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 11

MD experiment #2

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2021.12.8

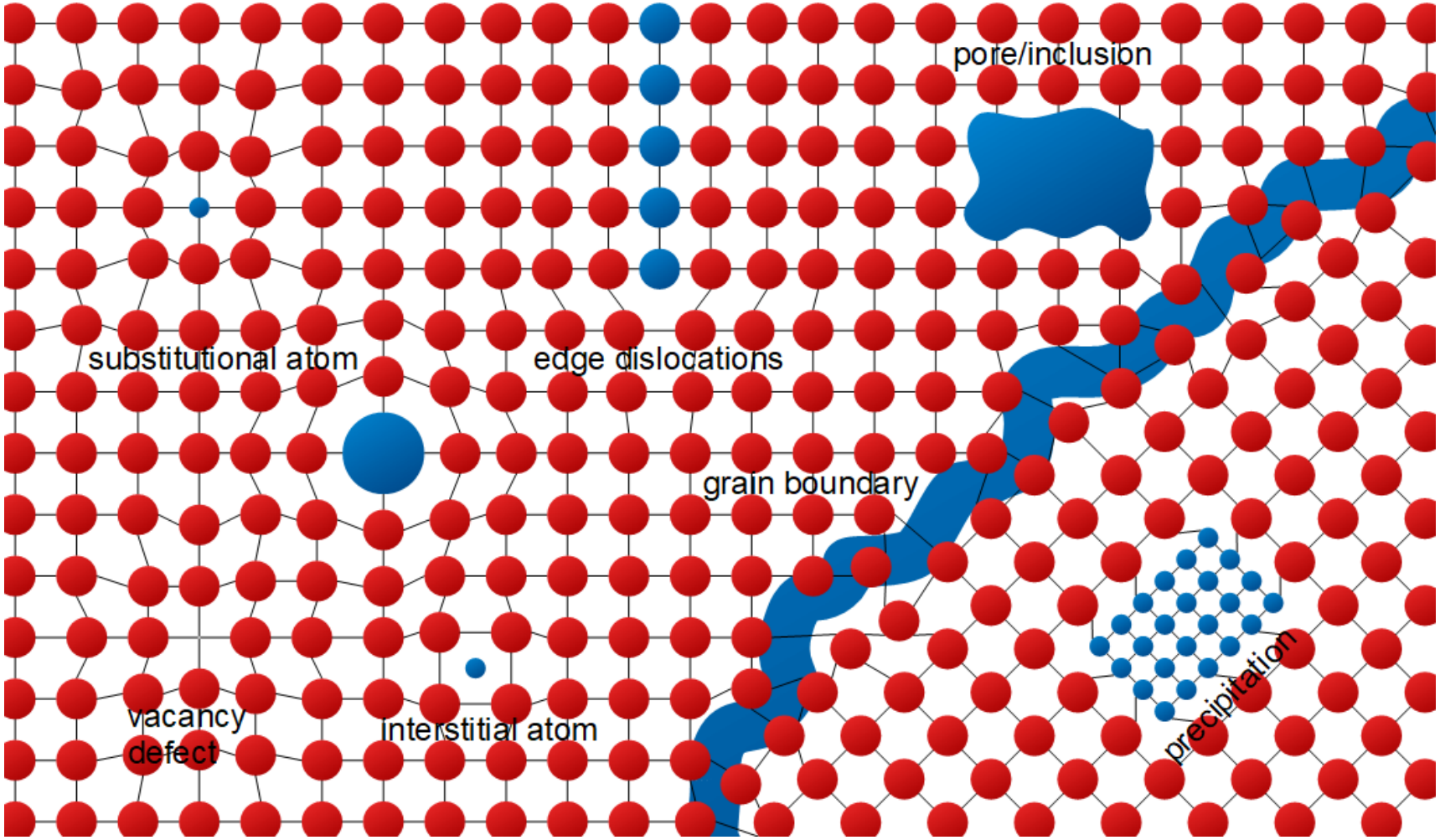
Contents: MD applications

- **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) Point defects, Diffusion coefficient (MD experiment #2)
     3) Dislocations (MD experiment #3)

- **Goals today**
  - Calculate formation energy for specific physical processes
  - Understand diffusion at atomic scale
  - Perform MD simulation with T & P control

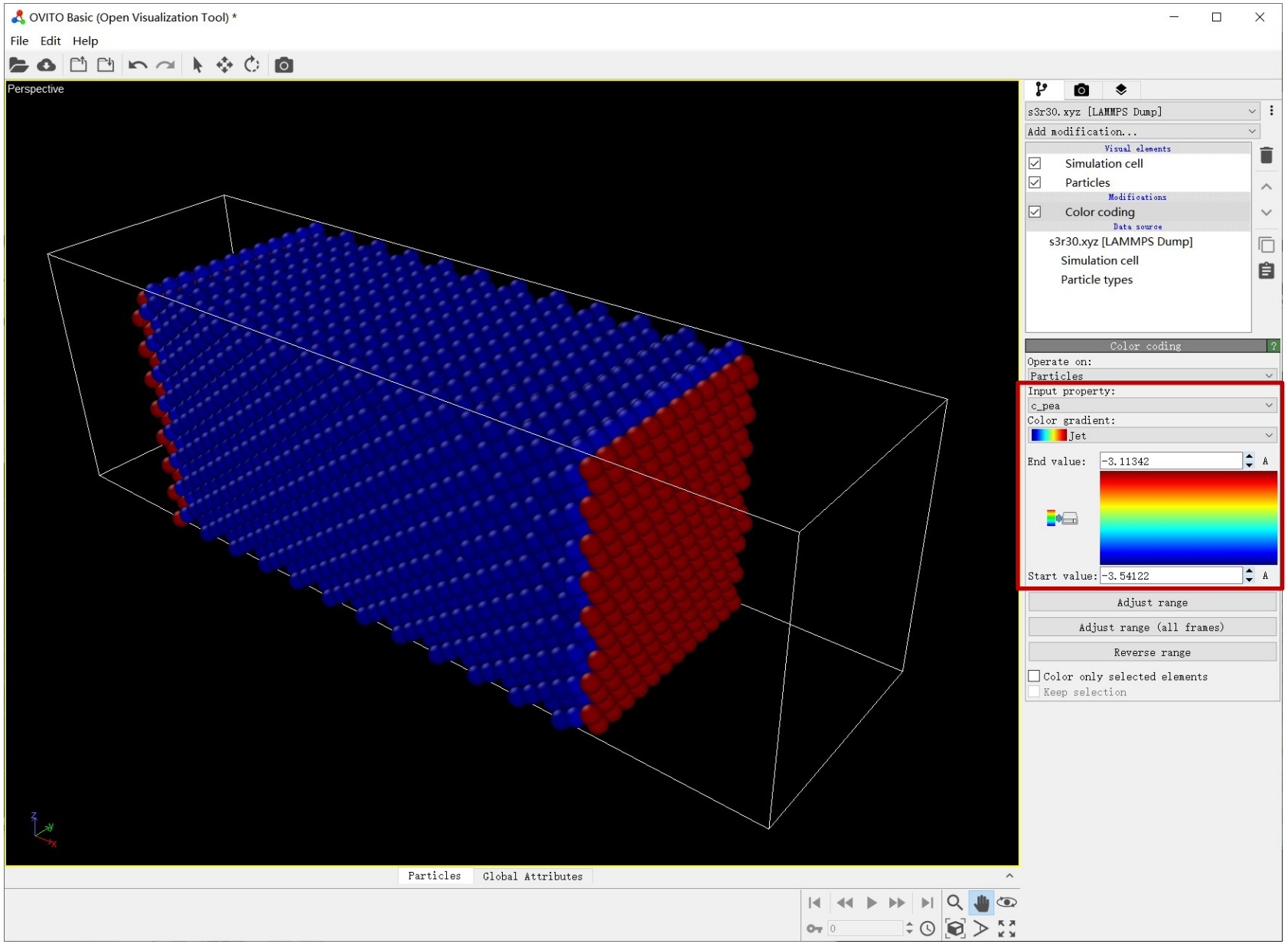
Defects in Crystals

"Crystals are like people: it's their defects that make them interesting." **– C. Frank**



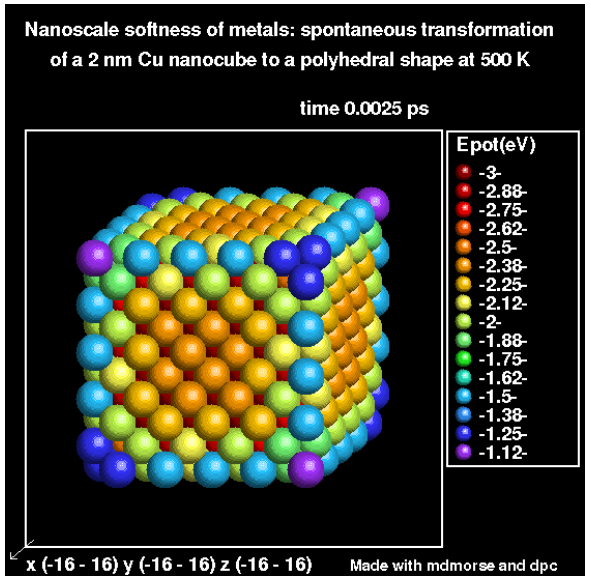
- Point defects
- Line defects
- Planar defects

surface energy



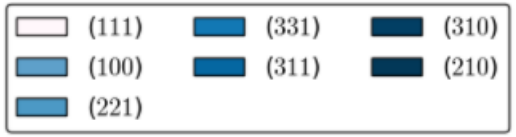
Previous homework

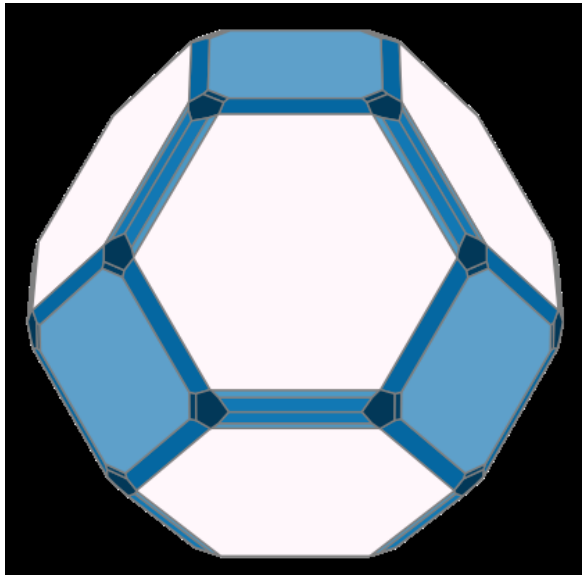
1. Calculate surface energy for (100), (110), (111) plane of fcc-Cu using LAMMPS, and compare with references.



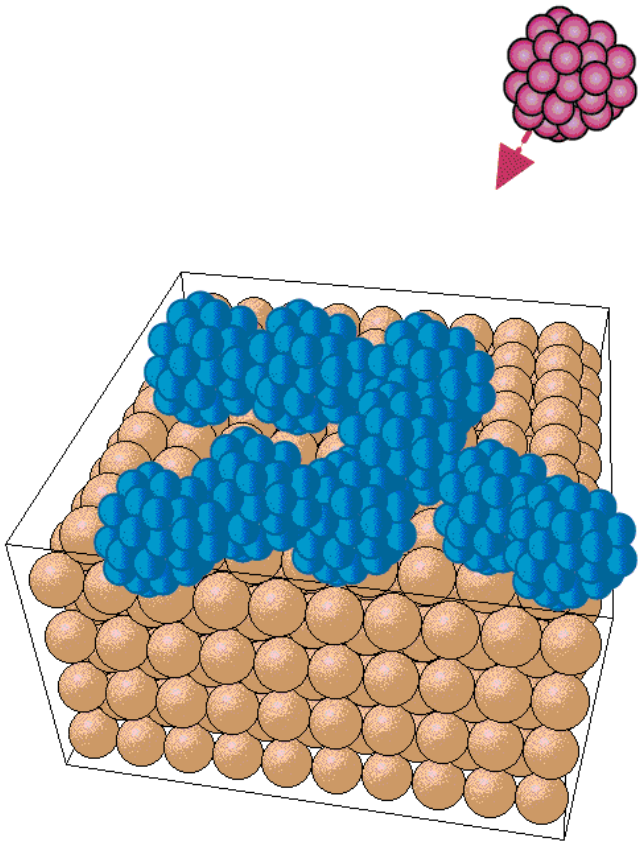
2. Visualize the structure by OVITO.

3. The morphology of nanocube Cu is mostly composed of _?_ plane. What controls its final shape? What's the theoretical ratios of different plane interceptions?

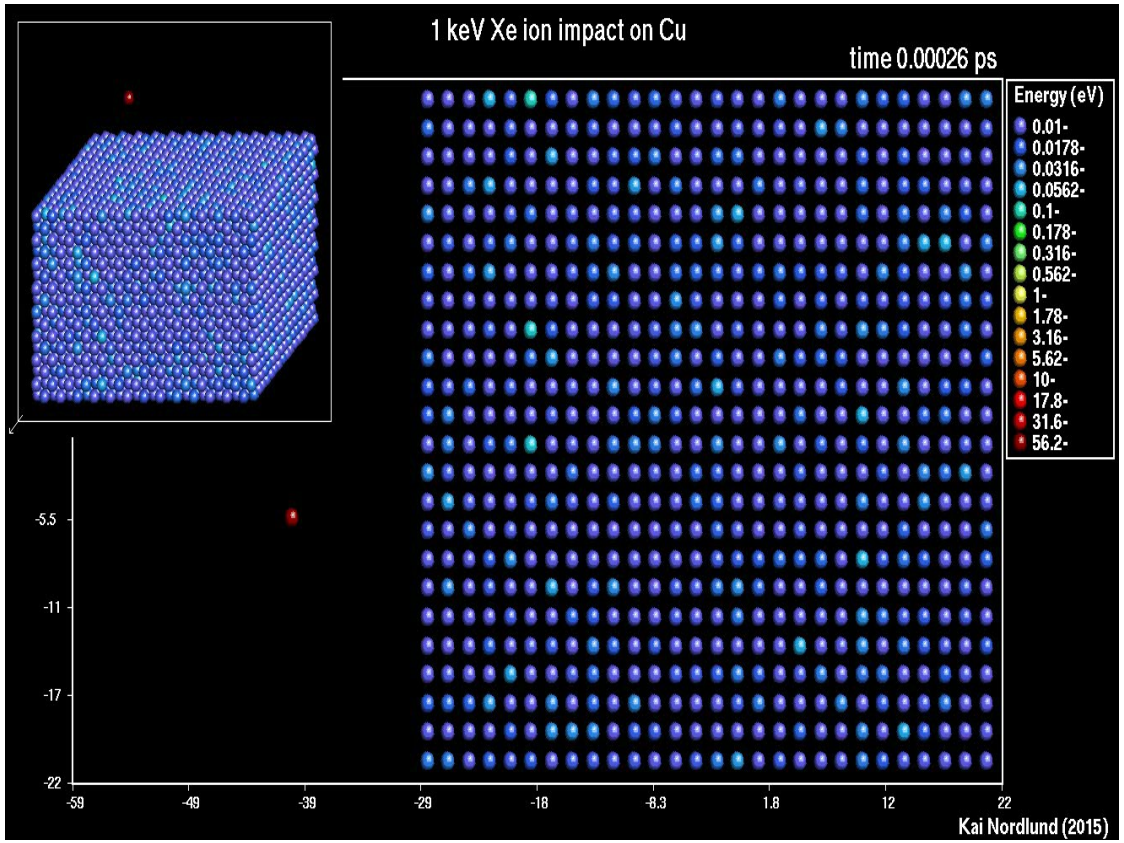




Irradiation damage



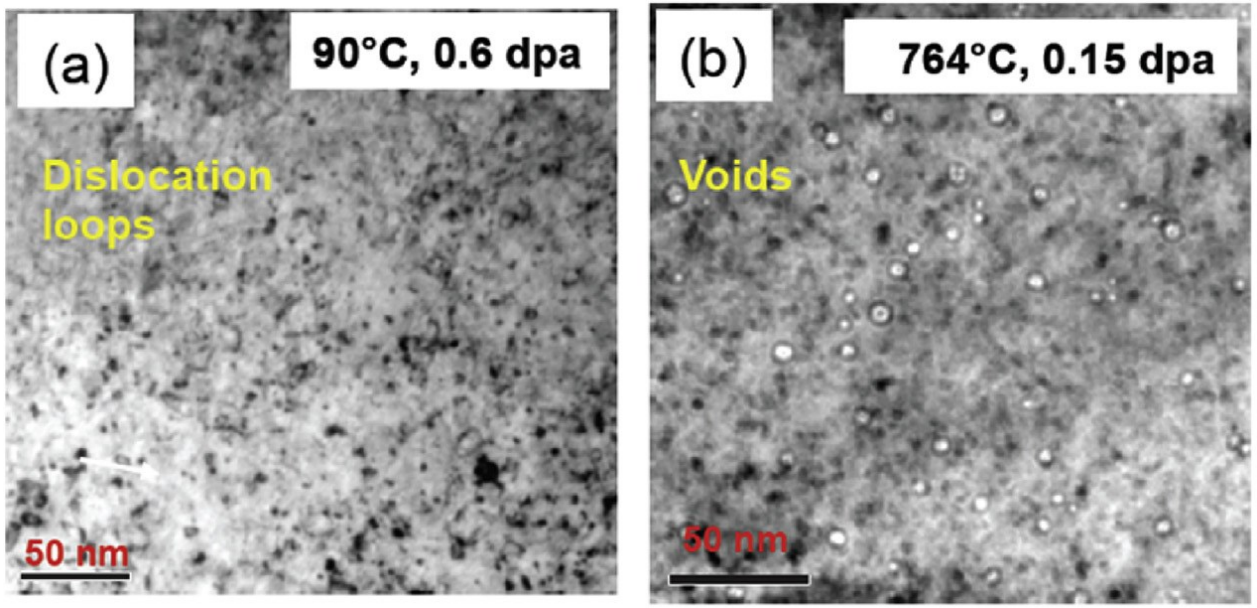
Irradiation effects of Ar gas cluster ion beam

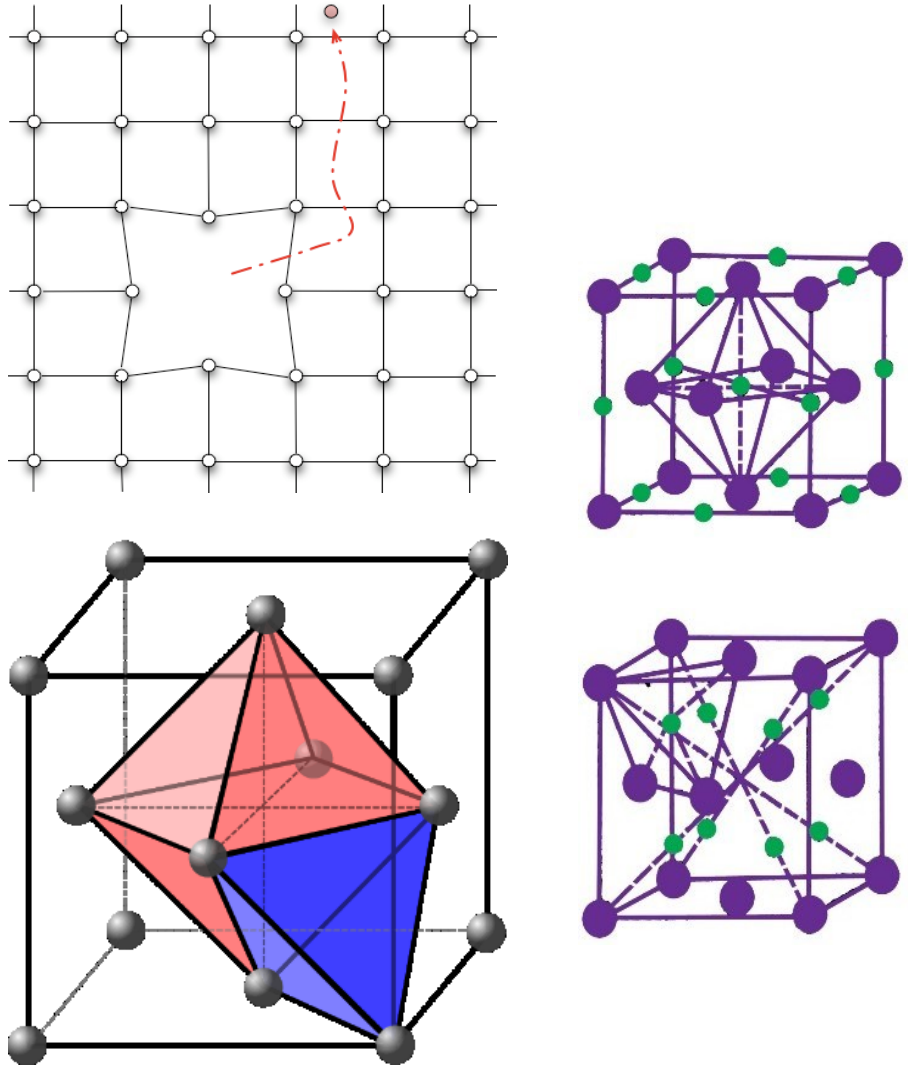


Collision cascades in Cu due to 1 keV Xe ion hitting
http://beam.helsinki.fi/~knordlun/anims.html

1. Point defects

- Formation of vacancies and interstitials
  - Frenkel pairs
  - Impurity atoms/ions
  - **Thermal** processes, equilibrium concentrations
  - Irradiation interstitial loops, voids

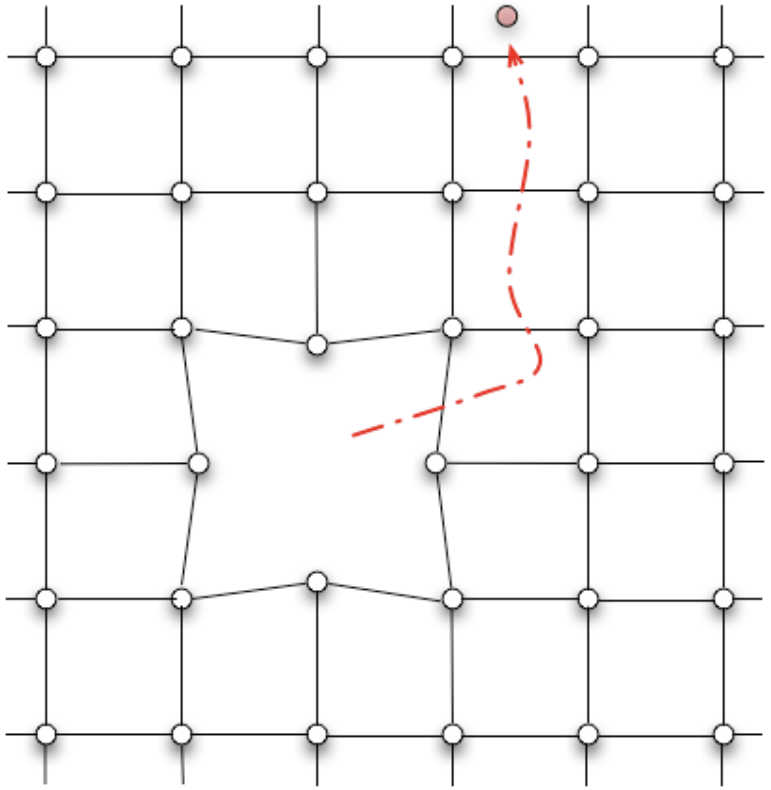




J. Nucl. Mater. 480, 235 (2016).

1.1 Vacancy Formation Energy E_V (T = 0 K)

$$E_V = E(N-1, N) - \frac{E(N,N)}{N} \cdot (N-1)$$



$E(m, N)$: total potential energy of a fully relaxed system containing m atoms occupying N perfect crystal lattice sites.

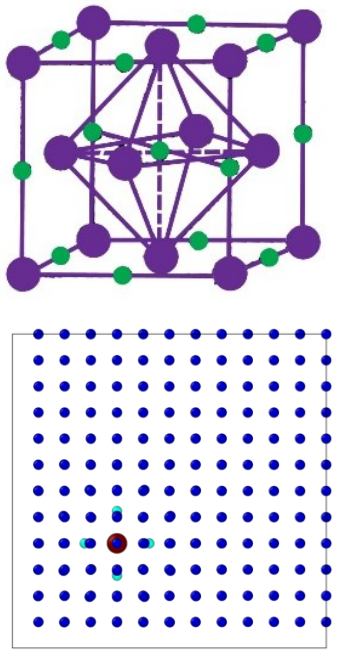
- E_V: work required to be done to break the bonds between an atom and its neighbors, and removing that atom to where it has **no interaction** (infinity) with the remaining system.

1.2 Interstitial Formation Energy E_I (T = 0 K)

$$E_I = E\left(N+1, N\right) - \frac{E(N,N)}{N} \cdot \left(N+1\right)$$

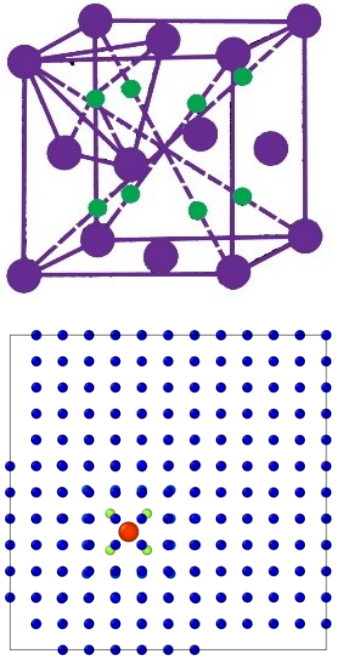
- E_I: energy required to create an interstitial structure from a corresponding perfect crystal lattice with the same number of atoms.

Octahedral (O) 八面体
(½,½,½) and (½,0,0)



O site added

Tetrahedral (T) 四面体
(¼,¼,¼)



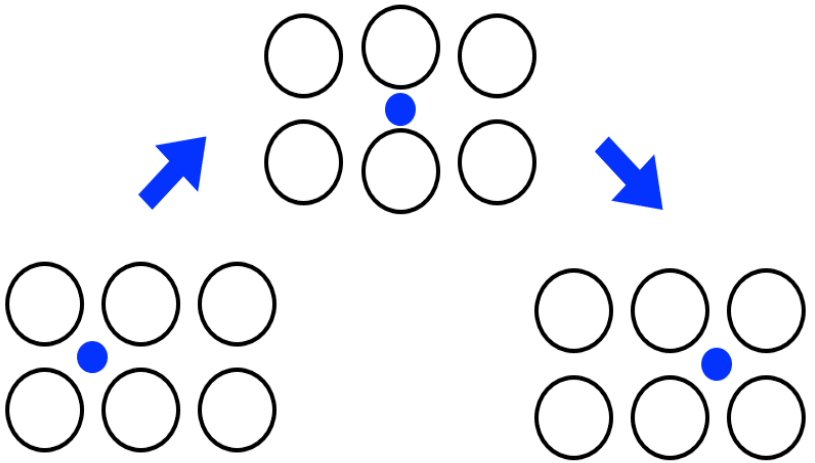
T site added

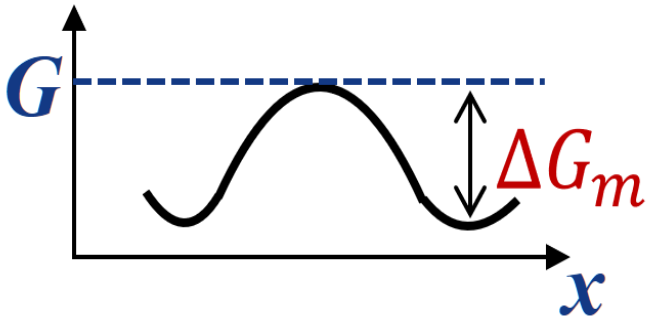
1.3 Effects of temperature on interstitial structure

- Thermal fluctuations could promote interstitial jumping from one site to another that is more energetically favorable.
- The jumping probability R, depends on temperature and can be described by Arrhenius equation

$$R = R_0 \exp\left(-\frac{G_m}{k_B T}\right)$$

  - R_0: attempt frequency, which is proportional to the vibration frequency of atoms.



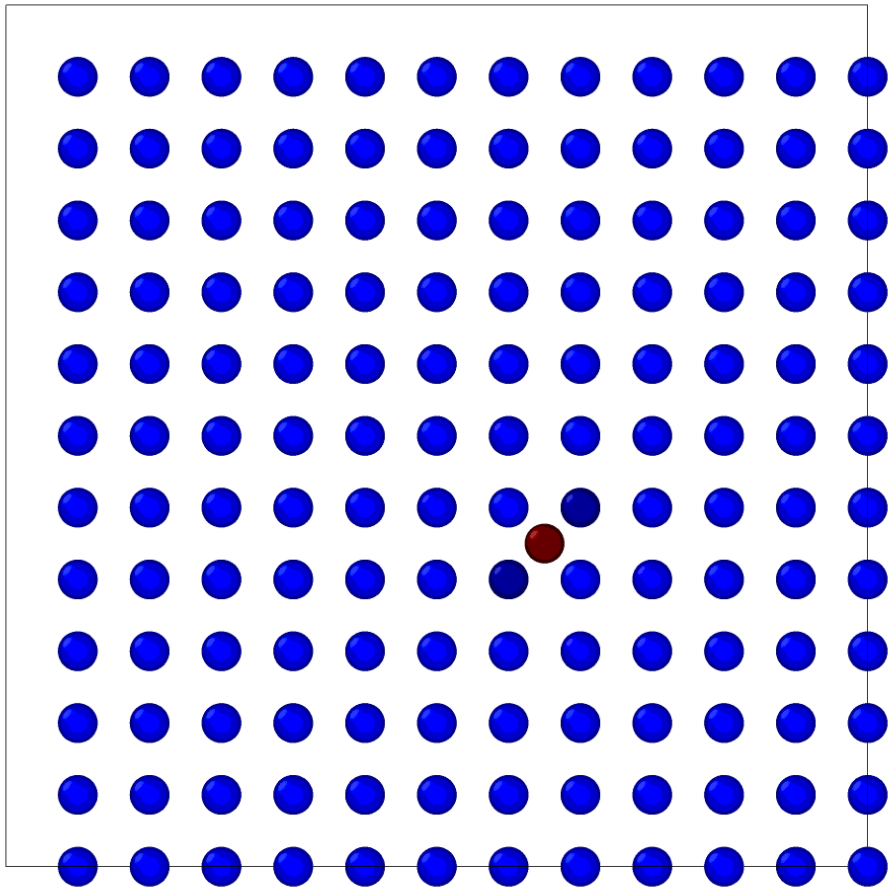


1.3 Interstitial Formation Energy via Thermal Activation

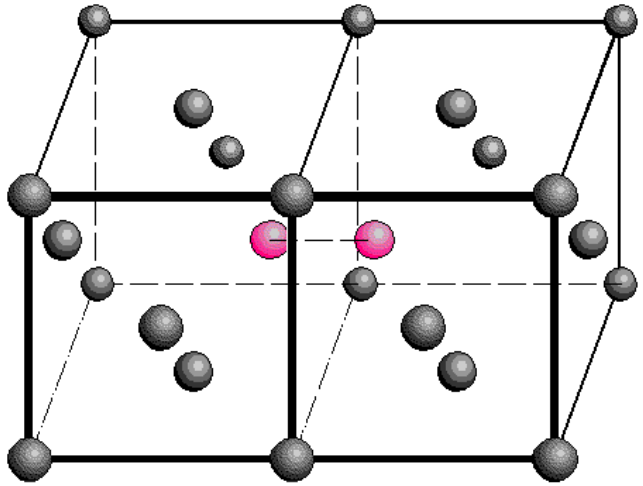
1. Initial perfect FCC cell with a 6 x 6 x 6 unit cell dimension
   - # of atoms N_A; the initial supercell with minimized energy E_A
2. Create an interstitial by inserting an atom
3. Heating up the supercell and relax
   - heating (NVT): increase the temperature from 0.5 K to 300 K
   - energy minimization (default conjugate gradient)
4. # of atoms N_B; the final energy E_B of the relaxed interstitial model
5. Calculate the interstitial formation energy, E_I (eV)

$$E_I = E_B(N+1, N) - \frac{E_A(N, N)}{N} \cdot N_B$$

Thermally activated interstitial motion

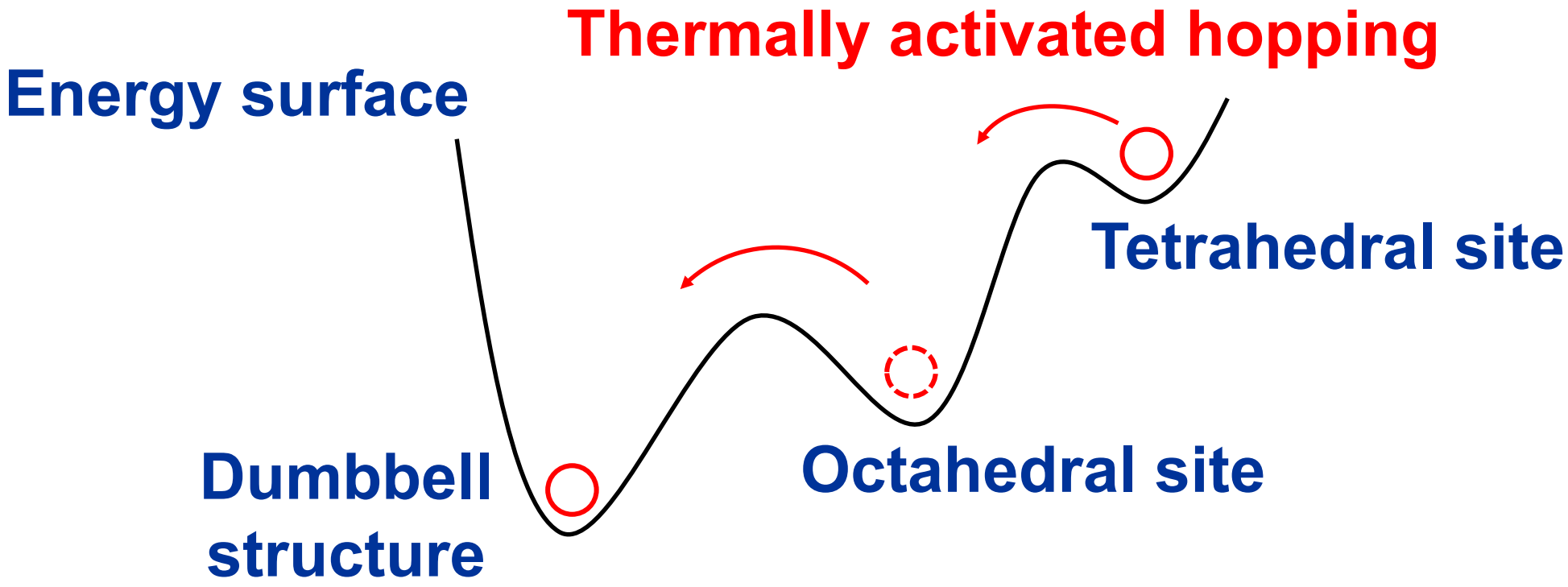


Dumbbell



- **Self-interstitials in FCC/BCC crystals**
  ➔ The atomic structure of minimum formation energy (dumbbell)

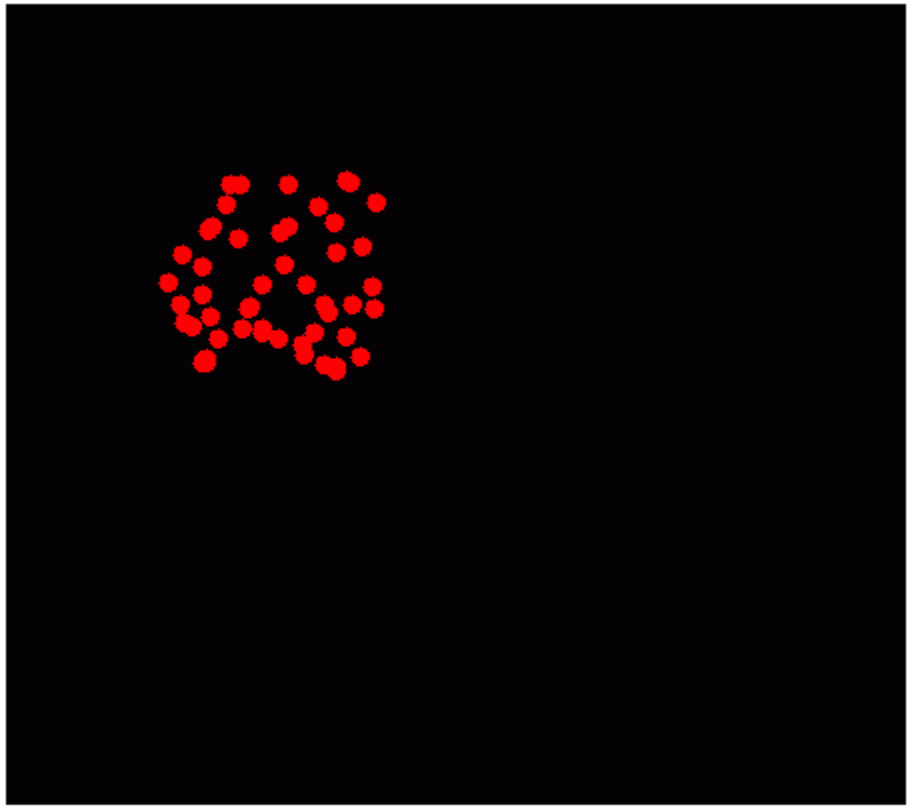
Hopping across energy barriers



- Q: How to calculate the minimum energy path and energy barrier?
- A: Nudged elastic band method in LAMMPS.

2. Diffusion: atomic vs continuum scale

Random motion of atoms



Fick's first 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.**

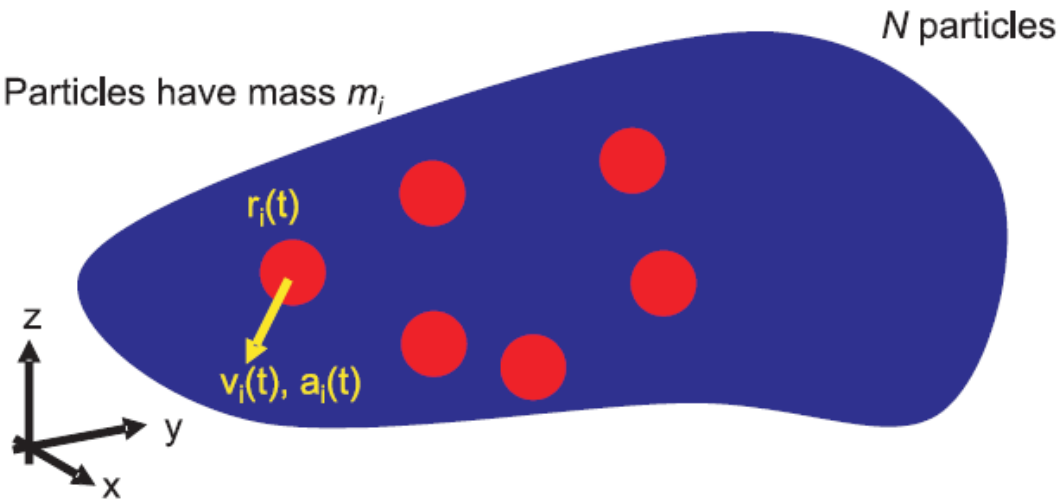
➢ **How does D depend on the motion of atoms that are undergoing diffusion, or how does D vary with the microstate of the system?**

2.1 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**

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



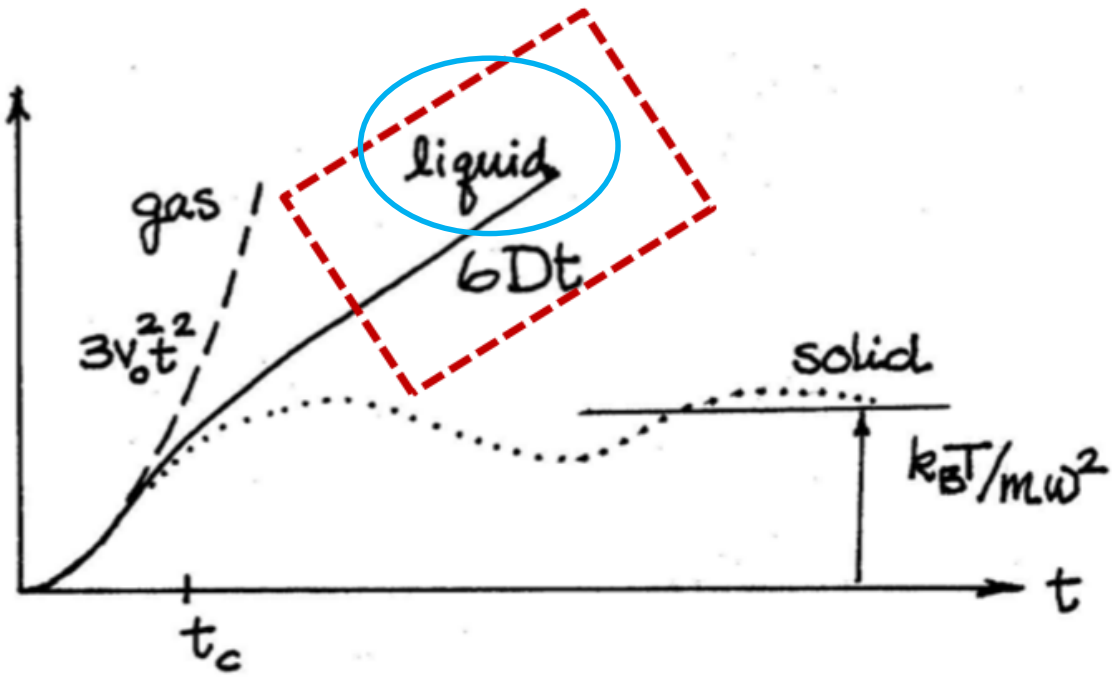
2.1 Mean square displacement $<\Delta^2 r(t)>$

- 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 6D**.

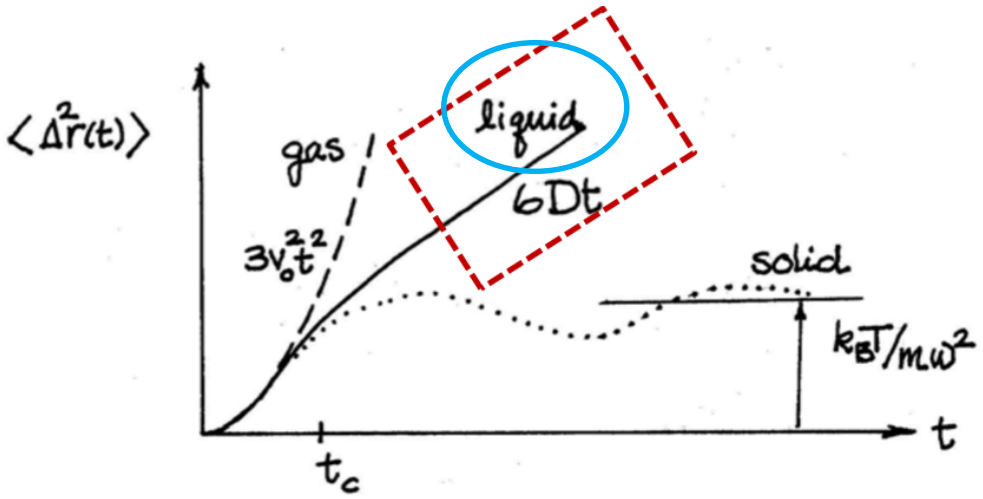
- **Solid**: Each atom is in its equilibrium position, and atoms feel the restoring forces due to the crystal bonding. One atom cannot diffuse too far from its lattice site, its motion is vibratory rather than diffusive. **MSD reaches a plateau**. (vibrational frequency)

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



2.2 Diffusion coefficient: $D = u^2/t$

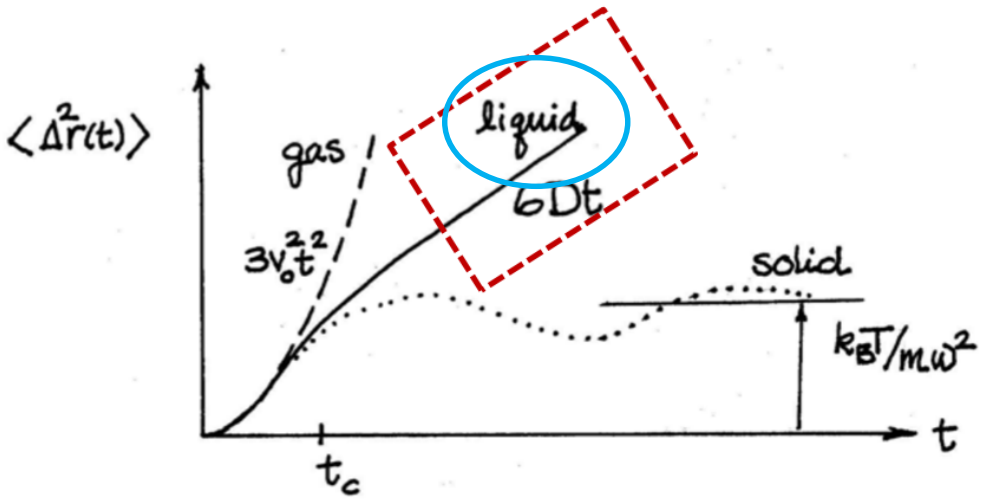
Temperature > $T_{melting}$




```
# 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.

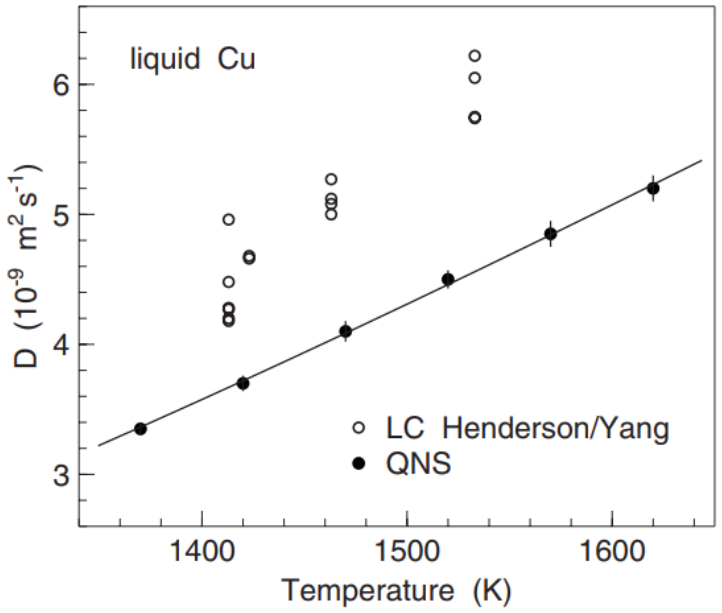


FIG. 2. Diffusion coefficients from quasielastic neutron scattering (filled circles) as a function of temperature. The line represents an Arrhenius function [Eq. (2)]. Values from a long capillary experiment (Ref. 19) are significantly larger (open circles).

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).

Homework (1)

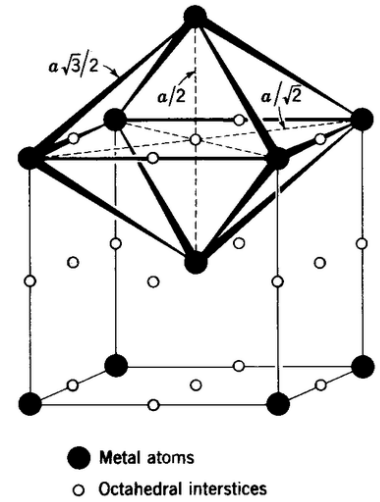
1. Calculate formation energy for Vacancy and Interstitial in fcc-Cu, fcc-Al, bcc-Fe at T = 0 K, and compare with reference.

	Cohesive energy/atom (eV)	E_V (eV)	E_{oct} (eV)	E_{tet} (eV)
Cu				
Al				
Fe				

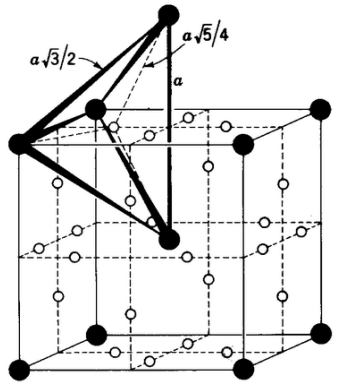
2. Calculate temperature effects on the migration of interstitial atoms in Cu.
   - Try different initial sites, relaxation T_{stop}, and final minimization temperature T_{min}, adjust heating rate, try deeper relaxation. Compare E_I and interstitial **trajectory** with that in Cu at different T.

- Due: Dec 15, 2021

O-site in bcc: (½,½,0), (½,0,0)



T-site in bcc: (¼,½,0) …



Homework (2)

3. Calculate self diffusion coefficient of Cu at different Temperature (above melting temperature 1358 K).

4. Determine the pre-factor D_0 and the activation energy on slide # 23.
   - Hint: $\ln\frac{D}{D_0} = -\frac{E_A}{k_B}(1/T)$, linear fit ln(D) = a − b·(1/T)➔ D_0 & E_A.

- Due: Dec 15, 2021

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	--			

Next Lecture：

MD Experiment #3

Appendix

$$J = -D\nabla c$$

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

$$J = -\eta\nabla v$$

- *J:* momentum flux, M_{net}/(A*dt)
- ∇v: velocity gradient
- η: viscosity (Pa·s)

$$J = -k\nabla T$$

- *J:* heat flux, Joule/(A*dt)
- ∇T: Temperature gradient
- k: thermal conductivity (Watt/m/K)