Molecular Dynamics

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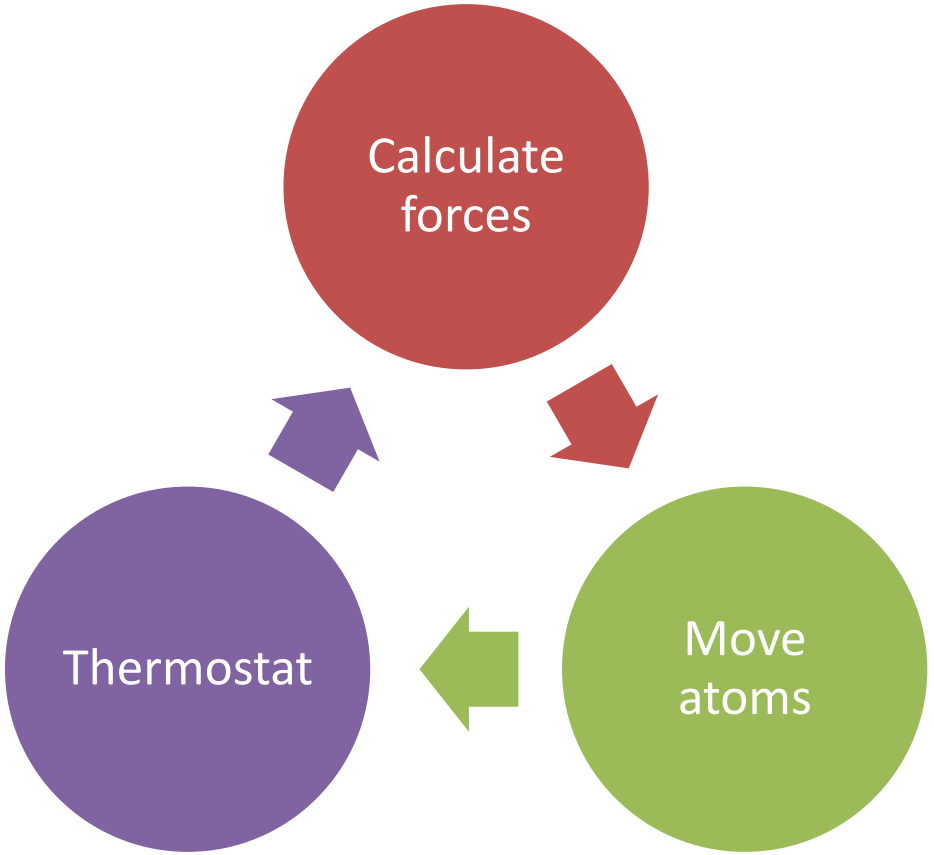
Outline

- What is MD?
- Why use MD?
- Strengths and limitations
- The different parts of MD:
  - Ensemble / thermostat
  - Atomic forces
  - Integrate equations of motion
- Analysis methods
- Assignment
- Examples

What is MD?

$$m_i \ddot{\boldsymbol{r}}_i = f_i$$

$$f_i = \frac{\partial}{\partial \boldsymbol{r_i}} U$$



Why use MD?

- Understand the effect of temperature and pressure on solids, liquids and gasses
- Examples:
  - Diffusion
  - Phase transformations
  - Thermodynamics
  - Nucleation and growth
  - Mechanical properties
  - …

Strengths and limitations

Classical MD

- Large systems, millions of atoms
- Limited number of elements
- Longer simulations

Ab initio MD

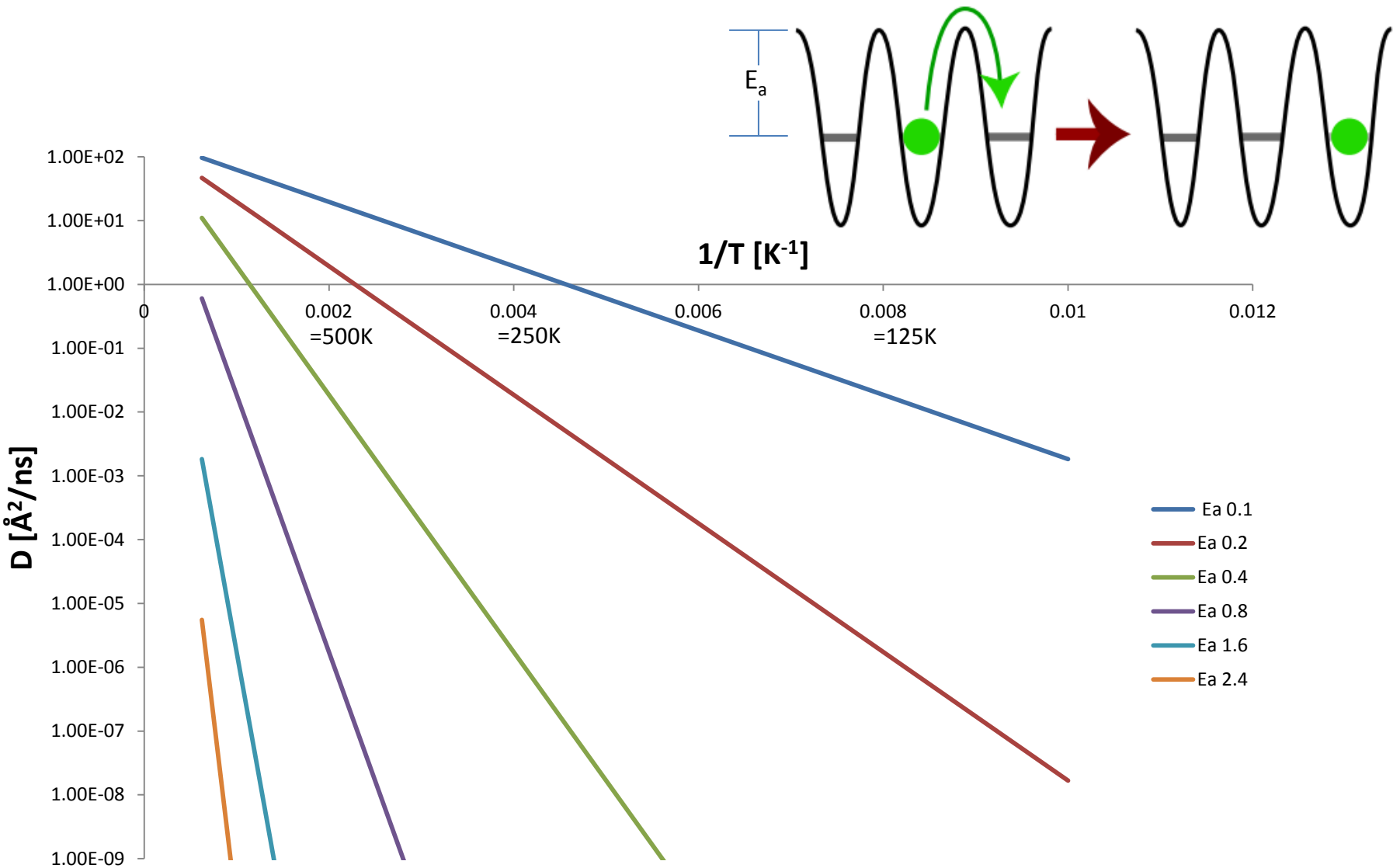
- Small systems, hundreds of atoms
- Many elements
- Short simulations <1ns

Hybrid, QM/MM

Accelerated MD

Metadynamics, Umbrella sampling

Strengths and limitations



Born-Oppenheimer MD

- Atomic dynamics and interaction treated on different time scales
- Classical treatment of atoms (no quantum mechanics)

Other types

- Car-Parrinello MD
- Parrinello-Rahman MD

The different parts of MD:
- **Ensemble** / thermostat

a group of items viewed as a whole rather than individually.

– Microcanonical ensemble, NVE

Isolated system with no heat exchange. Number of particles (N), volume (V), and energy (E) is conserved.

– Canonical ensemble, NVT

System in contact with heat bath through a thermostat. Number of particles (N), volume (V), and temperature (T) is conserved.

– Isothermal-Isobaric ensemble NPT

In a addition to a thermostat, a barostat is also used to conserve number of particles (N), pressure (P), and temperature (T) is conserved

What is temperature?

$$T(t) = \sum_{i=1}^{N} \frac{m_i \boldsymbol{v}_i{}^2(t)}{\mathrm{k}_B N_f}$$ Instantaneous temperature

$$N_f = 3N - 3$$ Number of degrees of freedom

m_i - mass for atom *i*
$v_i(t)$ - velocity for atom *i* at time *t*
N - number of atoms
k_B – Boltzmanns constant

The different parts of MD:
- Ensemble / **thermostat**

– Rescaling of velocities

The velocity distribution is rescaled with a factor, to obtaine temperature T.

– Andersen thermostat (http://dx.doi.org/10.1063/1.439486)

Probability, $P(t) = ve^{-vt}$, of an atom colliding with the heat bath and obtaining a new velocity from a Boltzmann distribution at temperature T.

– Nosé-Hover thermostat(s) (https://dx.doi.org/10.1103%2FPhysRevA.33.4253)

Adds a thermal reservoir to the dynamics. The mass, Q, (or chain of masses) of the heat bath needs to be adjusted to the simulated system.

– Langevin dynamics

Two force terms have been added: a dampening factor and a random collision term.

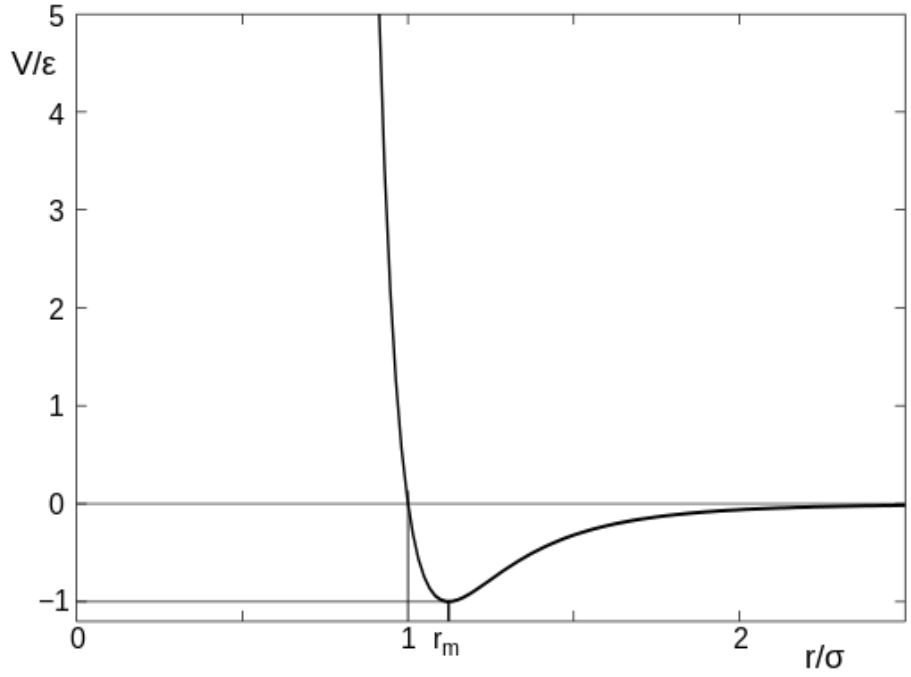
The different parts of MD:
- Atomic forces

- DFT
- Classical potentials
  - Lennard-Jones
  - EAM
  - Bond-order potentials
  - …

Lennard-Jones potential

$$U_i(r) = 4\varepsilon\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right)$$

- Potential only depends on the distance, r, between atoms
- Attractive and repulsive force
- Two parameters, ε and σ
- Works well for noble gasses



Embedded Atom Method (EAM)

$$U_i(\boldsymbol{r}) = F_\alpha\left(\sum_{i\neq j}\rho_\beta(r_{ij})\right) + \frac{1}{2}\sum_{i\neq j}\varphi_{\alpha\beta}(r_{ij})$$

Pair interraction function

Contribution of atom type β in position $\boldsymbol{r}_j$ to the charge density in position $\boldsymbol{r}_i$

Embedding function for atom type α in position $\boldsymbol{r}_i$

EAM potential energy for atom *i* of type α

The embedded atom method includes contribution from both pair interraction and electron density.
Catches more of the interractions in metallic materials.

The different parts of MD:
- Integrate equations of motion

Different type of algoritms used. One of the most common is the Velocity Verlet integration:

Step 1: $\boldsymbol{v}_i(t+dt) = \boldsymbol{v}_i(t) + \frac{1}{2}(\boldsymbol{a}_i(t) + \boldsymbol{a}_i(t+dt))dt$

Step 2: $\boldsymbol{r}_i(t+dt) = \boldsymbol{r}_i(t) + \boldsymbol{v}_i(t)dt + \frac{1}{2}\boldsymbol{a}_i(t)dt^2$

Step 3: $\boldsymbol{a}_i(t+dt)\, m_i = \frac{\partial}{\partial \boldsymbol{r_i}(t+dt)} U$

$\boldsymbol{v}_i$ – velocity of atom i, $\boldsymbol{a}_i$ – acceleration of atom i,

$\boldsymbol{r}_i$ – possition of atom i, dt – time step,

U – interaction potential

Analysis methods

- RDF
- MSD
- VACF
- VSD
- …
- Trajectories
- Look at movie…

Radial Distribution Function

- Local environment
- Gives information on bonding and local structure
- Number of neigbours in each shell

$$g(r) = \frac{1}{N}\sum_{i=1}^{N}\frac{N_i(r, r+dr)}{\rho * 4\pi * r^2 * dr}$$

Mean Square Displacement

MSD shows if atoms are diffusing or not

$$\langle |\boldsymbol{r}(t) - \boldsymbol{r}(t_0)|^2 \rangle = \frac{1}{N\, N_{t_0}} \sum_{t_0=0}^{t_{d-max}} \sum_{i=1}^{N} |\boldsymbol{r}_i(t_0 + t) - \boldsymbol{r}_i(t_0)|^2$$

In the linear regime, the MSD can be fitted to the Einstein relation to get the diffusion coefficient, D

$$\langle |\boldsymbol{r}(t) - \boldsymbol{r}(t_0)|^2 \rangle = 6 * D * t + C \qquad \text{2D}$$

Velocity auto-correlation

Velocity auto-corralation function.

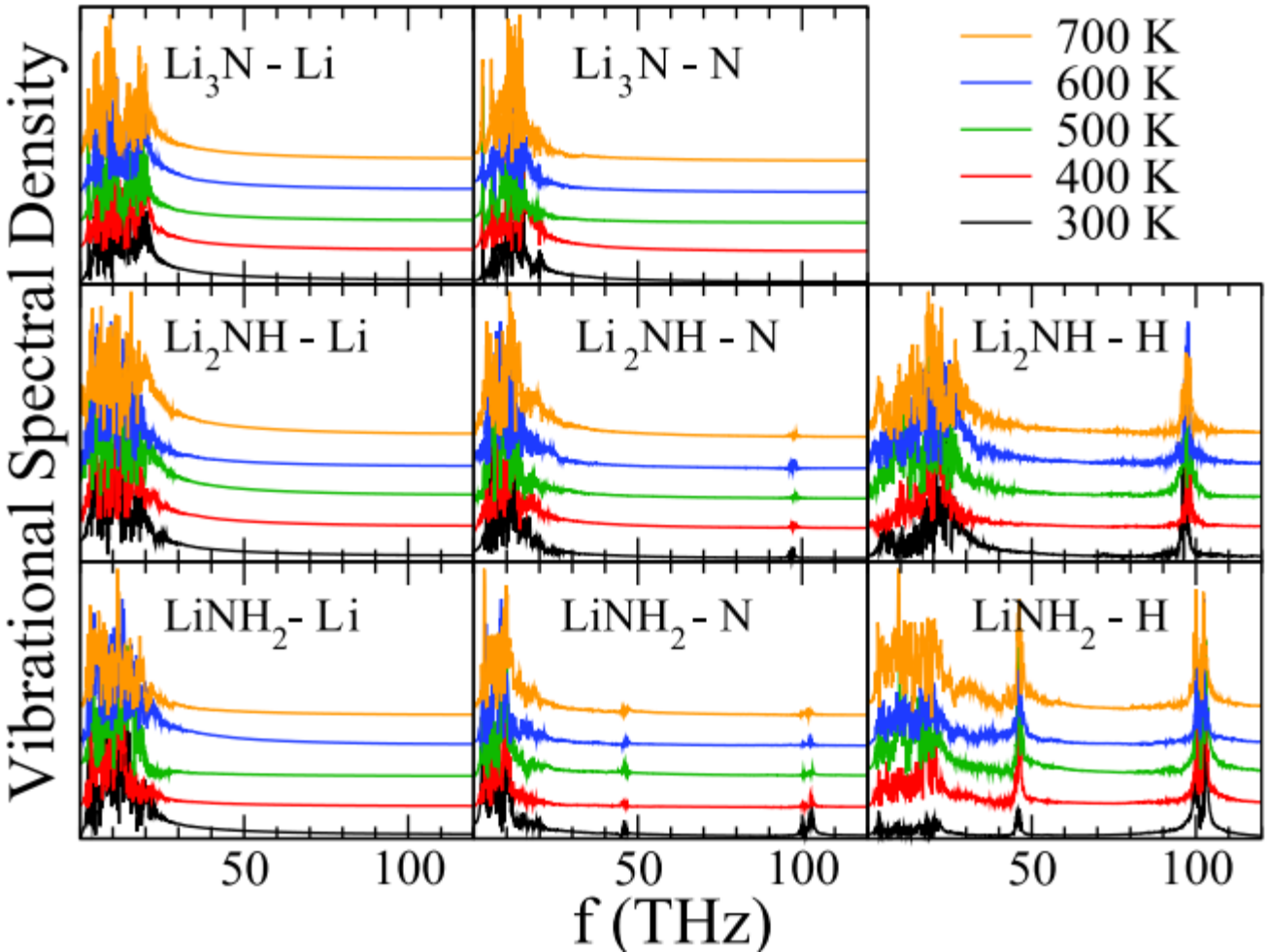
How the velocity of an atom is correlated over time

$$\Phi(t) = \frac{1}{N\, N_{t_0}(t)} \left\langle \sum_{t_0=0}^{N_{t_0}(t)} \sum_{i=1}^{N} \boldsymbol{v}_i(t_0) \cdot \boldsymbol{v}_i(t_0 + t) \right\rangle$$

A Fourier transform gives the vibrational spectral density

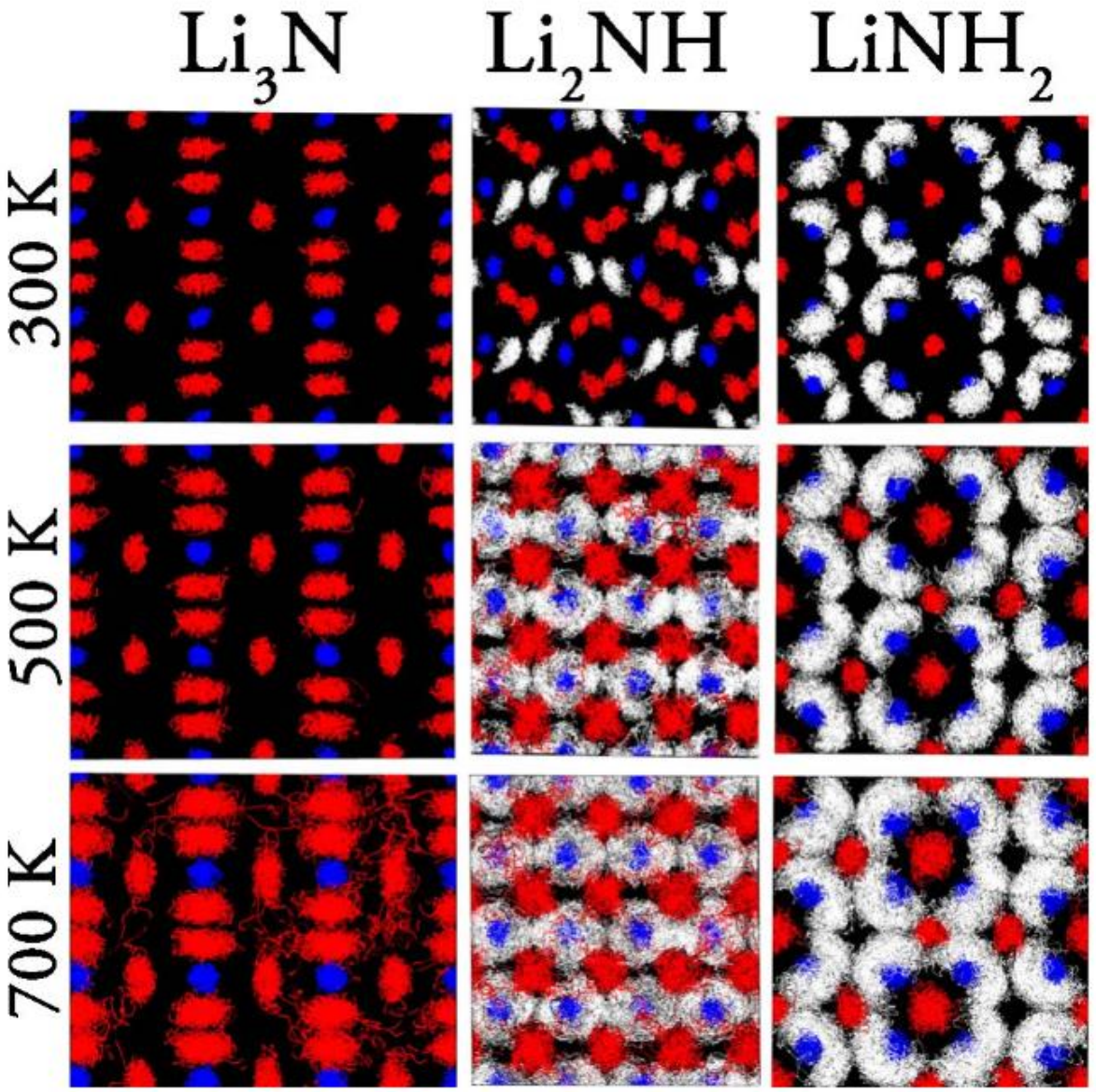
$$I(\omega) = \int_0^\infty e^{i\omega t} \Phi(t) dt$$

Example - Vibrational Spectral Density



Trajectories

Can give a good overview of what is happening



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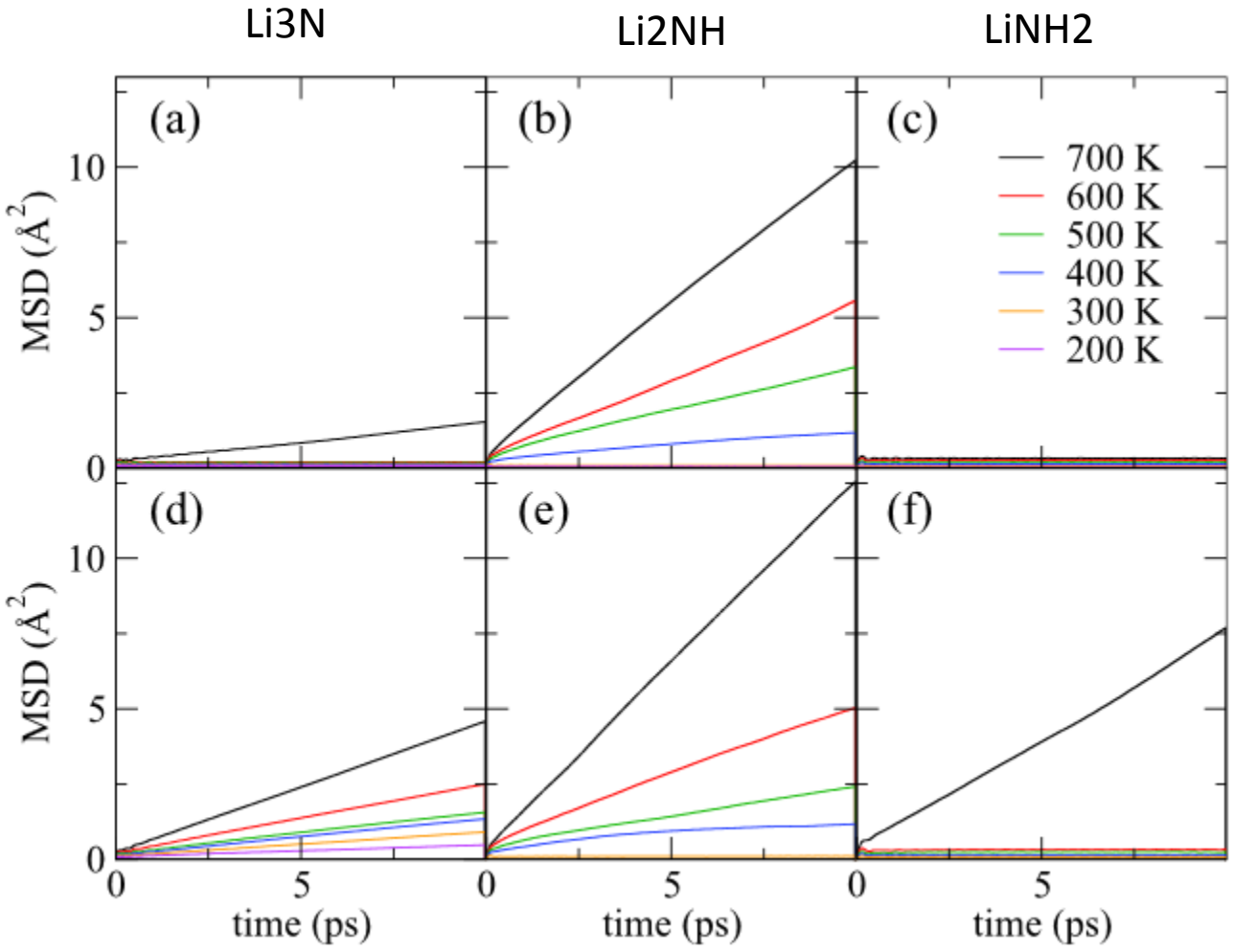
MSD for the same simulations



What could go wrong?

- Not thermalized simulation
- Energy leakage
- Boundary conditions
- …

Assignment

(I) Write a molecular dynamics code with:

- Velocity Verlet algoritm
- Force calculations using e.g. for example EAM or Lennard Jones potential
- (optional) thermostat

(II) Use the code to compute either a diffusion coefficient or a phase transformation temperature.

Visulization can either be integrated or using external tool like VMD (http://www.ks.uiuc.edu/Research/vmd/).

EAM potentials can be found at NIST (https://www.ctcms.nist.gov/potentials/).

Free choice of programming language.

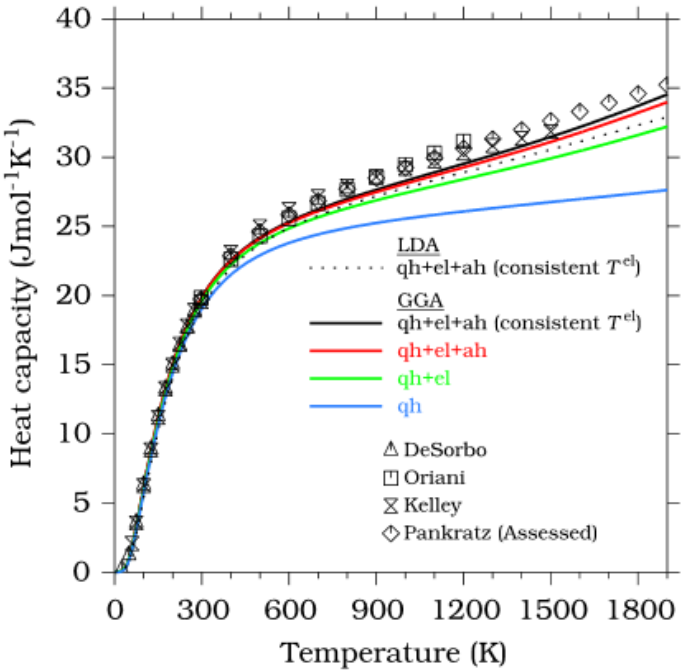
Examples

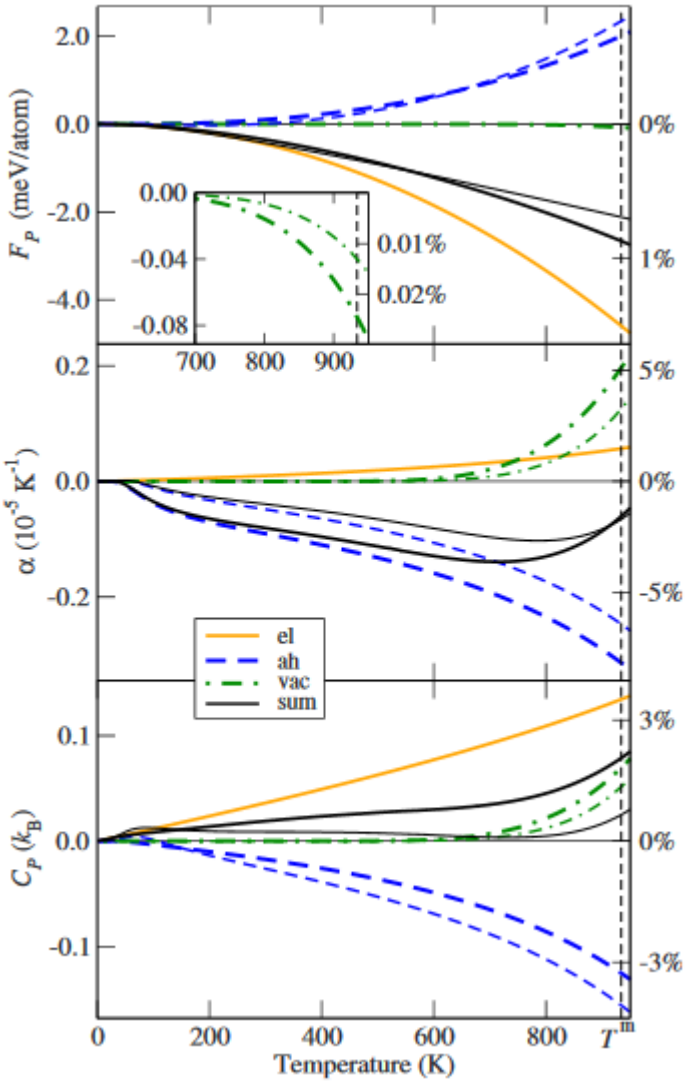
Ab initio up to the melting point: Anharmonicity and vacancies in aluminum

B. Grabowski, L. Ismer, T. Hickel, and J. Neugebauer
https://doi.org/10.1103/PhysRevB.79.134106

Finite temperature ab initio calculated thermodynamic properties of orthorhombic Cr3C2
B Kaplan, D Korbmacher, A Blomqvist, Blazej Grabowski

http://dx.doi.org/10.1016/j.calphad.2016.03.006





Temperature dependence of TiN elastic constants from ab initio molecular dynamics simulations

Peter Steneteg, Olle Hellman, Olga Yu. Vekilova, Nina Shulumba, Ferenc Tasnadi, and Igor A. Abrikosov

https://doi.org/10.1103/PhysRevB.87.094114

Lattice Vibrations Change the Solid Solubility of an Alloy at High Temperatures

Nina Shulumba, Olle Hellman, Zamaan Raza, Björn Alling, Jenifer Barrirero, Frank Mücklich, Igor A. Abrikosov, and Magnus Odén

https://doi.org/10.1103/PhysRevLett.117.205502