上海交通大學
材料科学与工程学院
School of Materials Science and Engineering, SJTU

MSE6701H Multiscale Materials Modeling and Simulation

Lecture 04

Molecular Statics & Temperature/Pressure Control

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Case study: Surface Energy

Surface energy:

excess energy associated with the presence of a surface.

$$\gamma = \frac{G_{\text{slab}} - G_{\text{bulk}}}{A_{\text{surface}}} \approx \frac{E_{\text{slab}} - E_{\text{bulk}}}{A_{\text{surface}}}$$

E_{slab}: total energy of system with surfaces

E_{bulk}: total energy of bulk system with same size as the slab

A_{surface}: surface area

Case study: Surface Energy

General steps:

① Calculate the total energy of bulk system.

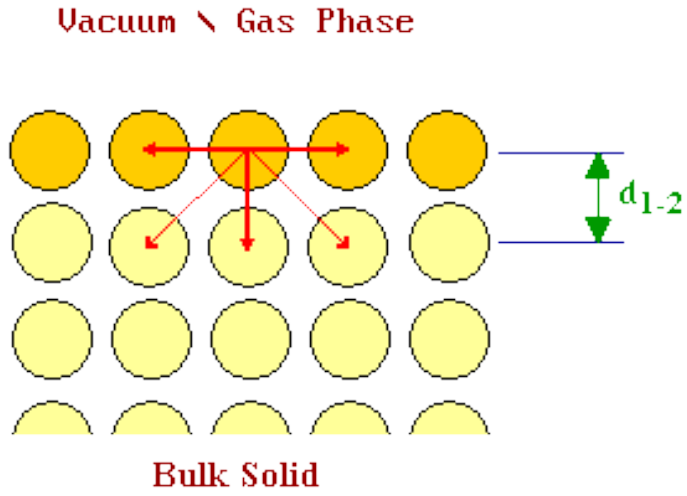
② Calculate the total energy of the slab system

a) Cleave a slab

b) Relax the slab

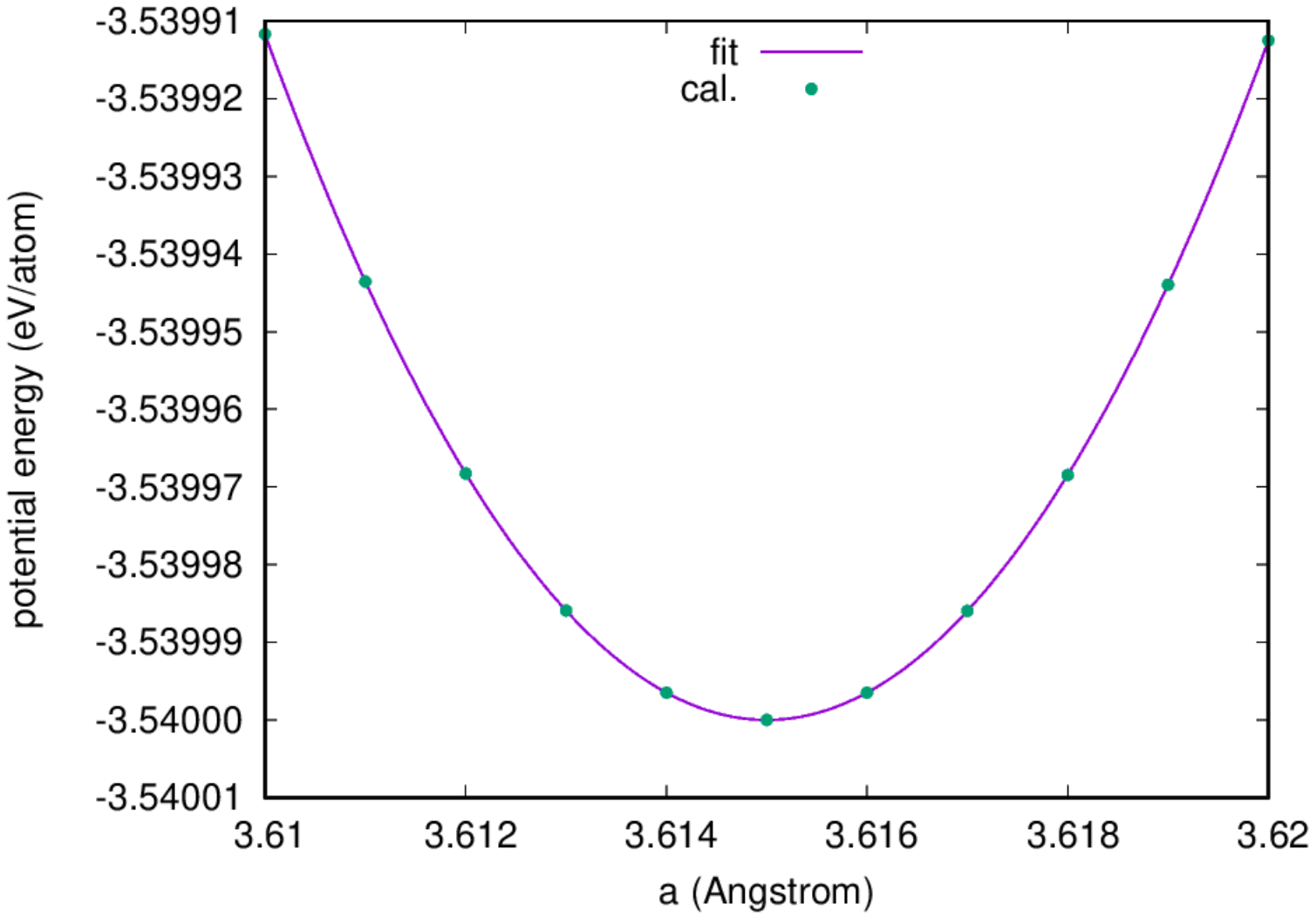
c) Get the total energy of the relaxed slab

③ Work out the surface energy



Total energy of bulk system

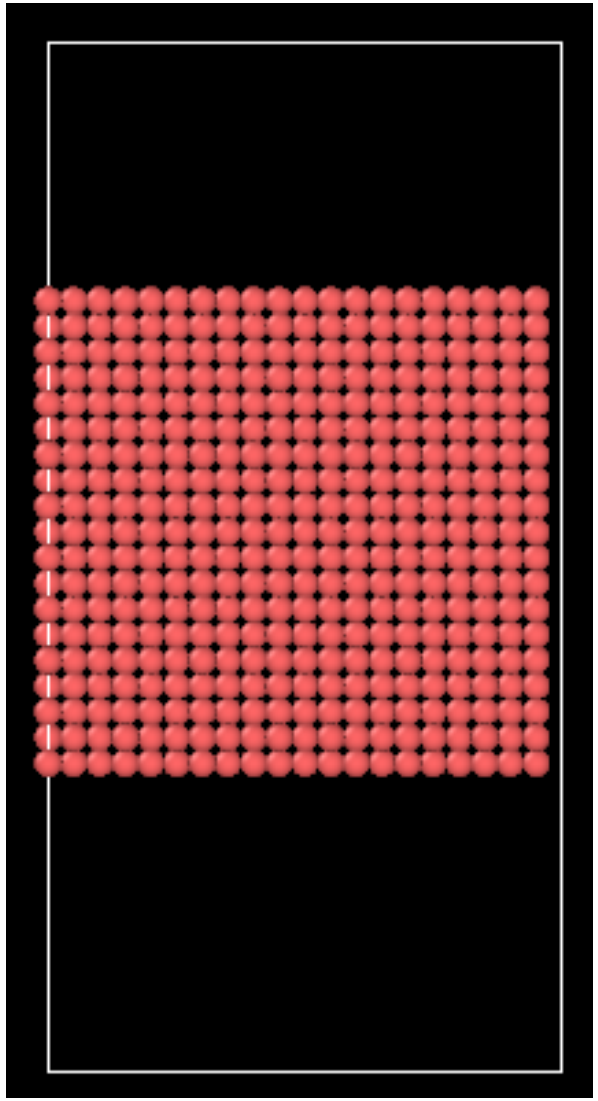
```
# LAMMPS input script for total energy calculation
units           metal
boundary        p p p
atom_style      atomic

lattice         fcc   3.615
region          box block 0 10 0 10 0 10
create_box      1 box
create_atoms    1 box

# Potential
pair_style      eam
pair_coeff      * * Cu_u6.eam

neighbor        0.2 bin
neigh_modify    delay 5

# Time step
timestep        0.001

# Variables to output
variable        vpa equal "vol / atoms"
variable        epa equal "pe  / atoms"

# MD
fix         1 all nve
run             0

# Output the energy
print       "${a} \${vpa} \${epa}" append ev.dat
```



a_0 = 3.615 Å, E_0 = -3.54 eV/atom

Slab cleavage

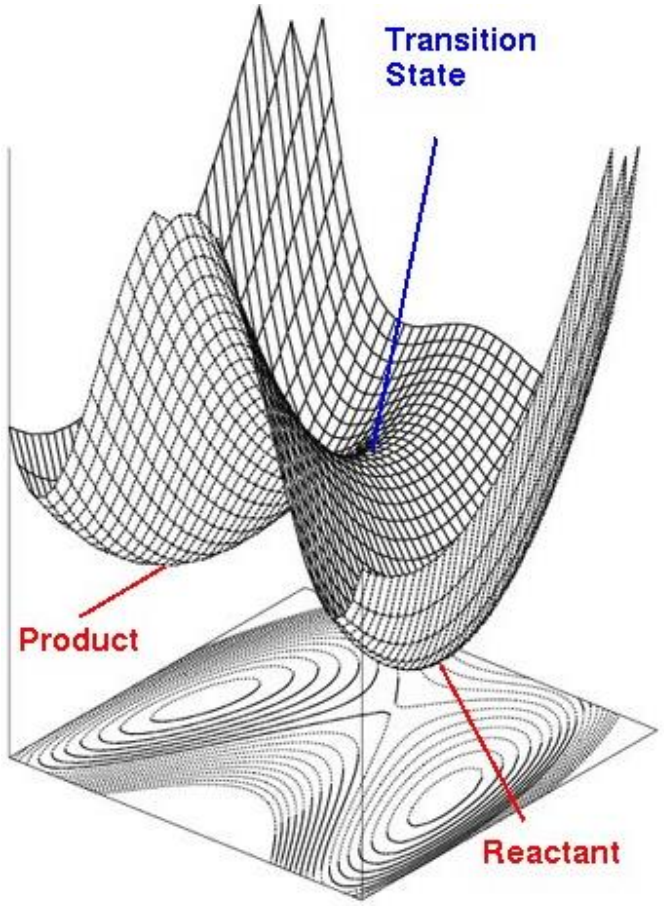
```
# Relaxation of Cu(001) surface
units         metal
boundary      p p p
atom_style    atomic

lattice       fcc 3.615
region        box  block 0 10 0 10 0 20
region        fill block 0 10 0 10 6 14
create_box    1 box
create_atoms  1 region fill

# Potential
pair_style    eam
pair_coeff    * * Cu_u6.eam

neighbor      0.2 bin
neigh_modify  delay 5

# Variables to output
variable      area equal "2.* lx * ly"
variable      delE equal "pe + atoms * 3.54"

# Thermal and trajectory
thermo_style  custom step pe pxx pyy pzz
thermo        10

dump          1 all atom 1000 dump.lammpstrj

# Minimization
min_style     cg
minimize      1e-12 1e-12 1000 10000
```



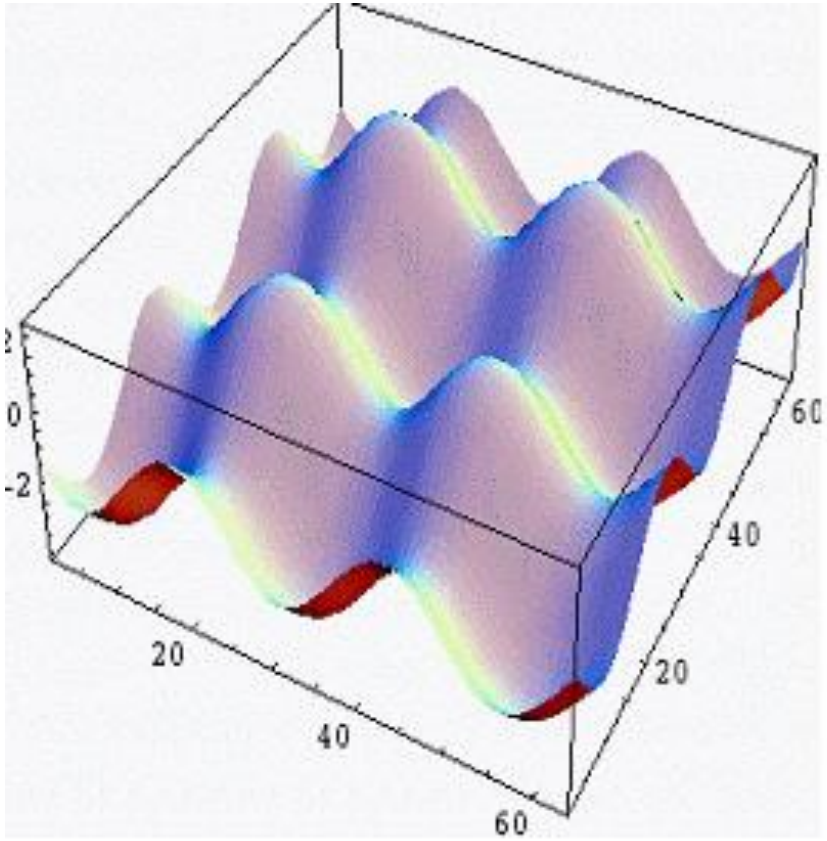
Other tools to create models

- ase
- pymatgen
- atomsk
- latgen
- ……

Minimization/optimization



$E(x)$



- Local minimum
- Global minimum
- Saddle point (transition state)

Minimization/optimization (Local)

$$E(x+\delta x) = E(x) + G(x)\delta x + \frac{1}{2}H(x)\delta x^2 + \ldots$$

Gradient **Hessian**

Force **Modulus**

Minimum:

$$\frac{\mathrm{d}\Delta E(x)}{\mathrm{d}\delta x} = 0$$

$$\frac{\mathrm{d}\left[E(x+\delta x) - E(x)\right]}{\mathrm{d}\delta x} \approx G(x) + H(x)\delta x = 0$$

$$\delta x = -\alpha H^{-1}(x) \cdot G(x)$$

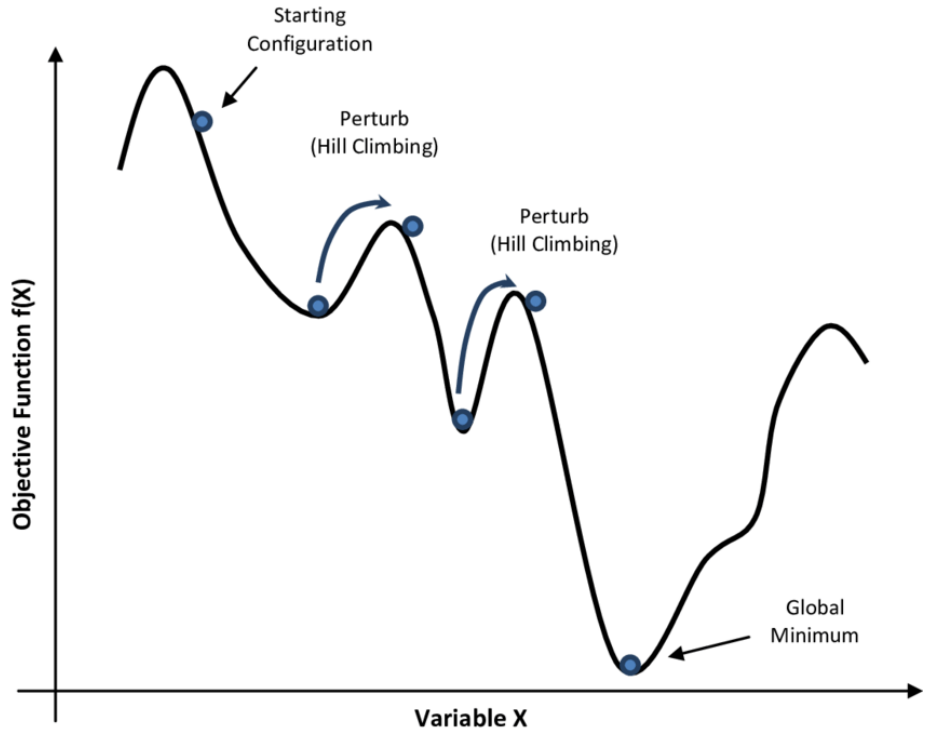
Local minimization algorithms

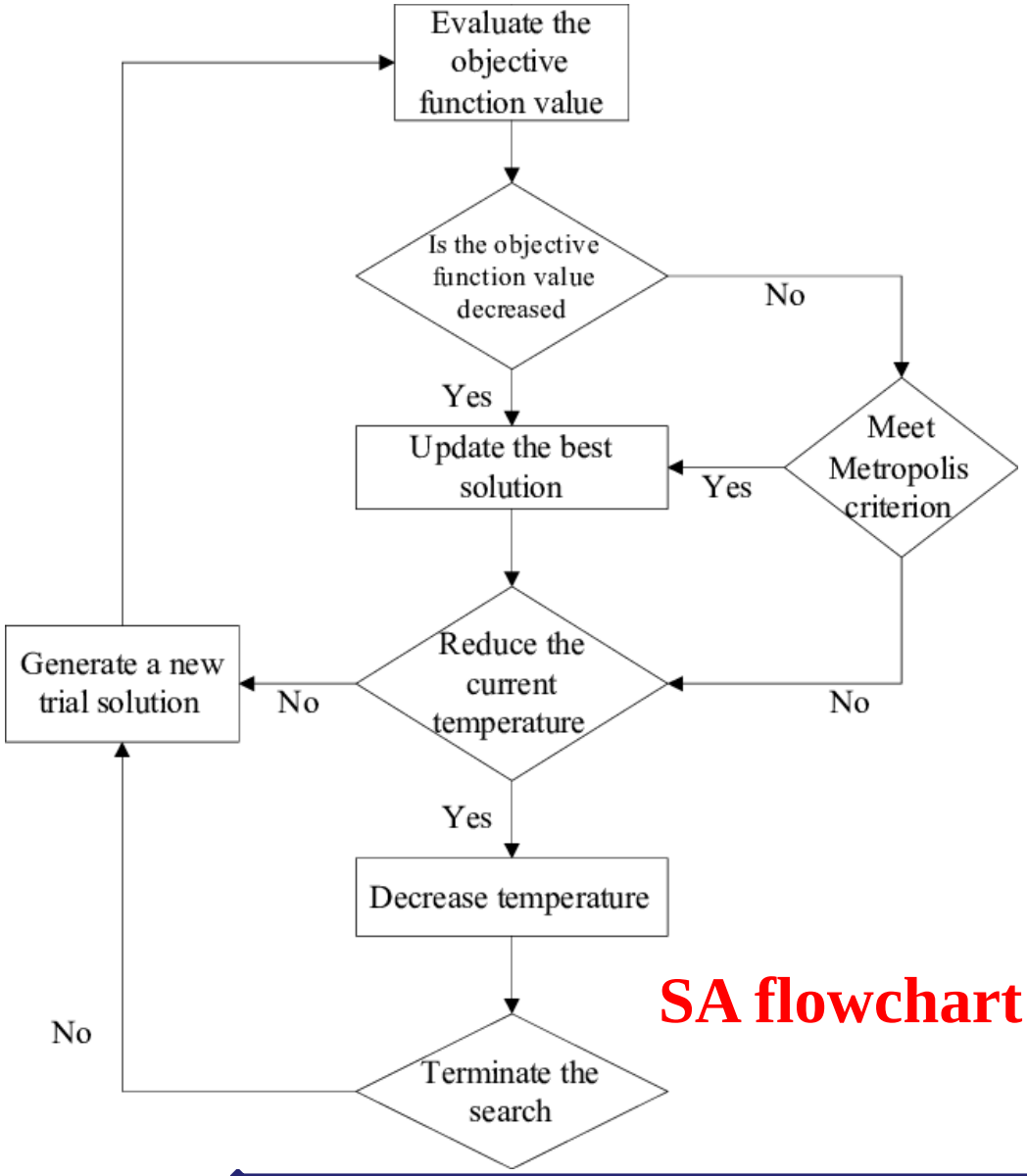
- **Energy and first derivatives based (forces)**
  - **steepest descents** (robust but slow) — min_style sd
  - **conjugate gradients** (robust and faster than sd) — min_style cg
  - **Hessian-free truncated Newton algorithm** — min_style htfn
  - **Damped MD** (fast when far from equilibrium) — min_style quickmin / min_style fire

- **Energy, first and second derivatives based** (fast but not necessarily stable)
  - **Newton-Raphson**
  - **BFGS updating of Hessian (reduces inversions)**

Global minimization

- Simulated annealing (SA)
- Genetic algorithms (GA)
- Particle swarm optimization (PSO)



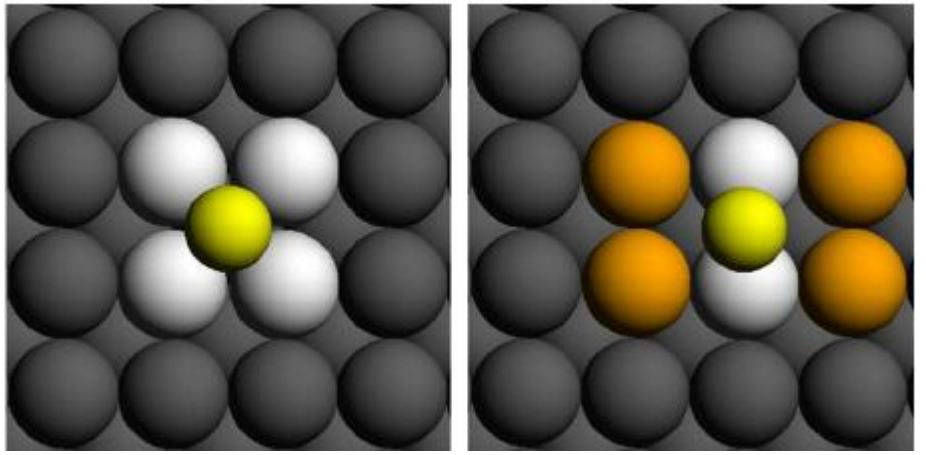


SA flowchart

Transition State Search

Transition State Theory

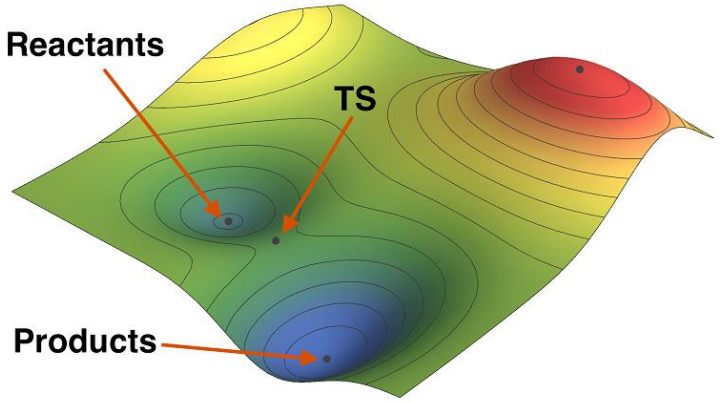
$$k = k_0 e^{-\frac{\Delta E}{k_B T}}$$



Stable Saddle

Methods:

- **Nudged Elastic Band (NEB)**
- **Dimer**
- **Activation-Relaxation-Technique (ARTn)**
- **….**



https://docs.lammps.org/neb.html

http://theory.cm.utexas.edu/vtsttools/neb.html

Case Study: Melting temperature

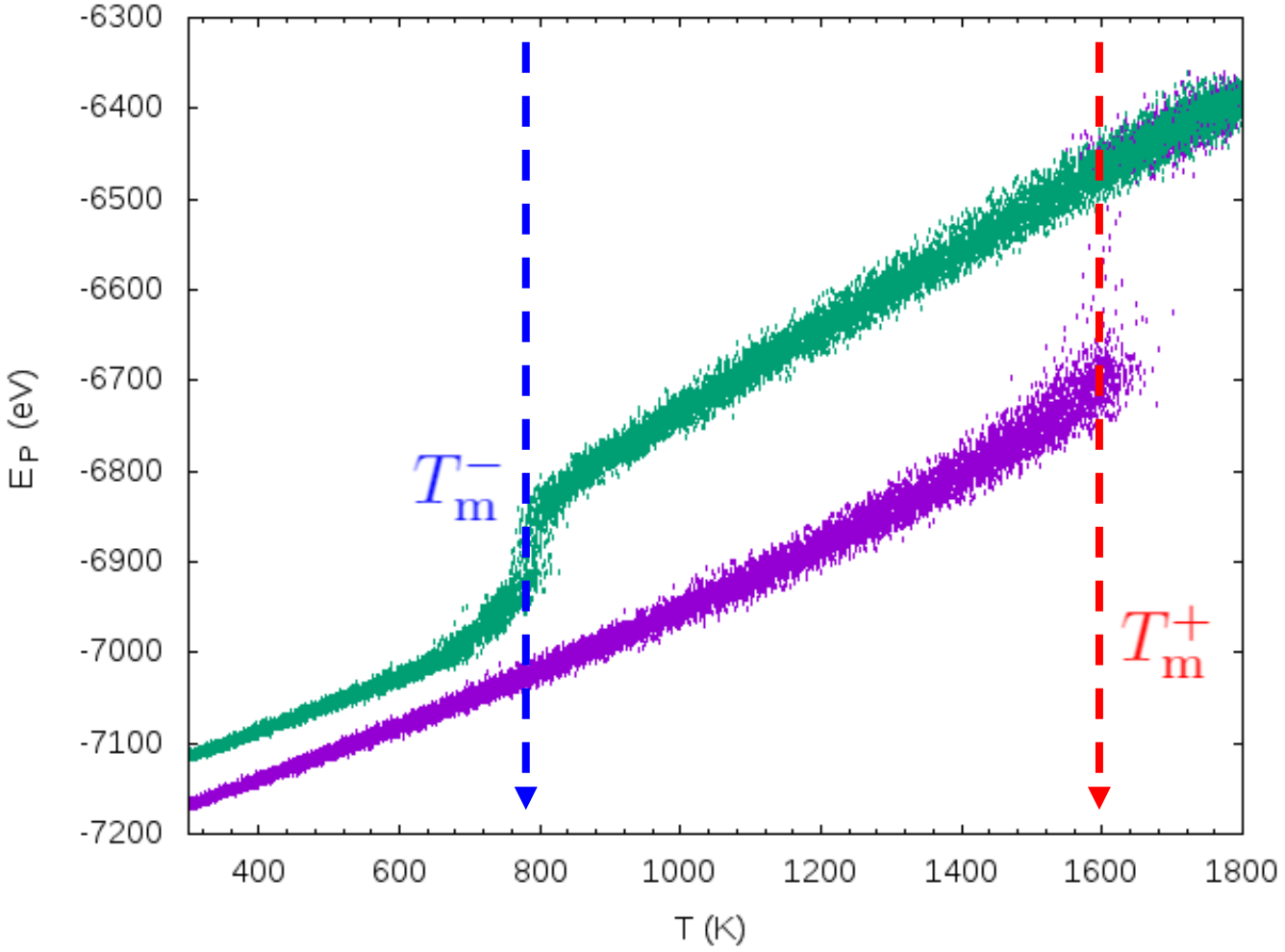
T_m of a solid is the temperature at which a substance changes state from solid to liquid at atmospheric pressure.

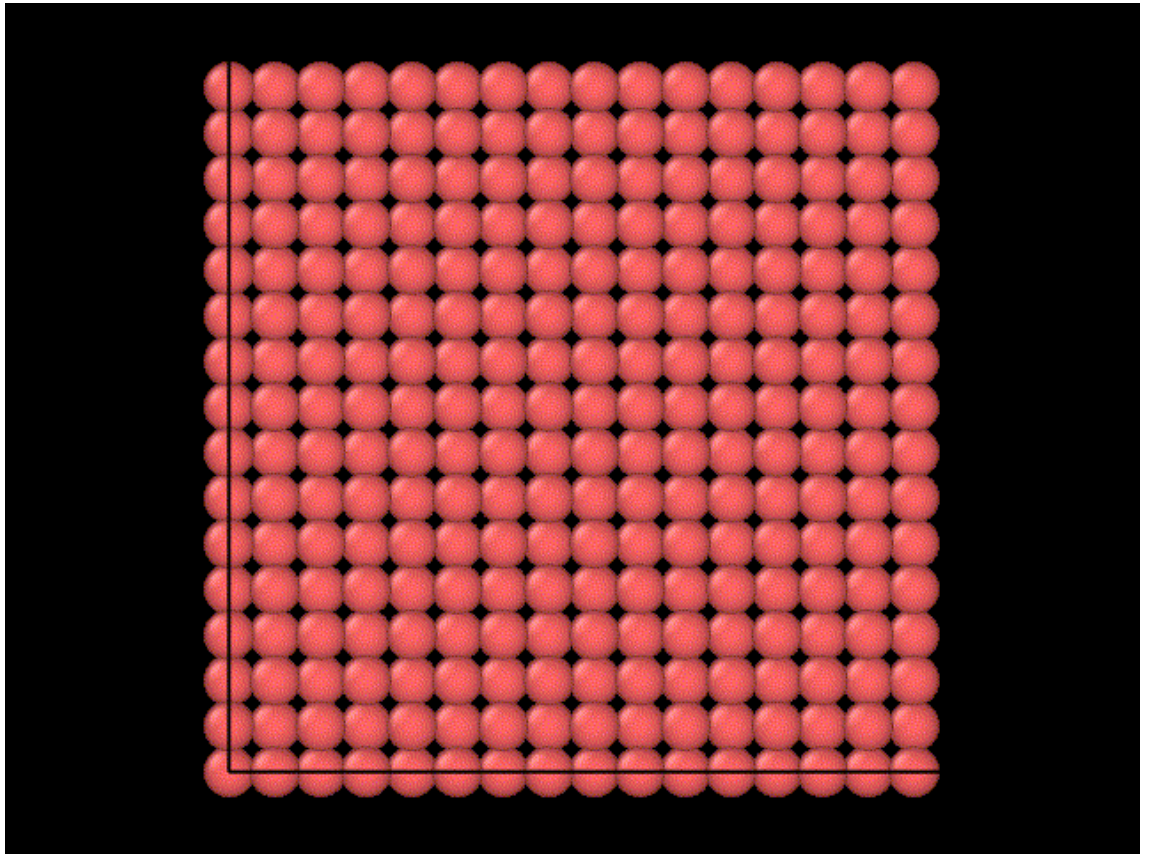
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	**H** –259.2																	**He** –269.7
2	**Li** 180.5	**Be** 1283											**B** 2027	**C** 4100	**N** –210.1	**O** –218.8	**F** –219.6	**Ne** –248.6
3	**Na** 98	**Mg** 650											**Al** 660	**Si** 1423	**P** 44.2	**S** 119	**Cl** –101	**Ar** –189.4
4	**K** 63.2	**Ca** 850	**Sc** 1423	**Ti** 1677	**V** 1917	**Cr** 1900	**Mn** 1244	**Fe** 1539	**Co** 1495	**Ni** 1455	**Cu** 1083	**Zn** 419.5	**Ga** 29.78	**Ge** 960	**As** 817	**Se** 217.4	**Br** –7.2	**Kr** –157.2
5	**Rb** 38.8	**Sr** 770	**Y** 1500	**Zr** 1852	**Nb** 2487	**Mo** 2610	**Tc** 2127	**Ru** 2427	**Rh** 1966	**Pd** 1550	**Ag** 960.8	**Cd** 320.9	**In** 156.2	**Sn** 231.9	**Sb** 630.5	**Te** 450	**I** 113.6	**Xe** –111.9
6	**Cs** 28.6	**Ba** 710	**La** 920	**Hf** 2222	**Ta** 2997	**W** 3380	**Re** 3180	**Os** 2727	**Ir** 2454	**Pt** 1769.3	**Au** 1063	**Hg** –38.9	**Tl** 303.6	**Pb** 327.4	**Bi** 271.3	**Po** 254	**At**	**Rn** –71

Mg 650 — Symbol; Melting point in °C

2000–3000 °C >3000 °C

Approach 1: Heating-cooling





Approximation $\bar{T}_m = \dfrac{T_m^+ + T_m^-}{2}$

Approach 2: solid-melt coexistence

General steps:

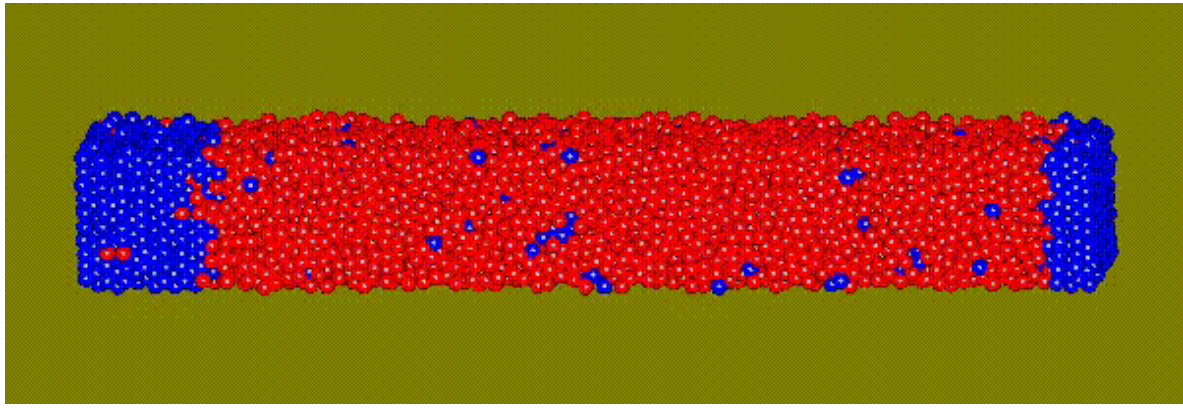
① Generate solid-melt interface

② Equilibrate at specified *T*, observe motion of interface

③ T corresponds to zero velocity corresponds to T_m.

Alternatives:

- Switch to NVE during late stage of 2
- Switch to NPH during late stage of 2
- Use two thermostats

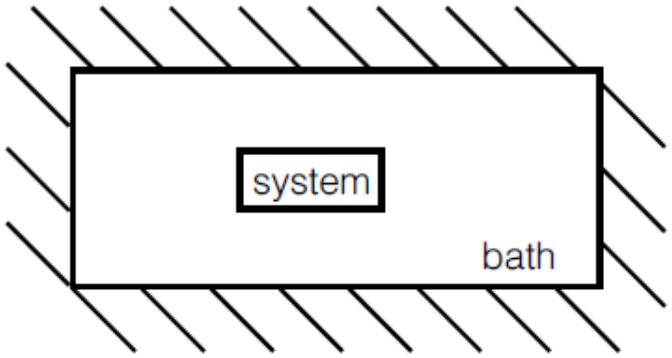


Thermodynamics Ensembles

- NVE: isolated system, microcanonical ensemble

  - Very rare cases
  - Newton's law

- NVT: equilibrated with a thermal bath, canonical ensemble



$$E_K = \frac{3}{2} N k_B T \qquad \langle A \rangle = \frac{\int A e^{-\beta E} \mathrm{d}^3 r \mathrm{d}^3 p}{\int e^{-\beta E} \mathrm{d}^3 r \mathrm{d}^3 p} = \frac{1}{t} \int_0^t A(\tau) \mathrm{d}\tau$$

$$\sigma_E^2 = \langle H^2 \rangle_{\mathrm{NVT}} - \langle H \rangle_{\mathrm{NVT}}^2 = k_B T^2 c_v.$$

$$\sigma_T^2 = \langle T^2 \rangle_{\mathrm{NVT}} - \langle T \rangle_{\mathrm{NVT}}^2 = \frac{2T^2}{N_{df}}.$$

Thermodynamics Ensembles

- NPT: isothermal-isobaric
- NPH: constant-pressure, constant-enthalpy

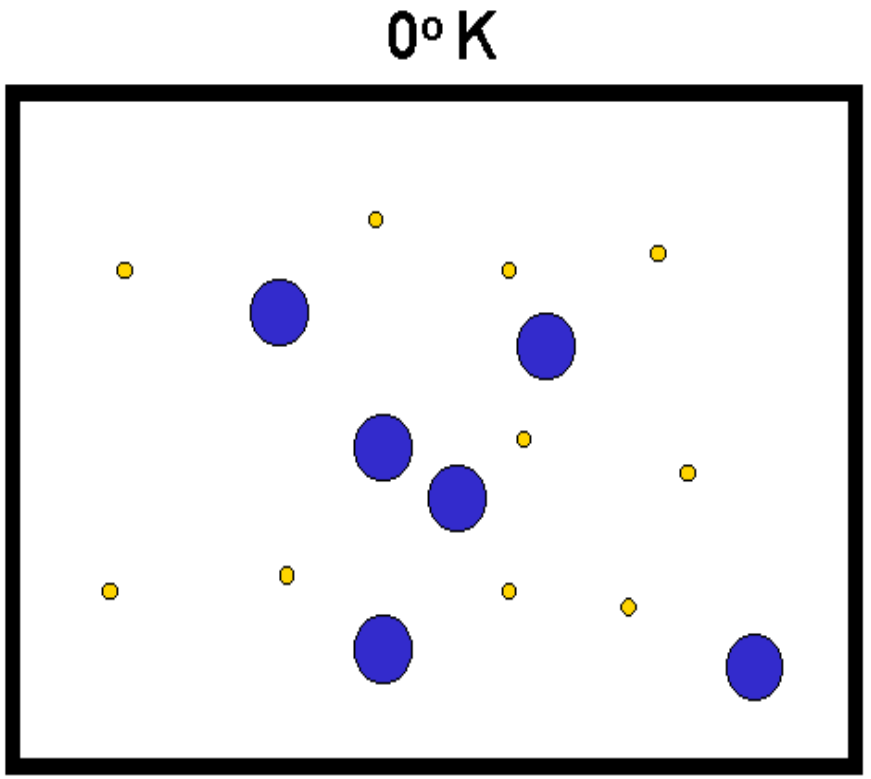
  Solid phase transformation

- μVT: grand canonical

  Phase transformation, (surface) adsorption…

Temperature control: thermostat

- Velocity scaling
  - isokinetics
  - Berendsen
- Stochastic thermostat
  - Andersen
  - Langevin
- Extended Lagrangian
  - Nose-Hoover
  - Nose-Hoover chain



$$E_K = \frac{3}{2} N k_B T = \frac{1}{2} \sum_i m_i v_i^2$$

Thermostat: isokinetic velocity scaling

Instantaneous temperature $T(t)$:

$$T(t) = \frac{1}{k_B N_{df}} \sum_{i,\alpha} m_i v_{i\alpha}^2$$

Isokinetics scaling:

$$\lambda = \sqrt{\frac{T_{\text{target}}}{T(t)}}, \qquad v'_{i\alpha} = \lambda v_{i\alpha}$$

Problem: cannot reproduce the variance in temperature for canonical system.

https://docs.lammps.org/fix_temp_rescale.html

Thermostat: Berendsen

$$\lambda = \sqrt{1 + \frac{\Delta t}{\tau}\left[\frac{T_{\text{target}}}{T(t)} - 1\right]}$$

$$v'_{i\alpha} = \lambda v_{i\alpha}$$

- No thermal noise.
- No clear proof that it reproduces canonical distribution.
- For weak coupling ($\tau > 0.01$ ps) it does lead to correct canonical averages.

https://docs.lammps.org/fix_temp_berendsen.html

Thermostat: Andersen

◆ Reset velocity of randomly selected atoms following a distribution.

Practical algorithm: at each MD step for each atom

① Draw a uniformly random number p in [0, 1];

② If $p < \frac{\Delta t}{\tau}$, draw another random number p_r that follows:

$$P(p_r) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left(-\frac{\beta {p_r}^2}{2m}\right)$$

③ Reset the momentum of current atom as p_r.

- Does reproduce the canonical ensemble
- It however breaks the continuity of MD trajectories
- Does not preserve energy and momentum.

Thermostat: Langevin

$$\mathbf{f}_i = -\nabla_{r_i} E - \frac{m}{\tau}\mathbf{v}_i + \mathbf{w}_i$$

Where $\mathbf{w}_i$ satisfies:

- **Gaussian distribution** $f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$
- $\langle w_i \rangle = 0$
- $\langle w_i w_j \rangle = \delta_{ij} \frac{2mk_BT}{\tau}$

Practically approximated by

$$w_i = \omega \sqrt{\frac{24mk_BT_{\text{target}}}{\tau \cdot \Delta t}} \qquad \omega \in [-0.5, 0.5]$$

https://docs.lammps.org/fix_langevin.html

Thermostat: Nose-Hoover

$$\mathbf{f}_i = -\nabla_{r_i} E - m\gamma \mathbf{v}_i$$

$$\dot{\gamma} = -N_{df} \frac{k_B T(t)}{Q} \left[\frac{T_{\text{target}}}{T(t)} - 1 \right]$$

Practical implementation:

$$\dot{\gamma} = -\frac{1}{\tau_{NH}} \left[\frac{T_{\text{target}}}{T(t)} - 1 \right]$$

https://docs.lammps.org/fix_nh.html

Barostat: Berendsen

Virial theorem

$$P_{\alpha,\beta} = \frac{1}{V}\left(\sum_i^N m_i v_{i\alpha} v_{i\beta} + \sum_{i>j} r_{ij,\alpha} \cdot f_{ij,\beta}\right)$$

$$P = \langle P_{\alpha,\alpha} \rangle = \frac{1}{d}\sum_\alpha^d P_{\alpha,\alpha} = \frac{N}{V} k_B T - \frac{1}{d}\sum_{i>j} \vec{r}_{ij} \cdot \frac{\partial \Phi_{ij}}{\partial \vec{r}_{ij}}$$

System coupled to external bath

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{P_{\mathrm{target}} - P(t)}{\tau_P}$$

Coordinate and volume variations

$$\dot{\mathbf{r}} = \mathbf{v} + \alpha \mathbf{r} \qquad \dot{V} = 3\alpha V$$

Barostat: Berendsen

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{1}{\beta V}\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{3\alpha}{\beta} \qquad \alpha = -\frac{\beta\left[P_{\mathrm{target}} - P(t)\right]}{3\tau_P}$$

For cubic system where $V = L^3$

$$\mu = 1 + \alpha = 1 - \frac{\beta\Delta t}{3\tau_P}\left[P_{\mathrm{target}} - P(t)\right] \qquad \vec{r}_i \to \mu\vec{r}_i \quad L \to \mu L$$

Equivalent expression

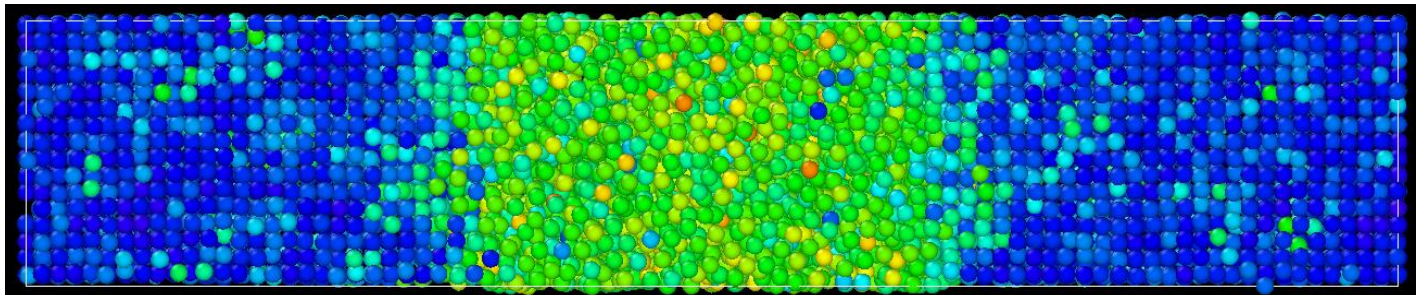
$$\mu = \left[1 - \frac{\Delta t}{\tau_P}\left(P_{\mathrm{target}} - P\right)\right]^{1/3}$$

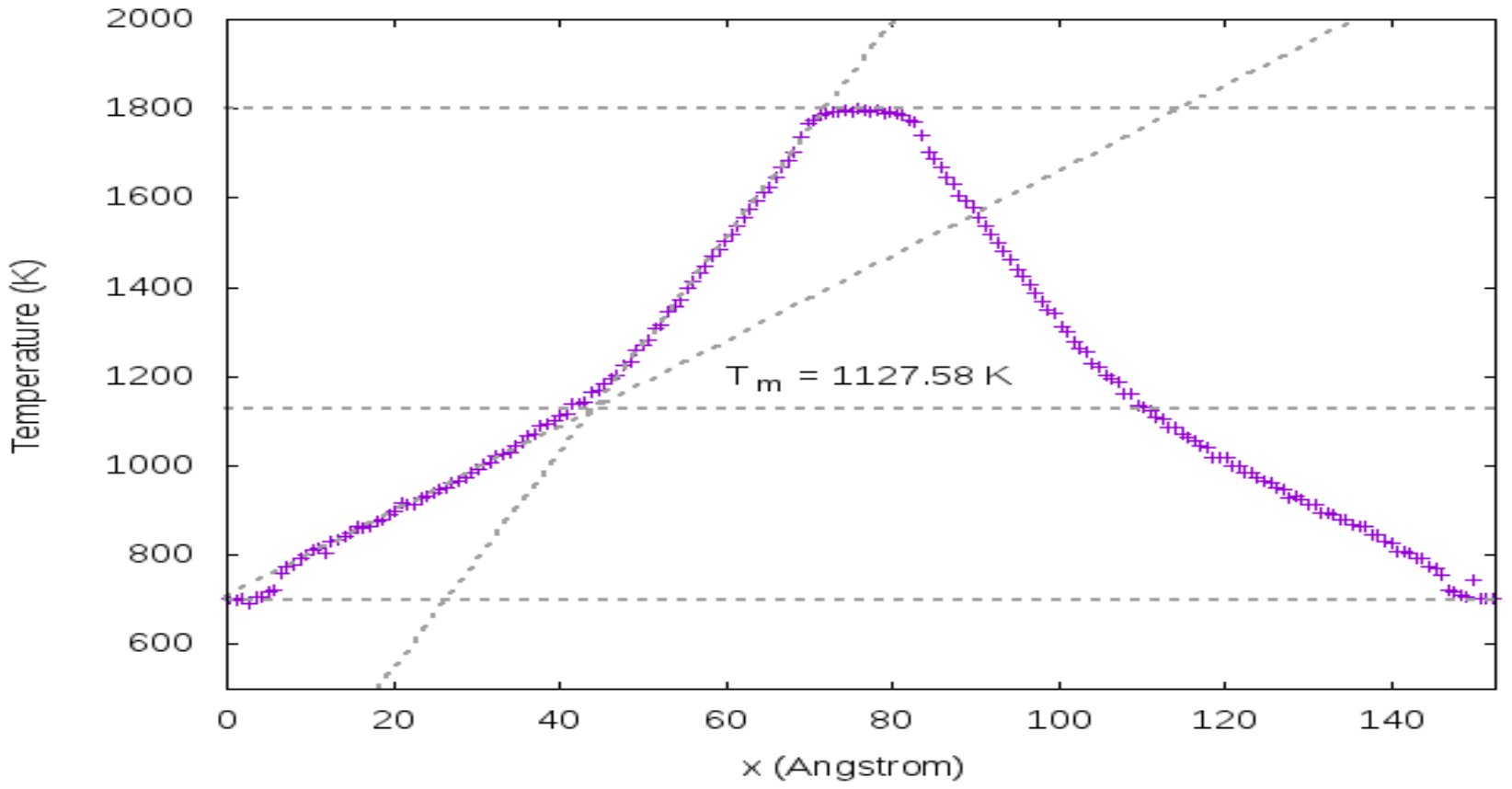
https://docs.lammps.org/fix_nh.html

https://docs.lammps.org/fix_press_berendsen.html

Melting temperature: Solid-melt Coexistence

```
# Relaxation of Cu(001) surface
units         metal
boundary      p p p
atom_style    atomic

# Initial configuration
lattice       fcc 3.615
region        box block 0 32 0 8 0 8
create_box    1 box
create_atoms  1 box

# Shift zero z to box center
variable      hx equal "(xhi - xlo)/2"
change_box    all x final -${hx} ${hx} remap units box

# Define regions and groups
region        low  block -46 46 INF INF INF INF side out units box
region        high block -11 11 INF INF INF INF units box

group         solid region low
group         melt dynamic all region high every 100

# Potential
pair_style    eam
pair_coeff    * * Cu_u6.eam

neighbor      0.5 bin
neigh_modify delay 5

# Compute local temperature
compute       TL solid temp
compute       TH melt temp
compute       kepa all ke/atom
compute       binchk all chunk/atom bin/1d x lower 0.001 units reduc

# initialization
velocity      all create 1000. 28459 dist gaussian

# Melting the liquid part
fix           1 all nve
fix           2 solid langevin 500.   500. 0.1 4321 zero yes
fix_modify    2 temp TL
fix           3 melt  langevin 2000. 2000. 0.1 4321 zero yes
fix_modify    3 temp TH
fix           4 all press/berendsen aniso 1. 1. 1. modulus 5000 coup
fix           5 all ave/chunk 10 20000 200000 binchk c_kepa ave one

# Thermal and trajectory
thermo_style custom step temp c_TL c_TH etotal pe press lx ly vol
thermo        100
dump          1 all atom 5000 dump.lammpstrj

# Run the simulation
run           1000000
```





Next Lecture：

Data Analysis and Property Calculations

Homework

Based on the examples in this course, generate Au(100), Au(110), Au(111) slab models, run minimization at 0K:

a) Calculate their surface energies at 0K;

b) Measure the change in interlayer separation of the surface, and compare to data in Table 1 of Solid State Communications **149**(37–38): 1561-1564, 2009.

c) Write a report on your experiments.

- Due: Nov. 3, 2022

Note:

- Append your lammps script but not the lengthy outputs.
- The possible potentials for Au could be found here:

https://www.ctcms.nist.gov/potentials/system/Au/ You can adopt any potential you prefer, but please specify explicitly.