



MSE6701H, Multiscale Materials Modeling and Simulation

- Electronic DFT
- Atomistic MD
- Mesoscale PF

Lecture 09

Molecular Dynamics under T, P constraints

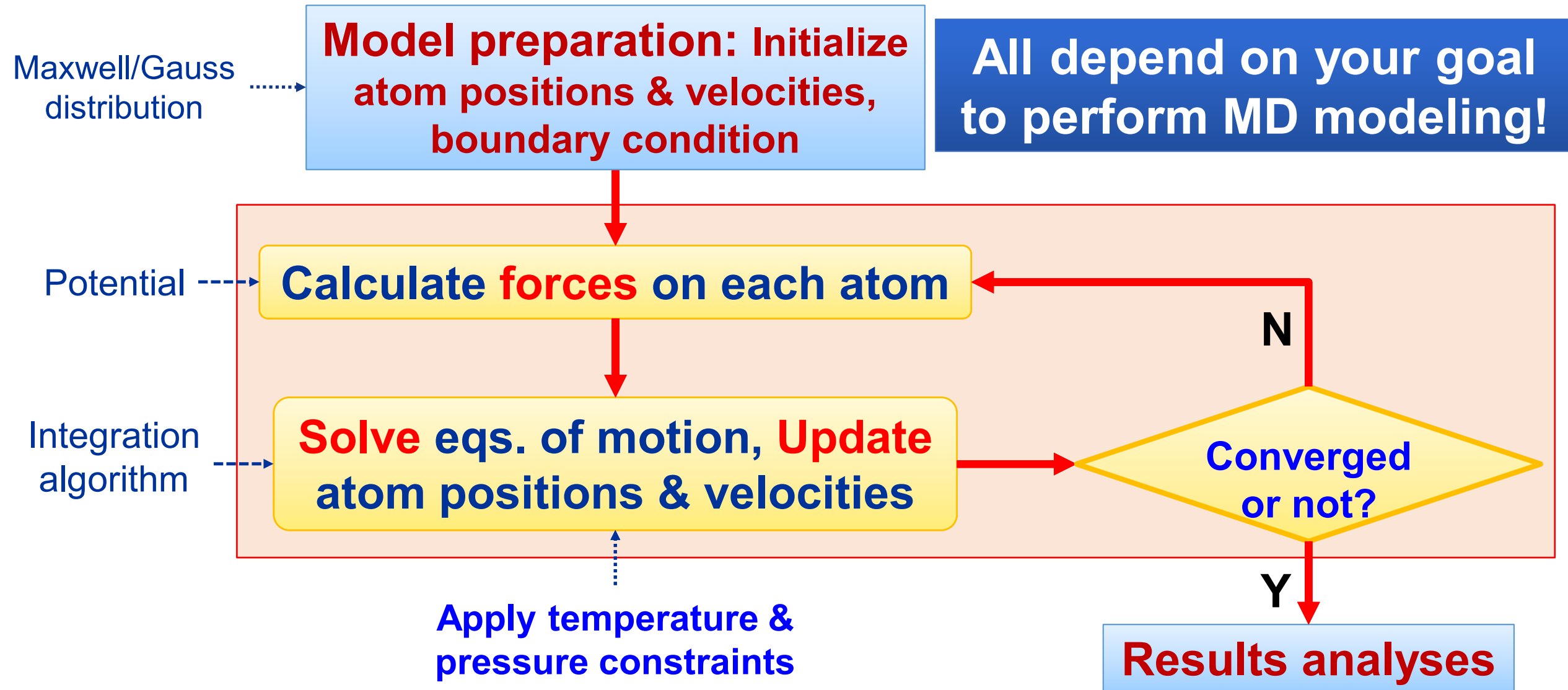
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2021.11.24

MD: overall flow chart

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➤ Goals

- Gain systematic knowledge on basic ideas of MD simulation.
- Apply MD to solve realistic issues in materials science & engineering.
- Apply MD to understand relationship between structure, mechanism and properties for typical problems in materials science & engineering.

Weeks	Contents
MD-1	✓ Development and algorithm
MD-2	✓ Interatomic potentials
MD-3	✓ Molecular Statics: energy minimization
*MD-4/5	• MD under T & P constraints; structure analyses
Experiments #1-2	1. Physical properties calculations: diffusion ... 2. Dislocation motion, plastic deformation

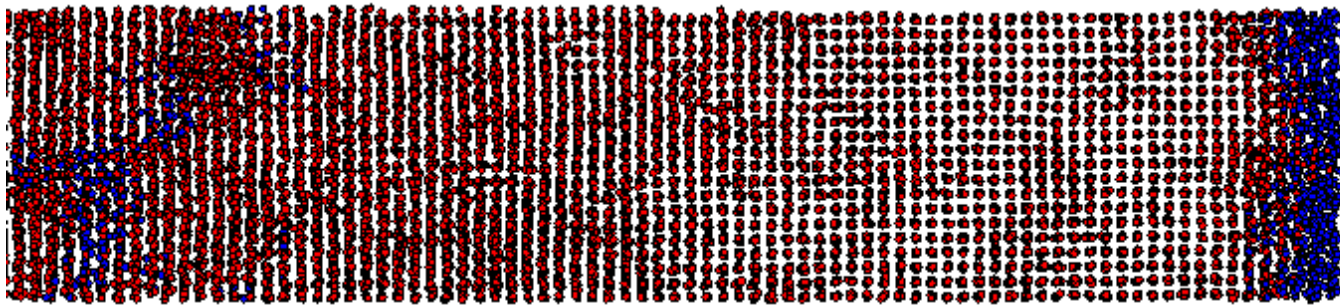
heterogeneous melting occurs near the back surface of the irradiated film

50 nm Ni Film

Absorbed Fluence: 430 J/m^2

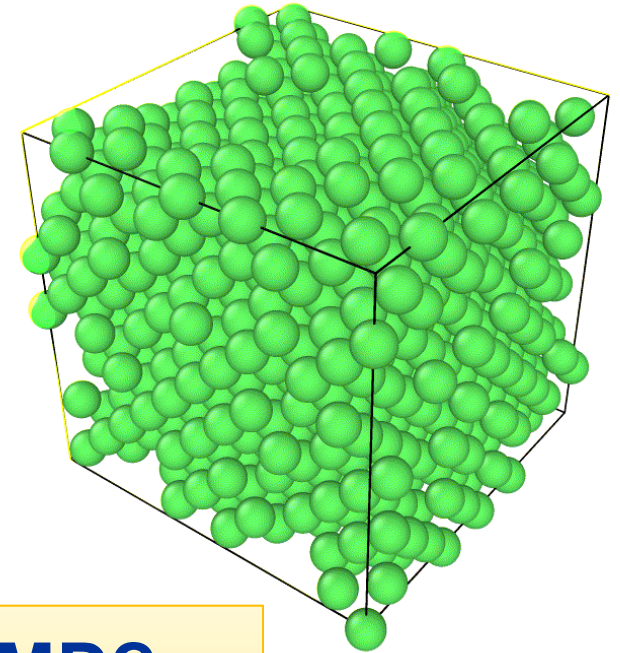
Depth: 38-55 nm

$t = 20 \text{ ps}$



http://ftp.aip.org/epaps/phys_rev_lett/E-PRLTAO-91-052334/

fcc-Al transforms to liquid as T increases



- **When & why control T in MD?**
- **How to control T in MD?**
- **How to characterize structures?**

1. Ensembles
2. Temperature control
 - Andersen method
 - Nose-Hoover thermostat
3. Structure analyses
4. Pressure control (next lecture)

➤ **Goals today**

- Tell when to control T, P
- Apply T constraints to specific problems
- Learn how to analyze crystal structures

Physically important conditions

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- ✓ Basic MD run under energy conservation: NVE
- 1. Biological reactions occur under constant Temperature: NVT
- 2. Chemical reactions occur open to atmosphere (P): NPT

- Properties of a system **depend on the applied constraints.**
 - each set of constraints corresponds to a different **ensemble**.

- **MD system**: microstate \leftrightarrow one point in $6N$ -dimensional $\{\mathbf{r}_i, \mathbf{p}_i\}$ space
 - observed macrostate = **time average**

$$E_{obs} = \langle E \rangle = \frac{1}{t_0} \int_0^{t_0} E(t') dt'$$

- **Statistical physics**: go through all the points in the phase space, but in an probabilistic way
 - macrostate = ensemble average

$$\langle E \rangle = \sum_{i=1}^{N_{\text{all}}} \rho_i E_i$$

ρ_i is **probability** density, depends on applied thermodynamic constraints!

➤ **Ergodicity: time average = ensemble average**

- Ideally, an ergodic system evolve long enough time will go through all points in $6N$ -dimensional $\{\mathbf{r}_i, \mathbf{p}_i\}$ space
- Realistically?
 - Some points are surrounded by high potential **energy barrier**

➤ Final state depends on the **certain thermodynamic constraints**

<https://svenschnieders.com/an-introduction-to-ergodicity/>

- Purpose
 - Go through all possible phase space efficiently
 - Obtain time averages = experimentally observed properties

- In MD, solving the Newton equation of motion = NVE ensemble

- How to simulate other important ensembles?
 - NVT, constant temperature
 - NPT, constant pressure

1.1 Microcanonical ensemble (NVE)

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- **NVE**: constant particle numbers N , volume V , and energy E .
- Equilibrium state
 - $E = K + U$ is constant
 - K and U fluctuate around their averages, thus T varies.
- **How?**
 - ✓ control E as a constant.

Completely isolated

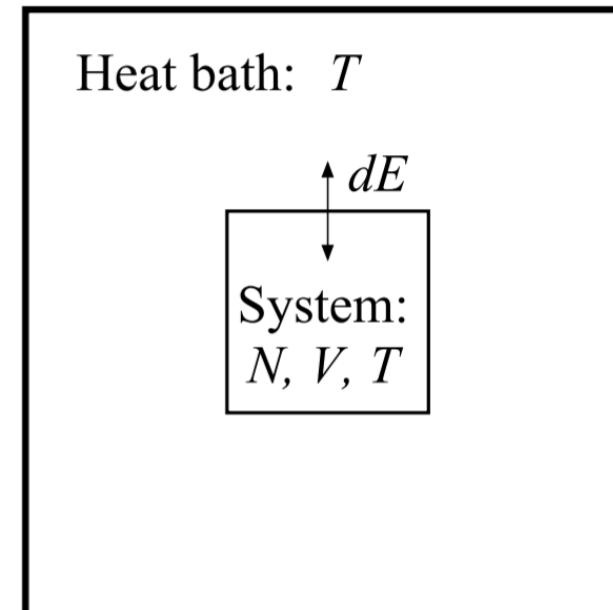
System:
 N, V, E

1.2 Canonical ensemble (NVT)

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- **NVT: Constant N , V & T , not isolated.** system is in contact with a heat bath of temperature T which is in equilibrium
 - **Energy exchange**, internal energy $dE \neq 0$, fluctuate
 - System (E_s) + bath (E_b) is isolated, but $E_s \ll E_b$

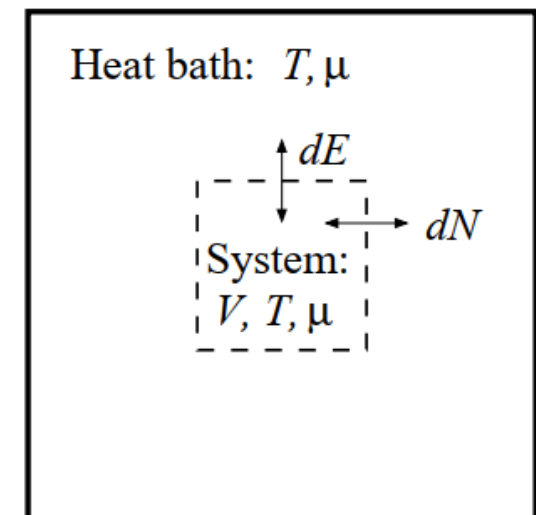
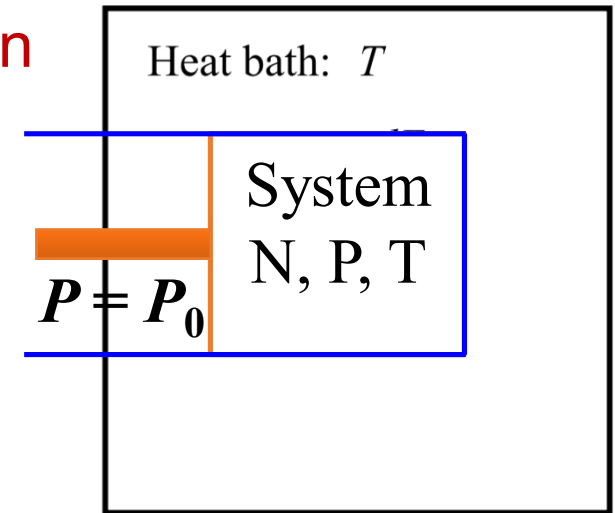
- **How?**
 - ✓ **Control T as a constant.**



1.3 other ensembles

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- Isobaric-isothermal ensemble NPT: constant pressure P and temp T
 - Common in lab constraints & phase transformation
 - Energy and volume fluctuate around mean value
- Grand canonical ensemble μVT
 - constant chemical potential μ .
 - N, P, E fluctuate
 - Effective in alloy design, particles are discrete

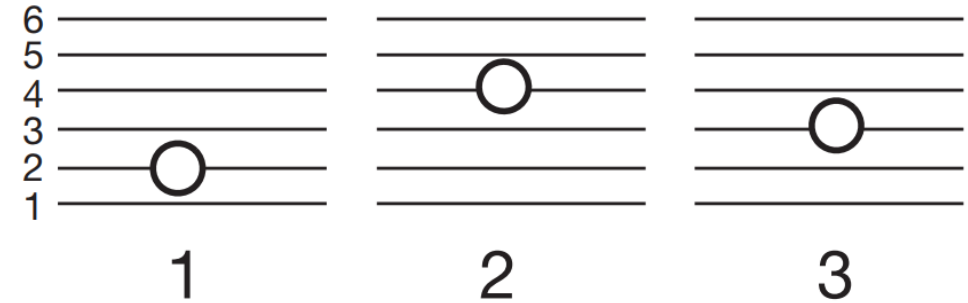


Example: *NVT* vs. *NVE*

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- A system of 3 atoms, with 6 possible energy levels: $E_n = ne_0$.

- Each microstate $\{E_1, E_2, E_3\}$
- Total $E = E_1 + E_2 + E_3$



- If *NVE*: e.g. total $E = 9e_0$
 - Microstate such as $\{2, 3, 4\}$, $\{3, 3, 3\}$ etc. has equal probability
 - Increase E , number of microstates rapidly increase. **Entropy?**
- If *NVT*
 - All energy states are possible, but probability is not equal
 - Probability $\propto \exp(-E_\alpha/k_B T)$

- For a given system of N atoms
 1. To approach thermo-states assembling the microcanonical (NVE) ensemble, you need to control (?)
 2. To approach thermo-states assembling the canonical (NVT) ensemble, you need to control (?)
 - A. Temperature
 - B. Internal energy
 3. How to define the temperature for a system of N atoms?

✓ Solution to Newton's equation → NVE

- Basic MD run under NVE
- However, isolated system with constant E is uncommon.
- In lab condition, control T or P is easier than control energy

$$\begin{aligned}\dot{\mathbf{r}}_i &= \mathbf{p}_i / m_i \\ \dot{\mathbf{p}}_i &= m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i\end{aligned}$$

➤ Physical ensembles

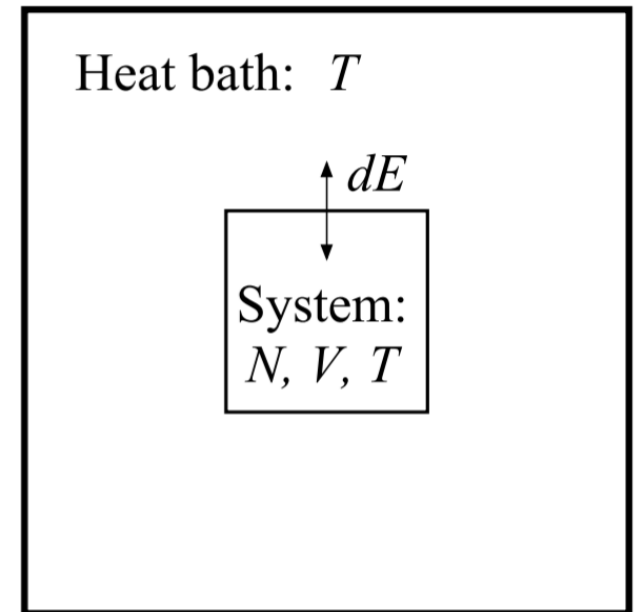
1. **Biological reactions occur under constant Temperature: NVT**
2. Chemical reactions occur open to atmosphere (P): NPT

1. Ensembles
2. Temperature control (NVT)
 - Andersen method
 - Nose-Hoover thermostat
3. Structure analyses
4. Pressure control

2.1 Thermostat: Andersen method

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- Exchange energy with surroundings: heat bath
- How: give the randomly selected atom (with some probability) **a new velocity** consistent with the **desired heat bath temperature**
- **Pros:** intuitive interpretation of NVT
- **Cons:** randomly assigned velocity is **unphysical** perturbation on the equation of motion for the selected atom



2.2 Thermostat: Nose-Hoover method (1)

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- **Idea:** Modify equation of motion to include a *non-Newtonian* term to maintain E_k .
- Constrained motion: $\ddot{\mathbf{r}}_i = \mathbf{F}_i / m_i - \lambda \dot{\mathbf{r}}_i$ artificial frictional force
 - λ : friction coefficient $\dot{\lambda} = (T(t) - T_0) / M_s \rightarrow 0$ means dynamics at steady
 - M_s : thermal “mass” that controls the rate of heat exchange with exterior

If $T > \text{desired } T_0$, λ increases \rightarrow velocity decreases, and vice versa
 $\rightarrow T$ fluctuates around desired T_0

2.2 Thermostat: Nose-Hoover method (2)

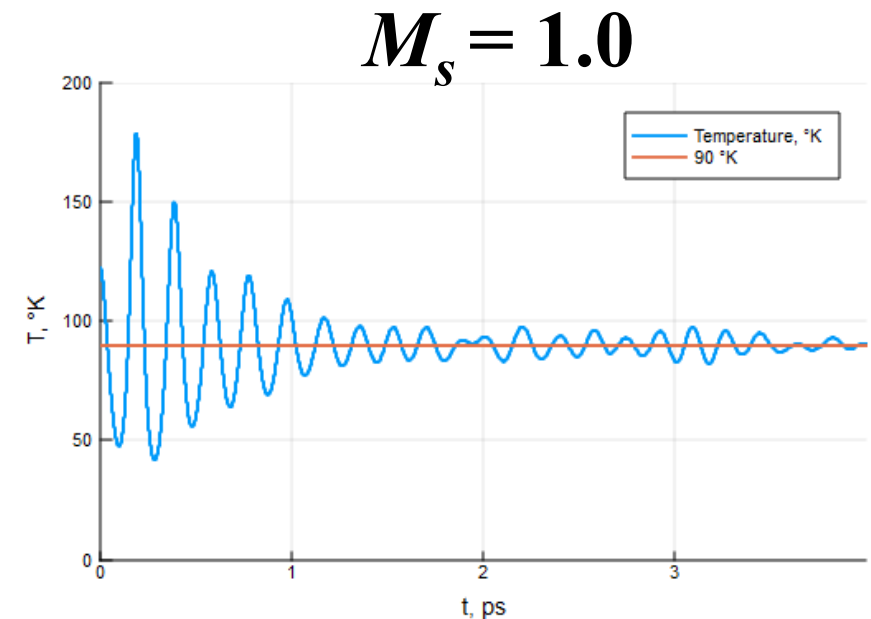
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➤ Pros

- leads to NVT (canonical distribution);
- The trajectories conserve the total energy of the *extended* system (\tilde{H})

➤ Cons

- Approach equilibrium: but oscillates (M_s)
- Large M_s : weak coupling with heat bath
- Small M_s : energy oscillate too much



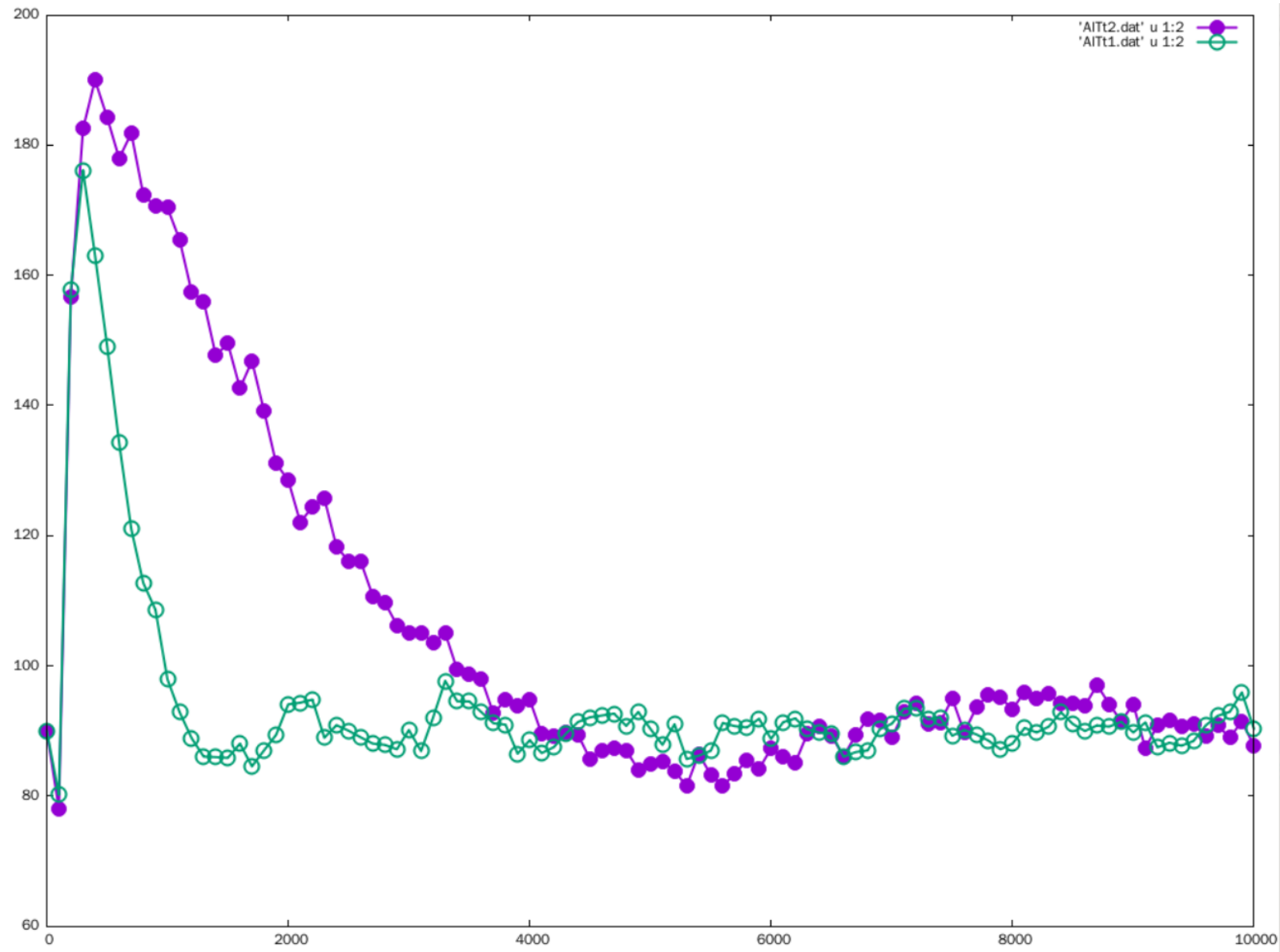
$$\tilde{H} = \sum_{i=1}^N \frac{1}{2} m_i |\mathbf{v}_i|^2 + U(\{\mathbf{r}_i\}) + \frac{1}{2} M_s \lambda^2 + 3 N k_B T \ln s$$

<http://www.acclab.helsinki.fi/~knordlun/moldyn/lecture06.pdf>

- **Don't control local T** when simulating thermal activated process.
- LAMMPS NVT: A Nose-Hoover thermostat will not work well for arbitrary values of *Tdamp*. If *Tdamp* is too small, the temperature can fluctuate wildly; if it is too large, the temperature will take a very long time to equilibrate. A good choice for many models is a *Tdamp* of around 100 timesteps. Note that this is NOT the same as 100 time units for most units settings.

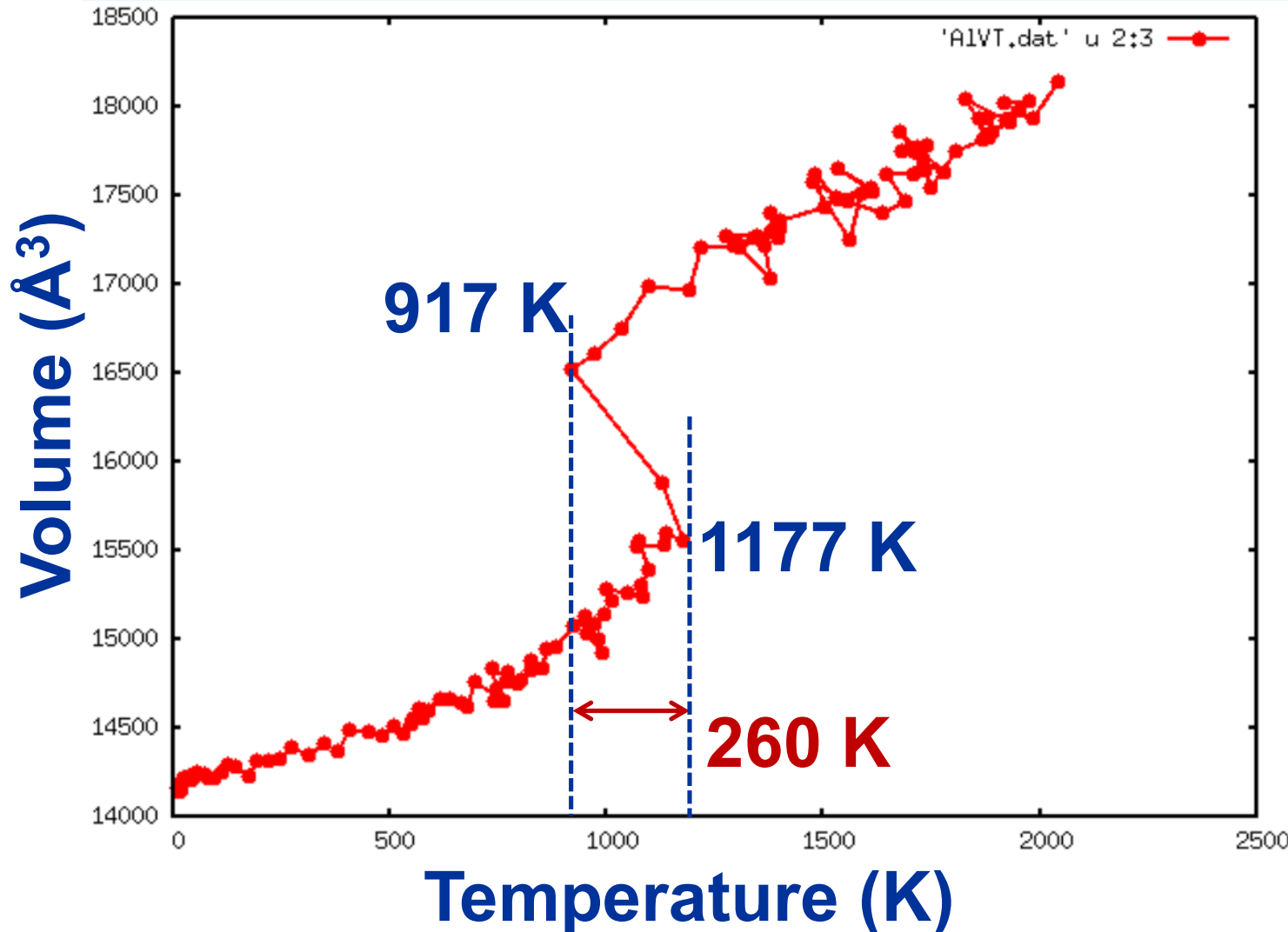
Example: effects of Tdamp

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Example: MD simulation of melting

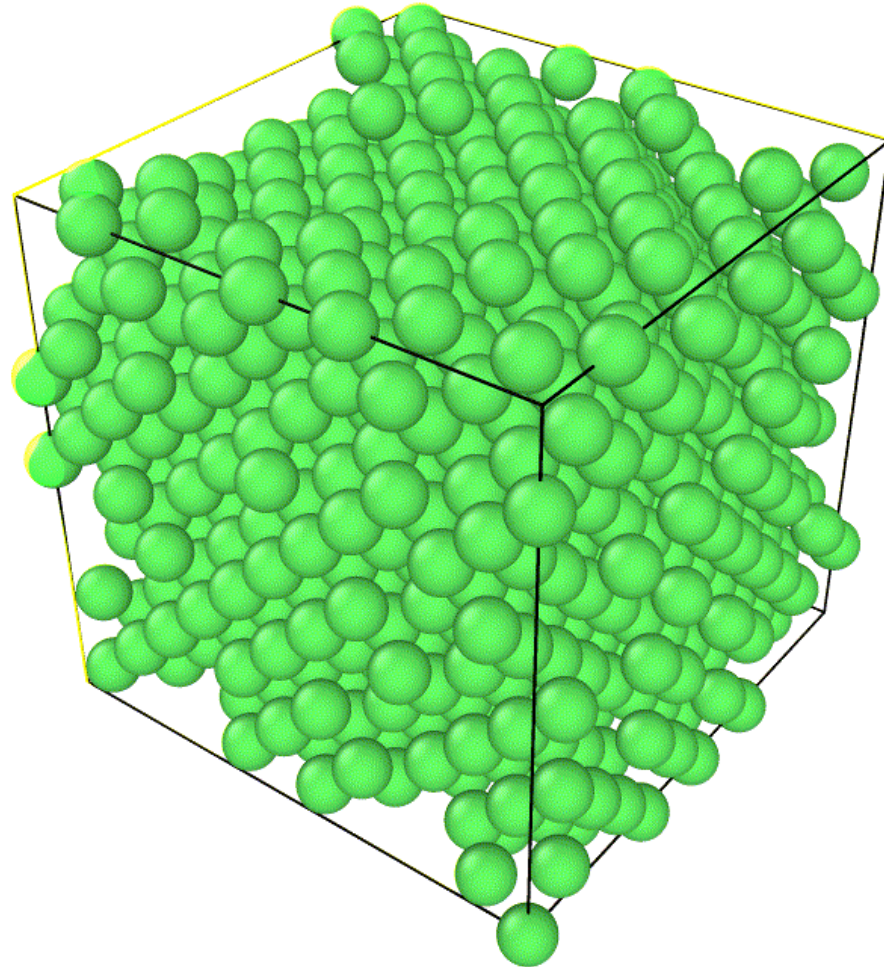
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1. PBC to simulate the bulk response
2. Experiments: melting starts at surface
3. Whole model starts to transform to liquid → instability. Requiring extra energy to overcome the energy barrier.

Structure with increasing Temperature

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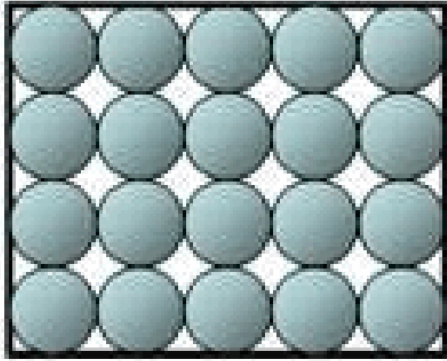


1. Ensembles
2. Temperature control (NVT)
 - Andersen method
 - Nose-Hoover thermostat
3. Structure analyses
4. Pressure control

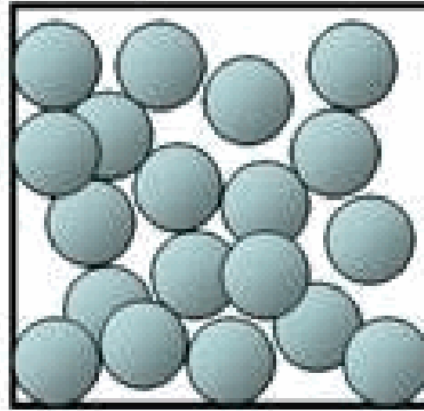
3.1 Why structure analyses

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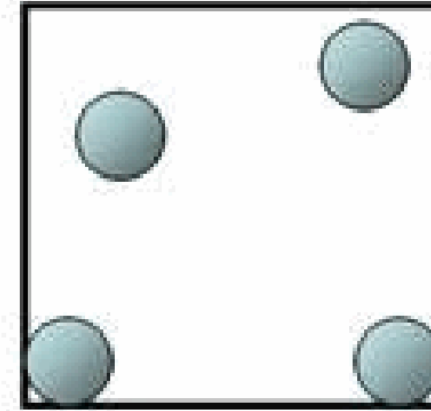
- When simulating phase transformation (melting)



Solid
Regular spacing



Liquid
Irregular spacing



Gas
More irregular spacing

- Concepts

- Measure distance of atoms to their neighbors
- Average over large number of atoms
- Average over time (MD) → structure evolution

3.2 Centro-Symmetry Parameter (1)

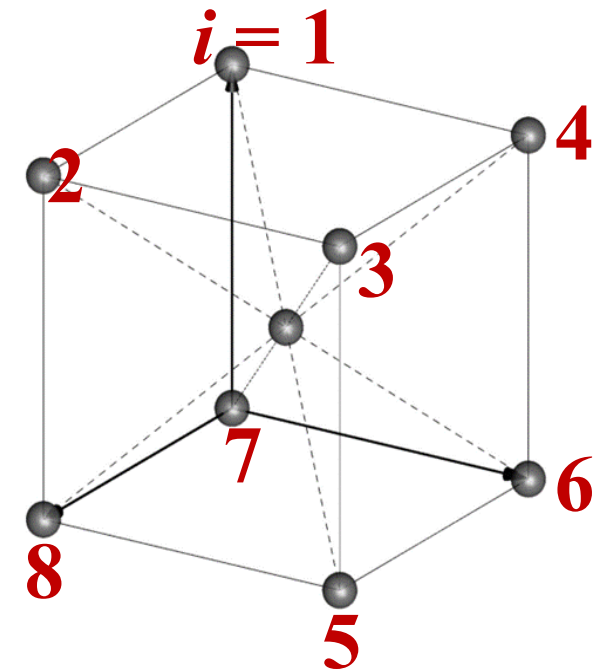
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➤ **Idea:** an atom possesses local centro-symmetry when for each of its neighbors at the relative position r , there is another neighbor at the relative position $-r$. (**inversion-symmetry** crystal, e.g. fcc, bcc ...)

➤ **How**

- $$\text{CSP} = \sum_{i=1}^{N/2} |\mathbf{r}_i + \mathbf{r}_{i+N/2}|^2$$

 N = number of nearest neighbors (NN)
- compute centro/atom



Kelchner, Plimpton, Hamilton, Phys Rev B, 58, 11085 (1998).

3.2 Centro-Symmetry Parameter (2)

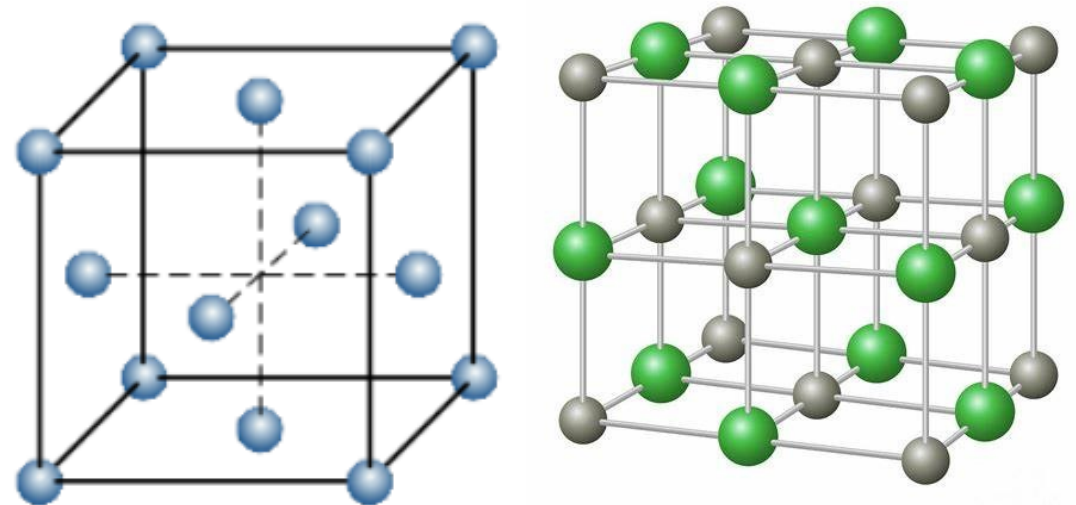
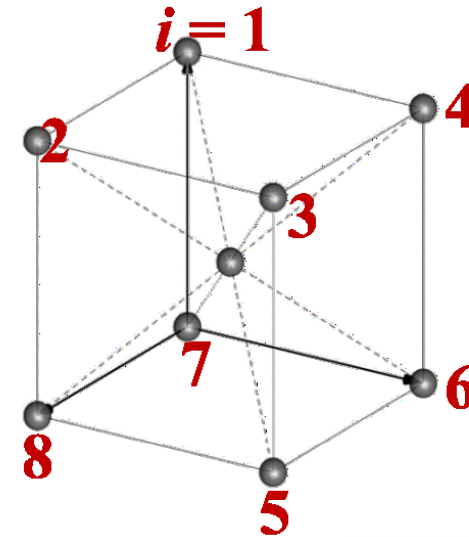
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$$\text{CSP} = \sum_{i=1}^{N/2} |\mathbf{r}_i + \mathbf{r}_{i+N/2}|^2$$

	BCC
Nearest neighbors (N)	8

Perfect crystal, CSP = ?

Whenever the local atomic arrangement deviates from the perfect crystal structure, the same two atoms may no longer be centro-symmetric. CSP ?



➤ RDF: pair distribution/correlation function

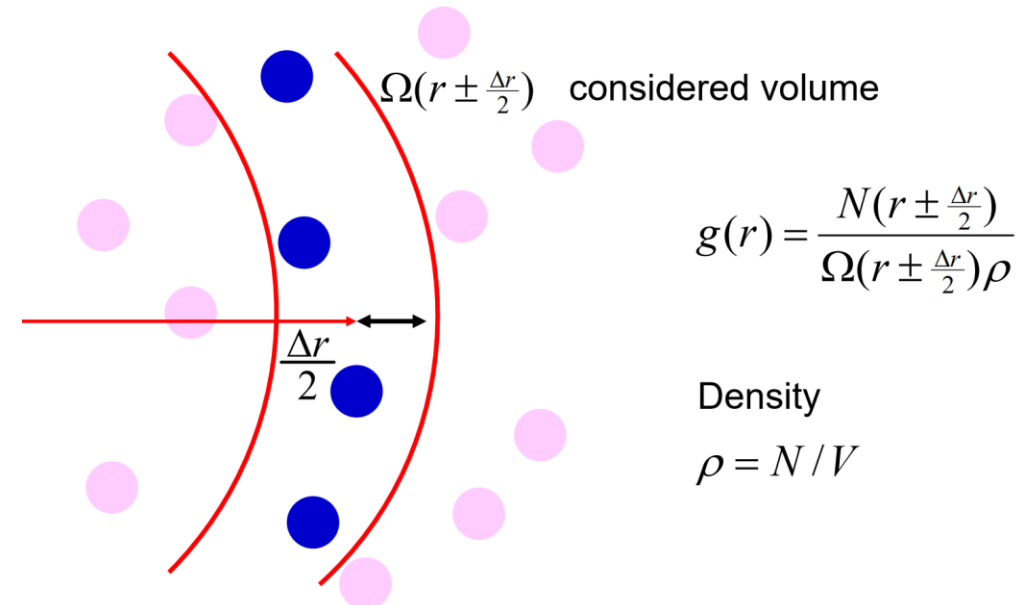
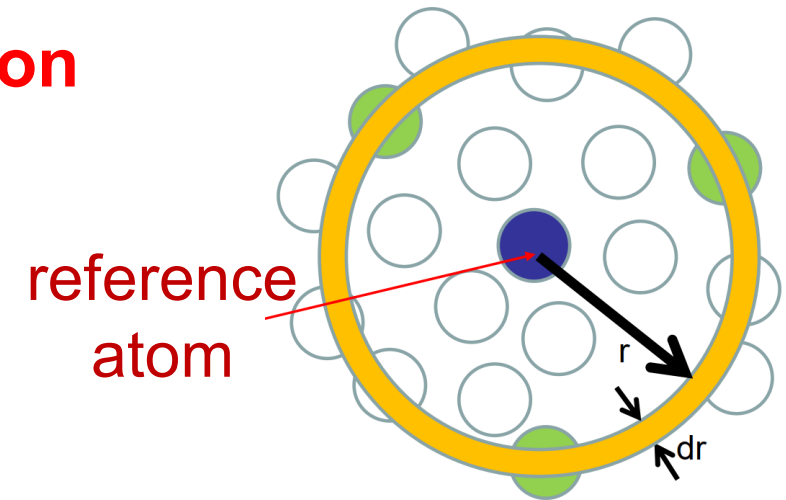
$$g(r) = \frac{\rho(r)}{\rho}$$

- $\rho(r)$: local density within Δr , $\Delta N/V_{\text{dr}}$
- ρ : overall density of atoms, N_{tot}/V
- Absolute value depends on Δr

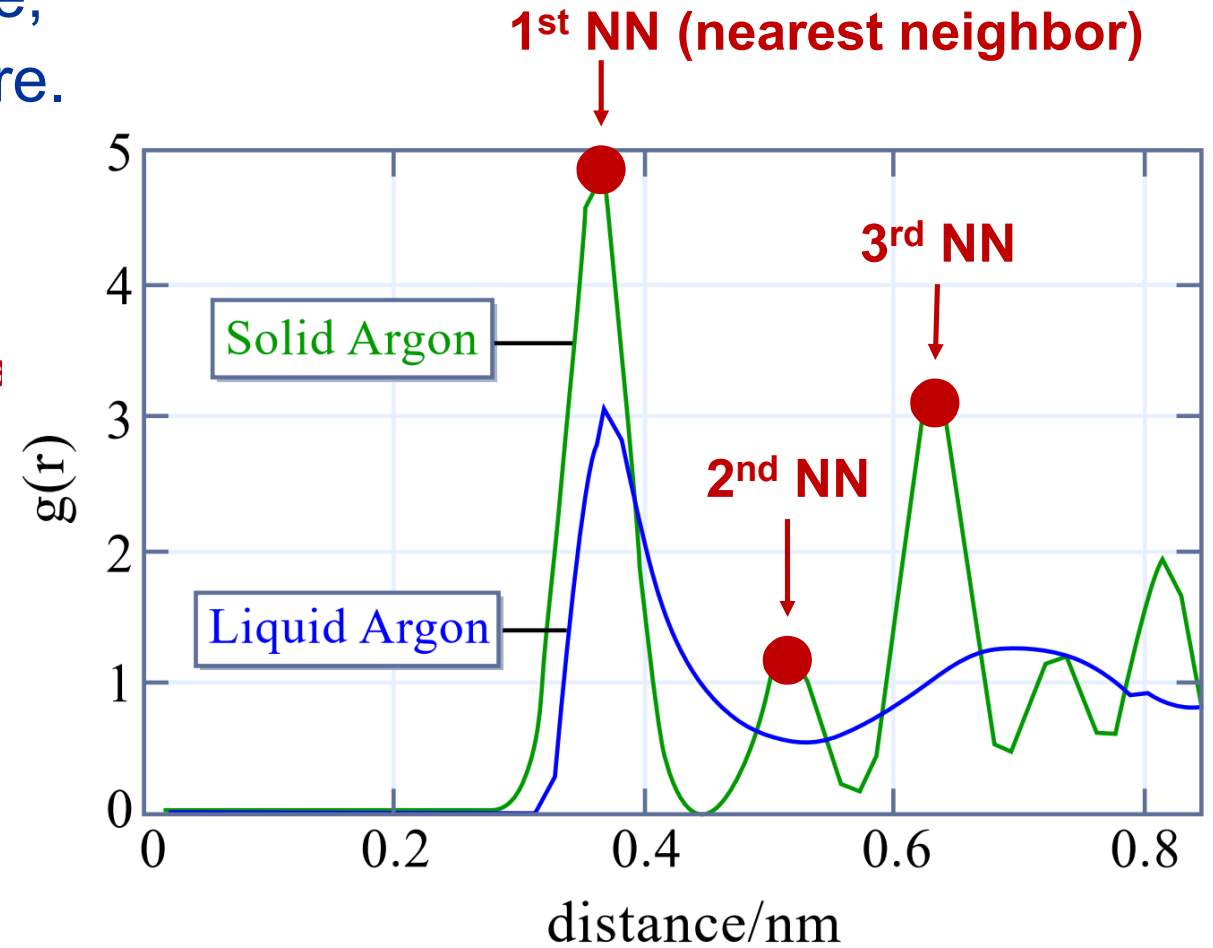
■ RDF can be measured experimentally

- x-ray or neutron-scattering

https://www.lptmc.jussieu.fr/user/mmi/IMI_lecture/lecture_5/OPEN_Micoulaut_lecture5_calculating_properties.pdf



- Peaks in RDF characterize NN distance, from which can infer the crystal structure.
- In fcc: 12, 6, 24 in first three shells.
- Comments about PDF
 - Describes how atoms are packed on **average**
 - Provide evolution of structure, but not about how fast atoms move.
 - **Instantaneous** disorder
 - compute rdf



$$1^{\text{st}} \text{ NN } r = a/\sqrt{2} = 0.38 \text{ nm}$$

3.4 Common Neighbor Analysis

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- **CNA:** atoms i and j are nearest neighbors if $r_{ij} \leq r_{\text{cut}}$.
compute cna/atom

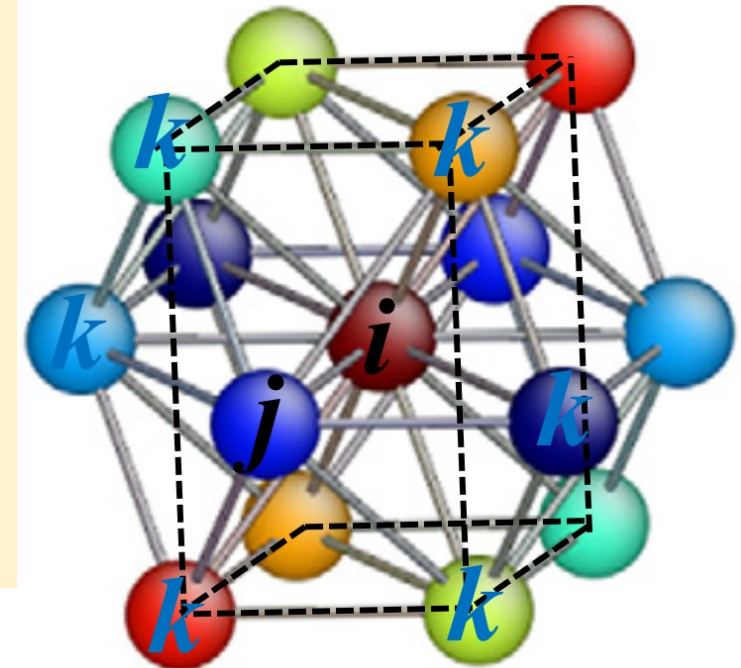
$$r_c^{fcc} = \frac{1}{2} \left(\frac{\sqrt{2}}{2} + 1 \right) a \simeq 0.8536 a$$

$$r_c^{bcc} = \frac{1}{2} (\sqrt{2} + 1) a \simeq 1.207 a$$

$$r_c^{hcp} = \frac{1}{2} \left(1 + \sqrt{\frac{4 + 2x^2}{3}} \right) a$$

- Starting with a pair of atom i – j , a set of four indexes (i-iv) is used to describe their common neighbors:
 - 1 or 2 indicates i and j are nearest neighbors (= 1) or not (= 2).
 - # of nearest neighbors k shared by the i – j pair (common neighbors)
 - # of bonds ($k \leftrightarrow k$) among the common neighbors
 - Differentiates diagrams with same (i-iii) and different bonding among common neighbors.

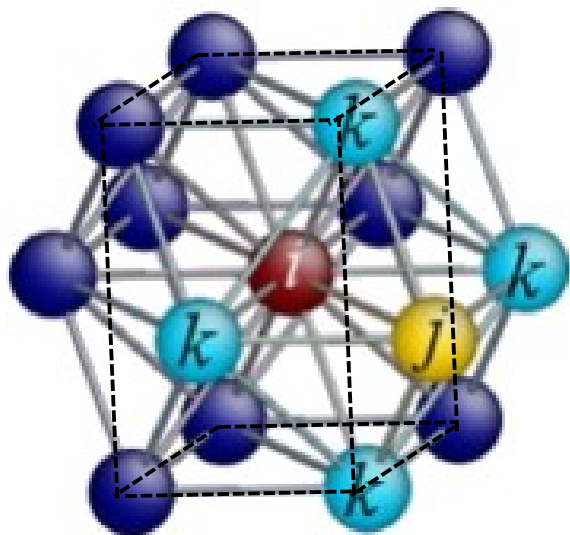
7 pairs, bcc: 1661



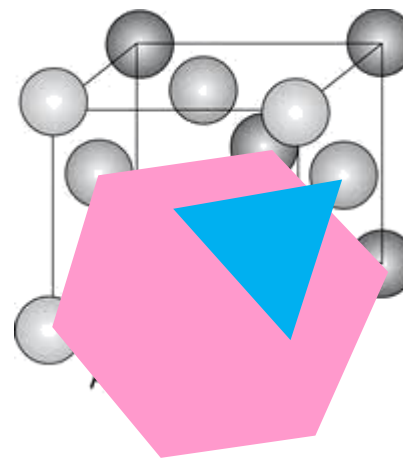
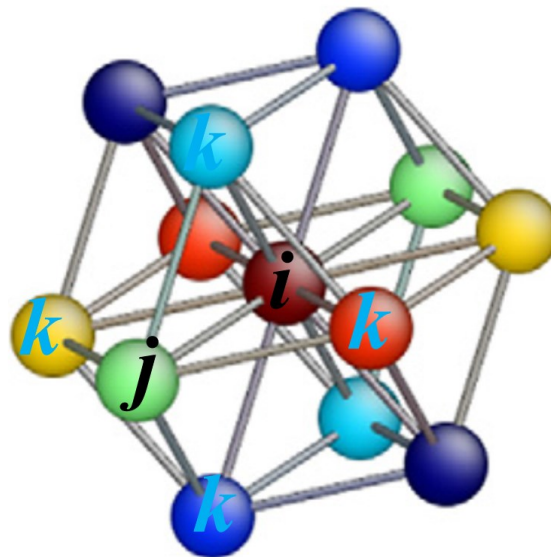
3.4 CNA analysis

- i. 1 or 2 indicates i and j are nearest neighbors ($= 1$) or not ($= 2$).
- ii. # of nearest neighbors k shared by the i - j pair (common neighbors)
- iii. # of bonds ($k \leftrightarrow k$) among the common neighbors
- iv. Differentiates diagrams with same (i-iii) and different bonding among common neighbors.

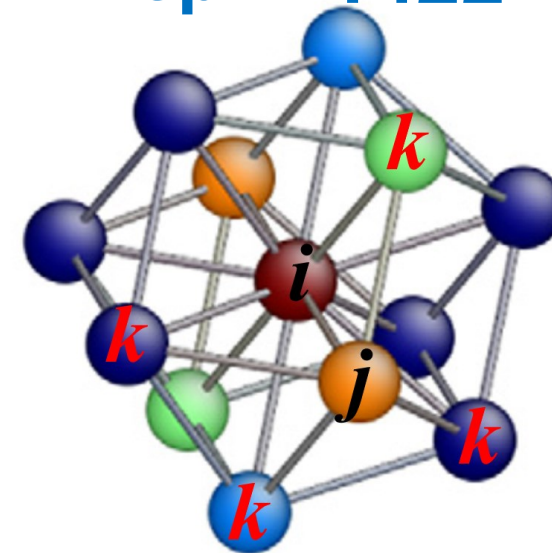
bcc: 1441



fcc: 1421



hcp: ? 1422



- Ensembles
- Temperature control
- Structure analyses

1. Numerical implementation of the Nose-Hoover equation of motion in updating position of atoms using velocity Verlet algorithm.
 2. Calculate melting point for Cu by MD using Mishin's EAM potential (2001), and compare it with reference. Visualize the structure using CSP and CNA analysis by OVITO.
- Due: Dec 1, 2021

Next Lecture:

Pressure (stress) control & MD Experiment #1



For continuous systems described by positions and momenta, the partition function takes the form

$$Q_{NVT} = \frac{1}{N!h^{3N}} \iint e^{-\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)/k_B T} d\mathbf{r}^N d\mathbf{p}^N, \quad (\text{G.14})$$

where the value of the Hamiltonian function $\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K(\mathbf{p}^N) + U(\mathbf{r}^N)$ is the total energy [223]. In Eq. (G.14), the limits of integration for the positional coordinates are such that they lie in the volume V . The components of the momenta can take on any values between $-\infty$ and ∞ .⁹

If the potential depends only on the positions,¹⁰ the integrals over momenta and positions are separable into a set of integrals over the momenta multiplied by a set of integrals over the positions. We can then evaluate the integrals over the momenta separately and, it turns out, analytically¹¹ and the partition function becomes

$$Q_{NVT} = \frac{1}{N!\Lambda^{3N}} \int e^{-U(\mathbf{r}^N)/k_B T} d\mathbf{r}^N, \quad (\text{G.15})$$

where $\Lambda = h/\sqrt{2\pi m k_B T}$ is the *thermal de Broglie wavelength*. The momenta thus do not appear directly in Q_{NVT} . For quantities that depend only on position, for example, the potential energy, averages take the form

$$\langle U \rangle = \frac{1}{Z_{NVT}} \int e^{-U(\mathbf{r}^N)/k_B T} U(\mathbf{r}^N) d\mathbf{r}^N, \quad (\text{G.16})$$

where the *configurational integral* is

$$Z_{NVT} = \int e^{-U(\mathbf{r}^N)/k_B T} d\mathbf{r}^N. \quad (\text{G.17})$$

Note that the de Broglie wavelength cancels out in Eq. (G.16).

1. Note averages in NVT satisfy

$$\langle K \rangle = \frac{\sum_{\alpha} \exp(-K_{\alpha}/k_B T) K_{\alpha}}{Q_{NVT}} = \frac{\int \exp\left(-\frac{K(\mathbf{p}^N)}{k_B T}\right) K(\mathbf{p}^N) d\mathbf{p}^N}{\int \exp\left(-\frac{K(\mathbf{p}^N)}{k_B T}\right) d\mathbf{p}^N}$$

2. $K(\mathbf{p}^N) = (p_x^2 + p_y^2 + p_z^2)/2m$

3. $\Rightarrow \langle K \rangle = \frac{3}{2} N k_B T$

The integrals over each coordinate of the momenta for each atom are $\int_{-\infty}^{\infty} \exp(-(p_x^2/2m)/k_B T) dp_x$. These are just Gaussian integrals of the form $\int_{-\infty}^{\infty} \exp(-ax^2) dx = \sqrt{\pi/a}$. Thus $\int_{-\infty}^{\infty} \exp(-(p_x^2/2m)/k_B T) dp_x = \sqrt{2\pi m k_B T}$ for each coordinate. For each atom we have three identical integrals multiplying each other, one for p_x , one for p_y , and one for p_z . Thus, the contribution from each atom is $(2\pi m k_B T)^{3/2}$. If all the atoms are the same, then we have a product of N such integrals, so the net contribution of K to the partition function is $(2\pi m k_B T)^{3N/2}$.