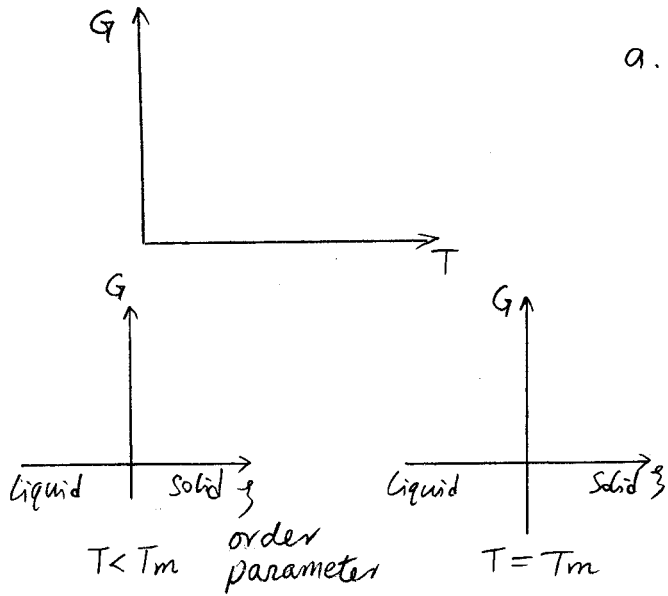


## 1. Experiment: Ice nucleation in supercooled water



a. Gibbs free energies of liquid/solid phases are equal at melting temperature  $T = T_m$ .

b. At  $T < T_m$ , liquid phase has higher free energy. So it is metastable

It will spontaneously go to the stable phase — solid phase.

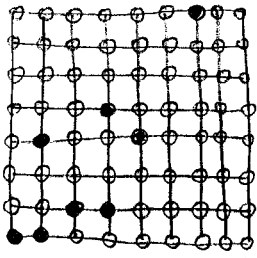
c. But the system may stay (arrested) in the metastable phase (supercooled water) for a long time by the kinetic barrier.

d. First order phase transition usually occurs by nucleation and growth.

Nucleation (of a small ice crystal) requires thermal fluctuation to overcome the free energy barrier.

## 2. Ising Model

Ising (1925) 1D, Onsager (1944) 2D



each lattice site is occupied by a spin  $S_i = \pm 1$

- $S_i = 1$  ↑
- $S_i = -1$  ↓

- a. 2D Ising model is an exactly solvable model that exhibits a phase transition

\* for more information, see ME346A Handout 11. Ising Model

- b. Hamiltonian

$$H(\{S_i\}) = -J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i \quad \text{--- (1)}$$

coupling strength
nearest neighbor pairs
external magnetic field

We will focus on the case of  $J > 0$  (ferromagnetic model)

- c. Spin dynamics (flips) at temperature  $T$  can be simulated by Monte Carlo (MC) using the metropolis algorithm.

\* more in the afternoon

- d. At thermal equilibrium, the probability of observing a given spin configuration  $\{S_i\}$  is specified by the Boltzmann distribution (or canonical distribution)

$$p(\{S_i\}) = \frac{1}{Z} e^{-\beta H(\{S_i\})}$$

↑  
normalization constant

spin configs with lower energy have higher probability

$$\beta = \frac{1}{k_B T}$$

↑  
Boltzmann's constant

We will assume  $J=1$ .

- e. when  $J > 0$ , neighboring spins "prefer" to be aligned
- ↑↑      ↓↓

when  $h > 0$ , spins "prefer" to be  $S_i = +1$

spins tend to align with external magnetic field.

- f. In the high temperature limit  $T \rightarrow \infty$  ( $\beta \rightarrow 0$ )  
all spin configurations are equally probable  
— disordered state

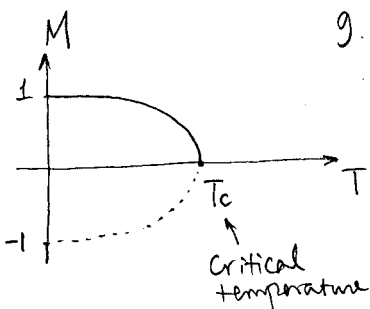
- g. In the low temperature limit  $T \rightarrow 0$  ( $\beta \rightarrow \infty$ )  
all spins prefer to be aligned collectively

most spins =  $-1$  ---- state A  
or  
most spins =  $+1$  ---- state B } two ordered states

So there must exist a critical temperature  $T_c$ .

$T > T_c$  disordered state

$T < T_c$  ordered states



magnetization

$$M = \frac{1}{N} \langle \sum_i S_i \rangle$$

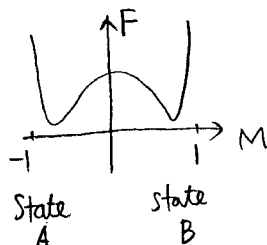
2D Ising model

$$k_B T_c = \frac{2J}{\ln(1+\sqrt{2})} = 2.269J$$

(at  $h=0$ )

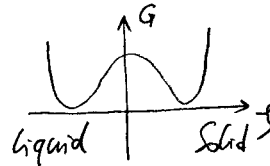
- h. We will focus on the case of  $T < T_c$

When  $h=0$



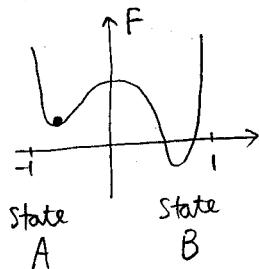
$F$ : Helmholtz  
free energy

think about water at  $0^\circ\text{C}$



States A and B have equal free energy  
and are equally probable.

when  $h > 0$



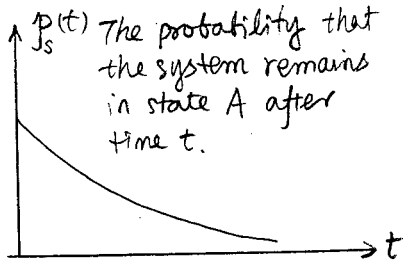
State A has higher free energy — metastable

State B has lower free energy — stable

But if the system is initialized in state A,  
it can stay there for a long time

### 3. Classical Nucleation Theory

Q: How long do we have to wait before the system jumps from state A to state B?



a. The waiting time is a random number

The probability of staying in state A after time  $t$

$$P_s(t) = 1 - e^{-It}$$

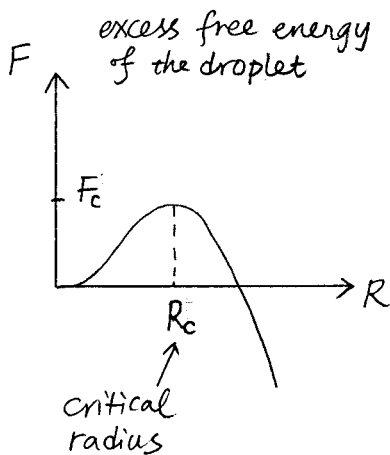
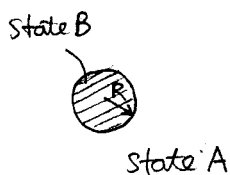
$P_s$ : for survival probability

$I$ : nucleation rate

$I(T, h)$  is what we are really after

depending on  $(T, h)$ ,  $j$  can be very low, e.g.  $10^{-30}$   
i.e. nucleation can be a rare event

We may never see a nucleation event if we run a MC simulation for a year (or a million years).



b. Volmer-Weber model (1926)

consider a spherical (3D) or circular (2D) droplet of the stable phase (state B) spontaneously formed (by fluctuation) in the sea of the metastable phase (state A)

3D

2D

$$F(R) = \sigma \cdot 4\pi R^2 - \Delta\mu \cdot \frac{4}{3}\pi R^3 \quad \text{--- (2)}$$

$\sigma$ : surface free energy (surface tension)  
 $\Delta\mu$ : chemical potential difference between the two phases

$$F(R) = \sigma \cdot 2\pi R - \Delta\mu \cdot \pi R^2 \quad \text{--- (3)}$$

maximum occurs at  $R = R_c$

$F_c \equiv F(R_c)$  is the free energy barrier that the system needs to overcome

the probability that the system finds itself at the top of the barrier is  $\sim e^{-\frac{F_c}{k_B T}}$

Volmer-Weber proposed that the nucleation rate can be estimated by

$$I \sim f_c^+ e^{-\frac{F_c}{k_B T}} \quad \text{----- (4)}$$

$\uparrow$   
 molecule  
 attachment rate

This is not a quantitative estimate.

Not specific enough about the prefactor.

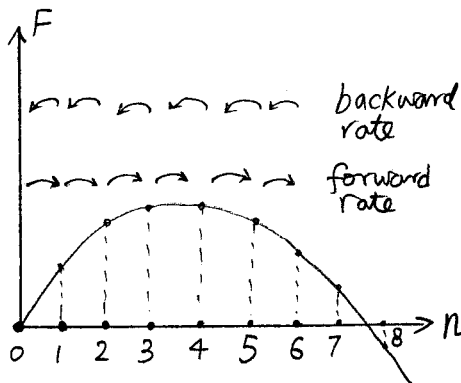
### c. Becker-Döring theory (1935)

Ref: J. D. Gunton and M. Droz

"Introduction to the Theory of Metastable and Unstable States"

Lecture Notes in Physics 183

Springer-Verlag (1983)



Coarse grain the system into a one-dimensional Markov chain specified by reaction coordinate

$n$ : # of molecules in droplet

droplet (or island)

state B -1



state A

Assume molecules only arrive or leave droplet one by one

(For Ising model, assume island of spin +1 only grows or shrinks by 1 spin at a time.)

Hence at each time,

$n$  either remains unchanged, or

$$n \rightarrow n+1$$

$$\text{or} \\ n \rightarrow n-1$$

by considering a steady state solution

(B.C. put systems reaching  $n = n_{\text{large}}$  back to state  $n=0$ )

Becker-Döring derived a quantitative prediction of the nucleation rate

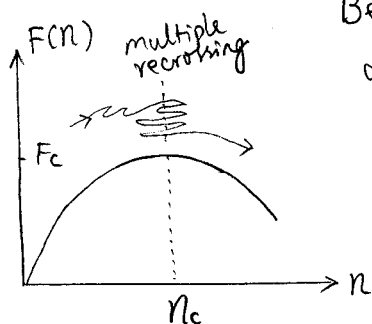
$$I = f_c^+ \Gamma e^{-\frac{F_c}{k_B T}} \quad \text{----- (5)}$$

where  $\Gamma \equiv \left( \frac{\eta}{2\pi k_B T} \right)^{1/2}$

$$\eta = - \left. \frac{\partial^2 F(n)}{\partial n^2} \right|_{n=n_c}$$

Zeldovich factor

↑  
multiple recrossing of  $n=n_c$  interface only counts as one nucleation event



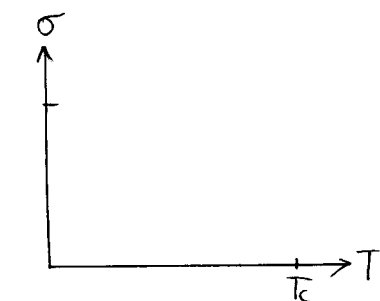
$$F_c = \max_n F(n)$$

for 2D Ising model,

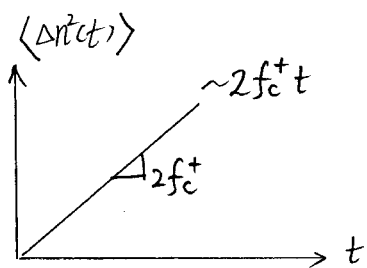
$$F(n) = \sigma_{\text{eff}}(T) \cdot 2\sqrt{\pi} \cdot n^{1/2} - \text{---} \cdot n \quad \text{----- (6)}$$

for 3D Ising model

$$F(n) = \sigma_{\text{eff}}(T) \cdot (36\pi)^{1/3} \cdot n^{2/3} - \text{---} \cdot n \quad \text{----- (7)}$$



Surface free energy is known accurately in 2D Ising model



$f_c^+$  (molecular attachment rate)

for Ising model, it means the rate at which the critical droplet fluctuates.

— similar to the "diffusion constant", along  $n$ -axis

consider an ensemble of islands, all with size  $n_c$  at  $t=0$ .

$$\langle \Delta n^2(t) \rangle \equiv \langle (n(t) - n_c)^2 \rangle$$

is the mean square deviation of the island size as a function of time

The Becker-Döring equation, Eq. (5)

is the most frequently used form of classical nucleation theory (CNT).

Q: Is it correct? (Does it apply to the Ising model?)

How can we test it?

Verdict is mixed!

Many Monte Carlo simulations of Ising model have been performed in the last few decades to test CNT.

## 4. Numerical Simulations to test CNT

Brute force MC simulation is out of the question because we are interested in the  $(T, h)$  regime where  $j$  is very small.

CNT really consists of two Parts

Part I:  $I = f_c^+ \Gamma e^{-\frac{F_c}{k_B T}}$  Eq. (5)

Part II:  $F(n) = \sigma_{\text{eff}}(T) \cdot 2\sqrt{\pi} \cdot n^{1/2} - 2hn$  Eq. (6)

↑ assumes surface energy of flat interface can be applied to curved surface of droplet

Strategy:

① suppose if we can compute  $I$ ,  $f_c^+$ ,  $\Gamma$ ,  $F_c$  independently, then we can plug them into Eq. (5) to see if Part I works.

$I$ : can be computed by Forward-Flux-Sampling (FFS) method.

Ref: Allen, Frenkel, and ten Wolde, J. Chem. Phys. 124, 024102 (2006),  
124, 194111 (2006).

$F(n)$ : can be computed by Umbrella Sampling (US) method.

Ref: Auer and Frenkel, Annu. Rev. Phys. Chem. 55, 333 (2004).

$$F(n) \rightarrow F_c, \Gamma$$

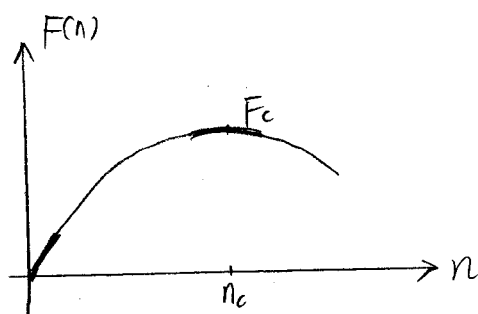
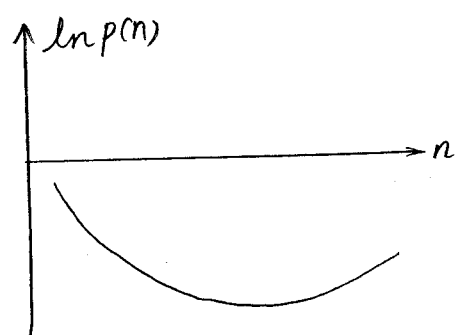
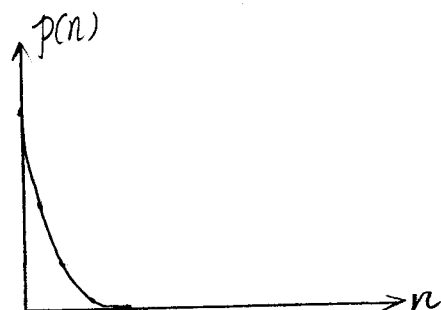
$f_c^+$ : can be computed from MC simulations starting from spin configurations with  $n=n_c$  (from FFS or US simulations)

②  $F(n)$  computed from US can be compared against Eq. (6) to test Part II of CNT.

## 5. Umbrella Sampling

a. conventional Monte Carlo simulation  
Metropolis algorithm

# of occurrence  
during MC simulation



→ randomly pick a spin  $i$   
 attempt to flip spin:  $S_i := -S_i$   
 compute energy change caused by the flip  

$$\Delta E = -2 \left( J \sum_{\text{nearest neighbors of } i} S_j + h \right) S_i$$
  
 if  $\Delta E < 0$ , accept the attempt  
 if  $\Delta E > 0$ , accept the attempt with probability  

$$P_{\text{acc}} = \exp\left(-\frac{\Delta E}{k_B T}\right)$$
  
 if the flip attempt is rejected, put it back,  
 i.e.  $S_i := -S_i$

one can show that this algorithm samples  
canonical distribution (see p. 2)

From an MC simulation, we can collect a  
histogram for the # of occurrence of spin +1  
islands of size  $n$ .

The histogram allows us to estimate the  
probability of finding an island of size  $n$   
at thermal equilibrium.

By definition,  

$$p(n) = e^{-\frac{F(n)}{k_B T}}$$

$$\therefore F(n) = -k_B T \ln p(n)$$

Hence, we can (in principle) estimate  $F(n)$   
by running Monte Carlo simulations.

The problem is that, in the region of interest,  
 $n \sim n_c$ ,  $p(n)$  is so small that we  
 don't get any data. e.g.  $p(n) \sim 10^{-20}$



Nonetheless, MC simulation can still tell us the shape of  $F(n)$  at  $n \approx 0$

Q: How to get  $F(n)$  at larger  $n$  values?

b. Bias potential

We can convince the computer to sample a different region on the  $n$ -axis, by changing the Hamiltonian e.g.

$$\tilde{H}(\{S_i\}) = \underbrace{-J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i}_{\text{original Hamiltonian}} + \underbrace{K (n(\{S_i\}) - \bar{n})^2}_{\text{bias potential}}$$

$\uparrow$  new Hamiltonian

For appropriate values of  $K, \bar{n}$ , the new simulation will generate spin configurations whose largest up-spin island  $n$  is in the neighborhood of  $\bar{n}$ .

$\uparrow$  sampling window       $\uparrow$  center of the window

The droplet (island) free energy of the new system is

$$\tilde{F}(n) = F(n) + K(n - \bar{n})^2$$

From the simulation histogram, we can estimate  $\tilde{p}(n)$

$$\rightarrow \tilde{F}(n) = -k_B T \ln \tilde{p}(n)$$

$$\rightarrow F(n) = \tilde{F}(n) - K(n - \bar{n})^2$$

Again, we obtain information about  $F(n)$ , but now in a different window, centered at  $\bar{n}$ .

\* Because it is expensive to compute largest cluster size  $n(\{S_i\})$ , the bias potential is not computed for every spin flip. After a number of spin flips using the original Hamiltonian, the whole sequence is accepted or rejected based on the bias potential.

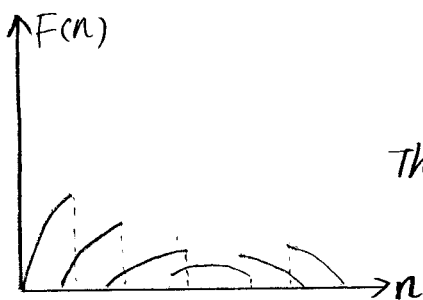
## c. overlapping the windows (or Umbrellas)

We have missed a detail so far. From the histogram method, we only know the relative probabilities, e.g.

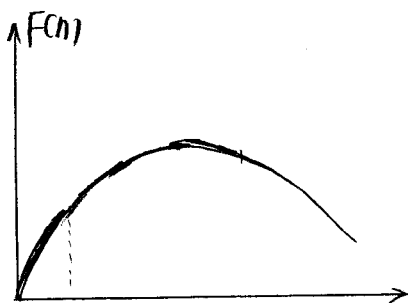
$$\frac{p(n_1)}{p(n_2)}, \text{ but not the absolute probabilities,}$$

This means, the  $p(n)$  curves we obtain is up to a multiplicative constant. (can be determined by requiring  $\sum_{n=0}^{\infty} p(n) = 1$ )

Thus, the  $F(n)$  curves we obtain is up to an additive constant.



We can add appropriate constants to different pieces of the  $F(n)$  curve obtained from U.S. at different windows (different  $\bar{n}$ ), so that we get one continuous curve,



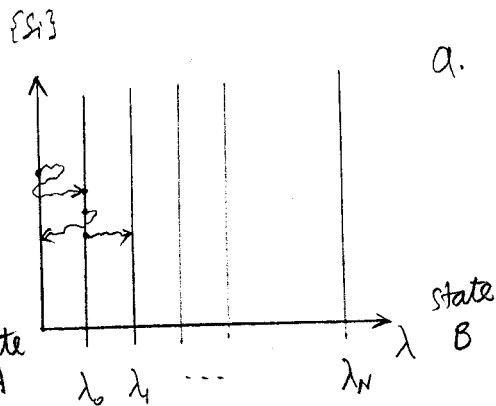
provided every window has some overlap with the neighboring windows.

## 6. Forward Flux Sampling

Because we want to compute the nucleation rate  $j$  numerically as a benchmark to test the Becker-Döring theory, the method we use should not rely on the same assumptions in the Becker-Döring theory.

- FFS was shown to work in non-markovian systems.
- FFS does not require detailed balance.
- The rate computed by FFS is independent of the choice of order parameter  $\lambda$  (we will set  $\lambda = n$ )

↑ size of largest cluster



a. define interfaces.

$$\lambda_A < \lambda_0 < \lambda_1 < \dots < \lambda_N$$

$\lambda \leq \lambda_A$  ----- corresponds to state A (spin ↓)

$\lambda \geq \lambda_N$  ----- corresponds to state B (spin ↑)

Fundamental assumption in FFS

$$I_0 \xrightarrow{\text{-----}} P(\lambda_N | \lambda_0)$$

$$I = I_0 P(\lambda_N | \lambda_0)$$

↑ nucleation rate, or rate of reaching state B  
 ↑ rate of nucleation a small nucleus, i.e. reaching interface  $\lambda_0$   
 ↑ probability of reaching interface  $\lambda_N$ , having already reached interface  $\lambda_0$ .

$$P(\lambda_N | \lambda_0) = P(\lambda_1 | \lambda_0) P(\lambda_2 | \lambda_1) \dots P(\lambda_N | \lambda_{N-1})$$

## b. FFS algorithm

i) start from state A, run conventional MC simulations for a long time, compute  $I_0$ , save a number of ( $\sim 500$ ) spin configurations whose  $n = \lambda_0$

ii) using the saved configurations at  $n = \lambda_0$  as initial condition, run conventional MC simulations (run multiple simulations from every initial condition) terminate each simulation when  $n \leq \lambda_A$  or  $n \geq \lambda_1$   
$$p(\lambda_1 | \lambda_0) = \frac{\# \text{ of times } n \geq \lambda_1}{\text{total } \# \text{ of simulation}}$$

finish this step after we have saved a sufficient number of ( $\sim 500$ ) spin configurations whose  $n = \lambda_1$

iii) use similar approach as ii) to compute  $p(\lambda_2 | \lambda_1)$  and save a number of spin configurations at  $n = \lambda_2$

iv) ...

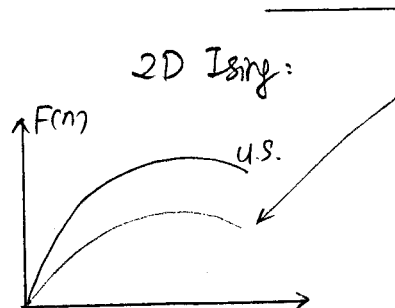
stop until we have obtained  $p(\lambda_N | \lambda_{N-1})$

## 6. How well does Becker-Döring theory work?

Part I works beautifully

$$I = f_c^+ T \exp\left(-\frac{F_c}{k_B T}\right) \quad \text{--- Eq. (5)}$$

for both 2D and 3D Ising model

for  $I$  over 20 orders of magnitude!(See numerical results,  $I^{FFS}$  v.s.  $I^{CNT}$ )Part II doesn't work so well.

2D Ising:

$$F(n) = \sigma_{\text{eff}}(T) \cdot 2\sqrt{\pi} \cdot n^{1/2} - 2h n \quad \text{--- Eq. (6)}$$

significantly underestimates  $F(n)$  from u.s.

but with two correction terms added

$$F(n) = \sigma_{\text{eff}}(T) \cdot 2\sqrt{\pi} \cdot n^{1/2} - 2h n + \frac{5}{4} k_B T \ln n + d(T)$$

↑  
constant, in the  
sense that it is  
independent of  $n$   
can be determined  
analytically.

3D Ising model ----- not very clear

For more details, see

S. Ryu and W. Cai. Phys. Rev. E 81, 030601(R) (2010)  
82, 011603 (2010).<http://www.stanford.edu/~caiwei/papers.html>

## 7. Numerical Demonstration of MD++

by Seungwon Ryu, after lunch.

## Numerical Homeworks

1. Run MC simulations of 2D Ising model at  $h=0$ , ( $J=1$ )  
(100x100)  
at several temperatures.

Plot averaged magnetization as a function of temperature,  
together with analytic solution.

$$M = [1 - (\sinh 2\beta)^{-4}]^{1/8}$$

2. Run FFS simulation of 2D Ising model ( $J=1$ )  
(100x100)  
at  $h=0.06$  and  $k_B T = 1.7$

Obtain nucleation rate

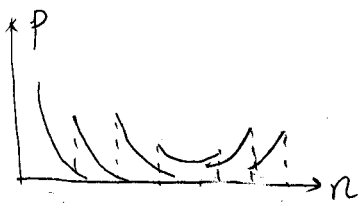
$$I = I_0 \cdot P(\lambda_n | \lambda_0)$$

Plot one spin configuration at each interface  $\lambda_i$

3. Run US simulation of 2D Ising model (100x100) ( $J=1$ )

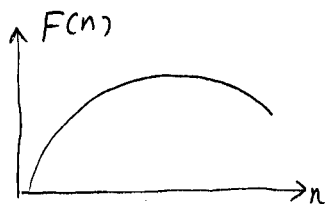
at  $h=0.06$  and  $k_B T = 1.7$

with 20 windows of half width  $w=8$ , centered at  
 $\bar{n} = 6 + 12i$ ,  $i=0, 1, 2, \dots, 19$ , respectively.



convert the probability data into

one continuous curve for the free energy  $F(n)$



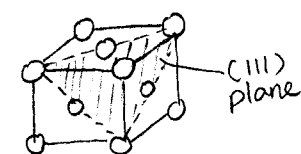
We have seen that the Becker-Döring theory

$$I = f_c^+ \Gamma \exp\left(-\frac{F^*}{k_B T}\right)$$

works well for the Ising model.

Here we will use it to predict the rate of dislocation nucleation under stress at finite temperature.

## 1. What is a dislocation



face-centered-cubic (FCC) crystal

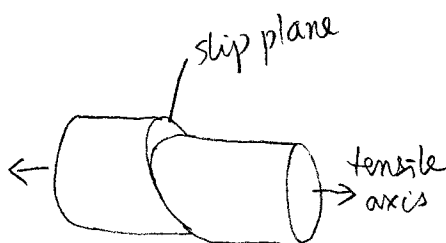
Al, Cu, Au, etc.

- a. Most engineering materials (metal, semiconductor) are crystals.

Atoms in a perfect crystal are arranged in a periodic structure.

A dislocation is a line defect in the crystal (more details later)

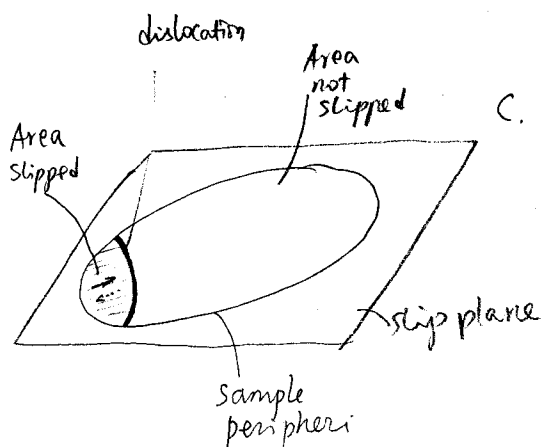
Dislocation motion is the fundamental mechanism of plastic deformation in metals.



(See Uchic's movie)

- b. Plastic deformation of metals occurs as slipping on crystallographic planes, e.g. (111) planes in FCC metals.

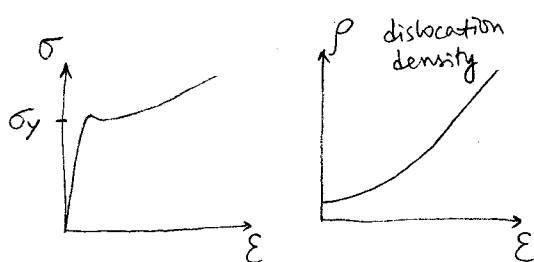
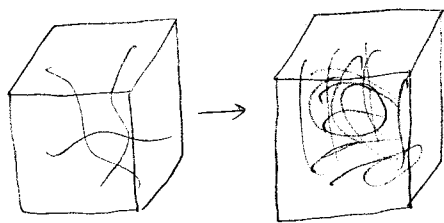
But simultaneously breaking (shearing) all the bonds across the slip plane requires a stress much higher than experimentally observed yield stress.



- c. What really happens is that part of the area on the slip plane slips first. The boundary between slipped and unslipped areas on the plane is a dislocation line.

The amount of slip is always a crystallographic vector, e.g.  $\underline{b} = \frac{a_0}{2} [110]$  in FCC metals. This is the Burgers vector of the dislocation. As the dislocation moves across the plane, the entire plane slips by  $\underline{b}$ .

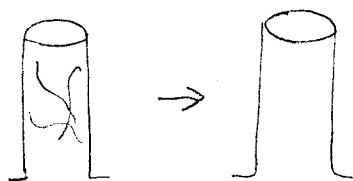
## 2. Dislocation multiplication versus nucleation



(See ParaDis movie)

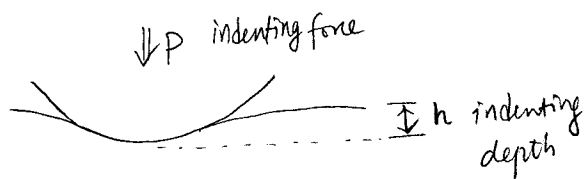
a. bulk crystal usually contains grow-in dislocations.

dislocation density increases by orders of magnitude (multiplication) during plastic deformation

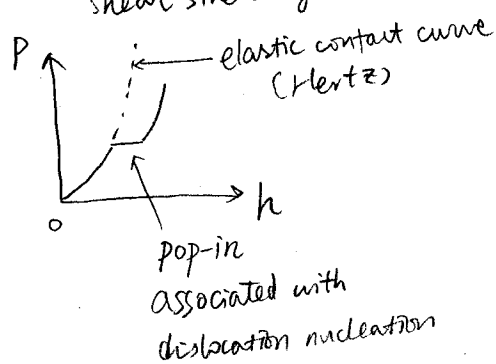


Shan et al. (2008)  
Nature Materials

b. In very small samples (e.g. micropillar, nanowire) all dislocations can leave the sample creating a "dislocation-starved" state. Continued plastic deformation requires supply of fresh dislocations, probably nucleated from the surface.



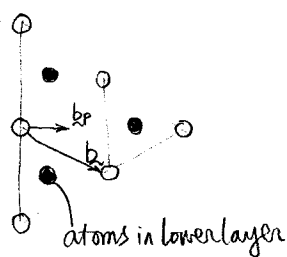
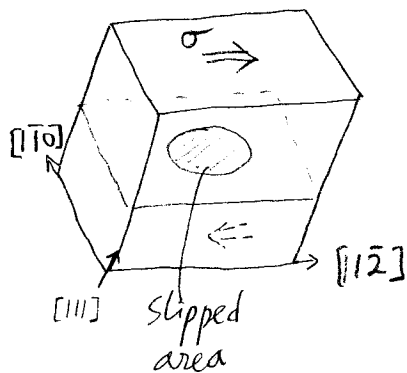
↑ incipient dislocation nucleate at maximum shear stress region



c. In nano-indentation experiment, the first "pop-in" event is usually associated with dislocation (loop) nucleation in the maximum shear stress region beneath the indenter.



### 3. Homogeneous dislocation nucleation



(111) plane

- a. For simplicity, we will focus on homogeneous nucleation of a dislocation loop in a crystal subjected to a uniform (and large) shear stress  $\sigma$

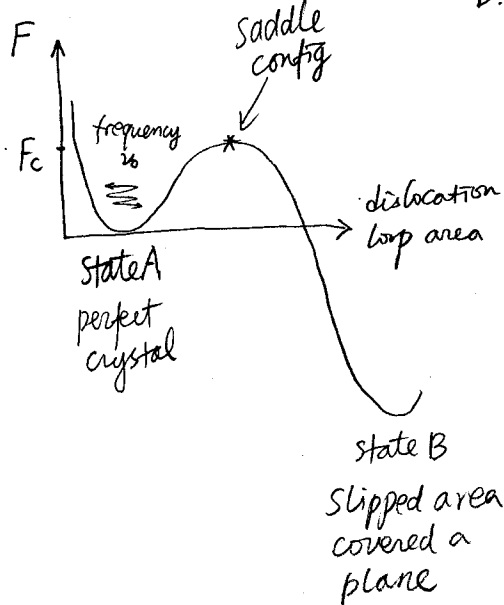
We want to predict the nucleation rate

$$I(T, \sigma)$$

$\sigma$  plays the role of the magnetic field  $h$  in the Ising model.

The nucleation rate function is linked to the "ideal strength" of the crystal.

The stress  $\sigma$  at which  $I(T, \sigma) \approx 1 s^{-1}$  is the stress at which a perfect crystal will collapse at the experimental time scale



- b. dislocation nucleation rate has often been estimated by Transition State Theory (TST)

$$I = \nu_0 \exp\left(-\frac{F_c(\sigma, T)}{k_B T}\right)$$

attempt frequency in metastable State A

----- we will check is this consistent with Becker-DeVries theory

free energy barrier

$\nu_0$  is usually taken to be the Debye frequency  
 $\nu_0 \approx 10^{13} \text{ Hz}$

$$I = \underbrace{\nu_0 \exp\left(\frac{S_c}{k_B}\right)}_{\text{pre-exponential factor if } E_c \text{ is used}} \exp\left(-\frac{E_c}{k_B T}\right)$$

$$F_c(\sigma, T) = \underbrace{E_c(\sigma, T)}_{\text{energy barrier}} - T \underbrace{S_c(\sigma, T)}_{\text{excess entropy of saddle config.}}$$

## 4. Chain of states Methods

- a. Most of existing methods applied to dislocation nucleation compute energy barrier at  $T=0$

$$F_c(\mathbf{c}, T=0) = E_c(\mathbf{c}, T=0)$$

Q: How large is the entropy  $S_c$ ?

The answer requires finite temperature simulations (later)

- b. Nudged-elastic-band (NEB) and String methods

(for more discussions, see "Computer Simulations of Dislocations", Bulatov and Cai, Oxford Univ. Press (2006). Chapter 7.)

The position of  $N$  atoms in the system can be specified by a  $3N$ -dimensional vector  $\underline{r}$

The  $3N$ -dimensional space of  $\underline{r}$  is called the configurational space. Every point in this space corresponds to a microstate of the system.

The interatomic interaction is described by the potential energy function  $U(\underline{r})$

Let  $\underline{r}_A$  and  $\underline{r}_B$  be two local minima of  $U(\underline{r})$

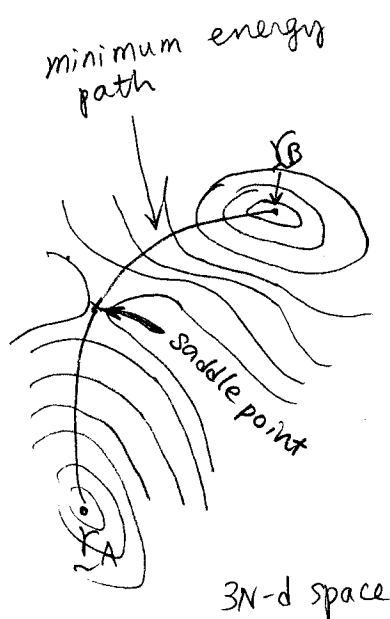
The region around  $\underline{r}_A$  is state A (perfect crystal)

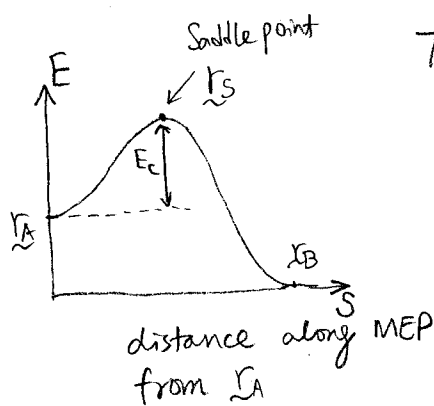
The region around  $\underline{r}_B$  is state B (slipped area covered a plane)

We are interested in the dislocation nucleation rate, which is the transition rate from state A to state B.

The NEB or string method search for the minimum energy path (MEP) connecting  $\underline{r}_A$  and  $\underline{r}_B$

Every point along MEP is an energy minimum in the directions perpendicular to the local tangent of MEP.





The energy maximum along MEP is called the Saddle point.

The energy barrier  $E_c(T=0)$  is the energy difference between the saddle point and  $r_A$

$$E_c(T=0) = U(r_S) - U(r_A)$$

To find MEP and hence saddle point, the NEB or string method creates a chain of states (allocates more 3N-d vectors)

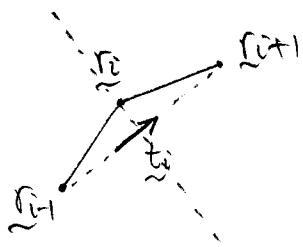
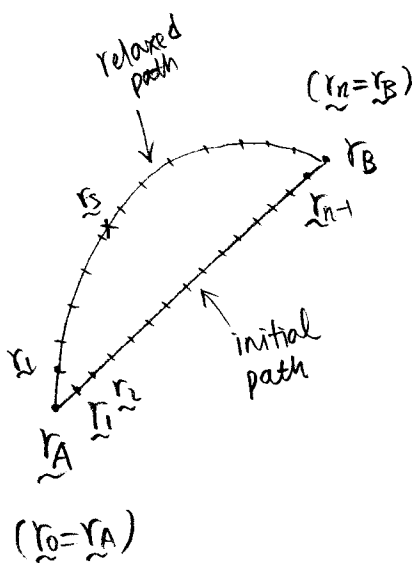
Usually, these vectors are initialized to be linear interpolations of  $r_A$  and  $r_B$

While  $r_0 = r_A$ ,  $r_n = r_B$  remain fixed,

$r_1, \dots, r_{n-1}$  are allowed to relax (minimize  $U(r_i)$ )

subjected to the constraint that the distance between neighboring states,

$L_1 \equiv |r_1 - r_0|$ ,  $L_2 \equiv |r_2 - r_1|$ ,  $\dots$ ,  $L_N \equiv |r_n - r_{n-1}|$  remain (close to) uniform along the chain.



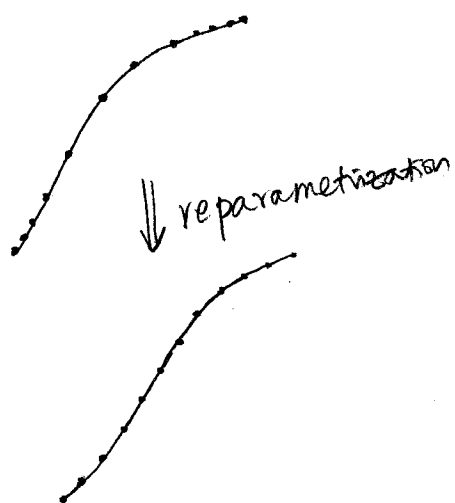
To minimize  $U(r_i)$  iteratively, we can simply move  $r_i$  along the force direction  $f_i \equiv -\frac{\partial U}{\partial r_i}$  in small steps.  $r_i := r_i - f_i \cdot \Delta$  (step size)

The NEB method implements the "equi-distance" constraint by modifying the force

$$t_i \equiv \frac{r_{i+1} - r_{i-1}}{|r_{i+1} - r_{i-1}|}$$

is the local tangent vector along MEP

$$f_i^{\text{NEB}} = \underbrace{f_i - (f_i \cdot t_i) t_i}_{\text{orthogonalize physical force with tangent vector } t_i} + \underbrace{K}_{\text{spring constant}} \underbrace{[(r_{i+1} + r_{i-1} - 2r_i) \cdot t_i] t_i}_{\text{artificial spring force to favor uniform sampling along MEP}}$$



The string method does not use the spring force (i.e.  $K=0$ ), but simply reparametrize the path sampled by  $\underline{r}_i$  to make the sampling uniform along the path.

This amounts to moving  $\underline{r}_i$  along  $\underline{r}_i$  by a distance computed based on the information of  $L_1, L_2, \dots, L_N$ .

The string method is conceptually simpler (no need to find an appropriate value for  $K$ ) and appears more stable.

— especially on rough energy surfaces.

### c. "Free-end" string method

(Keonwook Kang, Stanford, to be published)

Dislocation nucleation rate is vanishingly small unless stress is very high ( $\sim 1 \text{ GPa}$ )

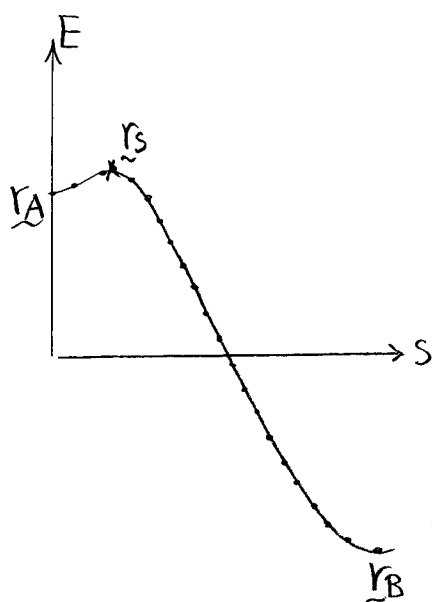
At high stress,  $U(\underline{r}_B)$  is much lower than  $U(\underline{r}_A)$  (say by  $\sim 10 \text{ eV} - 100 \text{ eV}$ )

The saddle point is much closer to  $\underline{r}_A$  than to  $\underline{r}_B$

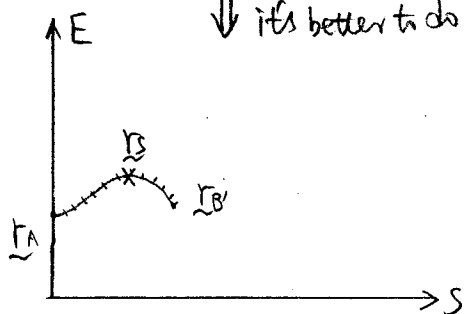
In this case, the MEP usually appears under-discretized (too coarse) near the saddle point, while many states are "wasted" between  $\underline{r}_S$  and  $\underline{r}_B$ .

We would prefer to truncate the chain to have a finer discretization near  $\underline{r}_S$ .

But the end of the path  $\underline{r}_B$  is no longer a local energy minimum, and should be allowed to move (relax).



↓ it's better to do this



Zhu et al. PNAS 104,3031 (2007) proposed the free-end NEB method, in which  $X_B'$  is constrained to stay on an energy isosurface.

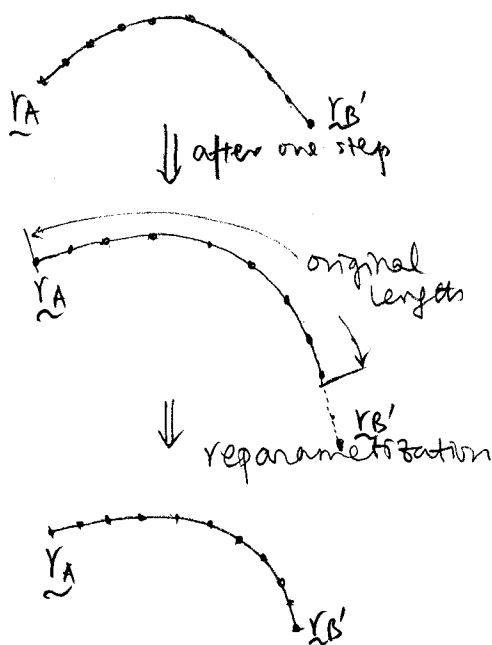
But we find it is non-trivial to find an appropriate spring constant  $K$  to make the new algorithm stable.

On the other hand, it is easy to generalize the string method to allow  $X_B'$  to relax but not to fall down all the way to  $X_B$ .

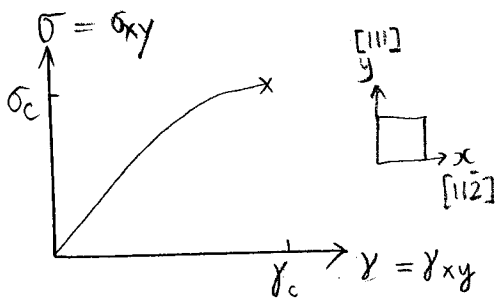
For example, we can require the total length of the path to remain constant after the reparametrization.

This amounts to truncating the path during the reparametrization step.

see free end string method result for partial dislocation nucleation in EAM Cu.



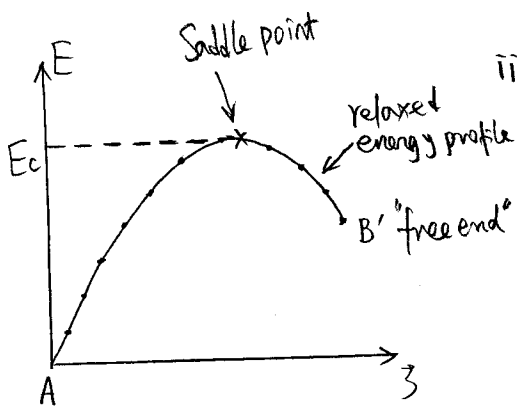
## d. Zero temperature results



i) First we need to get the (shear) stress-strain relationship (for the EAM Cu potential)

At each  $\gamma_{xy}$  value, we adjust all other strain components ( $\epsilon_{xx}, \epsilon_{yy}, \dots$ ) iteratively until the only non-zero stress component is  $\sigma_{xy}$

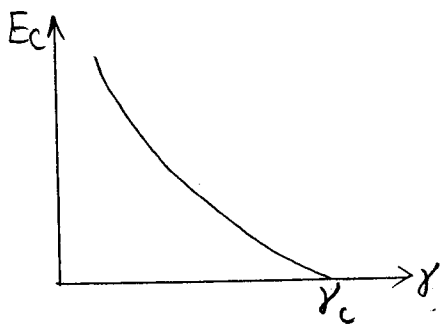
(see Seungghwa's numerical demo)



ii) At a given  $\gamma_{xy}$  value, (we also know the appropriate strain  $\epsilon_{xx}, \epsilon_{yy}, \dots$  so that only  $\sigma_{xy} \neq 0$ ) we perform string method calculation between state A and state B'

↑  
perfect crystal

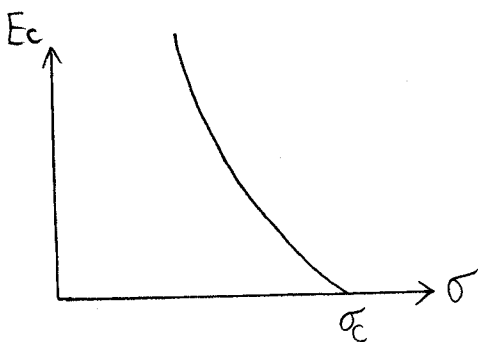
↑  
crystal containing a dislocation loop with radius > critical



iii) repeat ii) for different value of  $\gamma_{xy}$  ( $\sigma_{xy}$ )  
Plot  $E_c(\gamma_{xy})$  and  $E_c(\sigma_{xy})$

There is a critical strain  $\gamma_c$   
stress  $\sigma_c$

at which the energy barrier  $E_c \rightarrow 0$

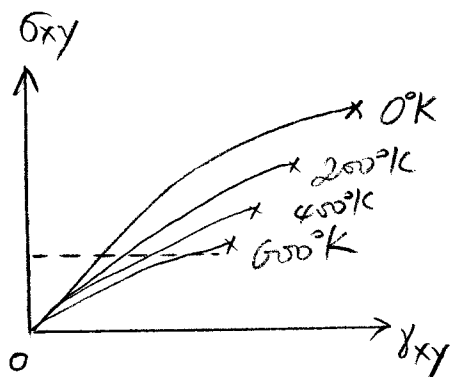


## 5. Finite Temperature Methods

$$\text{CNT: } I = f_c^+ T \exp\left(-\frac{F_c(\sigma, T)}{k_B T}\right)$$

a. First we need to find the thermal expansion strain at the given temperature  $T$  (at zero stress)

Then we need to obtain the shear stress-strain curves at finite temperature, by fixing  $\gamma_{xy}$  and adjusting other strain components until the only stress component is  $\sigma_{xy}$ .



The same stress produces increasing strain as temperature increases.

Notice shear modulus (slope at  $\gamma_y=0$ ) decreases with temperature  $T$ .

The critical strain  $\gamma_c$  also  
stress  $\sigma_c$   
decrease dramatically with  $T$ .

## b. Umbrella sampling of dislocation nucleation



$$\text{if } \max_{j \in \text{neighbor of atom } i} |r_{ij} - r_{ij}^0| > d_c$$

$\uparrow$  bond length       $\uparrow$  bond length in perfect crystal

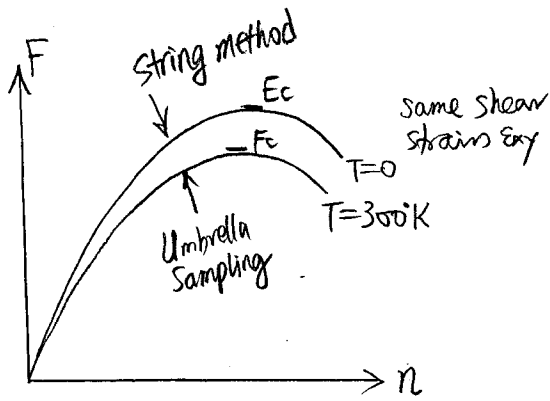
then atom  $i$  is labeled as

"slipped" atom (atom enclosed by dislocation loop)

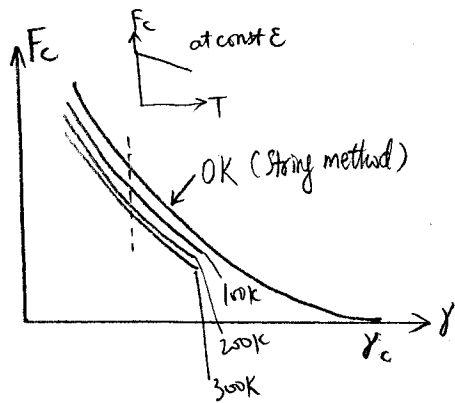
"Slipped" atoms closer to others than a cut off distance  $r_c$  are grouped into a cluster

$n_c$ : the # of atoms in the largest cluster  
is the global order parameter.

(Similar to the case of Ising model)

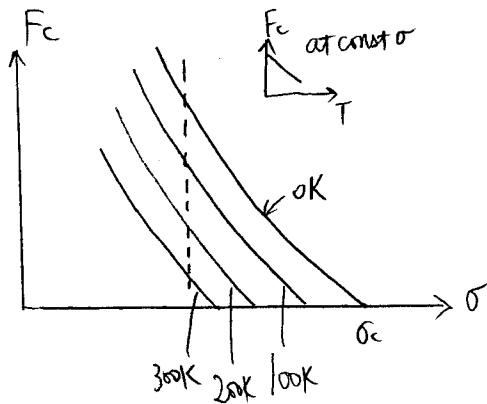


The free energy barrier at 300K is lower than the energy barrier at 0K.  
Q: why? what's the dominant mechanism?



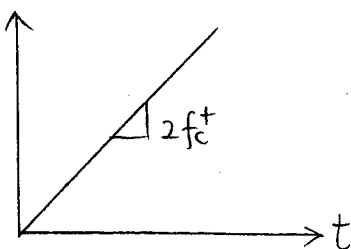
The drop of  $F_c$  with  $T$  at constant  $\sigma$  is much faster than that at constant  $\epsilon$ .

Q: why?



C. Attachment rate  $f_c^+$

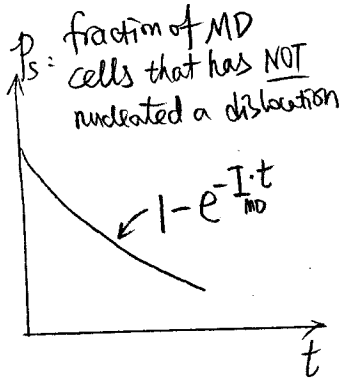
$$\langle (n(t) - n_c)^2 \rangle$$



compute by running Molecular Dynamics (MD) starting from critical nucleus. ( $n_c$ )



d. Put it all together, does it work?



Can be directly computed by MD at high  $T, \sigma$

$$I = N_{tot} \cdot f_c^+ \cdot \Gamma \cdot \exp\left(-\frac{F_c}{k_B T}\right)$$

# of nucleation sites

free energy normalized to probability per nucleation site

CNT prediction

(See Seung-Hwan's numerical results)

$$I^{MD} = 3.1 \times 10^8 \text{ Hz}$$

$$N_{tot} = 14976 \quad f_c^+ = 9.6 \times 10^{14} \text{ Hz} \quad \Gamma = 0.0554 \quad F_c = 0.6 \text{ eV}$$

$$I^{CNT} = 9.2 \times 10^7 \text{ Hz}$$

differences within error bar

## Numerical Homeworks

1. Run MD simulations of EAM Cu potential (in MDH)  
(Mishin)

to find out the thermal strain, at  $T=100\text{K}$ ,  $200\text{K}$ ,  $300\text{K}$ ,  $600\text{K}$ .

Plot thermal strain as a function of temperature  
and estimate the thermal expansion coefficient.

2. Obtain the  $\sigma_{xy}(\epsilon_{xy})$  relationship for the above potential model  
when  $\sigma_{xy}$  is the only non-zero stress component.  
at  $T=0\text{K}$ ,  $300\text{K}$ ,  $600\text{K}$ .

$x: [11\bar{2}]$

$y: [111]$

$z: [1\bar{1}0]$