

Lectures on Molecular Dynamics simulations of materials

Lecture 1: the theory behind molecular dynamics

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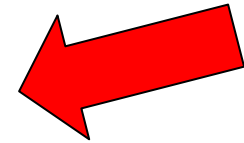
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Lectures on Molecular Dynamics simulations

Introduction

- What is molecular dynamics (MD)? Examples of current research
- What will I learn in these lectures?

Lecture 1: the theory behind molecular dynamics



- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD

Lecture 2: total energy and force calculations

- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: “averaging electrons out”

Lecture 3: advanced techniques and mesodynamics

- MD in under isothermal and isobaric conditions
- Coarse grain approaches and dynamics with implicit degrees of freedom

What is molecular dynamics?

Follow the dynamics (motion) of all the atoms in your material

Numerically solve classical equations of motion (Newton's):

Approximation

$$\vec{F}_i = m_i \vec{a}_i \quad \text{or} \quad \begin{cases} \dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \\ \dot{\vec{p}}_i = \vec{F}_i \end{cases}$$

Forces on atoms come from the total potential energy:

$$\vec{F}_i = -\vec{\nabla}_{r_i} V(\{r_j\}) \quad \leftarrow \text{Approximated (in almost all cases)}$$

Classical mechanics: Hamilton's picture

William Hamilton reformulation of classical mechanics (1800's)

Hamiltonian:

$$H(\{r_i\}, \{p_i\}) = V(\{r_i(t)\}) + \sum_{i=1}^{3N} \frac{p_i(t)^2}{2m_i} \quad i \text{ denotes atom and Cartesian component (x, y, or z)}$$

Equations of motion can be derived from the Hamiltonian:

$$\dot{r}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial r_i}$$

- These equations can only be solved analytically for very few cases
- MD solves the dynamics of many atoms (billions in supercomputers)

Classical mechanics: conserved quantities

$$H(\{r_i\}, \{p_i\}) = V(\{r_i(t)\}) + \sum_{i=1}^{3N} \frac{p_i(t)^2}{2m_i}$$

Let's calculate the time derivative of the Hamiltonian:

$$\frac{dH}{dt} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial r_i} \dot{r}_i + \frac{\partial H}{\partial p_i} \dot{p}_i \right)$$

Using the equations of motion we get:

$$\frac{dH}{dt} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial r_i} \frac{\partial H}{\partial p_i} + \frac{\partial H}{\partial p_i} \left(-\frac{\partial H}{\partial r_i} \right) \right) = 0 \quad \text{Total energy is conserved}$$

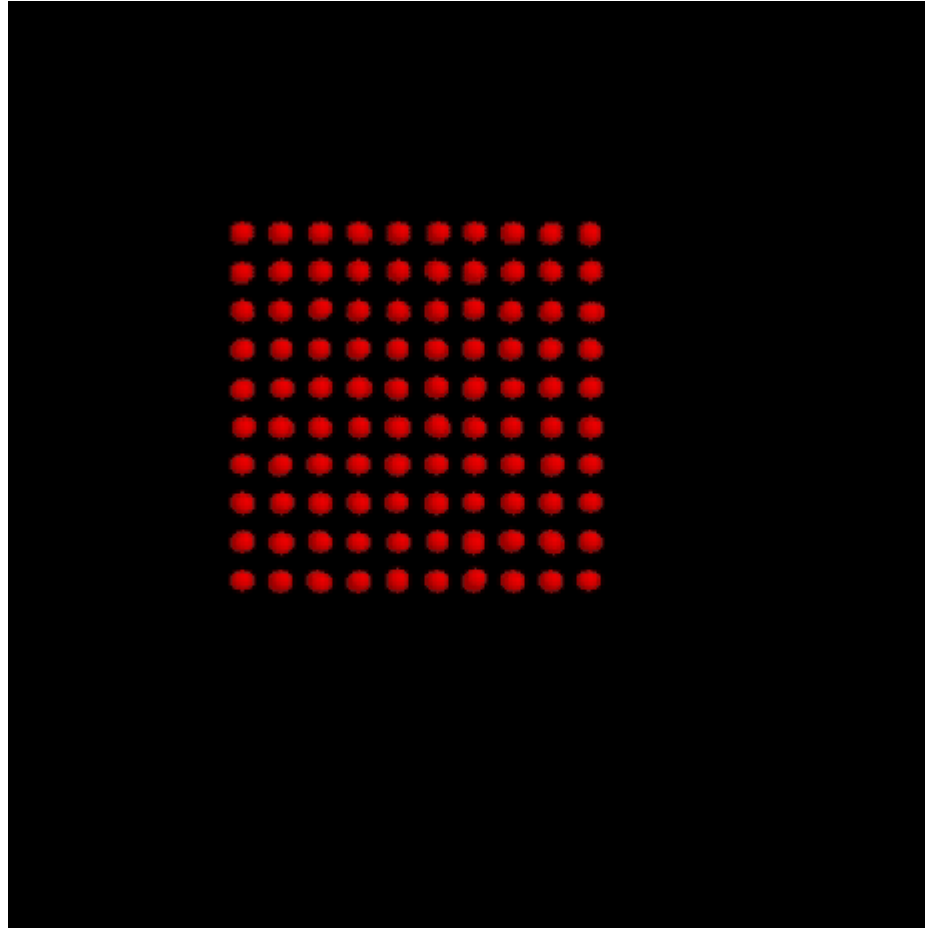
Other constants of motion are:

• Linear momentum: $\vec{P} = \sum_{i=1}^N \vec{p}_i$

• Angular momentum:

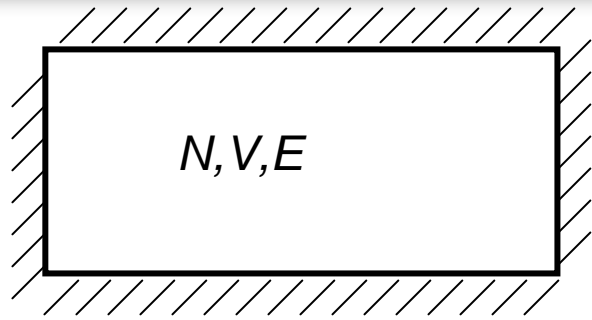
$$\vec{L} = \sum_{i=1}^N \vec{r}_i \times \vec{p}_i$$

Analysis/interpretation of MD: statistical mechanics



Goal: describe concepts that enable relating molecular dynamics with thermodynamics properties

Statistical mechanics



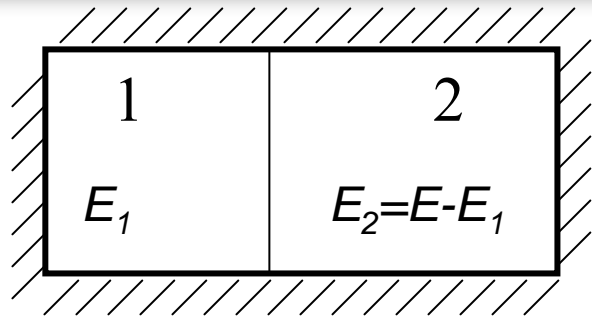
Consider N atoms in a rigid container of volume V with constant energy E

Number of different possible microscopic states:

$$\Omega(E, V, N) = \frac{1}{N! h^{3N}} \int_V d^{3N} r \int_{-\infty}^{\infty} d^{3N} p \delta(H(\{r_i\}, \{p_i\}) - E)$$

Postulate: the probability of the material being in any one of the $\Omega(N, V, E)$ is the same, i.e. all states are equally likely

Statistical mechanics



Consider a fictitious separation that divides the material in two subsystems

The energy of subsystem 1 is not constant

- What is the probability of subsystem 1 having energy E_1 ?

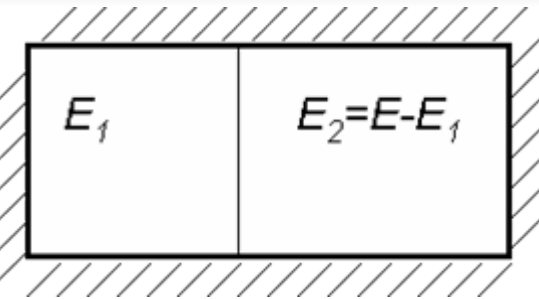
$$P(E_1, E - E_1) = \frac{\text{Number of microstates with } E_1}{\Omega(E, V, N)}$$

$$P(E_1, E - E_1) = \frac{\Omega_1(E_1, V_1, N_1) \cdot \Omega_2(E - E_1, V - V_1, N - N_1)}{\Omega(E, V, N)}$$

Additive measure of number of states:

$$\log P(E_1, E - E_1) = \log \Omega_1(E_1, V_1, N_1) + \log \Omega_2(E - E_1, V - V_1, N - N_1) + C$$

Statistical mechanics



Equilibrium state of the material:
Subsystems have the most likely energies,
i.e. maximum of $\log P(E_1, E - E_2)$

$$\frac{\partial \log P(E_1, E - E_1)}{\partial E_1} = 0 = \frac{\partial \log \Omega_1(E_1, V_1, N_1)}{\partial E_1} + \frac{\partial \log \Omega_2(E - E_1, V - V_1, N - N_1)}{\partial E_1}$$
$$0 = \frac{\partial \log \Omega_1(E_1, V_1, N_1)}{\partial E_1} - \frac{\partial \log \Omega_2(E_2, V_2, N_2)}{\partial E_2}$$

Two subsystems that can exchange energy are in equilibrium when:

$$\frac{\partial \log \Omega_1(E_1, V_1, N_1)}{\partial E_1} = \frac{\partial \log \Omega_2(E_2, V_2, N_2)}{\partial E_2}$$

$$\beta_1(E_1, V_1, N_1) = \beta_2(E_2, V_2, N_2) \quad \text{with:} \quad \beta = \frac{\partial \log \Omega(E, V, N)}{\partial E}$$

Statistical mechanics

$\log\Omega$ is important enough to have its own name: entropy

$$S = k \log\Omega(E, V, N)$$

Temperature:

$$\frac{\partial S(E, V, N)}{\partial E} = \frac{1}{T} \quad \frac{\partial \log\Omega(E, V, N)}{\partial E} = \beta = \frac{1}{kT}$$

Pressure:

$$\frac{\partial S(E, V, N)}{\partial V} = -\frac{P}{T}$$

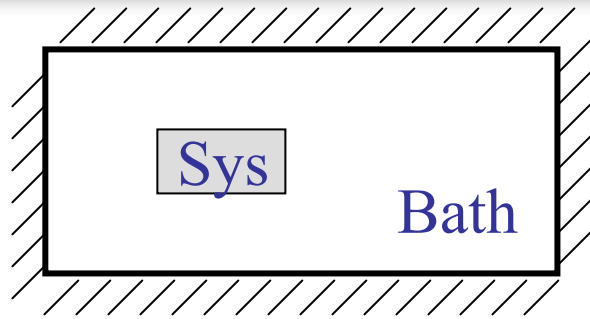
Chemical potential:

$$\frac{\partial S(E, V, N)}{\partial N} = \frac{\mu}{T}$$

Ludwig Boltzmann (1844-1906)



Statistical mechanics: canonical ensemble



$$E + E_{\text{bath}} = E_{\text{tot}} = \text{Constant}$$

Probability of system being in a microscopic $(\{r_i\}, \{p_i\})$ state with energy E :

$$P(\{r_i\}, \{p_i\}) = \frac{\Omega_{\text{bath}}(E_{\text{tot}} - H(\{r_i\}, \{p_i\}))}{\sum_{\text{microstates}} \Omega_{\text{bath}}(E_{\text{tot}} - E)}$$

Since $E \ll E_{\text{tot}}$ we expand $\log \Omega_{\text{bath}}$ around E_{tot} :

$$\log \Omega_{\text{bath}}(E_{\text{tot}} - E) = \log \Omega_{\text{bath}}(E_{\text{tot}}) - \left. \frac{\partial \log \Omega(E')}{\partial E'} \right|_{E_{\text{tot}}} E = \log \Omega_{\text{bath}}(E_{\text{tot}}) - \frac{E}{kT}$$

$$P(\{r_i\}, \{p_i\}) = \frac{e^{-\beta H(\{r_i\}, \{p_i\})}}{\sum_{\text{microstates}} e^{-\beta H(\{r_i\}, \{p_i\})}}$$

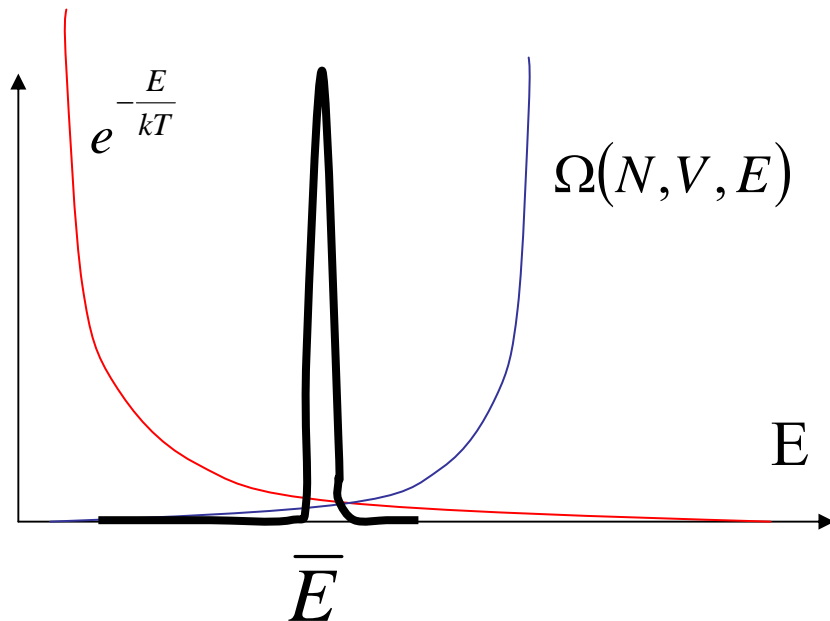
Maxwell-Boltzmann distribution

Canonical ensemble and thermodynamics

Maxwell-Boltzmann distribution $P(\{r_i\}, \{p_i\}) = \frac{e^{-\beta H(\{r_i\}, \{p_i\})}}{\sum_{\text{microstates}} e^{-\beta H(\{r_i\}, \{p_i\})}}$

Partition function: $Z(N, V, T) = \sum_{\text{microstates}} e^{-\beta H(\{r_i\}, \{p_i\})}$

$$Z(N, V, T) = \sum_E \Omega(N, V, E) e^{-\frac{E}{kT}} = \Omega(N, V, \bar{E}) e^{-\frac{\bar{E}}{kT}}$$



$$\log Z(N, V, T) = \log \Omega(N, V, E) - \frac{E}{kT}$$

Helmholtz free energy:

$$F = E - TS = -kT \log Z(N, V, T)$$

Canonical ensemble: averages

Consider a quantity that depends on the atomic positions and momenta:

$$A(\{r_i\}, \{p_i\})$$

In equilibrium the average values of A is:

$$\langle A \rangle = \sum_{microstates} A P_{micro} = \frac{\sum_{microstates} A(\{r_i\}, \{p_i\}) e^{-\beta H(\{r_i\}, \{p_i\})}}{\sum_{microstates} e^{-\beta H(\{r_i\}, \{p_i\})}} \quad \text{Ensemble average}$$

When you measure the quantity A in an experiment or MD simulation:

$$\frac{1}{\tau} \int_0^{\tau} dt A(\{r_i(t)\}, \{p_i(t)\}) \quad \text{Time average}$$

Under equilibrium conditions temporal and ensemble averages are equal

Canonical ensemble: equipartition of energy

Consider a variable that appears squared in the Hamiltonian:

$$H(\{r_i\}, \{p_i\}) = \lambda p_1^2 + V(\{r_i(t)\}) + \sum_{i=2}^{3N} \frac{p_i(t)^2}{2m_i} = \lambda p_1^2 + H'$$

$$\langle \lambda p_1^2 \rangle = \frac{\int d^{3N} p d^{3N} p \lambda p_1^2 e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}}{\int d^{3N} p d^{3N} p e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}} = \frac{\int d^{3N} p d^{3N-1} p e^{-\frac{H'}{kT}} \int dp_1 \lambda p_1^2 e^{-\frac{\lambda p_1^2}{kT}}}{\int d^{3N} p d^{3N-1} p e^{-\frac{H'}{kT}} \int dp_1 e^{-\frac{\lambda p_1^2}{kT}}}$$

Change of variable: $\frac{\lambda p_1^2}{kT} = x^2 \quad dp_1 = \frac{kT}{\lambda} dx$

$$\langle \lambda p_1^2 \rangle = \frac{(kT)^2}{\lambda} \frac{\int dx x^2 e^{-x^2}}{\frac{kT}{\lambda} \int dx e^{-x^2}} = \frac{1}{2} kT$$

Equipartition of energy: Any degree of freedom that appears squared in the Hamiltonian contributes $1/2kT$ of energy

Temperature in MD: equipartition of energy

$$\langle K \rangle = \frac{3N}{2} kT$$

In most cases c.m. motion is set to zero at time zero (constant of motion → it remains zero)

$$\langle K \rangle = \frac{3N-3}{2} kT$$

Often angular momentum is zeroed (and remains zero)

$$\langle K \rangle = \frac{3N-6}{2} kT$$

Temperature is related to **average** kinetic energy. Instantaneous temperature:

$$K(t) = \frac{N_{eff}}{2} kT(t)$$

Various important ensembles

Microcanonical (NVE)

Canonical (NVT)

Isobaric/isothermal (NPT)

Probability distributions

$$P(\{r_i\}, \{p_i\}) = \frac{1}{\Omega(E, V, N)}$$

$$P(\{r_i\}, \{p_i\}) = \frac{e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}}{Z(T, V, N)}$$

$$P(\{r_i\}, \{p_i\}, V) = \frac{e^{-\frac{1}{kT}[H(\{r_i\}, \{p_i\}) - PV]}}{Z_P(T, P, N)}$$

$$\Omega(E, V, N) = \sum_{micro} \delta(E - H(\{r_i\}, \{p_i\}))$$

$$Z(T, V, N) = \sum_{micro} e^{-\frac{E}{kT}}$$

$$Z_P(T, P, N) = \sum_V \sum_{micro} e^{-\frac{E - PV}{kT}}$$

Free energies

$$S = k \log \Omega(E, V, N)$$

$$F(T, V, N) = -kT \log Z$$

$$G(T, P, N) = -kT \log Z_p$$

Fluctuations

Fluctuations from equilibrium are also related to materials properties

$$\langle \delta A^2 \rangle = \frac{1}{\tau} \int_0^\tau [A(t) - \langle A \rangle]^2 dt = \langle A^2 \rangle - \langle A \rangle^2$$

Specific heat:

$$C_V = \left. \frac{\partial E}{\partial T} \right|_{NVT} \qquad \langle \delta H^2 \rangle_{NVT} = kT^2 C_V$$

Compressibility:

$$\beta_V = \left. \frac{1}{V} \frac{\partial V}{\partial P} \right|_{NVT} \qquad \langle \delta V^2 \rangle_{NPT} = k \langle V \rangle T \beta_T$$

Quantum effects

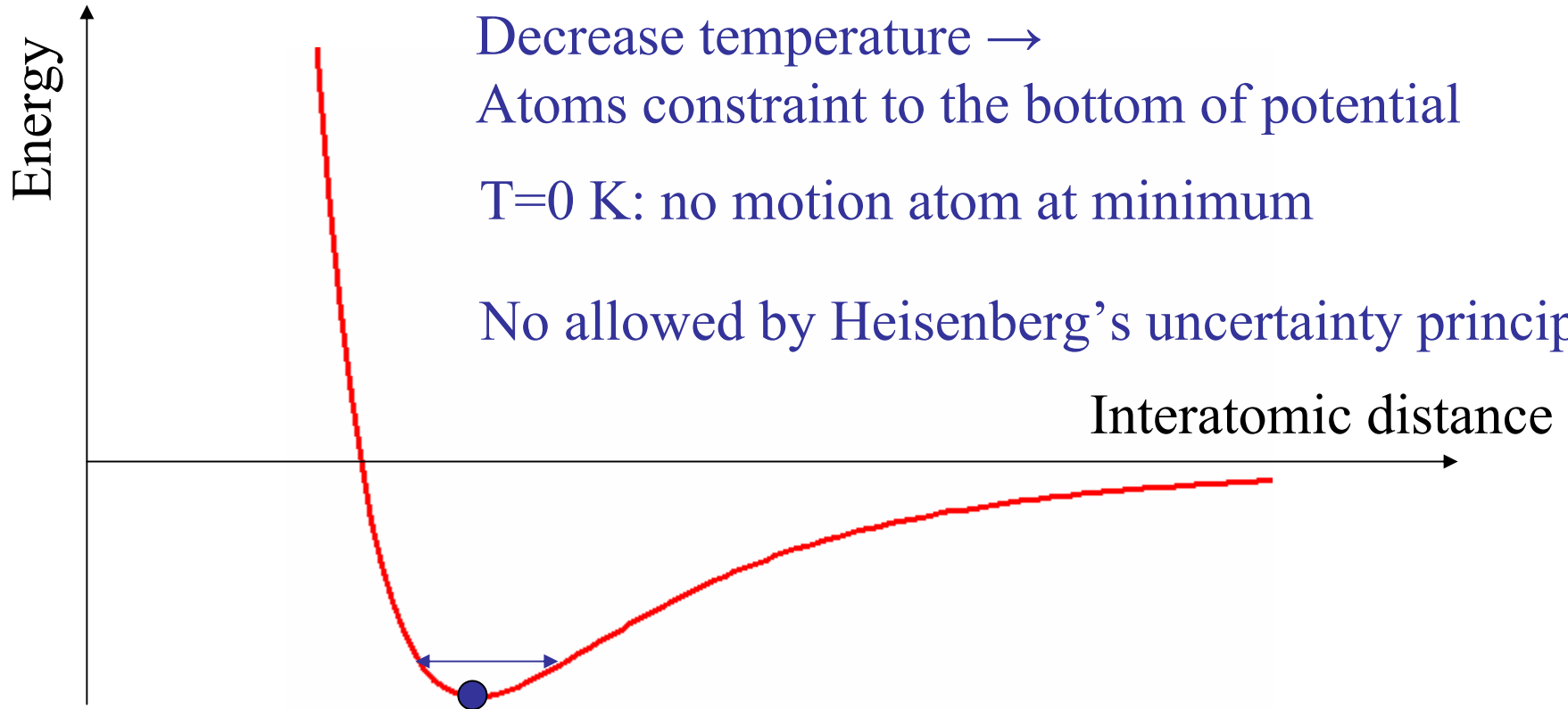
When does classical mechanics for atoms stop working?

Decrease temperature \rightarrow

Atoms constraint to the bottom of potential

$T=0$ K: no motion atom at minimum

No allowed by Heisenberg's uncertainty principle



Temperature at which quantum effects kick in depends on frequency

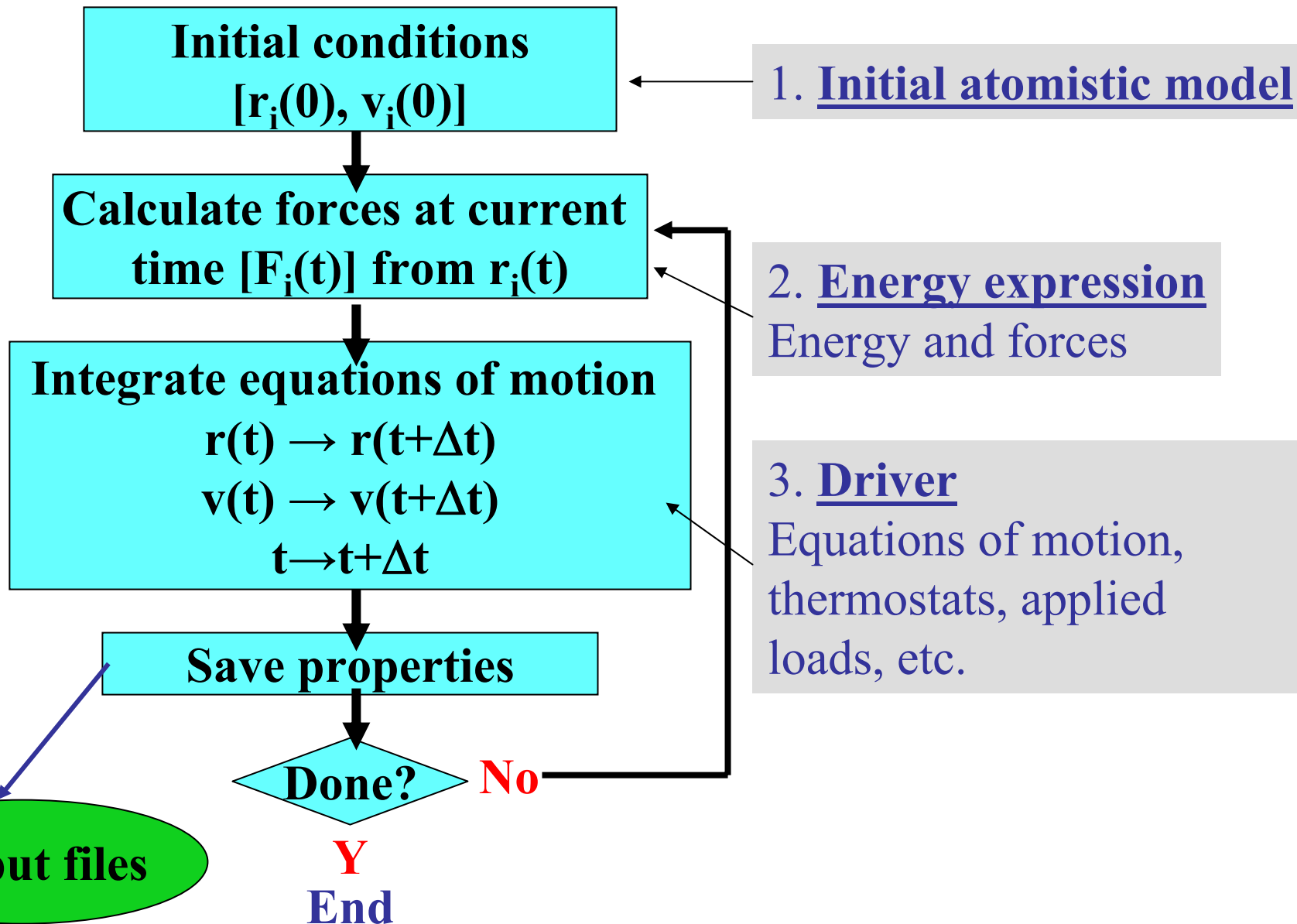
$kT \gg \hbar\omega$ Classical regime

$kT \sim < \hbar\omega$ Quantum regime

Statistical mechanics: further reading

- Kerson Huang: “*Statistical Mechanics*”
- Landau and Lifshitz: “*Course of Theoretical Physics Volume 5: Statistical Physics*”
- Balescu: “*Equilibrium and nonequilibrium statistical mechanics*”

MD: structure of an MD code



Integrating the equations of motion

$$\left. \begin{aligned} \dot{\vec{r}}_i &= \frac{\vec{p}_i}{m_i} \approx \frac{\vec{r}_i(t + \Delta t) - \vec{r}_i(t)}{\Delta t} & \vec{r}_i(t + \Delta t) &= \vec{r}_i(t) + \frac{\vec{p}_i}{m_i} \Delta t \\ \dot{\vec{p}}_i &= \vec{F}_i \approx \frac{\vec{p}_i(t + \Delta t) - \vec{p}_i(t)}{\Delta t} & \vec{p}_i(t + \Delta t) &= \vec{p}_i(t) + \vec{F}_i \Delta t \end{aligned} \right\} \text{Euler method}$$

Verlet algorithm: Taylor expansion of positions with time

$$r_i(t + \Delta t) = r_i(t) + \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 + \frac{1}{6}\dddot{r}_i(t)\Delta t^3 + O(\Delta t^4)$$

$$r_i(t - \Delta t) = r_i(t) - \dot{r}_i(t)\Delta t + \frac{1}{2}\ddot{r}_i(t)\Delta t^2 - \frac{1}{6}\dddot{r}_i(t)\Delta t^3 + O(\Delta t^4)$$

Sum two equations:

$$r_i(t + \Delta t) = 2r_i(t) - r_i(t - \Delta t) + \ddot{r}_i(t)\Delta t^2 + O(\Delta t^4)$$

Verlet algorithm: various equivalent formulations

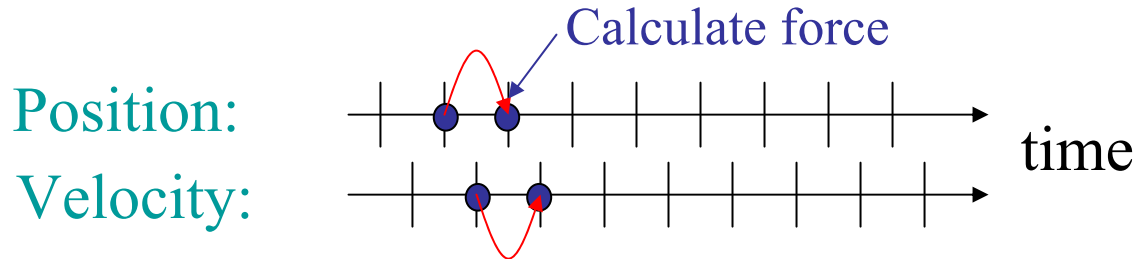
Velocity Verlet:
$$\left\{ \begin{array}{l} p_i\left(t + \frac{1}{2}\Delta t\right) = p_i(t) + \frac{1}{2}F_i(t)\Delta t \\ r_i(t + \Delta t) = r_i(t) + \frac{p_i\left(t + \frac{1}{2}\Delta t\right)}{m_i}\Delta t \\ p_i(t + \Delta t) = p_i\left(t + \frac{1}{2}\Delta t\right) + \frac{1}{2}F_i(t + \Delta t)\Delta t \end{array} \right.$$

Advance p half step

Advance r full step
(with p half step ahead)

Advance p half step
(with F at $t + \Delta t$)

Leap-Frog Verlet:
$$\left\{ \begin{array}{l} r_i\left(t + \frac{1}{2}\Delta t\right) = r_i\left(t - \frac{1}{2}\Delta t\right) + v_i(t)\Delta t \\ v_i(t + \Delta t) = v_i(t) + \frac{1}{m_i}F_i\left(t + \frac{1}{2}\Delta t\right) \end{array} \right.$$



Verlet algorithm: features and advantages

- Exactly time reversible
 - If velocities are reversed at a given time the algorithm traces back its steps
- Symplectic
 - Conserves volume in phase space (as Hamiltonian dynamics does)



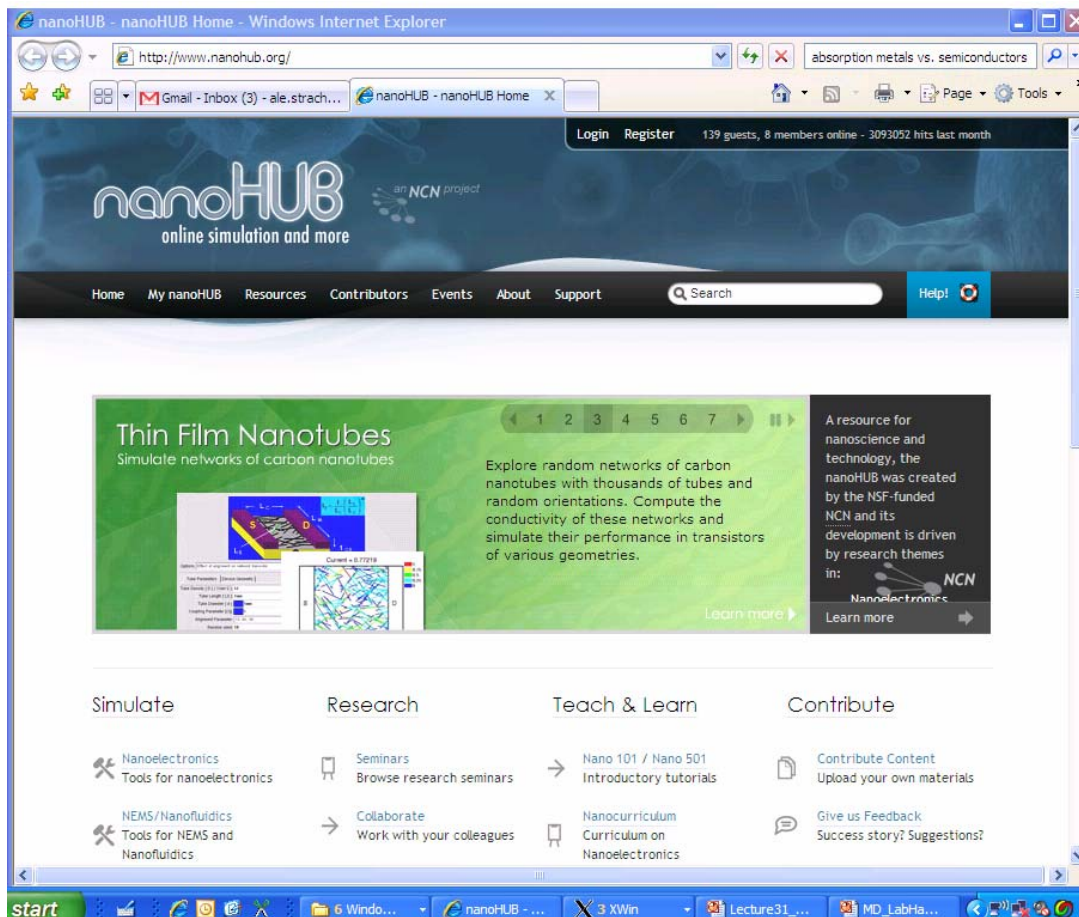
- No long-term energy drifts
- The trajectory stays very close to the constant energy hypersurface in phase space

Remember: $S = k \log \Omega(E, V, N)$

Run your own MD simulation

[nanoHUB](http://www.nanohub.org) (www.nanohub.org)

- Science portal developed by the Network of Computational Nanotechnology
- Provides services for online education, collaboration and simulation



The screenshot shows the nanoHUB website in a Windows Internet Explorer browser window. The address bar displays <http://www.nanohub.org/>. The page features a dark blue header with the nanoHUB logo and the tagline "online simulation and more". Below the header is a navigation menu with links for Home, My nanoHUB, Resources, Contributors, Events, About, and Support. A search bar and a Help! button are also present. The main content area includes a featured article titled "Thin Film Nanotubes" with a sub-heading "Simulate networks of carbon nanotubes". The article text describes exploring random networks of carbon nanotubes and simulating their performance in transistors. To the right of the article is a sidebar with a "Learn more" link and a logo for the Network of Computational Nanotechnology (NCN). Below the featured article is a grid of four categories: Simulate, Research, Teach & Learn, and Contribute. Each category has a list of sub-links and icons. The browser's taskbar at the bottom shows several open windows, including "6 Windo...", "nanoHUB - ...", "3 XWin", "Lecture31...", and "MD_LabHa...".

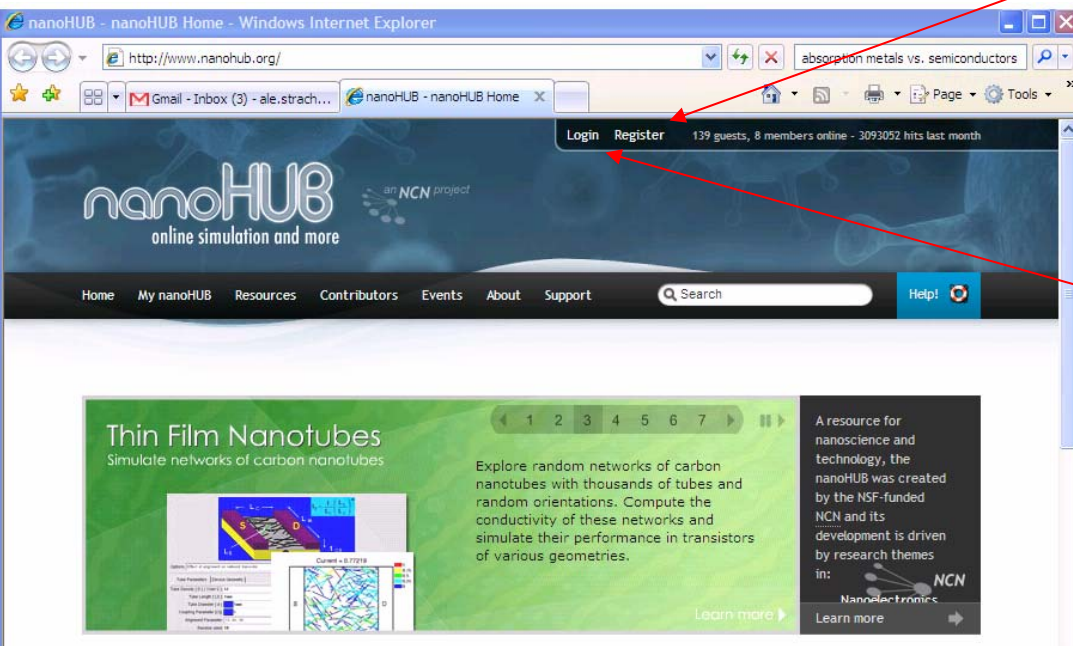
nanoMATERIALS simulation toolkit

nanoMATERIALS simulation toolkit @ nanoHUB

- General purpose tool for atomistic simulations of materials
- We are continuing to add features to the tool (electronic structure calculations are coming soon)

Register as a user of the nanoHUB:

Go to www.nanohub.org and click on: register



Login and then click select nanoMATERIALS tool from the tools menu

nanoMATERIALS and MD: further reading

Online lectures:

1. Materials strength: does size matter? nanoMATERIALS simulation toolkit tutorial

<http://www.nanohub.org/resources/2322/>

2. First Principles-based Atomistic and Mesoscale Modeling of Materials

<http://www.nanohub.org/resources/434/>

3. First Principles-Based Modeling of materials: Towards Computational Materials Design

<http://www.nanohub.org/resources/1239/>

Comments, more information?

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Question 1

Question 2

Question 3

Question 4

Question 5

Question 6

Question 7