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

MSE6701H, Multiscale Materials Modeling and Simulation

- ✓ Electronic DFT
- • **Atomistic MD**
- • Mesoscale PF

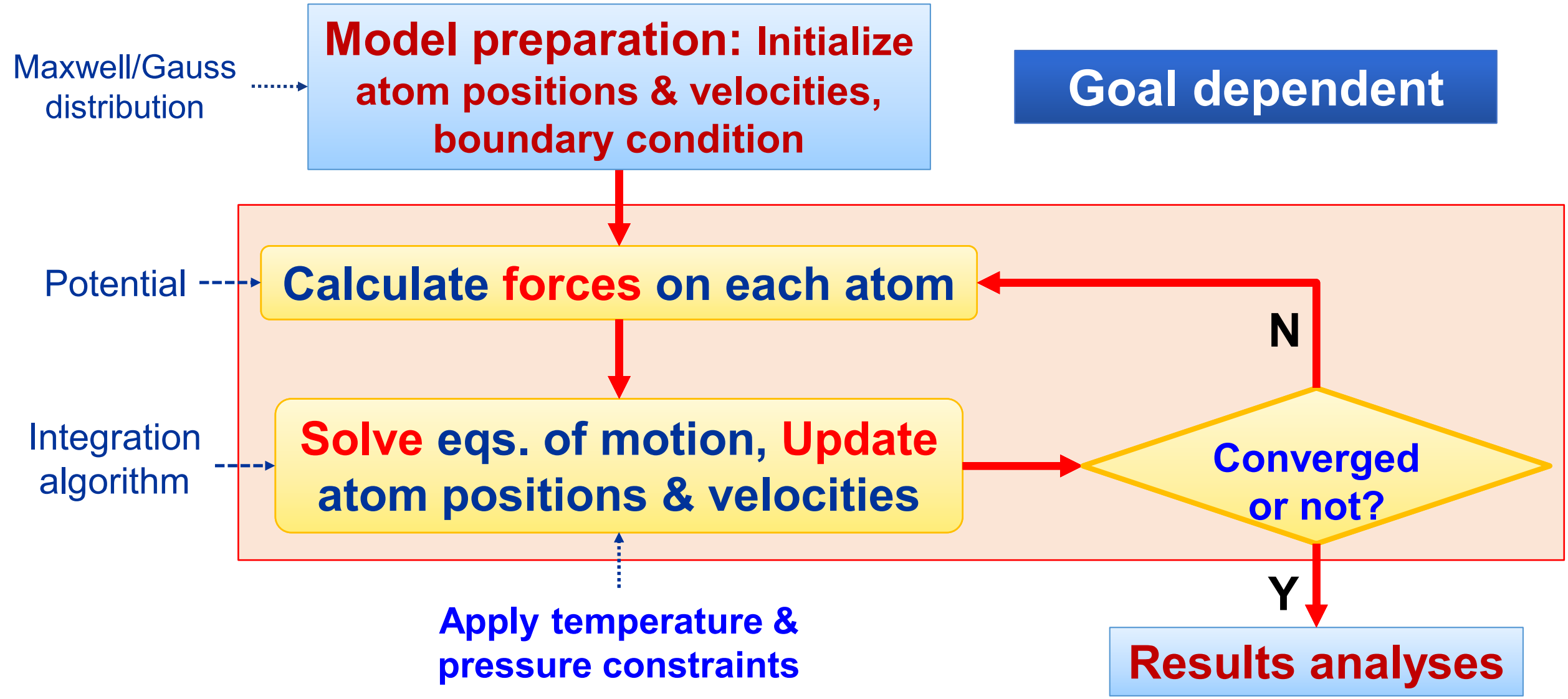
Lecture 10-P2

MD experiment #1

Guisen Liu (刘桂森)

2021.12.1

MD: overall flow chart



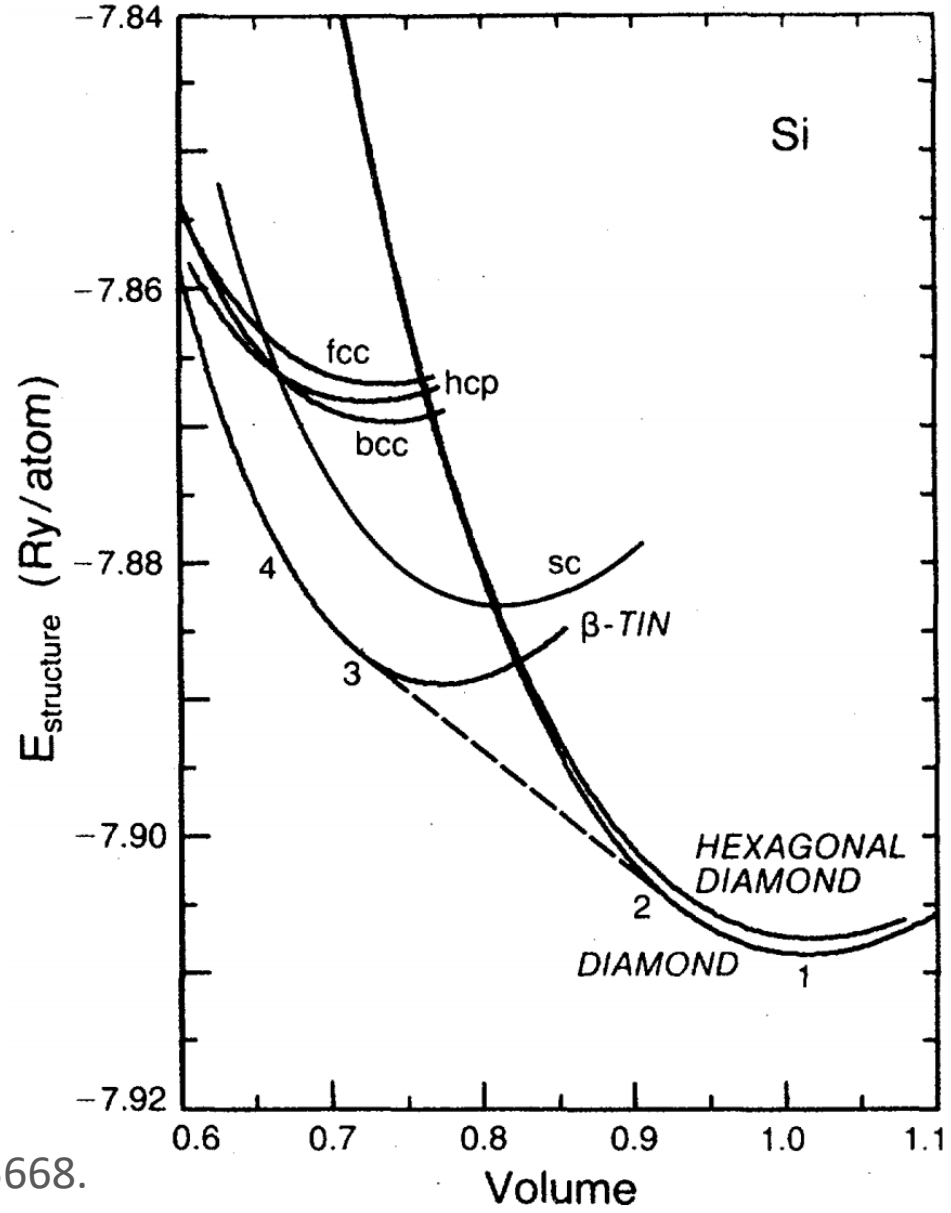
Contents: MD applications

- **Property evaluation**
  1. Structural properties such as RDF
  2. Physical properties: extract from atomic trajectories (averaged over time)
  3. Dynamical properties: time dependent properties (transport coefficient)
     1) Equilibrium lattice parameter, Bulk modulus, elastic moduli
     2) Diffusion coefficient

- **Goals**
  - Understand structure-property relation
  - Apply MD to calculate physical properties

The ground state (T = 0 K)

- Theoretical E-V curves ➔ predict phase transition under high pressure.
  - Energy-volume curves for seven phases Si.
  - Atomic volume is normalized to reference V for diamond Si at zero P.
  - Dashed line: common tangent (公切线) of the energy curves for the diamond phase and the β-tin (bct) phase.
  - Increase P, structure evolves from 1→2→3→4.



MT Yin and ML Cohen, Phys Rev B 26 (1982) 5668.

Calculate equilibrium lattice constant a_0

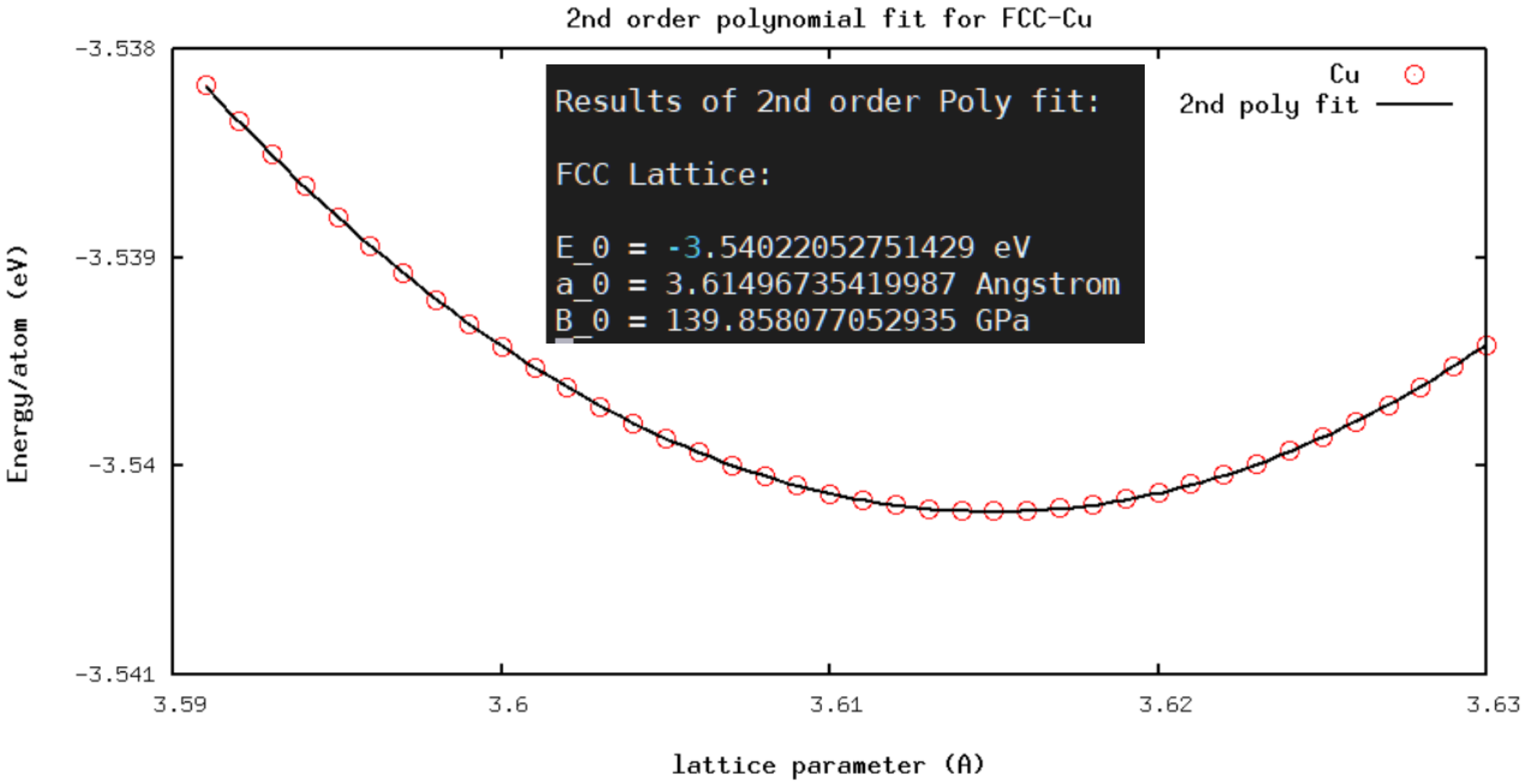
- Lattice energy E (eV) is a function of volume V (Å^3). The equilibrium lattice constant a_0 corresponds to the V that gives minimum of the $E(V)$ curve.

1) **Step 1: Give a structure, compute the potential energy for different volume values**
   a. Generate a 3x3x3 FCC copper (Cu) supercell with 108 atoms.
   b. LAMMPS writes "data" file containing lattice, volume per atom and energy per atom

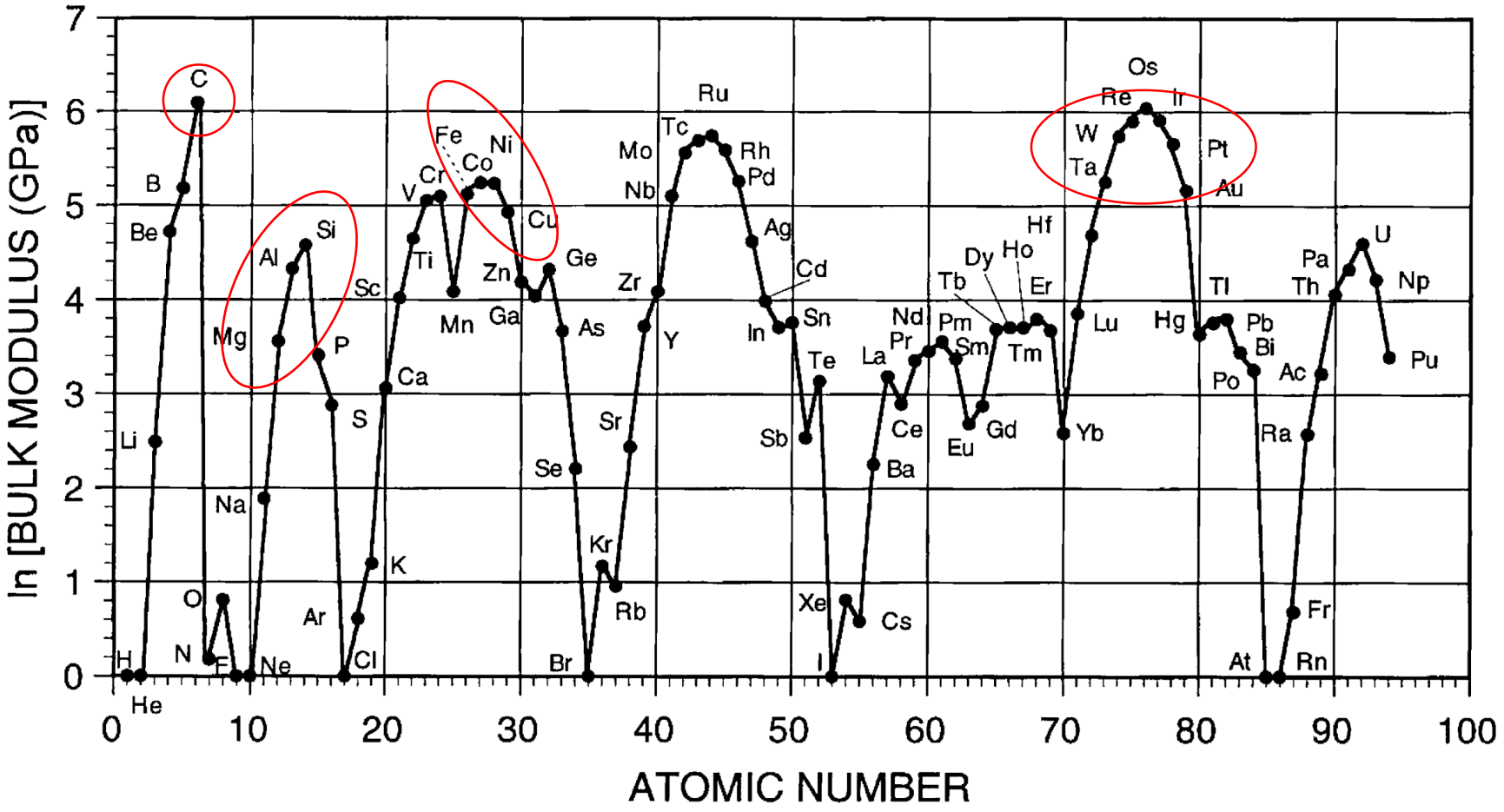
Lattice const. *a* (Å)	volume (Å^3)	energy (eV)
3.591	11.57673851775	-3.48875019885056
3.592	11.58641267200	-3.48888175993704
3.593	11.59609221425	-3.48900596416684
…	…	…

2) **Step 1: Give a structure, compute the potential energy for different volume values**
   a. Second order polynomial fit
   b. Murnaghan equation of state

2nd order polynomial fit of E(a)



Bulk moduli (B) of the elements



$\boldsymbol{B = -\left(\frac{dP}{dV/V}\right)_T}$, resistant to compression, is the ratio of the infinitesimal ***P* increase** to the resulting **relative decrease of volume**.

Isothermal compressibility: $\boldsymbol{\beta} = 1/B$ (used in P control)

$$\mu = \left[1 + \frac{\beta \Delta t \left(P(t) - P_0\right)}{\tau_p}\right]^{1/3}$$

Handbook of elastic properties of solids, liquids, and gases, 2nd vol. New York: Academic Press; 2001. p. 97 [Chap 7].
Note: Y-axis is **logarithmic** scale. Negative values are plotted along the base line.

Extract bulk modulus from E(a) relation at 0 K

- Bulk modulus $B \equiv -\frac{dP}{dV/V}$
  - *V*: unit cell volume. For cubic cell, $V = a^3 \rightarrow dV = 3a^2 da$
  - *P* : pressure. Change in energy change per atom

$$dE = -PdV \rightarrow P = -\frac{dE}{dV} = -\frac{NdE}{3a^2 da} \quad \text{with } N = 4 \text{ for one fcc unit cell}$$

- Bulk modulus as equilibrium state (0 K)

$$B = -\frac{dP}{dV/V} = \frac{N}{3a^2 \cdot 3a^2/a^3}\frac{d\left(dE/da\right)}{da} = \frac{N}{9a}\frac{d^2E}{da^2}, \rightarrow B_0 = \frac{N}{9a}\frac{d^2E}{da^2}\bigg|_{a=a_0}$$

- B: Curvature of E(a) near the minimum energy/atom

Appendix: Birch-Murnaghan (BM) equation of state

- To obtain minimum values for the discrete E-V points
  - Interpolate the discrete E-V points with *EOS* function, which is analytically derived from thermodynamics of internal energy in the vicinity of the minimum.
  - Birch-Murnaghan EOS

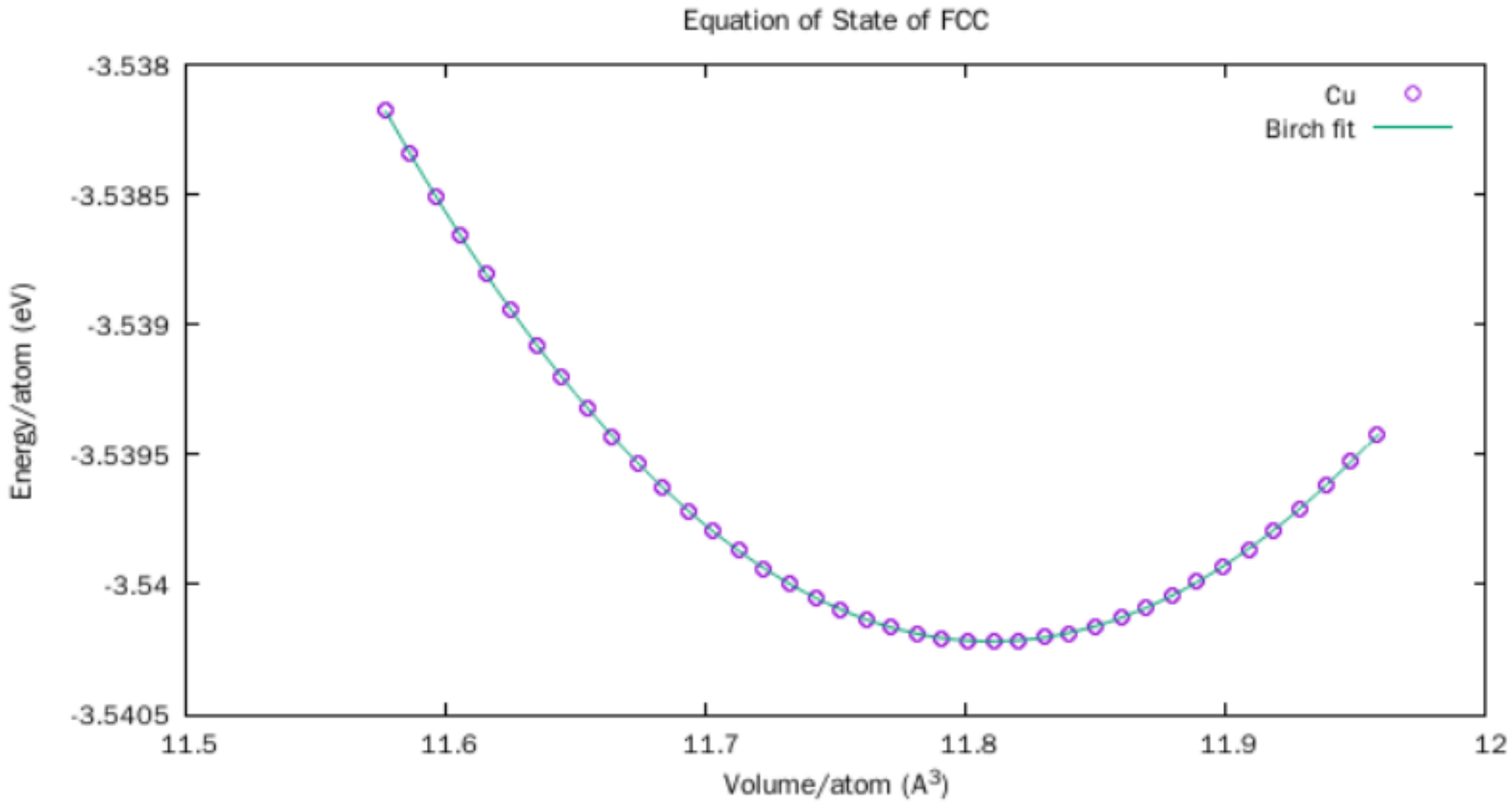
$$E(V) = E_0 + \frac{9V_0B_0}{8}\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]^2\left\{1 + \frac{1}{2}\left(B_0' - 4\right)\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\}$$

- V_0: equilibrium volume. V is the volume. $a_0 = (V_0)^{1/3}$.
- B_0: bulk modulus at V_0.
- $B_0' = (\partial B/\partial P)_T$: pressure derivative of B at V_0 and T.
- Euler strain

http://tutorials.crystalsolutions.eu/tutorial.html?td=eos&tf=eos_tut

(Birch, Intermetallic compounds: Principles and Practice, Vol I: Principles. pages 195-210)

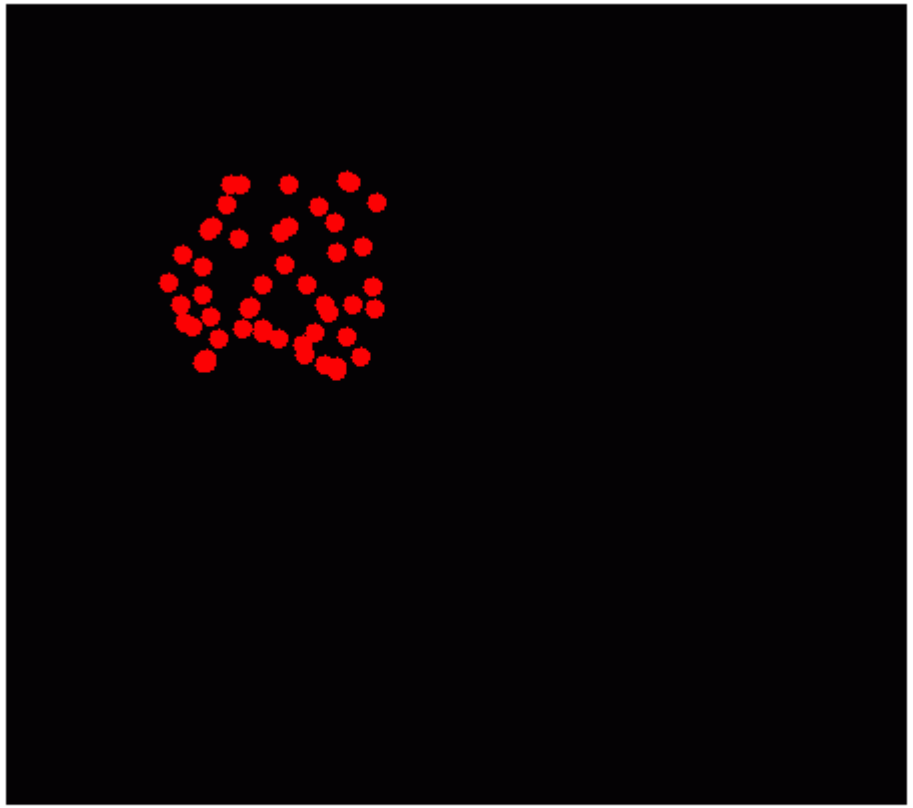
BM EOS fitting



How about elastic moduli Cijkl?

Diffusion: atomic vs continuum scale

Random motion of atoms



1^{st} Fick's law: $J = -D\nabla c$

- J: particle flux, net particle rate per unit area A [N/(A*dt)]
- c: particle density/concentration (kg/m^3, or #/m^3)
- ∇c: gradient of concentration
- D: diffusion coefficient (m^2/s)

✓ **Convert continuity to time dependent diffusion equation.**

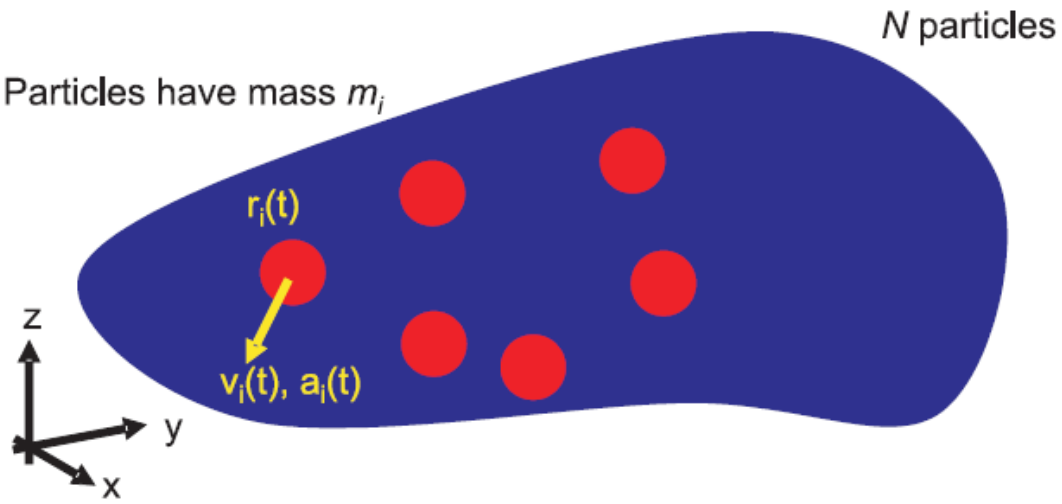
➢ **How does D depend on the motion of atoms that are undergoing diffusion, or how does D vary with the microstate of the system?**

Mean square displacement (MSD)

- **Diffusion is a transport phenomenon occurring on the molecular level.**
- MD tracks all the atoms moving around, i.e. the trajectory of any atom. **Statistically**, all the atoms must contribute equally to estimating the self-diffusion coefficient.

➢ **MSD function**

$$\left\langle \Delta^2 r(t) \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2$$



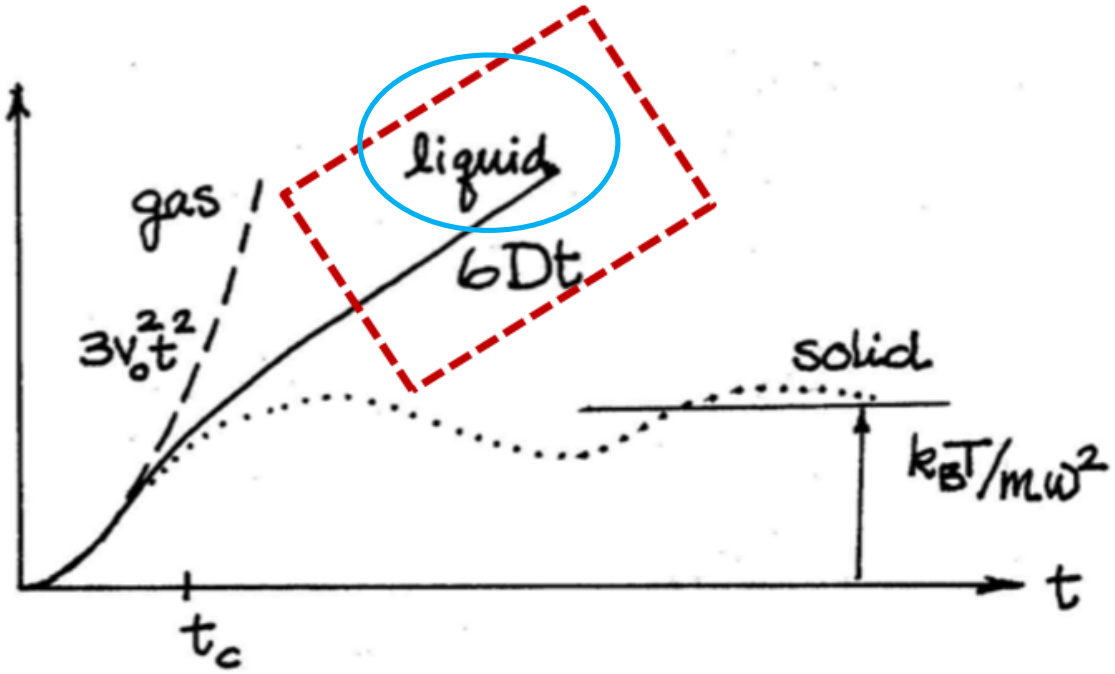
Mean square displacement (MSD) $<\Delta^2 r(t)>$

- Initially (short time): like ideal gas, inertial part of the motion of any physical system. $v_0^2 \sim k_B T/m$
- Later (long time): **dynamics** set in.

- **Liquid:** atom moves like Brownian motion. Each atom continuously collides with its neighbors as it diffuses through the liquid. ➔ **linear time dependence of MSD on D**.

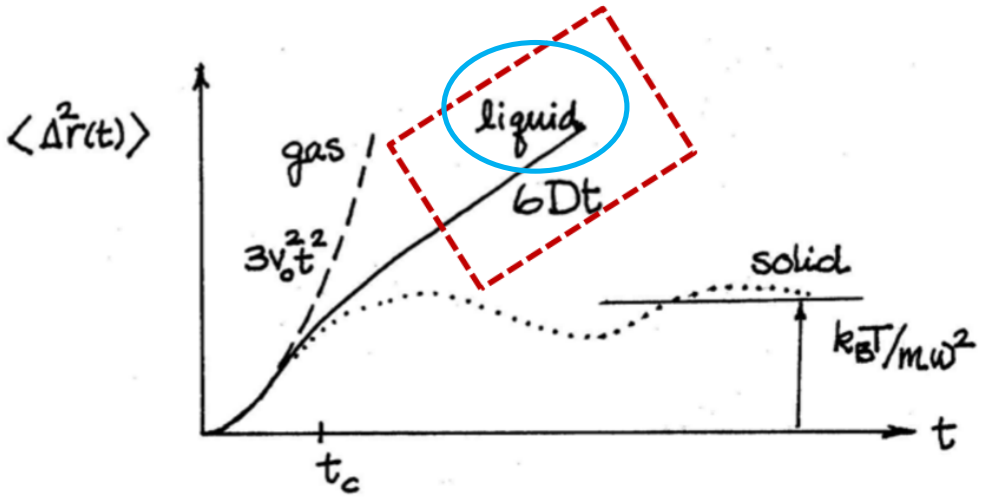
- **Solid**: Each atom is in its equilibrium position, and atoms feel the restoring forces due to the crystal bonding. One atom cannot diffuse too far from its lattice site, its motion is vibratory rather than diffusive. **MSD reaches a plateau**. (vibrational frequency)

MSD $<\Delta^2 r(t)>$



Diffusion coefficient: D = u^2/t

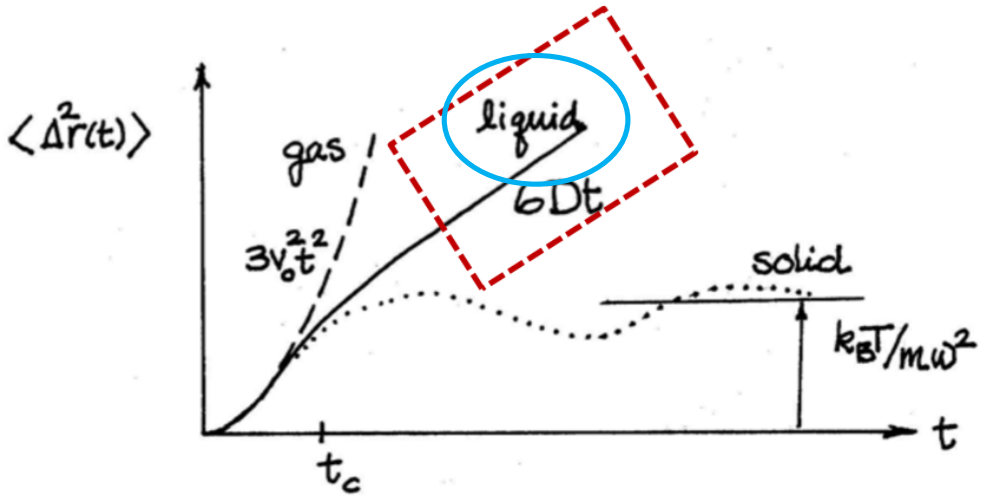
Temperature > $T_{melting}$




```
# msd = [dx, dy, dz,u^2=(dx^2+dy^2+dz^2)]
# summed and averaged displacements of atoms in the group
reset_timestep  0

variable        time equal step*$t

compute         msd all msd com yes
variable        msd equal c_msd[4] # c_msd[4] = u^2
fix             msd_tmp all vector 10 v_msd

variable        fitD equal slope(f_msd_tmp)/6/(10*dt) # in [A^2/ps]
variable        D2ps equal (v_msd)/6/(step*dt+1.0e-6)
variable        aveD equal 0.5*(v_D2ps+v_fitD)*10 # in [nm*m/s]=1e-9m^2/s

thermo_style    custom step v_msd v_fitD v_D2ps temp press vol
fix             print all print 10 &
"${time} ${msd} ${fitD} ${D2ps} ${aveD}" file tMSD.dat
```

compute msd all msd

2.3 Diffusion coefficient: control T & P




```
variable        a equal 3.615
variable        t equal 0.001
variable        T equal 1620
variable        Tdamp equal 100*$t
variable        p equal 1
variable        pdamp equal 1000*$t

units           metal
dimension       3
atom_style      atomic
timestep        $t
neighbor        2.0 bin
neigh_modify    delay 0 every 1

lattice         fcc $a
region          box block 0 $x 0 $y 0 $z
create_box      1 box
create_atoms    1 box

pair_style      eam/alloy
pair_coeff      * * ../CuYM.eam.alloy Cu

velocity        all create $T 1234567
fix             process all npt temp $T $T ${Tdamp} iso $p $p ${pdamp}
```

Temperature dependent D

- Diffusion is thermal aided process, thus strongly depends on T.

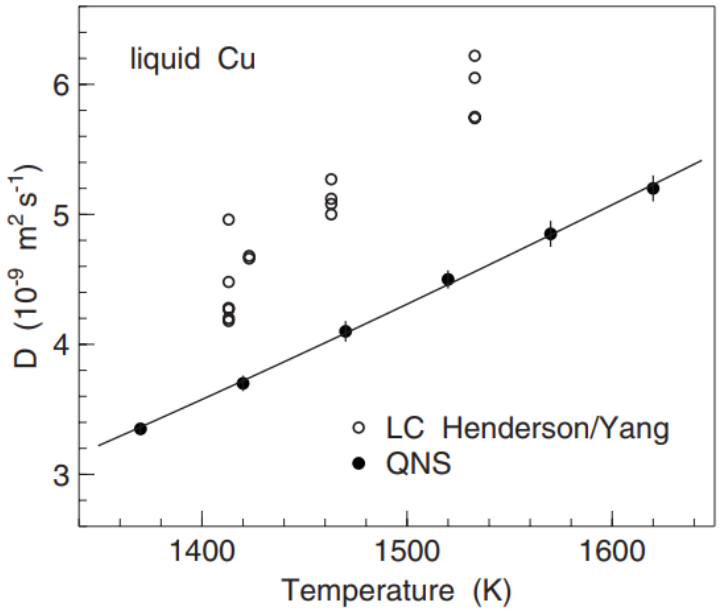


FIG. 2. Diffusion coefficients from quasielastic neutron scattering (filled circles) as a function of temperature. The line represents an Arrhenius function [Eq. (2)]. Values from a long capillary experiment (Ref. 19) are significantly larger (open circles).

Figure 2 shows the resulting QNS Cu self diffusion coefficients as a function of temperature. Values range from $(3.35 \pm 0.05) \times 10^{-9}$ m^2 s^{-1} at 1370 K to $(5.2 \pm 0.1) \times 10^{-9}$ m^2 s^{-1} at 1620 K (Table I). The temperature dependence D is best described with an Arrhenius behavior,

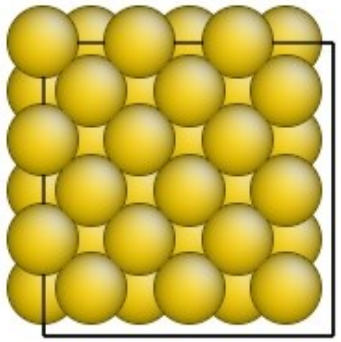
$$D = D_0 \exp(-E_A/k_B T), \qquad (2)$$

with a prefactor D_0 and an activation energy E_A. A best fit gives $E_A = (337 \pm 5)$ meV per atom and a $D_0 = (58.7 \pm 3) \times 10^{-9}$ m^2 s^{-1}.

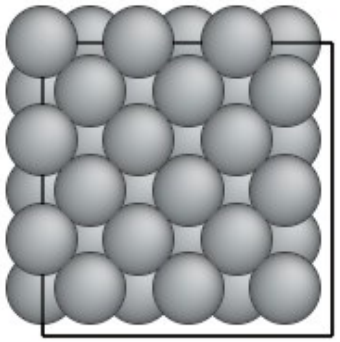
Question: determine D_0 and E_A?

A. Meyer: *Physical Review B.* 81(1), 012102 (2010).

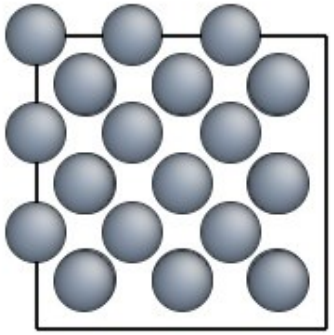
Lattice parameters & Bulk modulus at T = 0 K



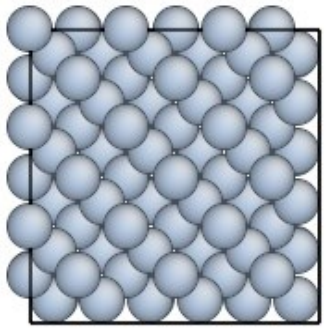
Cu



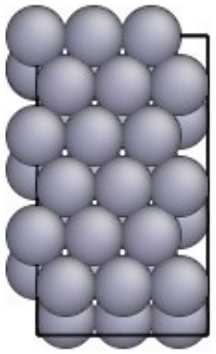
Al



Fe



Si



Mg

	Structure	Expt. a_0 (Å)	Expt. B (GPa)	a_0 (Å)	B (GPa)
Mg	HCP	3.209 (c/a=1.623)	35	? (c/a = ?)	?
Al	FCC	4.049	72	?	?
Si	Diamond	5.431	98	?	?
Fe	BCC	2.866	168	?	?
Cu	FCC	3.614	142	?	?

Diffusion coefficient for Cu

- Calculate self diffusion coefficient of Cu at different Temperature (above melting T = 1358 K).

- $\ln\frac{D}{D_0} = -\frac{E_A}{k_B}(1/T)$, linear fitting ln(D) = a – b·(1/T)➔ D_0 & E_A.

T (K)	Expt. *D* (10^{-9} m^2/s)	MD obtained *D* (10^{-9} m^2/s)	D_0 (m^2/s)	E_A (meV/atom)
1520	4.50 ± 0.07		?	?
1570	4.85 ± 0.10			
1620	5.20 ± 0.10			
1670	--			

Homework

1. Lattice parameters & Bulk modulus at T = 0 K for Mg, Al, Si, Fe, Cu

2. Diffusion coefficient (Page 18)

3. Name a few examples in materials science and engineering when applying temperature or/and pressure constraints are necessary.

- Due: Dec 8, 2021

Next Lecture：

MD Experiment #2