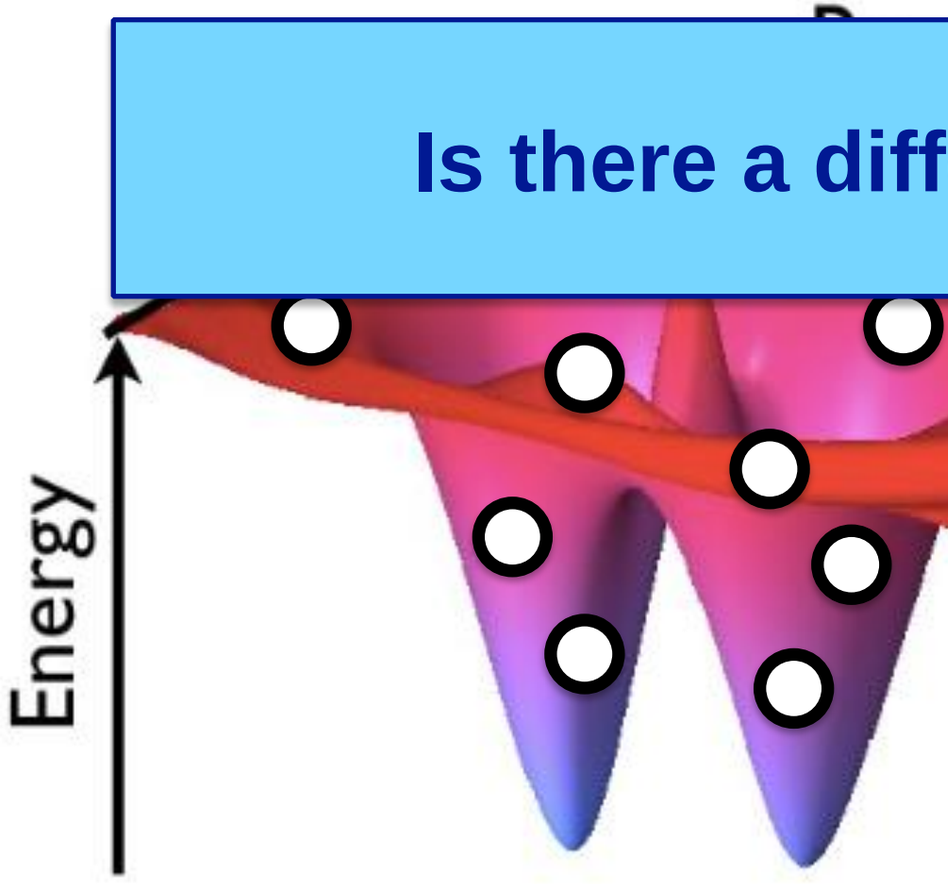
configuration (sampling points {*R*,*p*})

$$\langle A \rangle \approx \frac{1}{Z} \sum_{\mathbf{R}} \sum_{\mathbf{p}} e^{-\frac{H}{k_B T}} A(\mathbf{p}, \mathbf{R})$$

Compute by summing over configurations.

Statistical sampling

Is there a different way we can proceed?

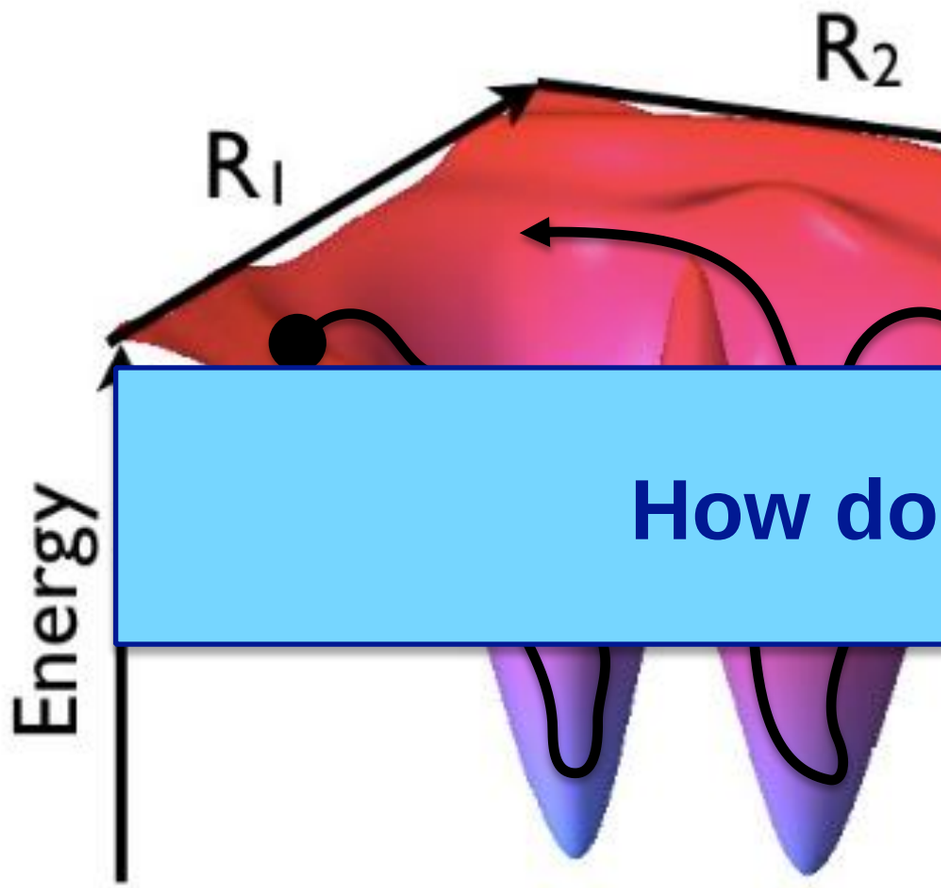


configuration (sampling points {*R*,*p*})

$$\langle A \rangle \approx \frac{1}{Z} \sum_{\mathbf{R}} \sum_{\mathbf{p}} e^{-\frac{H}{k_B T}} A(\mathbf{p}, \mathbf{R})$$

- **We might need a lot of configurations.**
- **We do not necessarily know how to find them.**

Statistical sampling



Time averages

How do we get the trajectory?

$$\langle A \rangle = \frac{1}{\tau} \int_0 dt\, A(\mathbf{p}(t), \mathbf{R}(t))$$

Ergodic hypothesis:

ensemble averages equal time averages

Remember lecture 1

We could propagate the Schrödinger equation:

$$\mathcal{H}\Psi(t) = \mathrm{i}\frac{\partial}{\partial t}\Psi(t)$$

This would treat the nuclei quantum mechanically, but that is maybe not what we want.

Back to classical nuclei and DFT.

The full Hamiltonian

$$H(\bullet\bullet\bullet \ \ldots \ \ominus\ominus\ominus \ldots)$$

$$\mathcal{H} = \overbrace{-\sum_{I=1}^{N_n} \frac{\nabla^2_{\mathbf{R}_I}}{2M_I}}^{T^n} + \overbrace{\sum_{I=1}^{N_n}\sum_{J>I}^{N_n} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}^{V^{nn}}$$

$$\underbrace{-\sum_{i=1}^{N_e} \frac{\nabla^2_{\mathbf{r}_i}}{2}}_{T^e} + \underbrace{\sum_{i=1}^{N_e}\sum_{j>i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V^{ee}} + \underbrace{\sum_{i=1}^{N_e}\sum_{J=1}^{N_n} \frac{-Z_J}{|\mathbf{r}_i - \mathbf{R}_J|}}_{V^{ne}}$$

The full Hamiltonian

$$H(\bullet\bullet\bullet \ \ldots \ \text{-}\ \text{-}\ \text{-} \ldots)$$

$$\mathcal{H} = \overbrace{-\sum_{I=1}^{N_n} \frac{\nabla^2_{\mathbf{R}_I}}{2M_I}}^{T^n} + \overbrace{\sum_{I=1}^{N_n}\sum_{J>I}^{N_n} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}^{V^{nn}}$$

$$+E^e_{\mathrm{DFT}}(\{\mathbf{R}\})$$

We have solved the electronic problem.

The full Hamiltonian

$$H(\bullet\bullet\bullet \ \ldots \ \ominus\ominus\ominus \ldots)$$

$$\mathcal{H} = \overbrace{-\sum_{I=1}^{N_n} \frac{\nabla^2_{\mathbf{R}_I}}{2M_I}}^{T^n} + \overbrace{\sum_{I=1}^{N_n}\sum_{J>I}^{N_n} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}^{V^{nn}} + E^e_{\mathrm{DFT}}(\{\mathbf{R}\})$$

potential energy surface

$$V(\{\mathbf{R}\})$$

Classical Hamiltonian for the nuclei

$$H(\bullet\bullet\bullet \ \ldots)$$

$$\mathcal{H} = \sum_{I=1}^{N_n} \frac{\mathbf{p}_I^2}{2M_I} + V(\{\mathbf{R}\})$$

classical Hamiltonian

Molecular dynamics

$$\mathcal{H} = \sum_{I=1}^{N_n} \frac{\mathbf{p}_I^2}{2M_I} + V(\{\mathbf{R}\})$$

classical Hamiltonian

$$\mathbf{F}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I} = -\frac{\partial V(\{\mathbf{R}\})}{\partial \mathbf{R}_I}$$

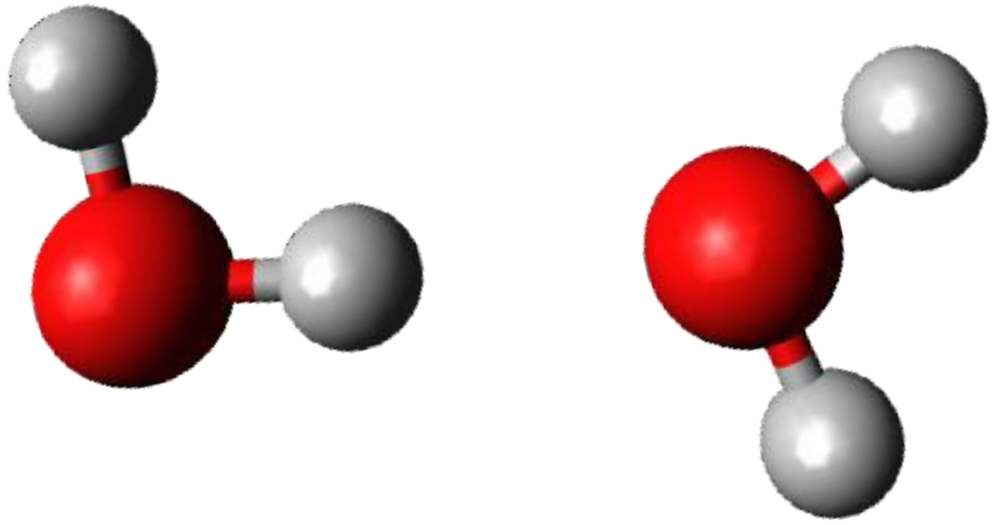
Forces

$$\mathbf{F}_I = M_I \ddot{\mathbf{R}}_I$$
$$= M_I \mathbf{a}_I$$

Newton's equation of motion

Molecular dynamics — moving atoms

$$\mathbf{F}_I = M_I \ddot{\mathbf{R}}_I$$



at time *t*

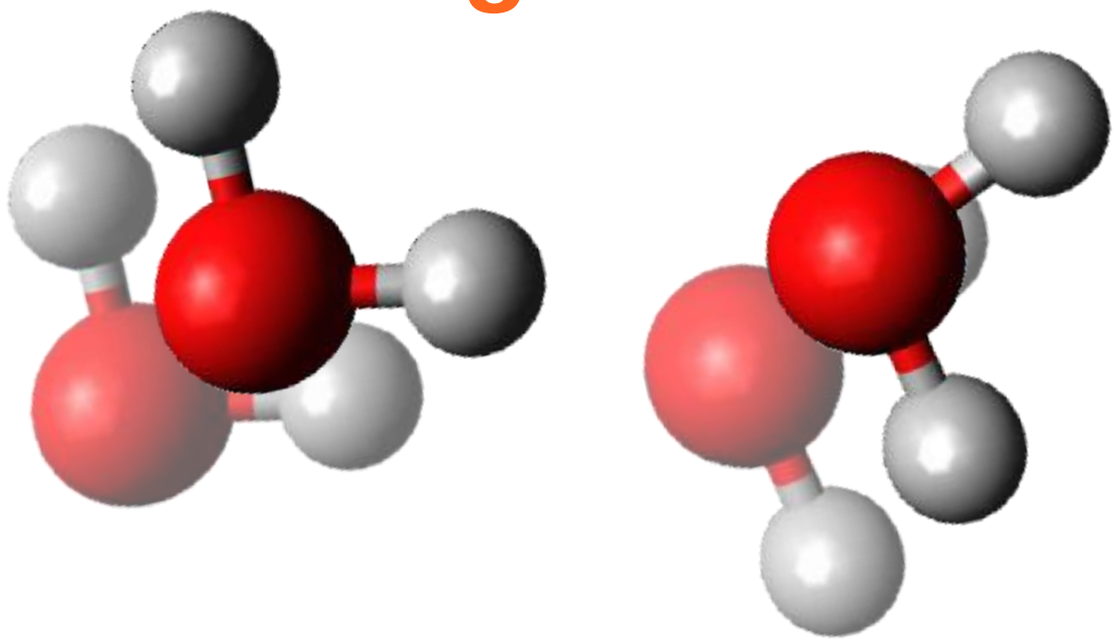
.

velocities: $\mathbf{v}_I(t) = \dot{\mathbf{R}}_I(t)$

positions: $\mathbf{R}_I(t)$

Molecular dynamics — moving atoms

$$\mathbf{F}_I = M_I \ddot{\mathbf{R}}_I$$



at time *t* + *Δt*

velocities: $\mathbf{v}_I(t + \Delta t)$

positions: $\mathbf{R}_I(t + \Delta t)$

move atoms according to forces

Numeric integration — naive propagation

We start from Taylor expansion:

$$\mathbf{R}(t+\Delta t) = \mathbf{R}(t) + \dot{\mathbf{R}}\Delta t + \frac{1}{2}\ddot{\mathbf{R}}\Delta t^2 + \frac{1}{6}\dddot{\mathbf{R}}\Delta t^3 + \ldots$$

Usual approximation: truncation

$$\mathbf{R}(t+\Delta t) = \mathbf{R}(t) + \dot{\mathbf{R}}\Delta t + \frac{1}{2}\ddot{\mathbf{R}}\Delta t^2$$

velocity *v*

acceleration *a*

Numeric integration — naive propagation

- **Not time reversible!**
- **Does not conserve volume in phase space!**
- **Suffers from energy drift!**

Usual approximation: truncation

$$\mathbf{R}(t+\Delta t) = \mathbf{R}(t) + \dot{\mathbf{R}}\Delta t + \frac{1}{2}\ddot{\mathbf{R}}\Delta t^2$$

velocity *v*

acceleration *a*

Numeric integration — Verlet algorithm

Taylor expansion for + *Δt and - Δt*

$$\mathbf{R}(t+\Delta t) = \mathbf{R}(t) + \dot{\mathbf{R}}\Delta t + \frac{1}{2}\ddot{\mathbf{R}}\Delta t^2 + \frac{1}{6}\dddot{\mathbf{R}}\Delta t^3 + \ldots$$

$$\mathbf{R}(t-\Delta t) = \mathbf{R}(t) - \dot{\mathbf{R}}\Delta t + \frac{1}{2}\ddot{\mathbf{R}}\Delta t^2 - \frac{1}{6}\dddot{\mathbf{R}}\Delta t^3 + \ldots$$

The sum gives:

$$\mathbf{R}(t+\Delta t) + \mathbf{R}(t-\Delta t) = 2\mathbf{R}(t) + \ddot{\mathbf{R}}\Delta t^2 + \mathcal{O}(\Delta t^4)$$

Numeric integration — Verlet algorithm

Taylor expansion for + *Δt and - Δt*

$$\mathbf{R}(t+\Delta t) = \mathbf{R}(t) + \dot{\mathbf{R}}\Delta t + \frac{1}{2}\ddot{\mathbf{R}}\Delta t^2 + \frac{1}{6}\dddot{\mathbf{R}}\Delta t^3 + \ldots$$

$$\mathbf{R}(t-\Delta t) = \mathbf{R}(t) - \dot{\mathbf{R}}\Delta t + \frac{1}{2}\ddot{\mathbf{R}}\Delta t^2 - \frac{1}{6}\dddot{\mathbf{R}}\Delta t^3 + \ldots$$

The sum gives, which is:

$$\mathbf{R}(t+\Delta t) = 2\mathbf{R}(t) - \mathbf{R}(t-\Delta t) + \ddot{\mathbf{R}}\Delta t^2$$

Numeric integration — Verlet algorithm

- **Time reversible!**
- **Conserve volume in phase space!**
- **No energy drift!**

The sum gives, which is:

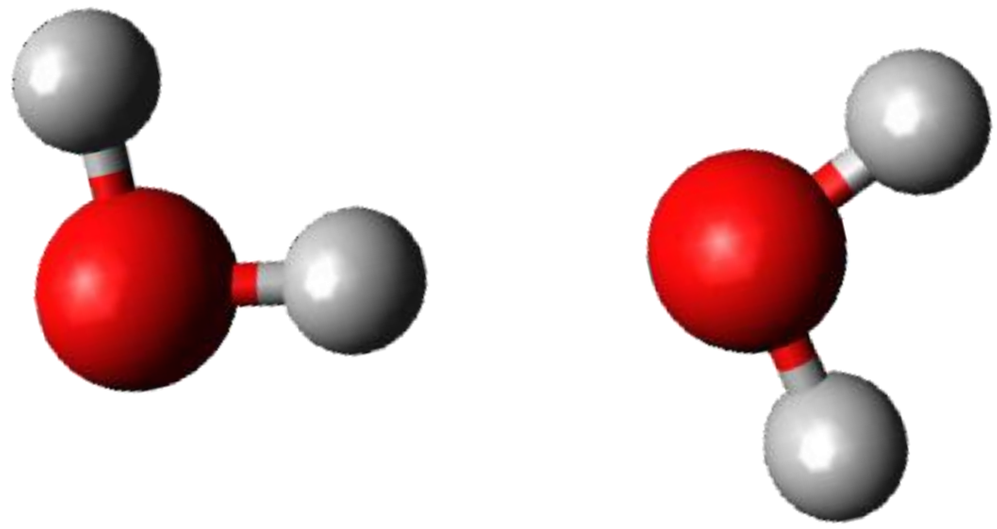
$$\mathbf{R}(t+\Delta t) = 2\mathbf{R}(t) - \mathbf{R}(t-\Delta t) + \ddot{\mathbf{R}}\Delta t^2$$

Molecular dynamics in practice

Initial *v(0), R(0)*

Converge DFT calculation

Calculate forces



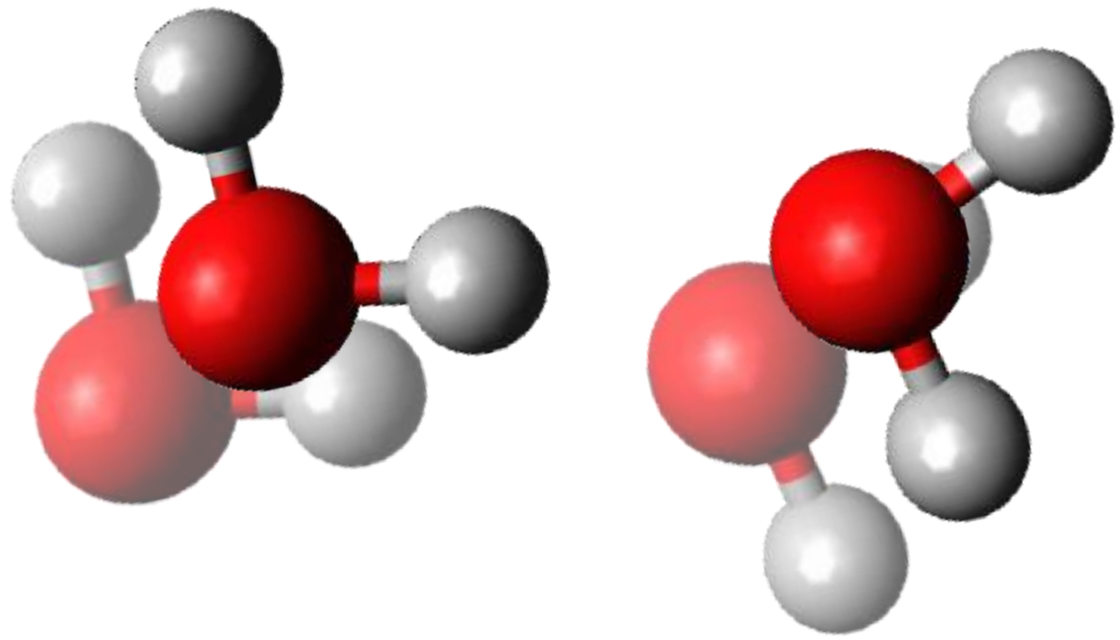
Molecular dynamics in practice

Initial *v(0), R(0)*

Converge DFT calculation

Calculate forces

Apply Verlet algorithm to get *v(t+Δt), R(t+Δt)*



Molecular dynamics in practice

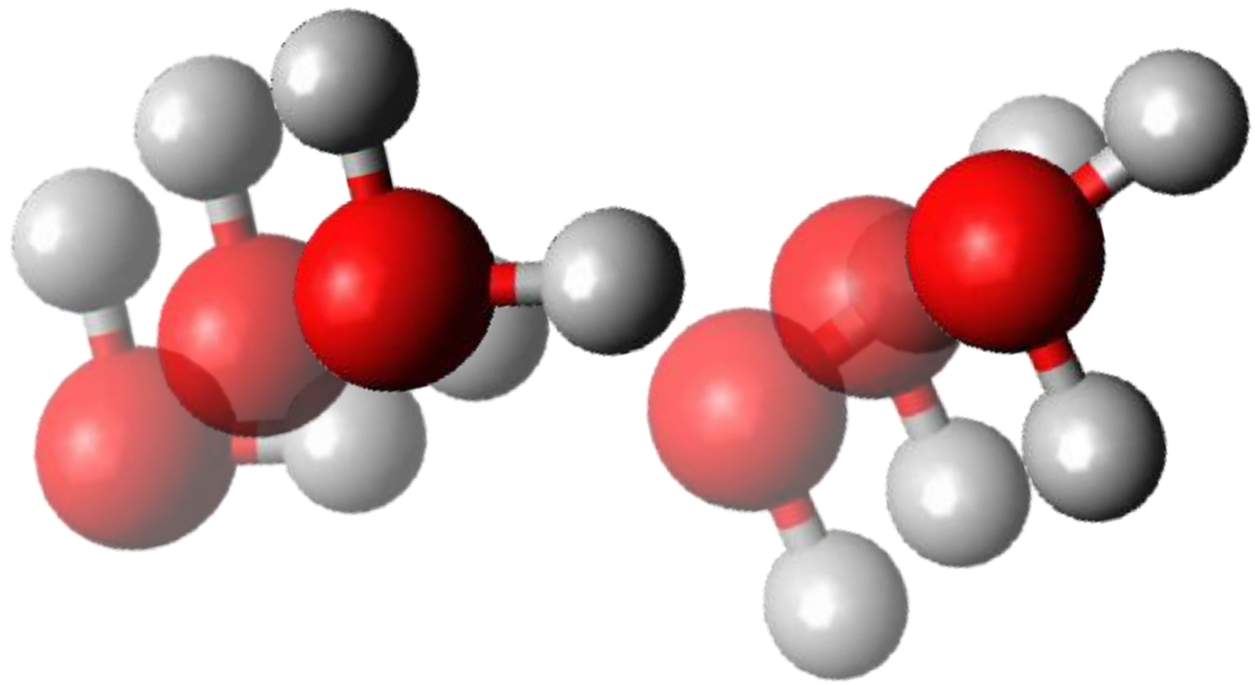
Initial *v(0), R(0)*

Converge DFT calculation

Calculate forces

Apply Verlet algorithm to get *v(t+Δt), R(t+Δt)*

repeat



Questions – DFT MD in practice?

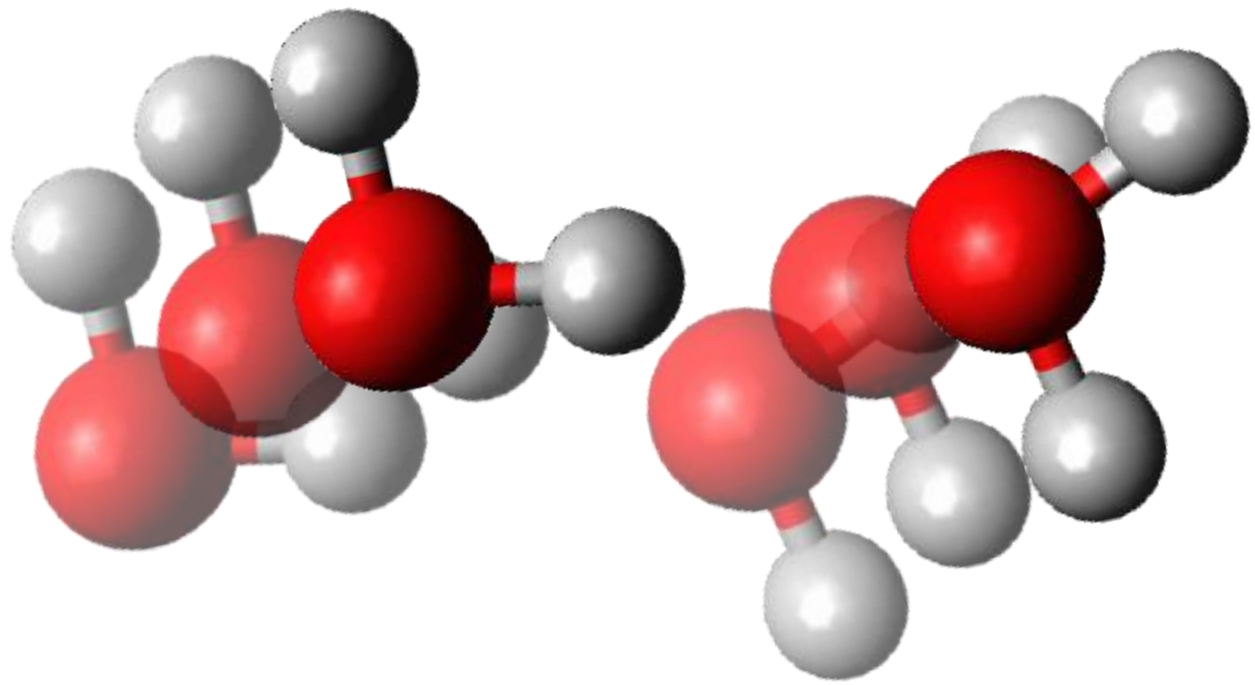
Initial *v(0), R(0)*

Converge DFT calculation

Calculate forces

Apply Verlet algorithm to get *v(t+Δt), R(t+Δt)*

repeat



Thermodynamic ensembles

	conserved quantities
Micro-canonical ensemble (NVE)	**# particles, volume, energy**
Canonical ensemble (NVT)	**# particles, volume, temperature**
NPT or NPH ensemble (for phase transitions)	**# particles, pressure, temperature or enthalpy**
Grand-canonical ensemble (μVT) (for ad- or desorption)	**chemical potential, volume, temperature**

FHI-aims MD settings

FHI-aims technical detail:

settings for molecular dynamics calculations:

MD_run time ensemble	:	specify total simulation time and the MD ensemble
MD_time_step deltat	:	set the MD time step
sc_accuracy_forces	:	request an appropriate force accuracy

V. Blum et al. Computer Physics Communications 180, 2175 (2009)

Thermodynamic ensembles

	conserved quantities
Micro-canonical ensemble (NVE)	**# particles, volume, energy**
Canonical ensemble (NVT)	# particles, volume, temperature
NPT or NPH ensemble (for phase transitions)	# particles, pressure, temperature or enthalpy
Grand-canonical ensemble (μVT) (for ad- or desorption)	chemical potential, volume, temperature

typical MD ensemble (follows directly from Newton's equation of motion)

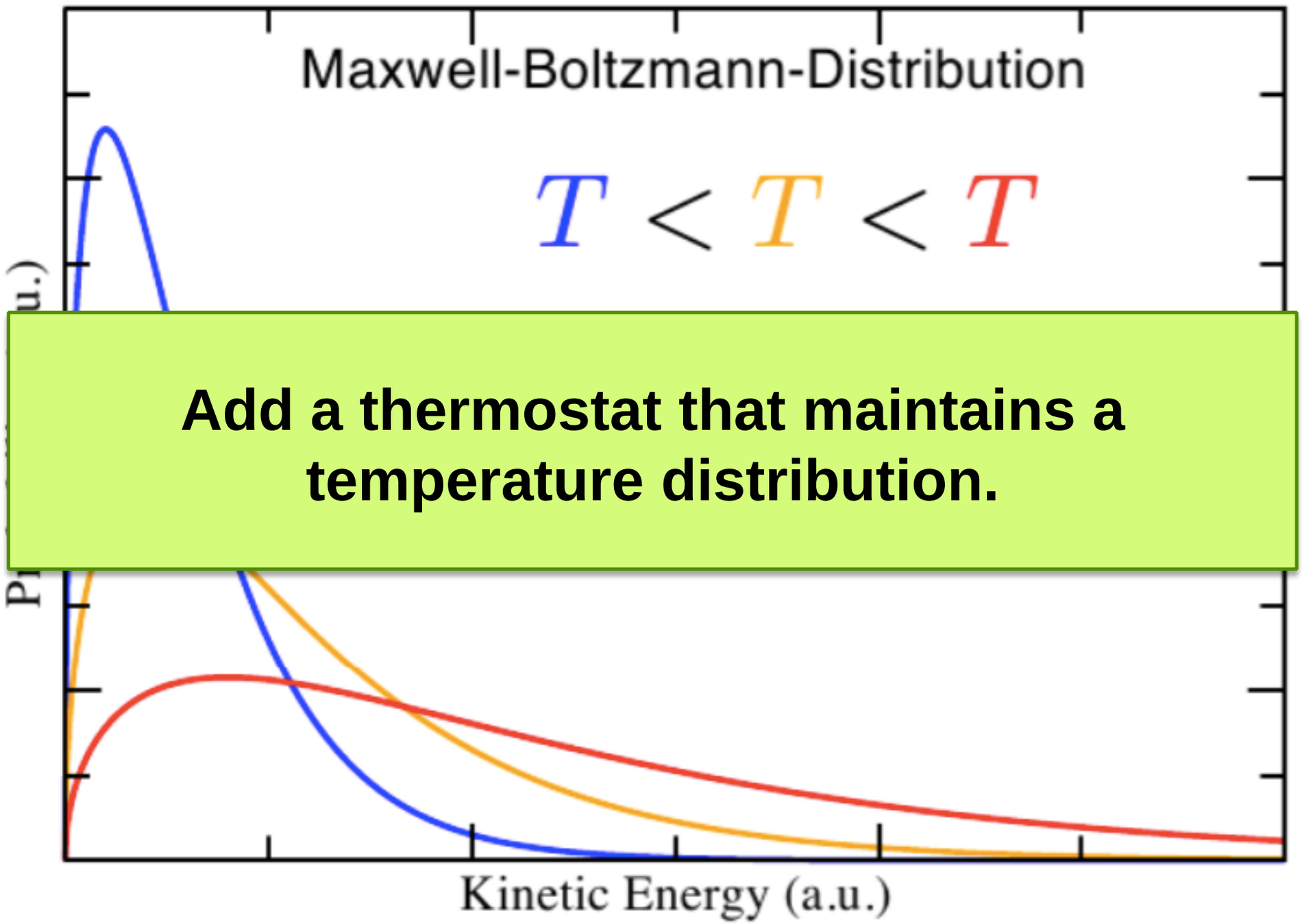
Thermodynamic ensembles

	conserved quantities
Micro-canonical ensemble (NVE)	# particles, volume, energy
Canonical ensemble (NVT)	**# particles, volume, temperature**

What about this ensemble?

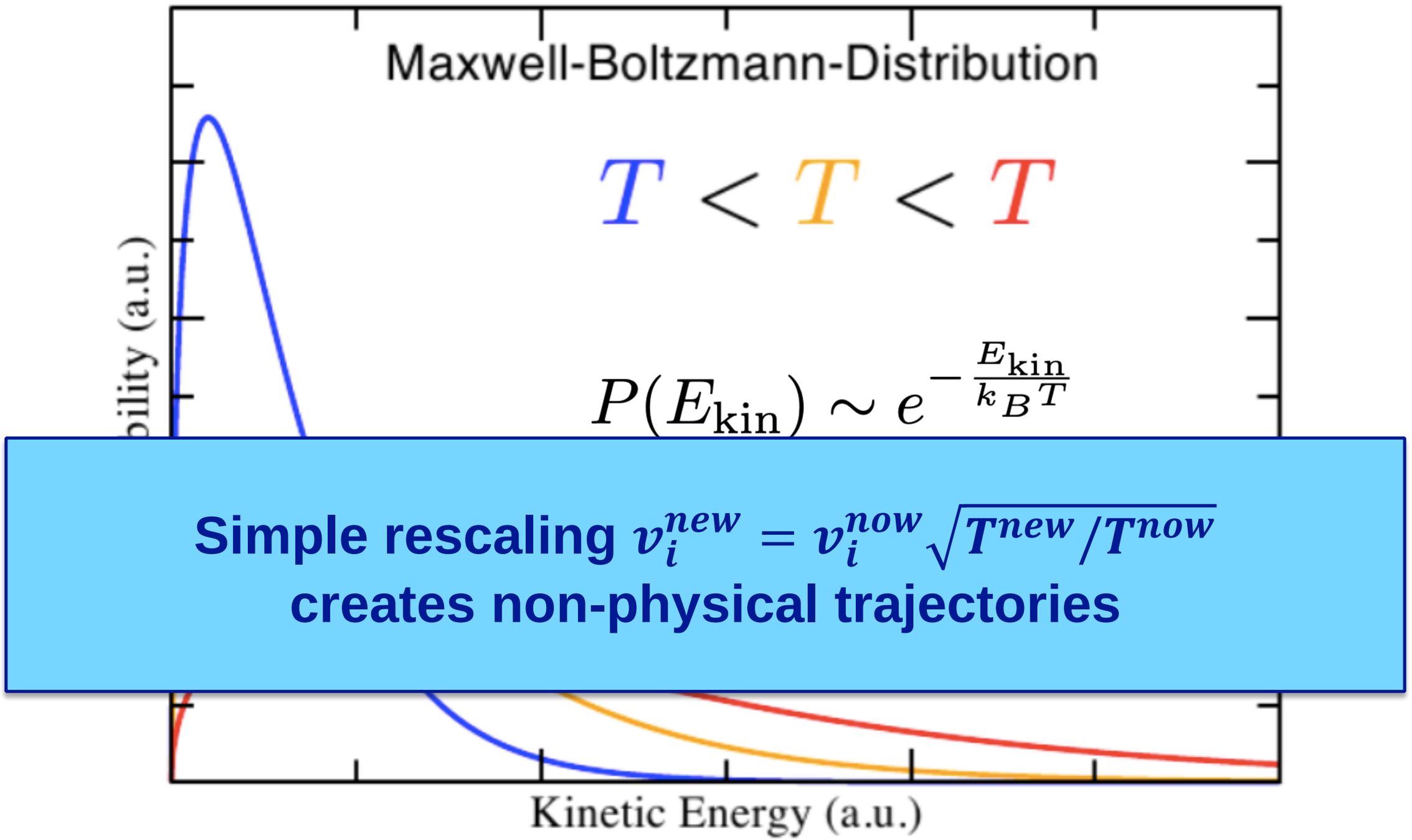
Need to maintain a constant temperature.

Temperature distributions



Add a thermostat that maintains a temperature distribution.

Temperature distributions



Simple rescaling $v_i^{new} = v_i^{now} \sqrt{T^{new}/T^{now}}$ creates non-physical trajectories

Nosé-Hoover thermostat

$$\mathcal{H} = \sum_{I=1}^{N_n} \frac{(\mathbf{p}'_I)^2}{2M_I} + V(\{\mathbf{R}\}) + \frac{p_\eta^2}{2Q} + 3Nk_BT\eta$$

original Hamiltonian

heat bath (in form of fictitious oscillator)

One of possible thermostats giving appropriate trajectories (close to the wanted T)

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S. Nosé, J. Chem. Phys. 81, 511 (1984)
W. G. Hoover, Phys. Rev. A 31, 1695 (1985)

Nosé-Hoover thermostat

fictitious mass

$$\mathcal{H} = \sum_{I=1}^{N_n} \frac{(\mathbf{p}'_I)^2}{2M_I} + V(\{\mathbf{R}\}) + \frac{p_\eta^2}{2Q} + 3Nk_BT\eta$$

original Hamiltonian

heat bath (in form of fictitious oscillator)

$$\mathbf{p}'_I = \frac{\mathbf{p}_I}{s}$$

scaled momenta

S. Nosé, J. Chem. Phys. 81, 511 (1984)
W. G. Hoover, Phys. Rev. A 31, 1695 (1985)

Nosé-Hoover thermostat

fictitious mass

$$\mathcal{H} = \sum_{I=1}^{N_n} \frac{(\mathbf{p}'_I)^2}{2M_I} + V(\{\mathbf{R}\}) + \frac{p_\eta^2}{2Q} + 3Nk_BT\eta$$

original Hamiltonian

heat bath (in form of fictitious oscillator)

$$\dot{\mathbf{p}}'_I = \mathbf{F}_I - \frac{p_\eta}{Q}\mathbf{p}'_I$$

momenta are damped by fictitious mass

This is what maintains a constant temperature.

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S. Nosé, J. Chem. Phys. 81, 511 (1984)
W. G. Hoover, Phys. Rev. A 31, 1695 (1985)

Questions?

fictitious mass

$$\mathcal{H} = \sum_{I=1}^{N_n} \frac{(\mathbf{p}'_I)^2}{2M_I} + V(\{\mathbf{R}\}) + \frac{p_\eta^2}{2Q} + 3Nk_BT\eta$$

original Hamiltonian

heat bath (in form of fictitious oscillator)

$$\dot{\mathbf{p}}'_I = \mathbf{F}_I - \frac{p_\eta}{Q}\mathbf{p}'_I$$

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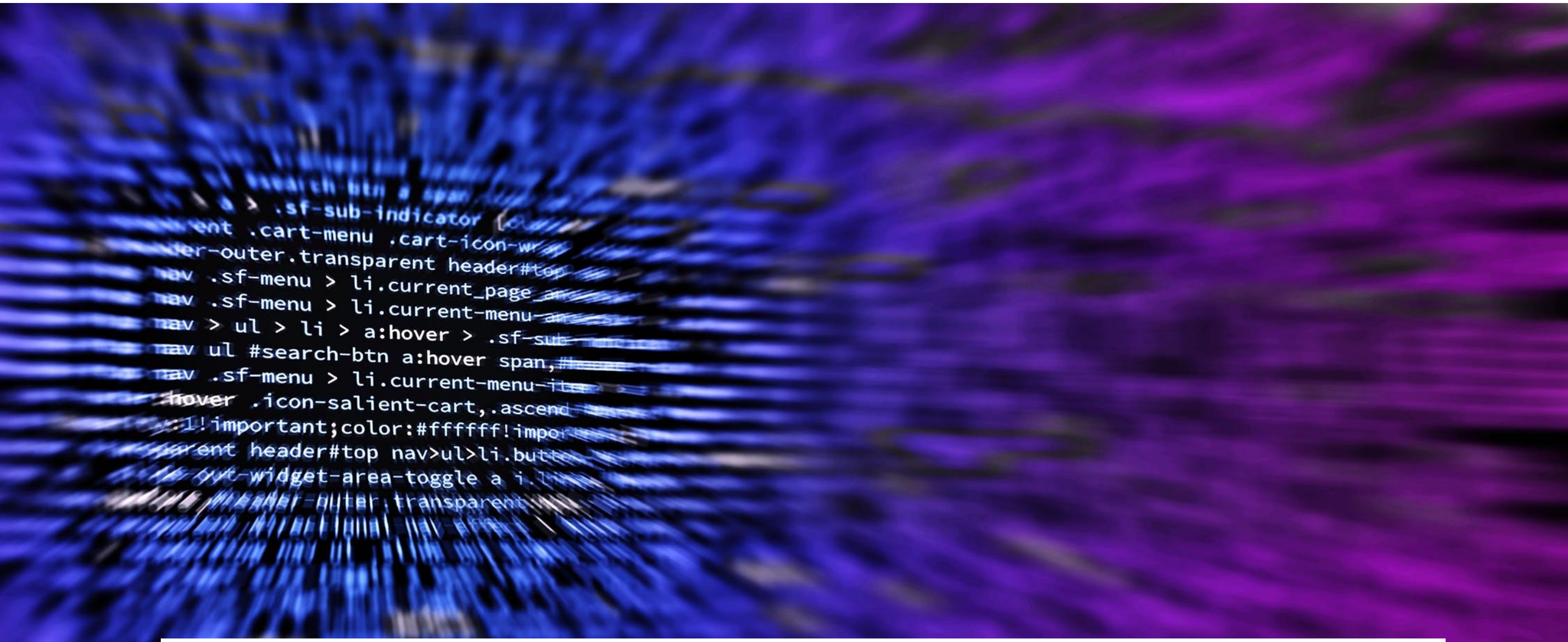
Computational Project



Preassignment for next Monday:

Read *Planning a Computational Project* chapter (on MyCourses->Lectures>Lecture 5)

Questions?

Enjoy our "DFT MD & dispersion interactions" tutorial:

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- **/work/courses/unix/PHYS/E0546/TUTORIALS**
- **Ask for printouts**

Interesting links related to the tutorial: More information on Thermostats:https://nanohub.org/resources/7576/download/Martini_L4_TemperatureControl.pdf
https://www2.mpip-mainz.mpg.de/~andrienk/journal_club/thermostats.pdf
http://www.courses.physics.helsinki.fi/fys/moldyn/lectures/L5.pdf
And also FHI-aims manual.

Don't forget to put your name in the list of attendance!

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