

## CSRC Summer Short Course on Monte Carlo Methods

## Free Energy and Umbrella Sampling Methods

Wei Cai Stanford University

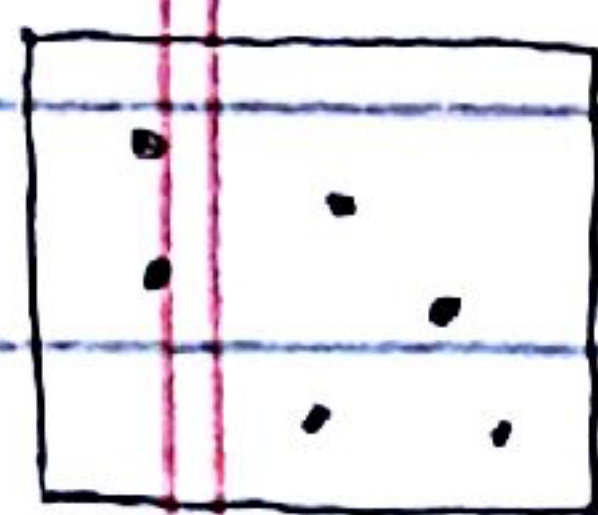
## Part I. Free Energy Methods

## 1. Definitions of Model Systems

## Atomic System (N atoms)

coordinates  $\{q_i\}$   $i=1, 2, \dots, 3N$ momenta  $\{p_i\}$ 

$$\text{Hamiltonian } H(\{q_i, p_i\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U(\{q_i\})$$

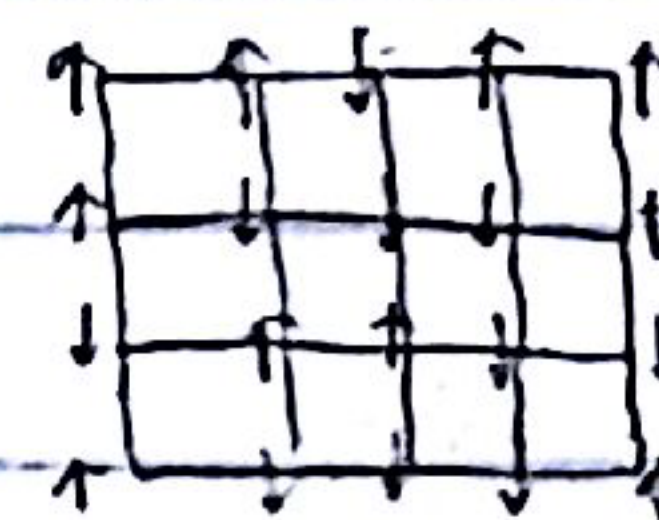
 $U(\{q_i\})$  interatomic potential

## Ising Model (N spins)

spins  $\{S_i\}$   $i=1, 2, \dots, N$ 

$$S_i = \begin{cases} +1 & \uparrow \\ -1 & \downarrow \end{cases}$$

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

 $\langle i,j \rangle$ : all nearest neighbor pairs

Canonical Ensemble describes equilibrium distribution at finite temperature  $T$

probability density of finding the system at phase space point  $(q_i, p_i)$  ( $\beta \equiv \frac{1}{k_B T}$ )

$$P(q_i, p_i) = \frac{1}{Z} e^{-\beta H(q_i, p_i)} = \frac{1}{Z} e^{-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}} e^{-\beta U(\{q_i\})}$$

normalization factor

$$\tilde{Z} = \int \prod_{i=1}^{3N} dq_i dp_i e^{-\beta H(q_i, p_i)}$$

$$\text{partition function } Z = \frac{1}{N! h^{3N}} \tilde{Z}$$

 $k_B$ : Boltzmann's constant $h$ : Planck's constant

probability of finding the system at spin configuration  $\{S_i\}$

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

normalization factor (partition function)

$$Z = \sum_{\{S_i\}} e^{-\beta H(\{S_i\})}$$

Canonical Ensemble can be generated by Monte Carlo (e.g. Metropolis) Algorithm.

This means that (canonical) ensemble average can be evaluated by 'time' average in MC simulation.

Many experimentally measurable quantities can be expressed as an ensemble average and hence can be computed as a 'time' average.

e.g. average potential energy

$$\langle U \rangle = \int \prod_{i=1}^{3N} dq_i dp_i P(q_i, p_i) U(\{q_i\}) = \frac{\int \prod_{i=1}^{3N} dq_i e^{-\beta U(\{q_i\})} U(\{q_i\})}{\int \prod_{i=1}^{3N} dq_i e^{-\beta U(\{q_i\})}}$$

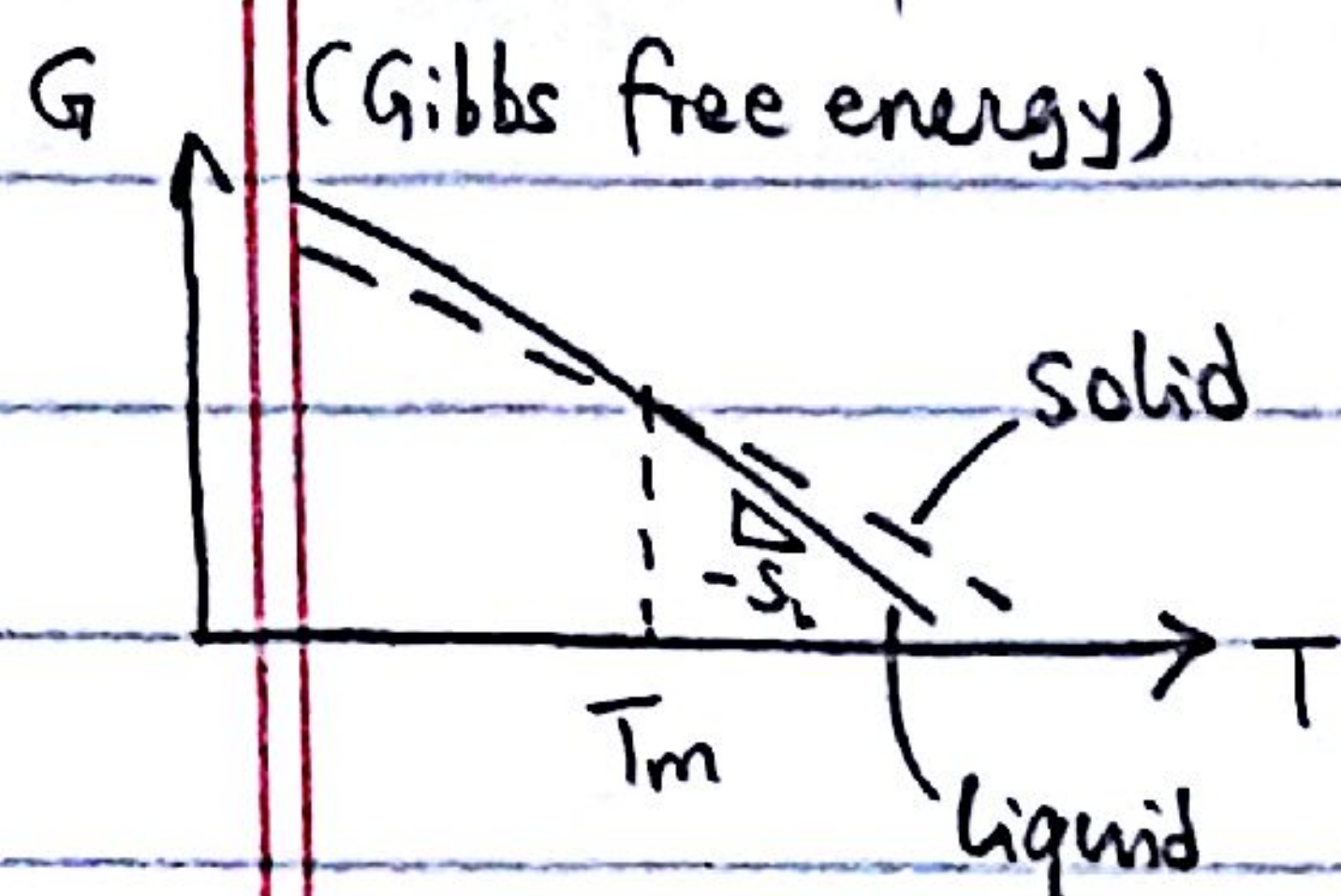
average magnetization  $M = \sum_i S_i$ 

$$\langle M \rangle = \sum_{\{S_i\}} e^{-\beta H(\{S_i\})} \left( \sum_i S_i \right)$$



## 2. Significance of free energy

Atomic system can exhibit several phases (gas, liquid, solid)



$$G(N, P, T) = -SdT + Vdp + \mu dN$$

$$S = - \left( \frac{\partial G}{\partial T} \right)_{N, P}$$

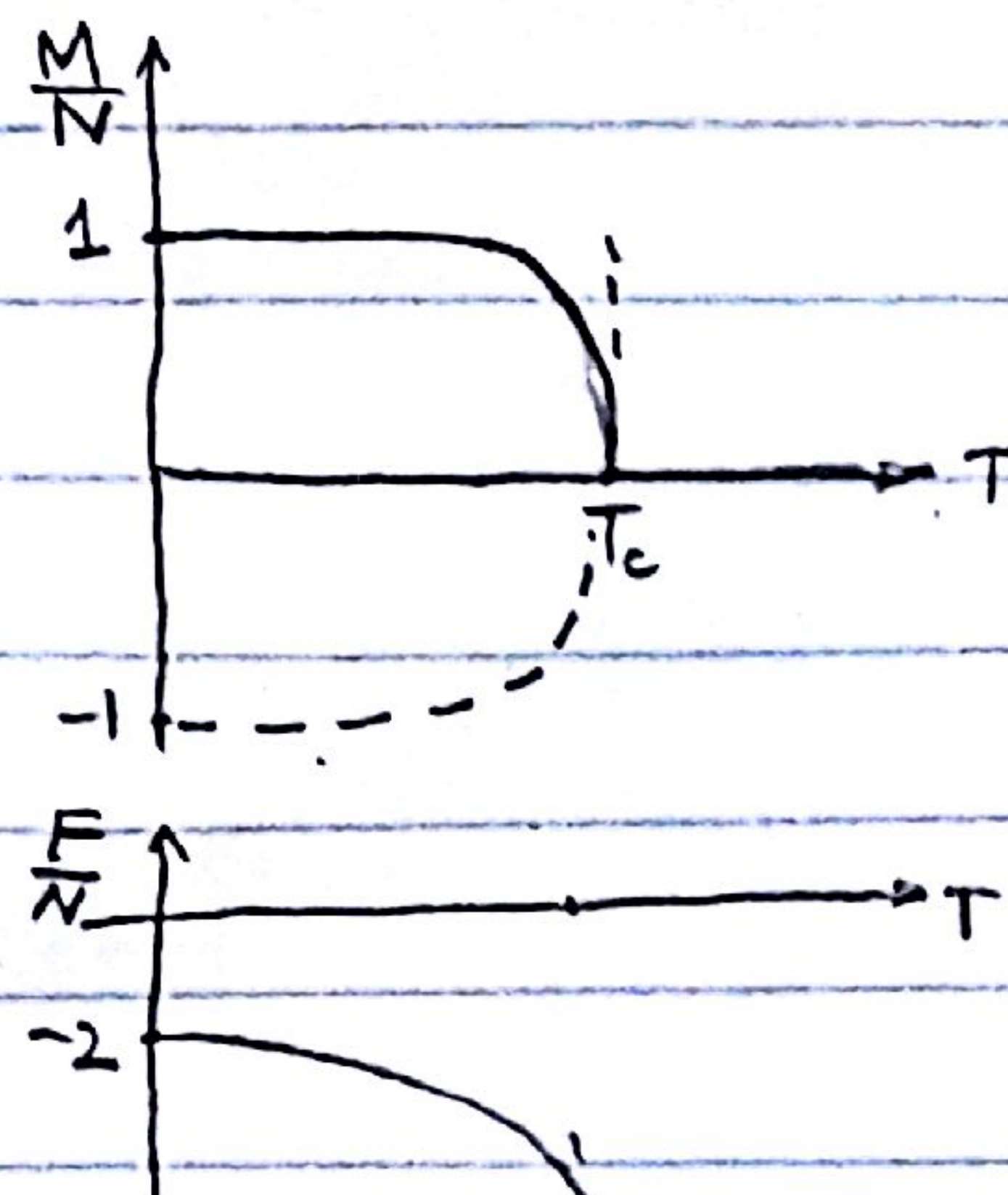
$$G = E - TS + PV$$

under zero pressure ( $p=0$ )

Gibbs free energy  $G = F = E - TS$  (Helmholtz free energy)

Free energy (as a function of  $T$ ) is needed for accurate prediction of melting point  $T_m$ .

2D/3D Ising model exhibit two ferromagnetic phases below  $T_c$



Derivatives of (Helmholtz) free energy contain singularity at critical temperature  $T_c$

At constant temperature, system evolves (spontaneously) in the direction that minimizes free energy.

Other examples: protein folding, hydrophobic interaction.

## 3. Definition of free energy

Atomic system

$$F = -k_B T \ln Z$$

$$= -k_B T \ln \left( \frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dq_i dp_i e^{-\beta H(\mathbf{q}, \mathbf{p})} \right)$$

Ising Model

$$F = -k_B T \ln Z$$

$$= k_B T \ln \left( \sum_{\{s_i\}} e^{-\beta H(\{s_i\})} \right)$$

The free energy does not have the form of an ensemble average. Therefore it cannot be (directly) calculated from 'time' average.

Therefore, free energy calculation requires more advanced methods.



#### 4. Derivative of free energy as ensemble average

Imagine a Hamiltonian containing a parameter  $\lambda$ .

e.g.

$$H(\mathbf{q}, \mathbf{p}) = \sum_i \frac{p_i^2}{2m} + \lambda U(\mathbf{q})$$

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

$\lambda=1$  corresponds to original system of interest.

$\lambda=0$  another system in which there are no interactions, (i.e. ideal gas)

another example: suppose  $H_1(\mathbf{q}, \mathbf{p})$  is the system of interest,

$H_0(\mathbf{q}, \mathbf{p})$  is a reference system whose free energy is known.

parameterized Hamiltonian  $H(\mathbf{q}, \mathbf{p}, \lambda) = (1-\lambda)H_0(\mathbf{q}, \mathbf{p}) + \lambda H_1(\mathbf{q}, \mathbf{p})$

$$\lambda=1, H(\mathbf{q}, \mathbf{p}, \lambda) = H_1(\mathbf{q}, \mathbf{p})$$

$$\lambda=0, H(\mathbf{q}, \mathbf{p}, \lambda) = H_0(\mathbf{q}, \mathbf{p})$$

Free energy of parameterized Hamiltonian is now a function of  $\lambda$

$$F(\lambda) = -k_B T \ln \left( \frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dq_i dp_i e^{-\beta H(\mathbf{q}, \mathbf{p}, \lambda)} \right)$$

note  $F(\lambda=1)$  is the free energy of interest.

$$\frac{\partial F}{\partial \lambda} = \frac{(-k_B T) \frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dq_i dp_i e^{-\beta H(\mathbf{q}, \mathbf{p}, \lambda)} \cdot \left( -\beta \right) \frac{\partial H(\mathbf{q}, \mathbf{p}, \lambda)}{\partial \lambda}}{\frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dq_i dp_i e^{-\beta H(\mathbf{q}, \mathbf{p}, \lambda)}} = \left\langle \frac{\partial H(\mathbf{q}, \mathbf{p}, \lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

Define  $f_{\lambda} \equiv -\frac{\partial H(\mathbf{q}, \mathbf{p}, \lambda)}{\partial \lambda}$  as generalized force on parameter  $\lambda$

$$\text{then } -\frac{\partial F}{\partial \lambda} = \langle f_{\lambda} \rangle = \frac{\int \prod_{i=1}^{3N} dq_i dp_i e^{-\beta H(\mathbf{q}, \mathbf{p}, \lambda)} f_{\lambda}(\mathbf{q}, \mathbf{p}, \lambda)}{\int \prod_{i=1}^{3N} dq_i dp_i e^{-\beta H(\mathbf{q}, \mathbf{p}, \lambda)}}$$

$\therefore -\frac{\partial F}{\partial \lambda}$  equals to the ensemble average of generalized force  $f_{\lambda}$

$$F(\lambda=1) - F(\lambda=0) = \int_0^1 \frac{\partial F}{\partial \lambda} d\lambda = \int_0^1 \left\langle \frac{\partial H(\mathbf{q}, \mathbf{p}, \lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda$$

The free energy difference between two systems can be evaluated from an integral of ensemble averages.



## 5 Method of Thermodynamic Integration (TI)

e.g. suppose  $H(\{s_i\}, \lambda) = -\lambda J \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i$

$\lambda=1$ :  $H(\{s_i\}, \lambda) = H_1(\{s_i\}) = -J \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i$  is the system of interest

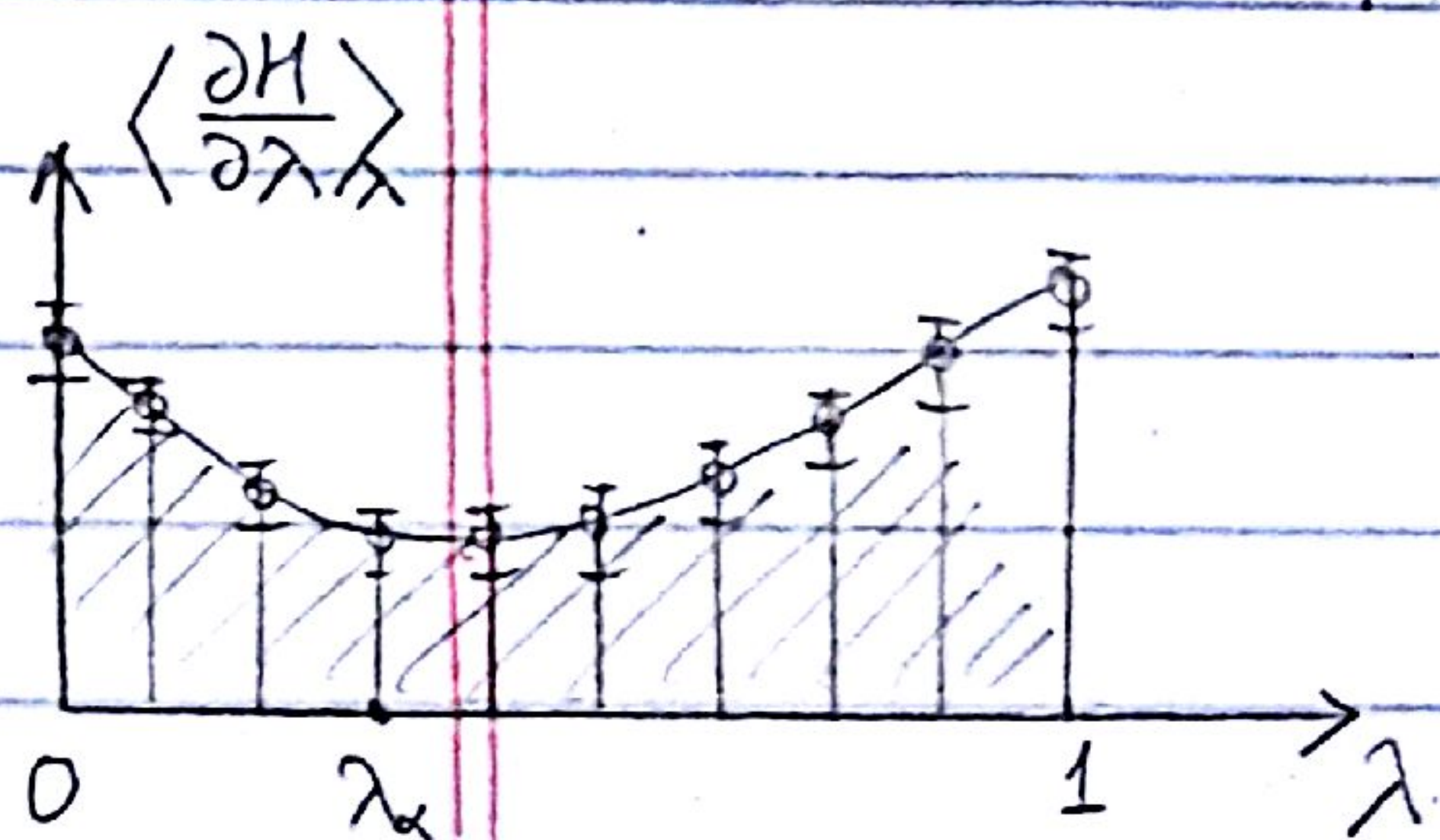
$\lambda=0$ :  $H(\{s_i\}, \lambda) = H_0(\{s_i\}) = -h \sum_i s_i$  is a reference system of non-interacting spins.

$F_0 = -k_B T \ln Z_0$  reference free energy

$$Z_0 = \sum_{\{s_i\}} e^{-\beta(-h \sum_i s_i)} = \sum_{\{s_i\}} \prod_i e^{\beta h s_i} = (e^{\beta h} + e^{-\beta h})^N = (2 \cosh \beta h)^N$$

$$F_0 = -k_B T \ln (2 \cosh \beta h)^N = -N k_B T \ln (2 \cosh \beta h) \quad \text{i.e. known analytically}$$

Our goal is to find the free energy  $F_1$  of system  $H_1(\{s_i\})$  which is generally not known in 2D/3D.



$$\frac{\partial H(\{s_i\}, \lambda)}{\partial \lambda} = -J \sum_{\langle ij \rangle} s_i s_j$$

$$\left\langle \frac{\partial H(\{s_i\}, \lambda)}{\partial \lambda} \right\rangle_{\lambda} = \left\langle -J \sum_{\langle ij \rangle} s_i s_j \right\rangle_{\lambda} \quad \text{is the ensemble}$$

average, which can be computed from "time" average of Monte Carlo simulation using  $H(\{s_i\}, \lambda)$ .

See computer simulations, 2, 88 (2000).

### Algorithm 1. (TI)

1. Choose number of subdivision points  $N_s$ . define  $\lambda_\alpha = \frac{\alpha}{N_s}$ ,  $\alpha=0, 1, \dots, N_s$ .

2. For each  $\lambda_\alpha$ , perform Monte Carlo simulation using Hamiltonian

$$H(\{s_i\}, \lambda_\alpha) = -\lambda_\alpha J \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i$$

3. For each Monte Carlo simulation using  $\lambda_\alpha$ . Compute time average of  $-J \sum_{\langle ij \rangle} s_i s_j$

the result is called  $\left\langle -J \sum_{\langle ij \rangle} s_i s_j \right\rangle_{\lambda_\alpha}$

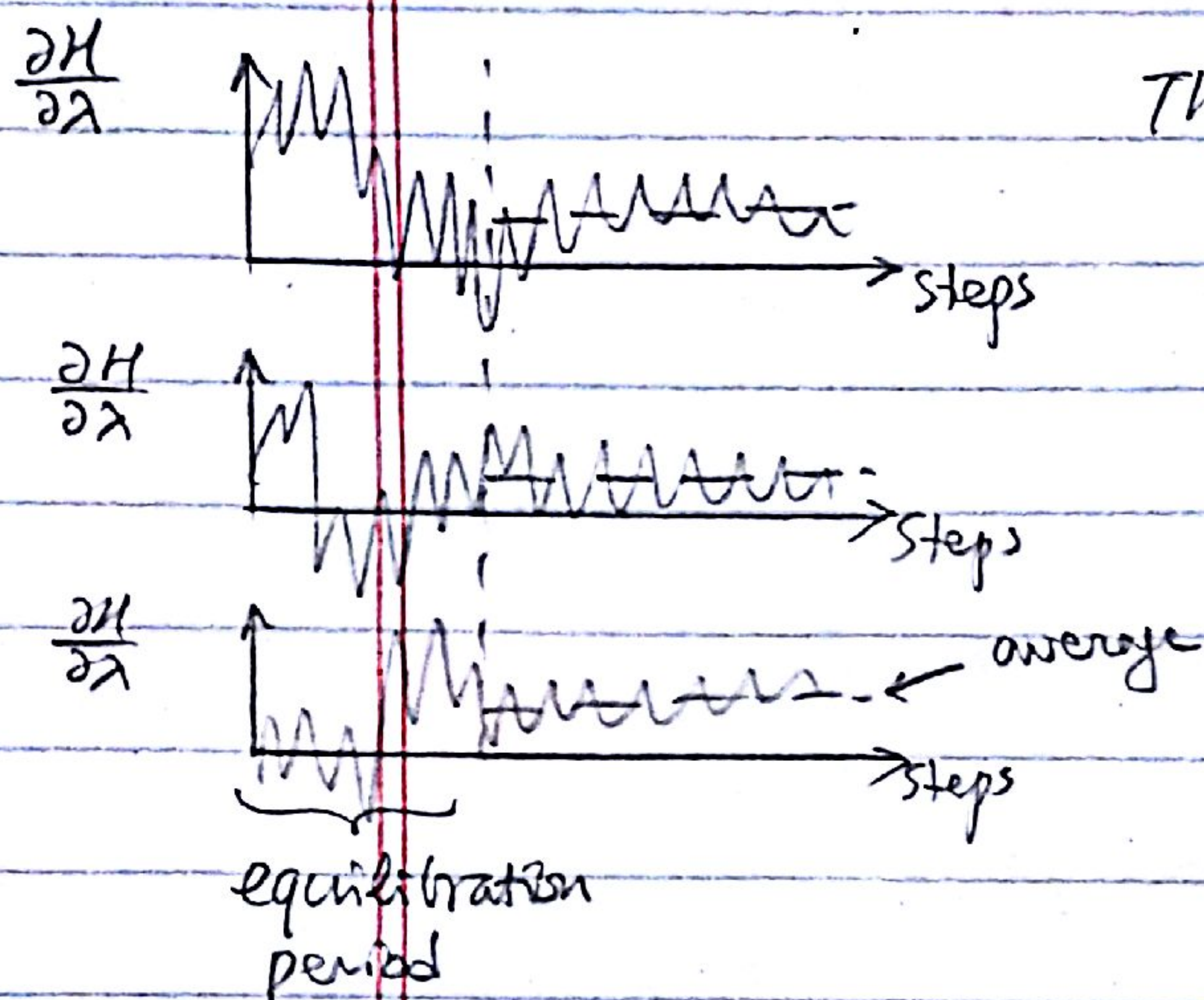
4. Numerically integrate  $\frac{\partial F}{\partial \lambda}$  (trapezoid rule)

$$F_1 - F_0 = \frac{1}{2} \left\langle -J \sum_{\langle ij \rangle} s_i s_j \right\rangle_{\lambda_0} + \sum_{\alpha=1}^{N_s-1} \left\langle -J \sum_{\langle ij \rangle} s_i s_j \right\rangle_{\lambda_\alpha} + \left\langle -J \sum_{\langle ij \rangle} s_i s_j \right\rangle_{\lambda_{N_s}}$$



## 6. Problems with the TI method

- a. Not sure how to choose number of subdivision points  $N_s$  optimally.  
 too small  $N_s$  leads to discretization error in numerical integration  
 too large  $N_s$  leads to high computational cost.
- b. Each Monte Carlo simulation with different  $\lambda$  runs independently



The initial equilibration period of each simulation is "wasted", because we cannot collect data before equilibrium is reached.

Each simulation needs to run sufficiently long to reduce statistical error in the ensemble average.

- c. Not clear if we should run fewer long simulations (small statistical error) or many short simulations (small discretization error).

## 6. Method of Adiabatic Switching (AS)

Idea: A long Monte Carlo simulation in which  $\lambda$  gradually changes from 0 to 1

If the changes of  $\lambda$  happens sufficiently slowly, we may expect that the system is always close to the equilibrium distribution corresponding to the instantaneous value of  $\lambda$ .

For clarity, let us introduce a 'time' to the Monte Carlo simulation.

Suppose each Monte Carlo step takes one unit of time. So the total simulation time  $t_{sim}$  is just the total simulation steps.

Define the 'dynamic work' during the non-equilibrium Monte Carlo simulation.

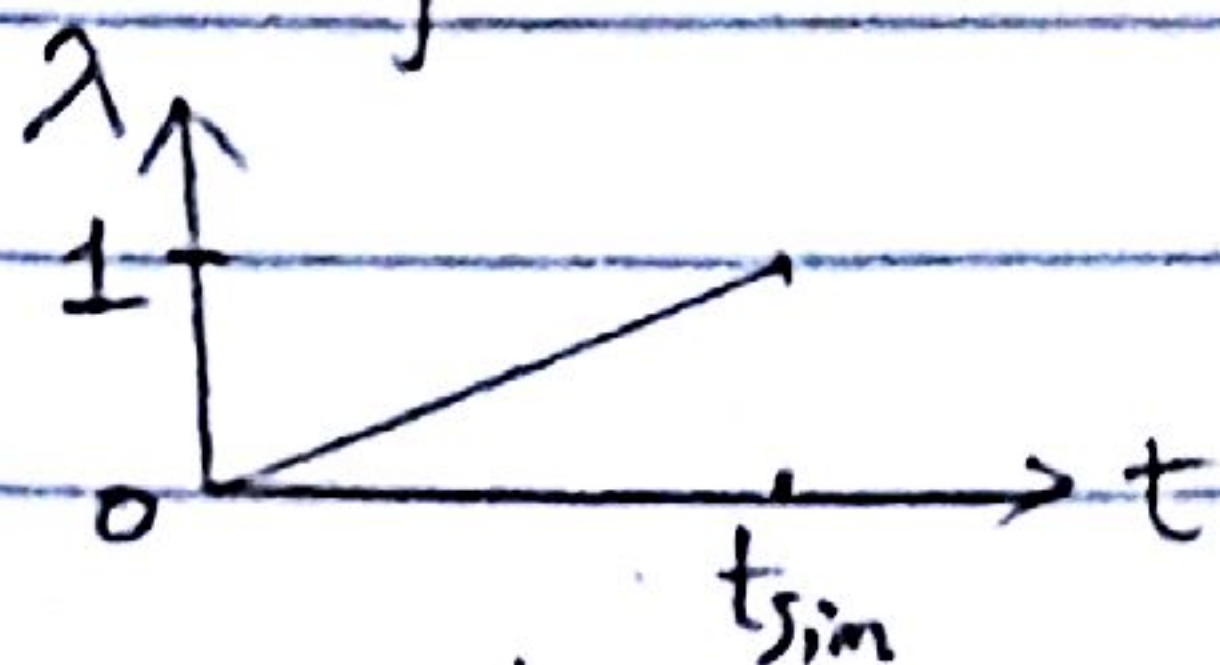
$$W_{dyn} = \int_0^{t_{sim}} \frac{\partial H(\lambda(t))}{\partial \lambda} \frac{d\lambda(t)}{dt} dt = \sum_{t=1}^{t_{sim}} \frac{\partial H(\lambda(t))}{\partial \lambda} \frac{d\lambda(t)}{dt}$$



$\lambda(t)$  is called the switching function.

$$\lambda(t=0) = 0, \quad \lambda(t=t_{\text{sim}}) = 1.$$

The simplest switching function is a linear function.



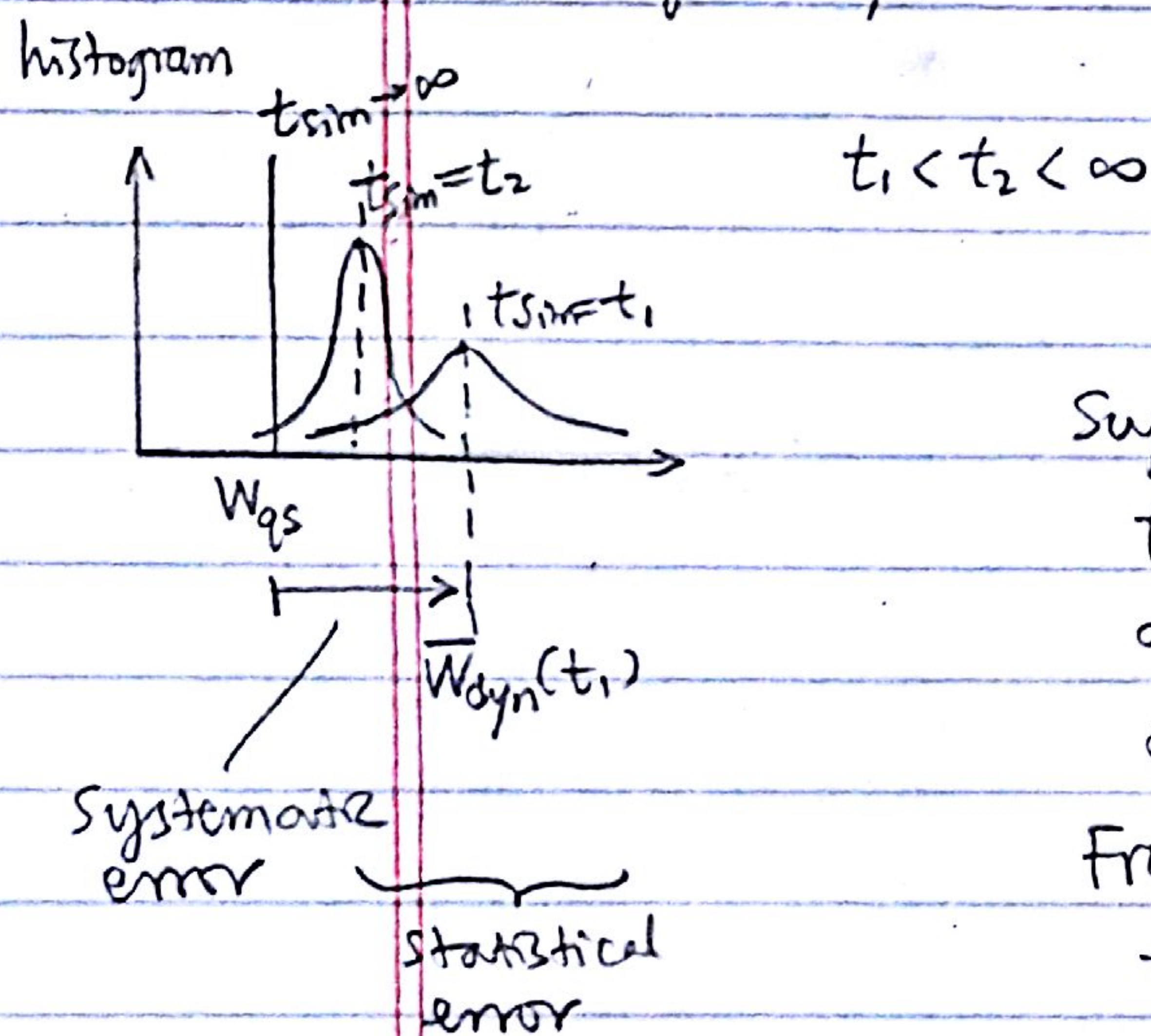
but other non-linear switching functions usually performs better (see below)

In the limit of infinitely long simulation, we recover the quasi-static (q.s.) limit, where the system is always at equilibrium

$$\lim_{t_{\text{sim}} \rightarrow \infty} W_{\text{dyn}} = W_{\text{qs}} \equiv \int_0^1 \left\langle \frac{\partial H(\lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda = F_1 - F_0$$

In reality,  $t_{\text{sim}}$  is always finite, so  $W_{\text{dyn}}$  deviates from  $W_{\text{qs}}$

Actually  $W_{\text{dyn}}$  is a random number distributed around  $W_{\text{qs}}$  (if  $t_{\text{sim}}$  is long)



Suppose we run MC simulation with switching time  $t_{\text{sim}} = t_1$  many times. Each simulation will give us a different  $W_{\text{dyn}}$ . We can build a histogram of  $W_{\text{dyn}}$ .

From the histogram, we can see that  $W_{\text{dyn}}$  contains two error sources: systematic error and statistical error

If we use a longer switching time  $t_2$ , then both systematic error and statistical error will reduce.



### 7. Dissipation in Adiabatic Switching (AS)

Define  $E_{diss} \equiv \overline{W_{dyn}} - W_{qs}$

↑  
averaged work  
from many switching  
simulations  $t_{sim} = t_i$

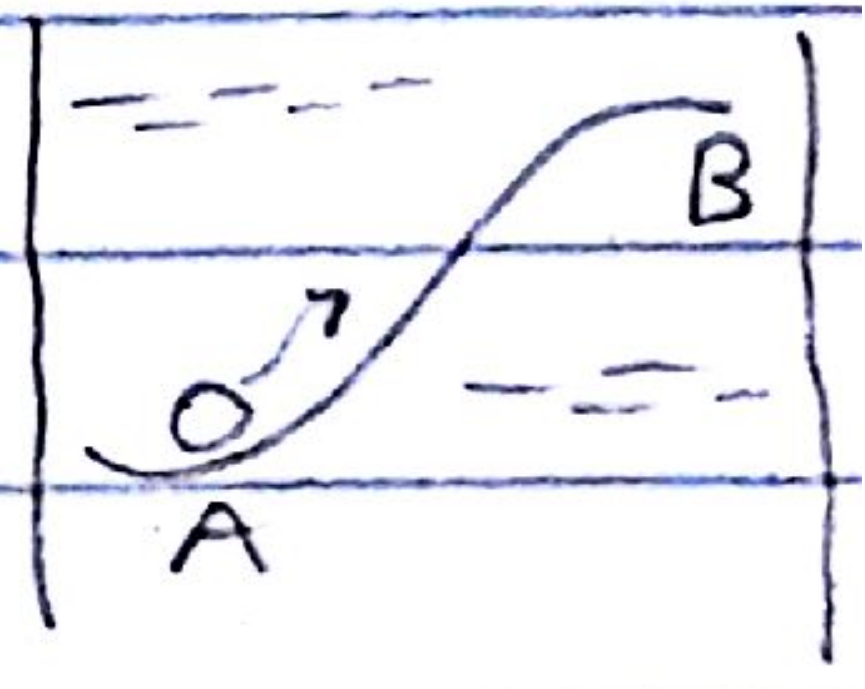
↑  
work in the quasi state limit  
 $t_{sim} \rightarrow \infty$   
 $W_{qs} = F_1 - F_0$

It can be shown analytically (and numerically) that

$$E_{diss} > 0$$

So  $E_{diss}$  is the energy dissipated during the non-equilibrium process of switching the Hamiltonian from  $H_0$  to  $H_1$

(Imagine moving a sphere through water from point A to point B the work done include the potential energy difference  $E_B - E_A$  as well as dissipation due to viscosity of water.

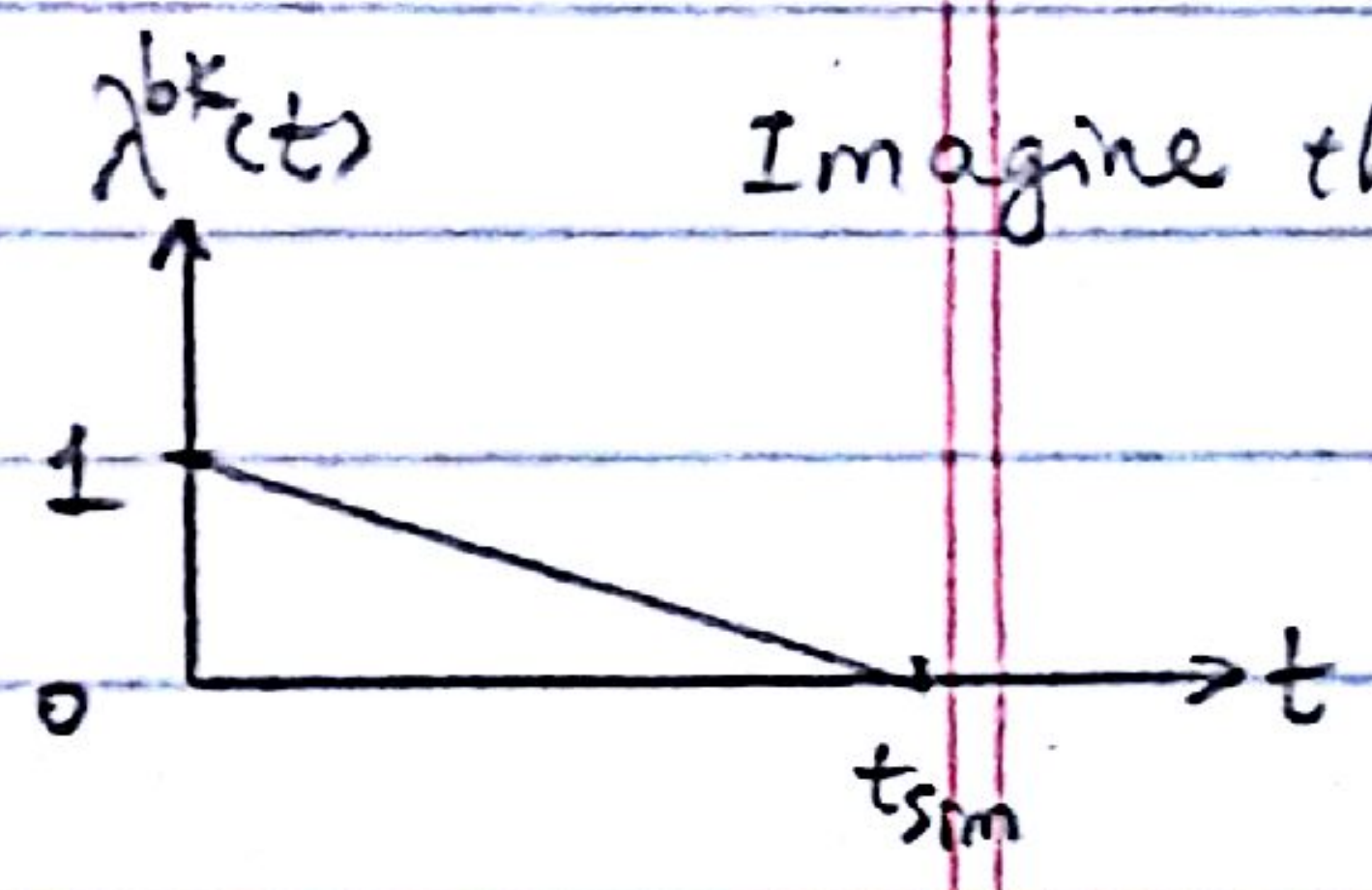


The dissipated work decreases with decreasing speed of the sphere.)

Note that the dissipation is always positive ( $E_{diss} > 0$ ) regardless of whether  $F_1 - F_0$  is positive or negative.

This allows us to estimate the magnitude of  $E_{diss}$

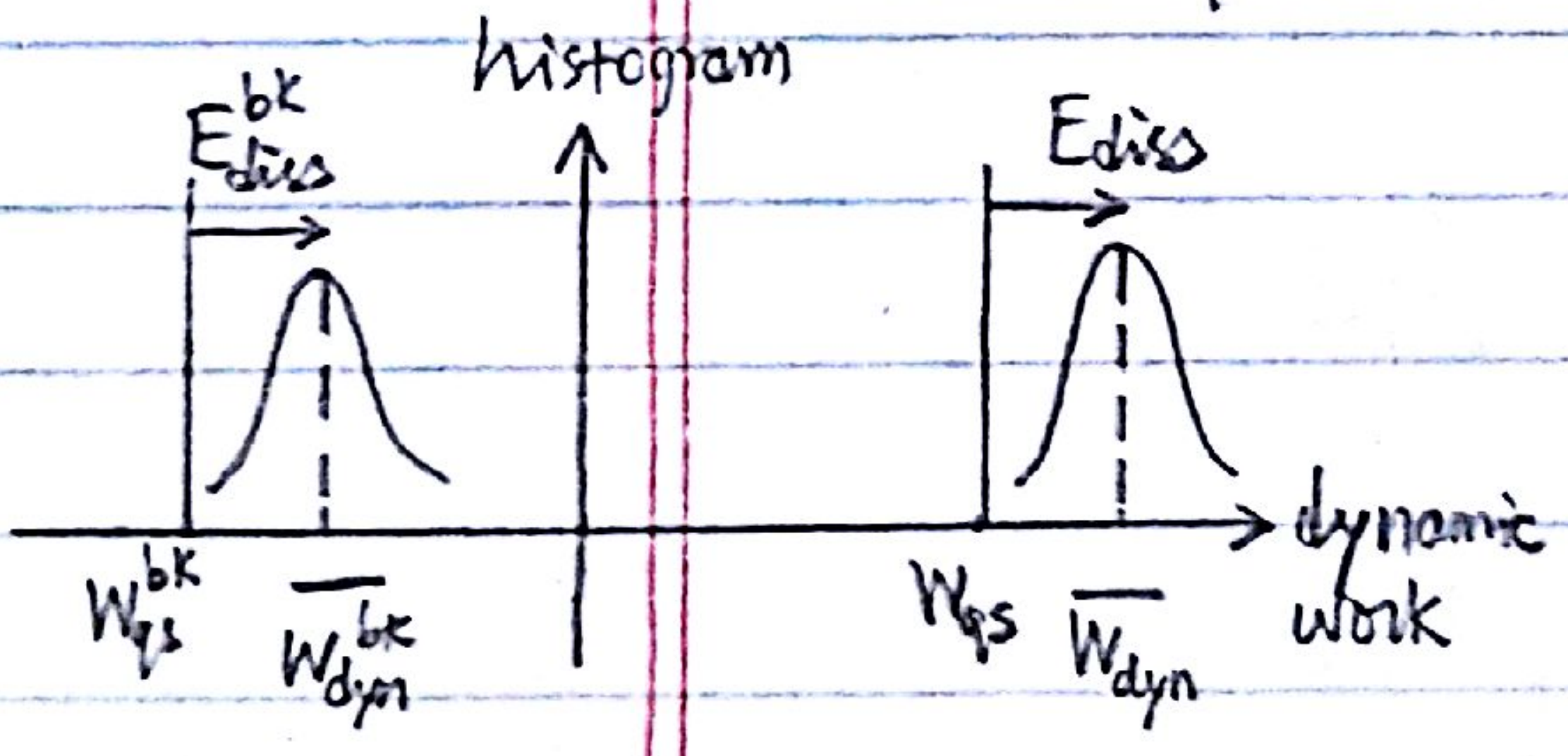
Imagine that we also perform a series of backward switching simulation.



$$\lambda^{bk}(t=0) = 1, \quad \lambda^{bk}(t=t_{sim}) = 0$$

The work done is  $W_{dyn}^{bk} = \int_0^{t_{sim}} \frac{\partial H(\lambda)}{\partial \lambda} \frac{d\lambda^{bk}(t)}{dt} dt$

In the quasi-state limit  $\lim_{t_{sim} \rightarrow \infty} W_{dyn}^{bk} = W_{qs}^{bk} = -W_{qs} = F_0 - F_1$



Define  $E_{diss}^{bk} \equiv \overline{W_{dyn}^{bk}} - W_{qs}^{bk} > 0$

dissipation is always positive regardless of direction

recall  $E_{diss} \equiv \overline{W_{dyn}} - W_{qs} > 0$

add together

$$E_{diss} + E_{diss}^{bk} = \overline{W_{dyn}} + \overline{W_{dyn}^{bk}} > 0$$

$$(W_{qs}^{bk} + W_{qs} = 0)$$



If we expect  $E_{\text{diss}} \approx E_{\text{diss}}^{\text{bk}}$  (not strictly true)

then  $E_{\text{diss}} \approx \frac{1}{2} (\overline{W}_{\text{dyn}} + \overline{W}_{\text{dyn}}^{\text{bk}})$  ← this is a simple estimate of dissipation.

$$F_1 - F_0 = W_{\text{qs}} = \overline{W}_{\text{dyn}} - E_{\text{diss}} \approx \frac{1}{2} (\overline{W}_{\text{dyn}} - \overline{W}_{\text{dyn}}^{\text{bk}})$$

— this is a better estimator for the free energy difference.

However, in general,  $E_{\text{diss}} \neq E_{\text{diss}}^{\text{bk}}$ ,

so  $W_{\text{qs}} \neq \frac{1}{2} (\overline{W}_{\text{dyn}} - \overline{W}_{\text{dyn}}^{\text{bk}})$ , i.e. the systematic error is still present.

The only way to reduce systematic error is to increase switching time  $t_{\text{sim}}$ .

The way to reduce the statistical error is to repeat switching simulations and compute average  $\overline{W}_{\text{dyn}}$  (and  $\overline{W}_{\text{dyn}}^{\text{bk}}$ ).

## 8. Switching function.

In principle, any continuous monotonic function that satisfies boundary condition

$$\begin{cases} \lambda(t=0) = 0 \\ \lambda(t=t_{\text{sim}}) = 1 \end{cases} \text{ can be used as a switching function.}$$

We have been using the simplest choice:  $\lambda = \frac{t}{t_{\text{sim}}}$ .

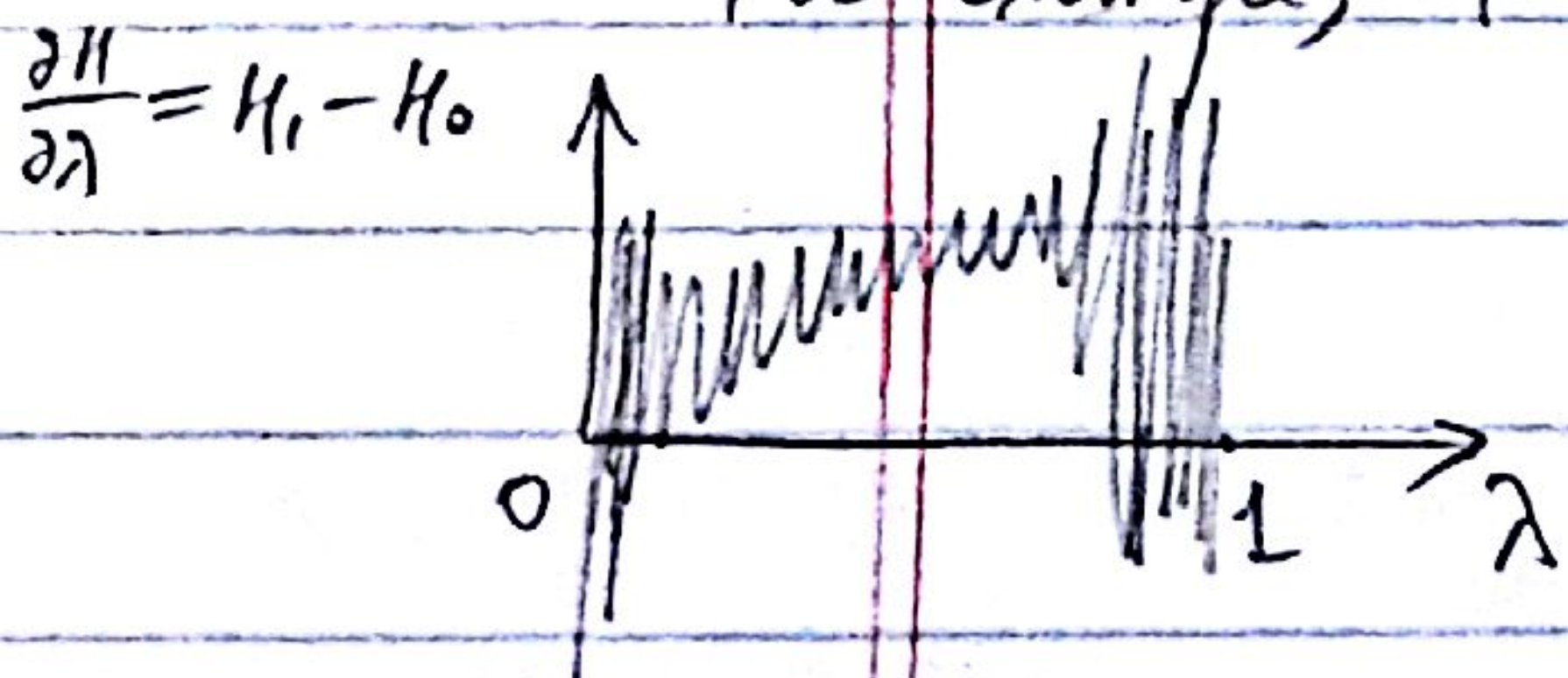
but this is often not the optimal choice.

The optimal switching function minimizes the systematic and statistical error for a given number of total simulation steps  $t_{\text{sim}}$ .

It is generally impossible to find the exact optimal switching function, and there is no need to. General guide lines exist for finding good switching functions.

We should switch slowly ( $\frac{d\lambda}{dt}$  small) where the integrand  $\frac{\partial H}{\partial \lambda}$  fluctuates a lot.

For example, for  $H(\mathbf{q}, \mathbf{p}; \lambda) = (1-\lambda)H_0(\mathbf{q}, \mathbf{p}) + \lambda H_1(\mathbf{q}, \mathbf{p})$ ,  $\frac{\partial H}{\partial \lambda} = H_1 - H_0$  usually fluctuates a lot at  $\lambda \approx 0$  and  $\lambda \approx 1$ .

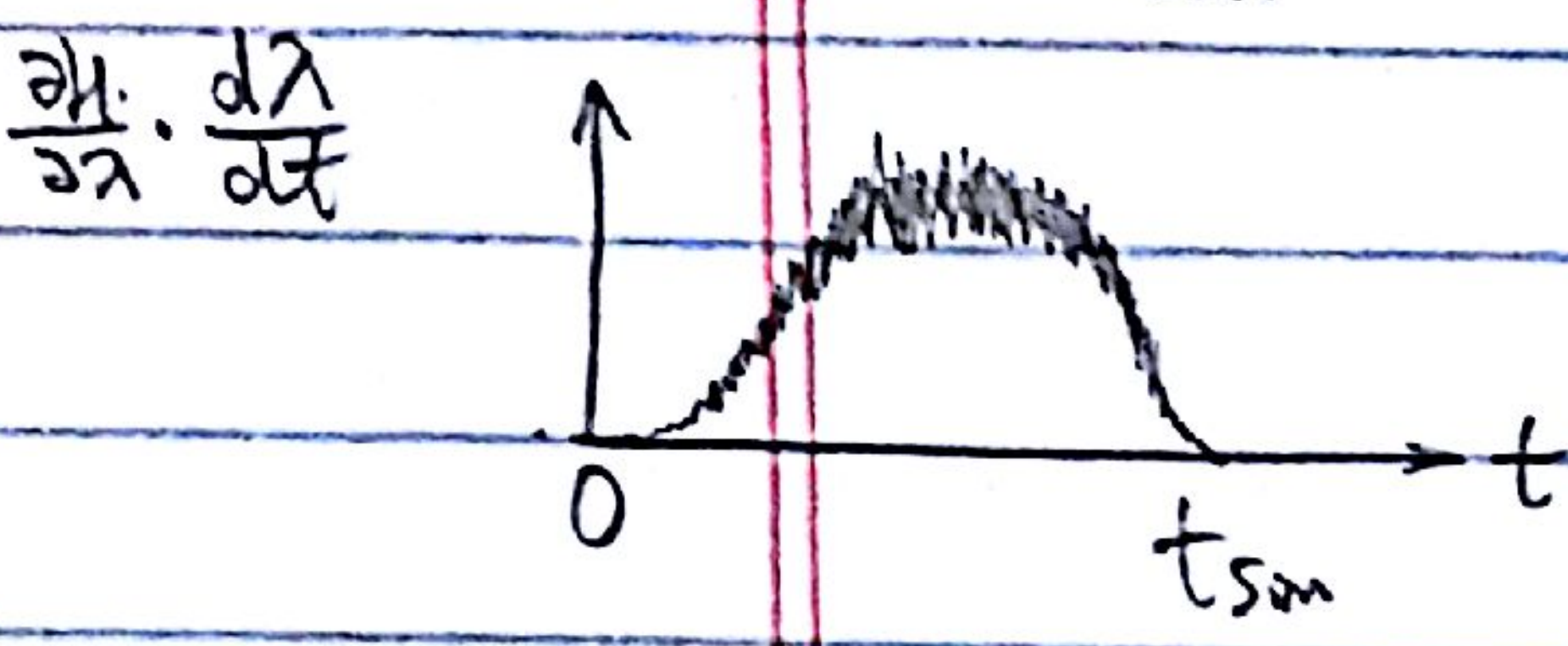
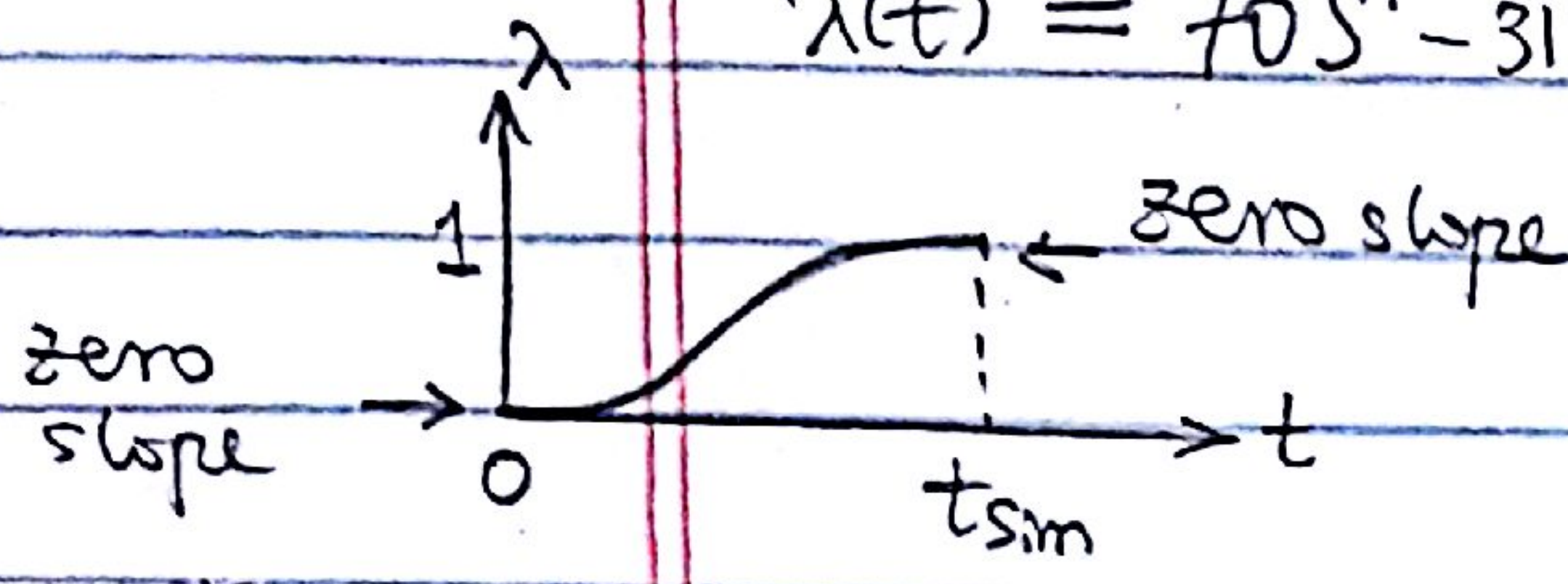


Hence we would like to use a switching function  $\lambda(t)$  that has small slope at  $t \approx 0$  and  $t \approx t_{\text{sim}}$ .



A reasonable choice is

$$\lambda(t) = 70S^9 - 315S^8 + 540S^7 - 420S^6 + 126S^5, \text{ where } S = t/t_{sim}$$



$$W_{dyn} = \int_0^{t_{sim}} \frac{\partial H}{\partial \lambda} \frac{d\lambda}{dt} dt$$

The integrand now has much smaller fluctuation because  $\frac{d\lambda}{dt} = 0$  at  $t=0$  and  $t=t_{sim}$

### 9. Switching along the Temperature Axis

It is often of interest to compute free energy as a function of temperature (such as in melting point calculations.)

Here we use Ising model as an example again.

For simplicity, let us assume  $h=0$  (no external magnetic field)

$$H(\{S_i\}) = -J \sum_{\langle i,j \rangle} S_i S_j \quad F_1(T) = -k_B T \ln \left( \sum_{\{S_i\}} e^{\beta J \sum_{\langle i,j \rangle} S_i S_j} \right), \quad \beta \equiv \frac{1}{k_B T}$$

We then introduce parameter  $\lambda$  to the Hamiltonian

$$H(\{S_i\}, \lambda) = -\lambda J \sum_{\langle i,j \rangle} S_i S_j, \quad F(T, \lambda) = -k_B T \ln \left( \sum_{\{S_i\}} e^{\beta \lambda J \sum_{\langle i,j \rangle} S_i S_j} \right)$$

The method above allows us to compute

$$F_1(T) = F(T, \lambda=1) \cong F(T, \lambda=0) + \int_0^1 \frac{\partial H(\lambda)}{\partial \lambda} \frac{d\lambda}{dt} dt$$

where  $F(T, \lambda=0) = -N k_B T \ln 2$

However,  $F(T, \lambda)$  at intermediate  $\lambda$  values ( $0 < \lambda < 1$ ) have physical meanings too.

$$F(T, \lambda) = F_1\left(\frac{T}{\lambda}\right) \longleftarrow \text{It is the free energy of the original system at another temperature } \frac{T}{\lambda}.$$

pick some reference temperature  $T_0$

$$F_1\left(\frac{T_0}{\lambda(t)}\right) = F(T_0, \lambda(t)) \cong -N k_B T \ln 2 + \int_0^t \frac{\partial H(\lambda)}{\partial \lambda} \frac{d\lambda}{dt} dt \longleftarrow \text{This allows us to compute } F_1 \text{ as a function of } T = \frac{T_0}{\lambda}.$$



## 10. Free Energy of Atomic Systems.

see: [http://micro.stanford.edu/wiki/Computing\\_Melting\\_Point\\_by\\_Free\\_Energy\\_Method](http://micro.stanford.edu/wiki/Computing_Melting_Point_by_Free_Energy_Method)

Solid	Liquid
pick a temperature ( $T_1 < T_m$ )	pick a temperature ( $T_2 > T_m$ )
use Harmonic Oscillators (e.g. Einstein model) as reference system $H_0$	use Ideal Gas as reference system $H_0$
Compute $F_S - F_0$ at $T_1$ (solid)	Compute $F_L - F_0$ at $T_2$ (liquid)
Compute $F_S(T)$ by switching along T-axis	Compute $F_L(T)$ by switching along T-axis.
do several forward and backward switchings for each switching run	do several forward and backward switchings for each switching run.

## Reference free energy

3N-harmonic oscillators

$$\text{(Quantum)} \quad F = \sum_{i=1}^{3N} \left[ \frac{\hbar \omega_i}{2} + k_B T \ln(1 - e^{-\beta \hbar \omega_i}) \right]$$

$\omega_i = \sqrt{\frac{k_i}{m}}$  is vibrational frequency.

$$\text{(Classical)} \quad F = \sum_{i=1}^{3N} -k_B T \ln \frac{k_B T}{\hbar \omega_i}$$

Ideal gas (N atoms in volume V)

$$F = -N k_B T \left[ \ln \left( \frac{V}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right) + 1 \right]$$



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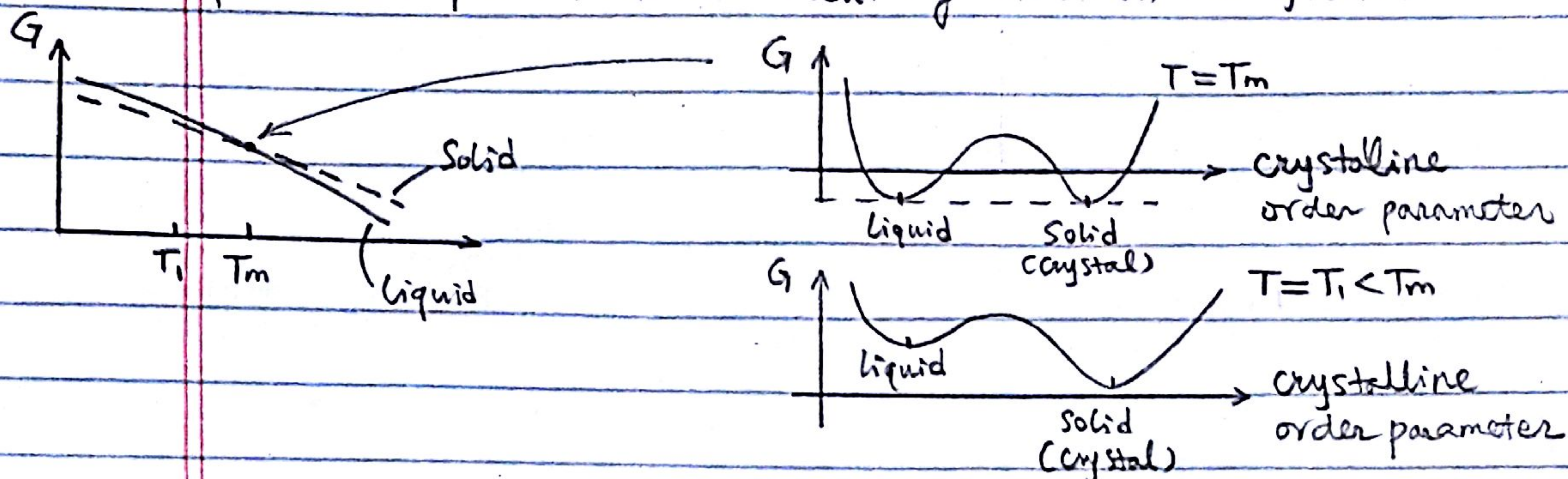
Stanford University

Part II. Umbrella Sampling Method for Free Energy Barrier

## 1. Nucleation Phenomenon

Nucleation is an important phenomenon that occurs in a wide range of systems.

Most first order phase transitions occur by nucleation and growths.



Example: supercooled water (see movies)

At  $T = T_i < T_m$  (below melting point, i.e. supercooled), the liquid phase has higher free energy than the solid (crystalline) phase.

This means that, in principle, the liquid should transform to solid (i.e. freezes) after a sufficiently long time.

However, water can be kept as a liquid below the freezing point (e.g. at  $-2^\circ\text{C}$ ) for a very long time if left undisturbed.

This is because for liquid to transform into solid, it needs to overcome a free energy barrier (nucleation barrier).

At low temperatures, the rate to overcome the nucleation barrier can be very low, hence the liquid can be kinetically trapped in the supercooled state without turning into a solid (crystal).



## 2. Classical Nucleation Theory

The mechanism for first order phase transition is usually by nucleation-and-growth.

For example, a small nucleus of solid phase can form by thermal fluctuation within the liquid phase.

For simplicity, assume the nucleus is a sphere with radius  $R$ .

The free energy change of the system by forming the nucleus can be approximated as

$$\Delta G \approx \underbrace{-\Delta\mu \cdot \frac{4}{3}\pi R^3}_{\substack{\text{chemical} \\ \text{potential} \\ \text{difference} \\ \text{between} \\ \text{liquid and solid} \\ (\Delta g_L - \Delta g_S)}} + \underbrace{\gamma_{LS} \cdot 4\pi R^2}_{\substack{\text{surface} \\ \text{energy} \\ \text{area}}}$$

$\Delta G$  reaches maximum ( $\Delta G_c$ ) at  $R=R_c$  critical radius.

The probability of finding the system at  $R=R_c$  is  $\sim e^{-\frac{\Delta G_c}{k_B T}}$

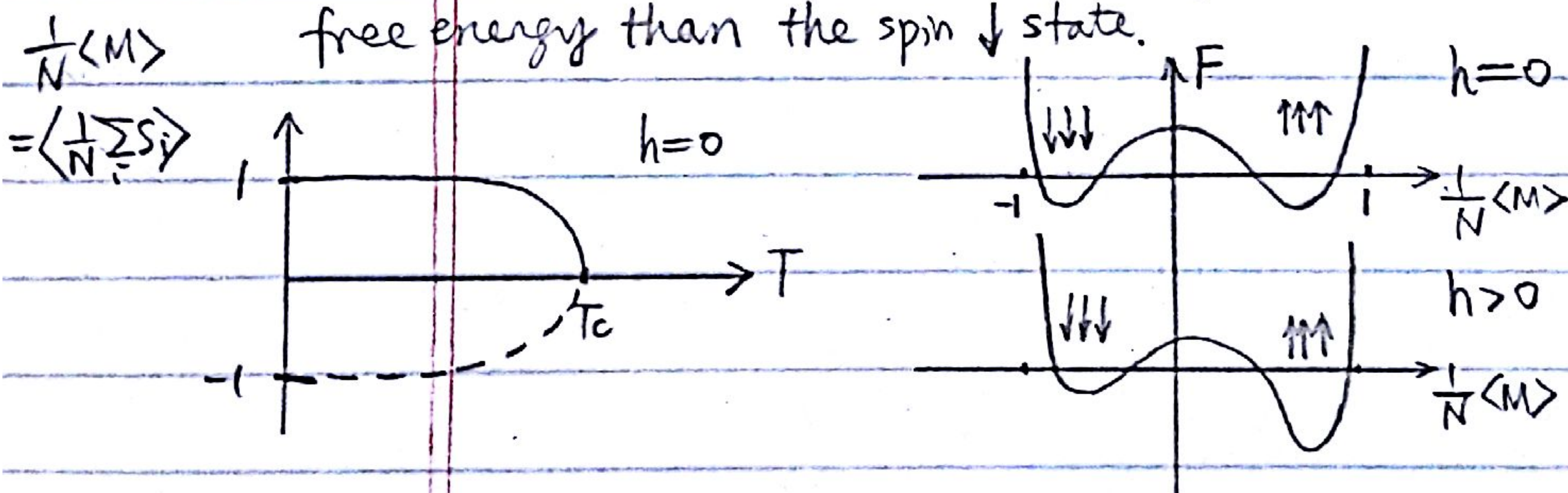
If  $\Delta G_c \gg k_B T$ , the rate of nucleation can be very low.

## 3. Nucleation in Ising Model

We shall use the Ising model to discuss the nucleation phenomenon in detail.

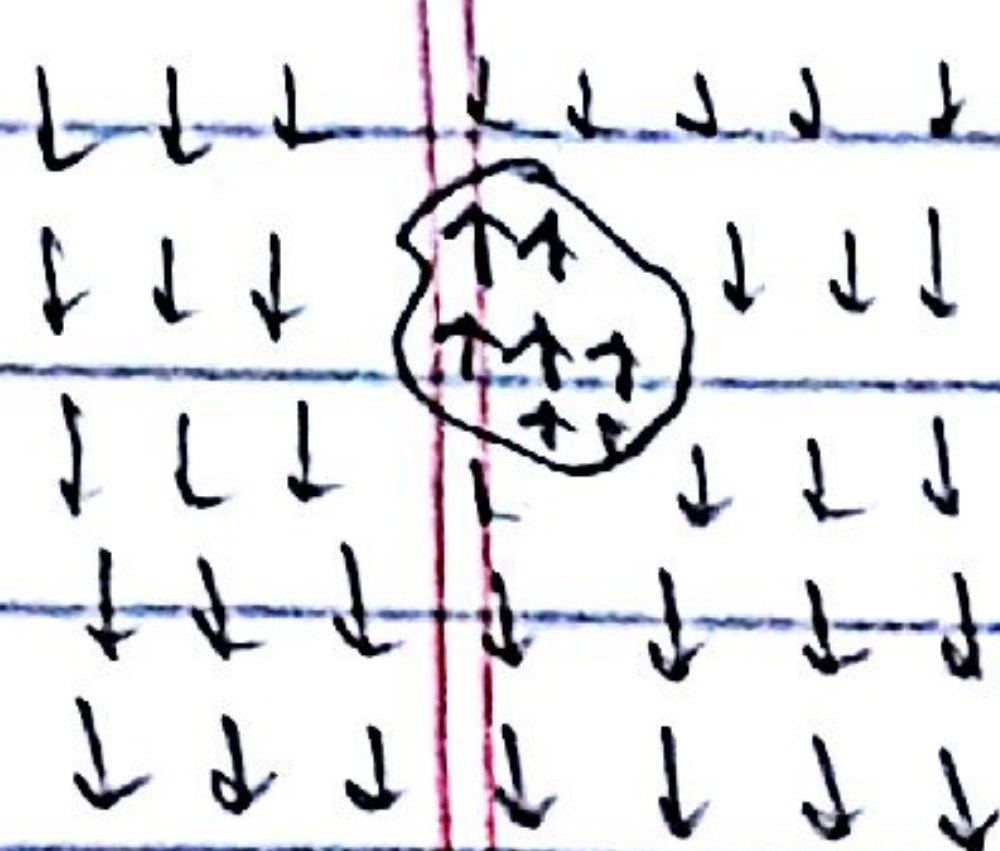
At  $T < T_c$ , the system can be found in one of the two ferromagnetic phases, in which most of the spins point in the same direction (up or down, +1 or -1).

If  $h=0$ , the two phases are equally probable. If  $h>0$ , then the spin  $\uparrow$  has lower free energy than the spin  $\downarrow$  state.



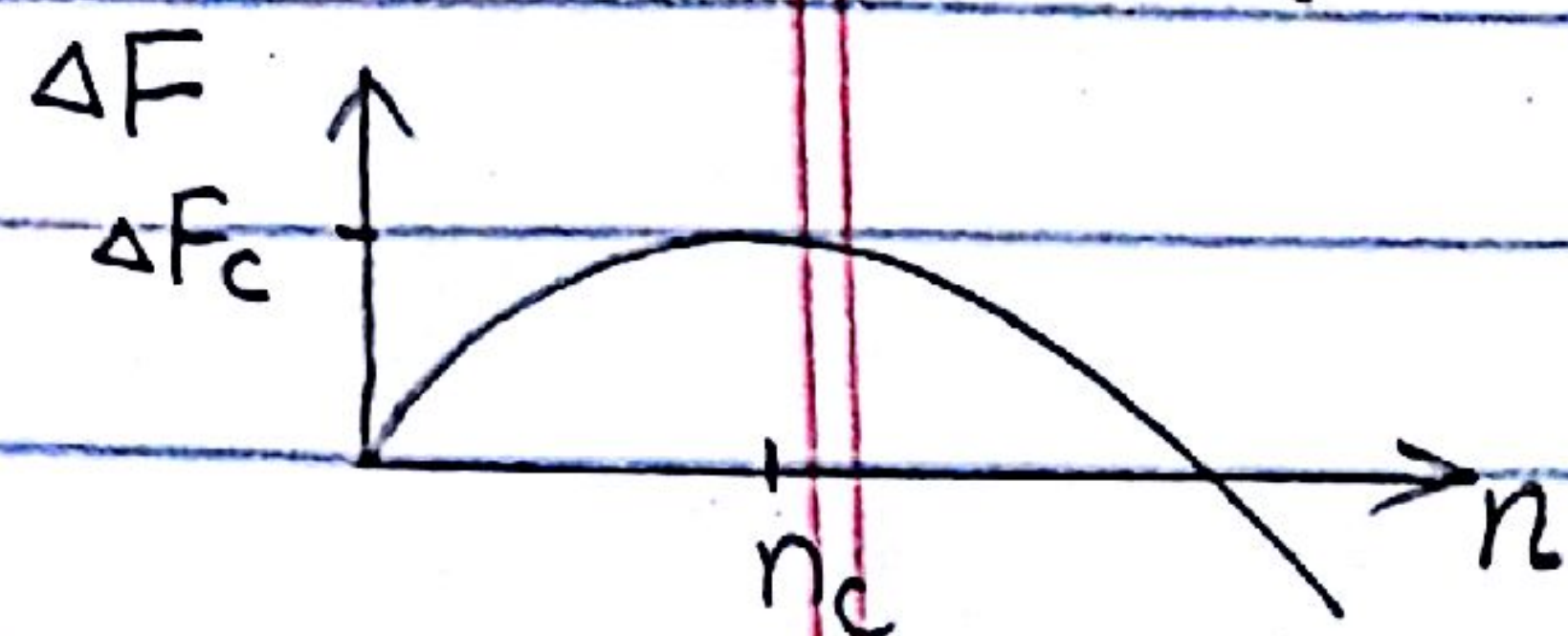
But if the system is already in the spin  $\downarrow$  state, it may stay there for a long time and eventually transform to spin  $\uparrow$  state by nucleation.





The nucleus is a cluster of spin  $\uparrow$  embedded in a 'sea' of spin  $\downarrow$

We shall measure the size of the nucleus by the number  $n$  of spins in the cluster.



In 2D Ising model, if we assume the cluster has a circular shape with radius  $R$ ,  $\pi R^2 \cong n$ ,  $R \cong \sqrt{\frac{n}{\pi}}$

$$\text{Perimeter length } 2\pi R = 2\pi \sqrt{\frac{n}{\pi}} = 2\sqrt{\pi n}$$

The free energy change by forming a nucleus of size  $n$  can be estimated by  $\Delta F \cong \underbrace{-2h \cdot n}_{\text{energy difference between } \downarrow \text{ and } \uparrow} + \underbrace{\gamma \cdot 2\sqrt{\pi n}}_{\text{'surface' energy between spin } \uparrow \text{ and spin } \downarrow \text{ phases}}$

Our goal is to use Monte Carlo simulations to compute  $\Delta F(n)$  without approximations.

From  $\Delta F(n)$ , we can easily find the maximum  $\Delta F_c$ , and then calculate the nucleation rate.

(See Phys. Rev. E (Rapid Comm.) 81, 030601(R), 2010; PRE 82, 011603, 2010)

The Becker-Döring theory (BDT) predicts that the nucleation rate is

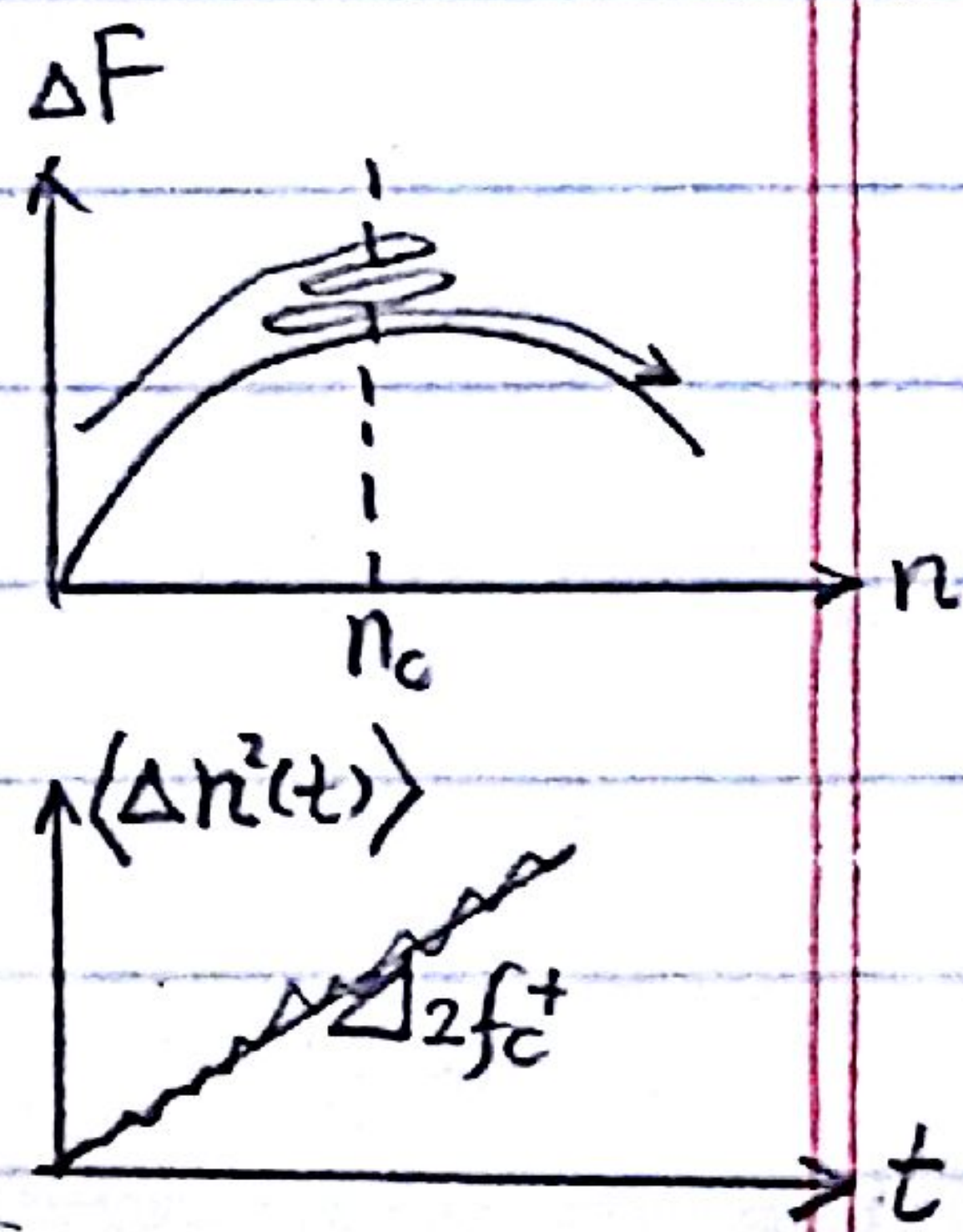
$$I = f_c^+ \Gamma e^{-\frac{\Delta F_c}{k_B T}}$$

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

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

is the Zeldovich factor to account for multiple recrossing of  $n=n_c$  surface by a single nucleation event.

$2f_c^+$  is the slope of the 'mean square displacement' curve for the size fluctuation of clusters with initial size  $n_c$ .





#### 4. Free Energy as a Function of Cluster Size

The free energy of the Ising Model is defined as

$$F = -k_B T \ln Z, \quad \text{partition function } Z = \sum_{\{S_i\}} e^{-\beta H(\{S_i\})}$$

where the sum in the partition function is over all possible spin configurations.

Q: What does it mean when we say free energy for a cluster of size  $n$ ,  $F(n)$ ?

$$F(n) = -k_B T \ln \hat{Z}(n), \quad \hat{Z}(n) = e^{-\beta F(n)}$$

where partition function  $\hat{Z}(n) = \sum_{\{S_i\}} e^{-\beta H(\{S_i\})}$   
 s.t. largest cluster size =  $n$

Note  $Z = \sum_{n=0}^{\infty} \hat{Z}(n)$ , i.e.  $\hat{Z}(n)$  is a partial sum which only include some of the terms in  $Z$

Q: Why do we want to define  $F(n)$  this way?

The probability of finding the system in a particular spin configuration  $\{S_i\}$

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

The probability of finding the system containing a largest cluster of size  $n$

$$p(n) = \sum_{\substack{\{S_i\} \\ \text{s.t. largest} \\ \text{cluster size} = n}} p(\{S_i\}) = \frac{1}{Z} \sum_{\substack{\{S_i\} \\ \text{s.t. largest} \\ \text{cluster size} = n}} e^{-\beta H(\{S_i\})} = \frac{\hat{Z}(n)}{Z} = \frac{1}{Z} e^{-\beta F(n)}$$

compare these two expressions, we see that  $p(n)$  also has the Boltzmann form, with the free energy  $F(n)$  replacing the energy  $H(\{S_i\})$ .

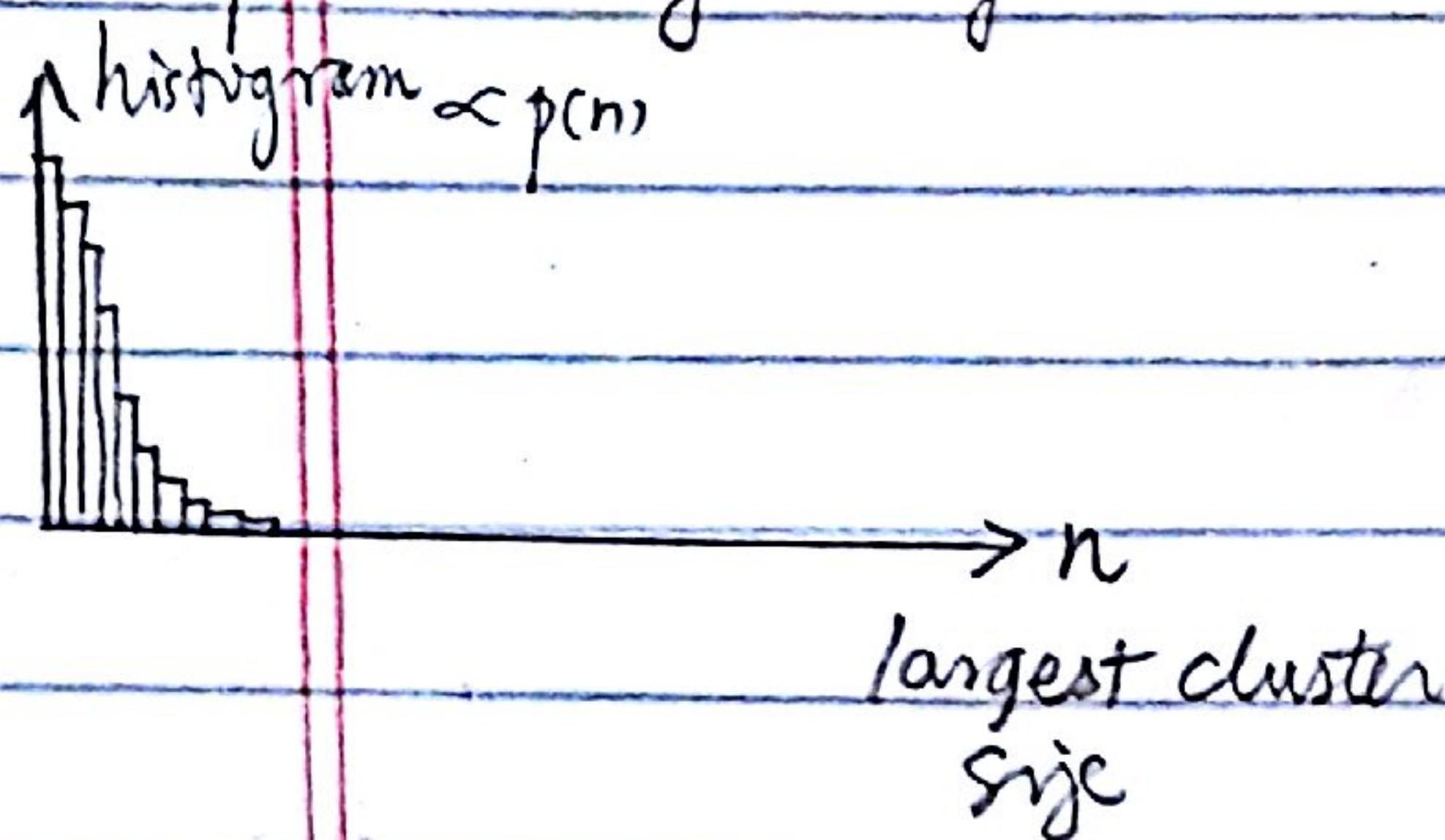
$$p(n) = \frac{1}{Z} e^{-\beta F(n)}, \quad F(n) = -k_B T \ln[p(n) \cdot Z] \quad \hat{Z}(n) = p(n) \cdot Z$$



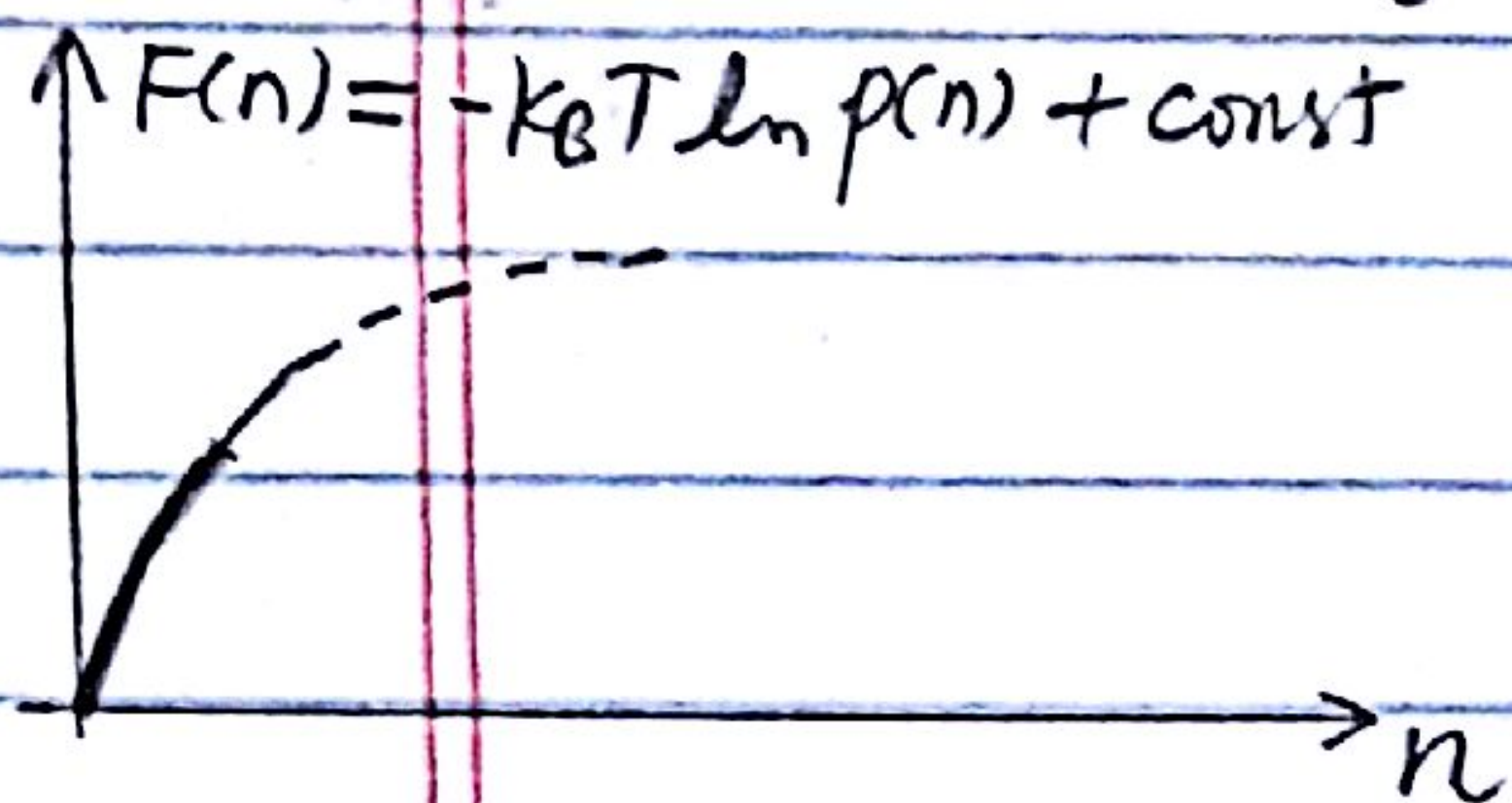
## 5. Compute Free Energy from Probability (Histogram)

Given the relation between  $p(n)$  and  $F(n)$ , we can (hypothetically) construct the  $F(n)$  curve from histogram of largest cluster size  $\propto p(n)$

Just do usual Monte Carlo simulation and record largest cluster size  $n$  periodically during the simulation, and build a histogram.



Take logarithm of the histogram, and multiply  $-k_B T$ , we obtain  $F(n)$  up to a constant.



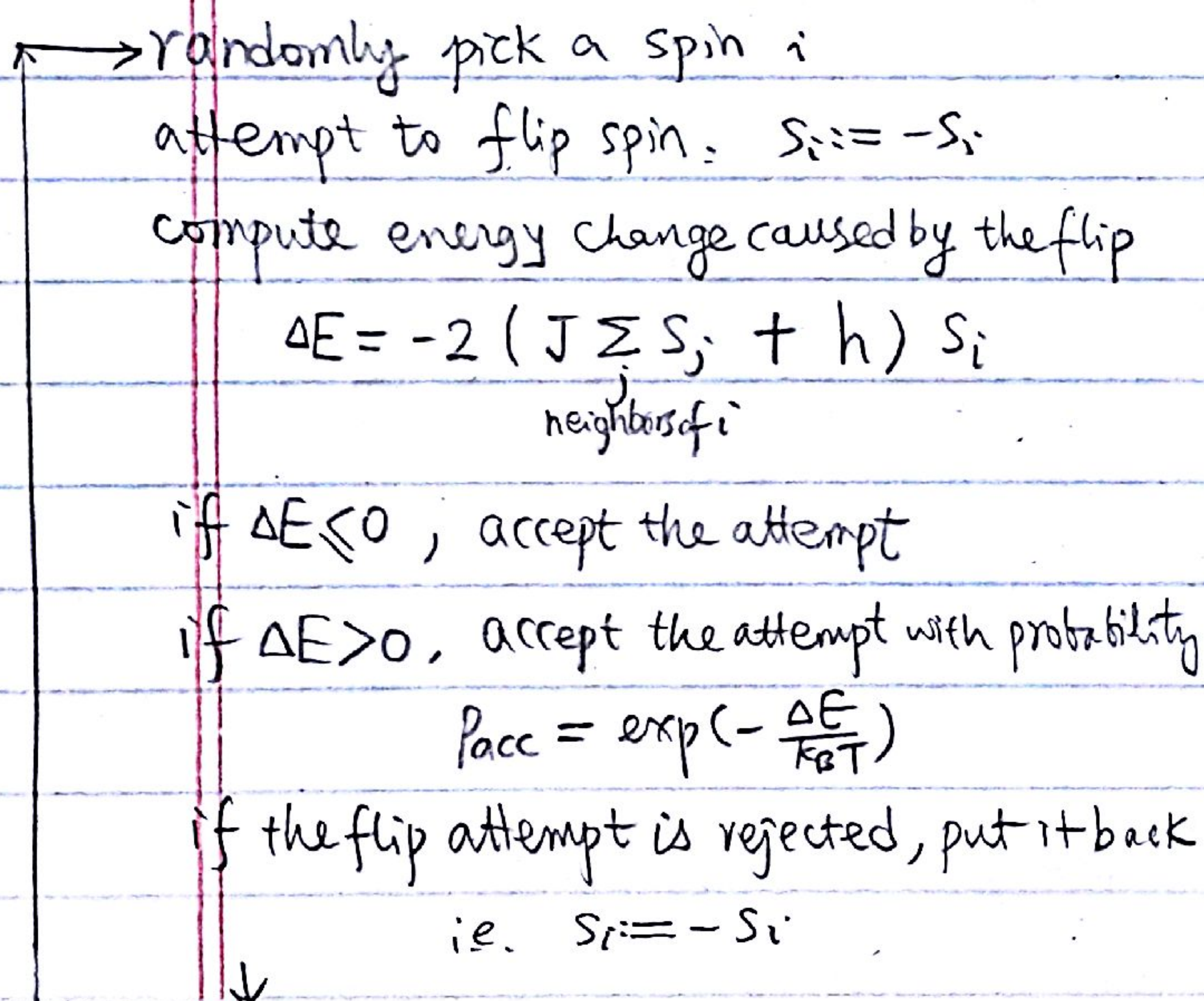
However, we won't be able to obtain the free energy barrier  $\Delta F_c$  with this approach.

The probability of sampling configurations containing a large cluster size  $n$  is very small. So the histograms with large  $n$  quickly becomes empty. Logarithm of zero is undefined.

We need to modify the Monte Carlo simulation so that we can sample configurations with large clusters.

## 6. Umbrella sampling

### a. conventional Monte Carlo simulation (Metropolis algorithm)





## b. bias potential

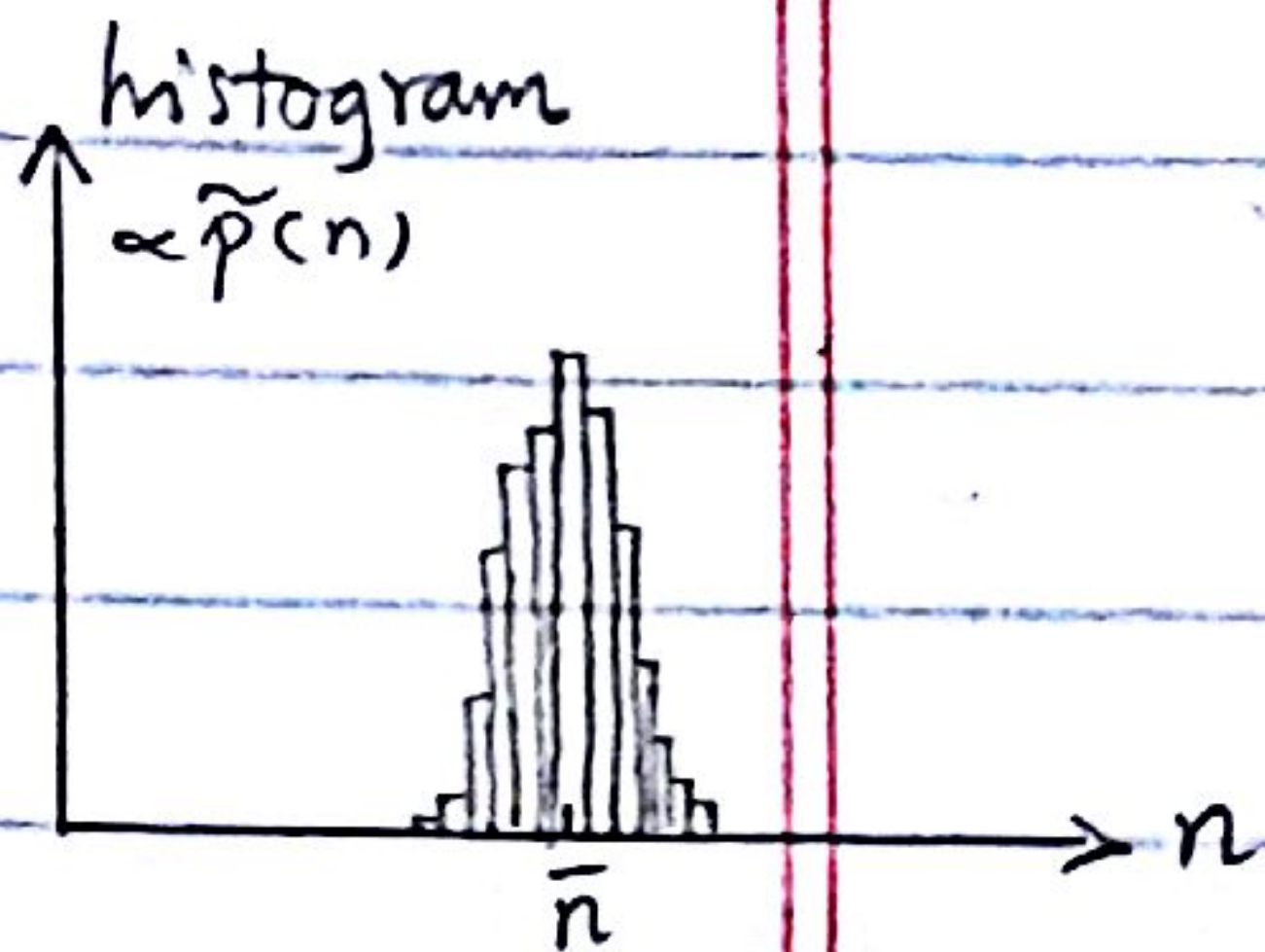
We can induce the sampling of configurations containing large clusters by modifying the Hamiltonian

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

constants
↓

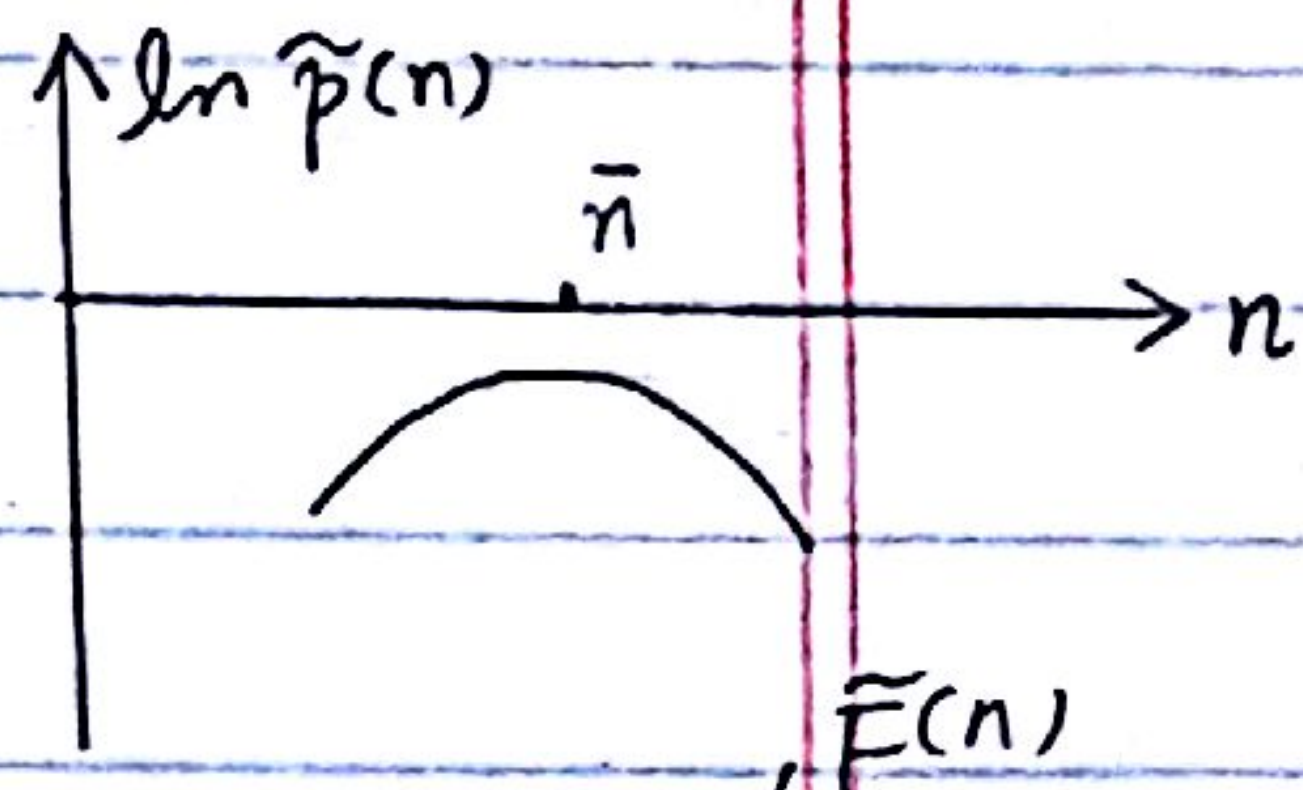
new Hamiltonian
original Hamiltonian
bias potential

$n(\{S_i\})$  is the largest cluster size of spin configuration  $\{S_i\}$



The only modification to the Monte Carlo algorithm is the calculation of energy change caused by spin flip

$$\Delta E = -2 \left( J \sum_{\langle i,j \rangle} S_j + h \right) S_i + \underbrace{\Delta U_{\text{bias}}}_{\text{change of bias potential caused by spin flip}}$$



For sufficiently large  $K$ , the new Monte Carlo simulation will generate spin configurations whose largest spin ↑ cluster size  $n$  is in the neighborhood of parameter  $\bar{n}$ .



The cluster free energy of the new system can be obtained from  

$$\tilde{F}(n) = -k_B T \ln \tilde{p}(n) \quad (\text{up to a constant})$$

The new free energy function is related to the original one as  

$$\tilde{F}(n) = F(n) + \underbrace{K(n - \bar{n})^2}_{\text{bias potential}} \quad (+ \text{arbitrary constant})$$

The free energy function of the original system is obtained as

$$\begin{aligned} F(n) &= \tilde{F}(n) - K(n - \bar{n})^2 \\ &= -k_B T \ln \tilde{p}(n) - K(n - \bar{n})^2 \end{aligned}$$

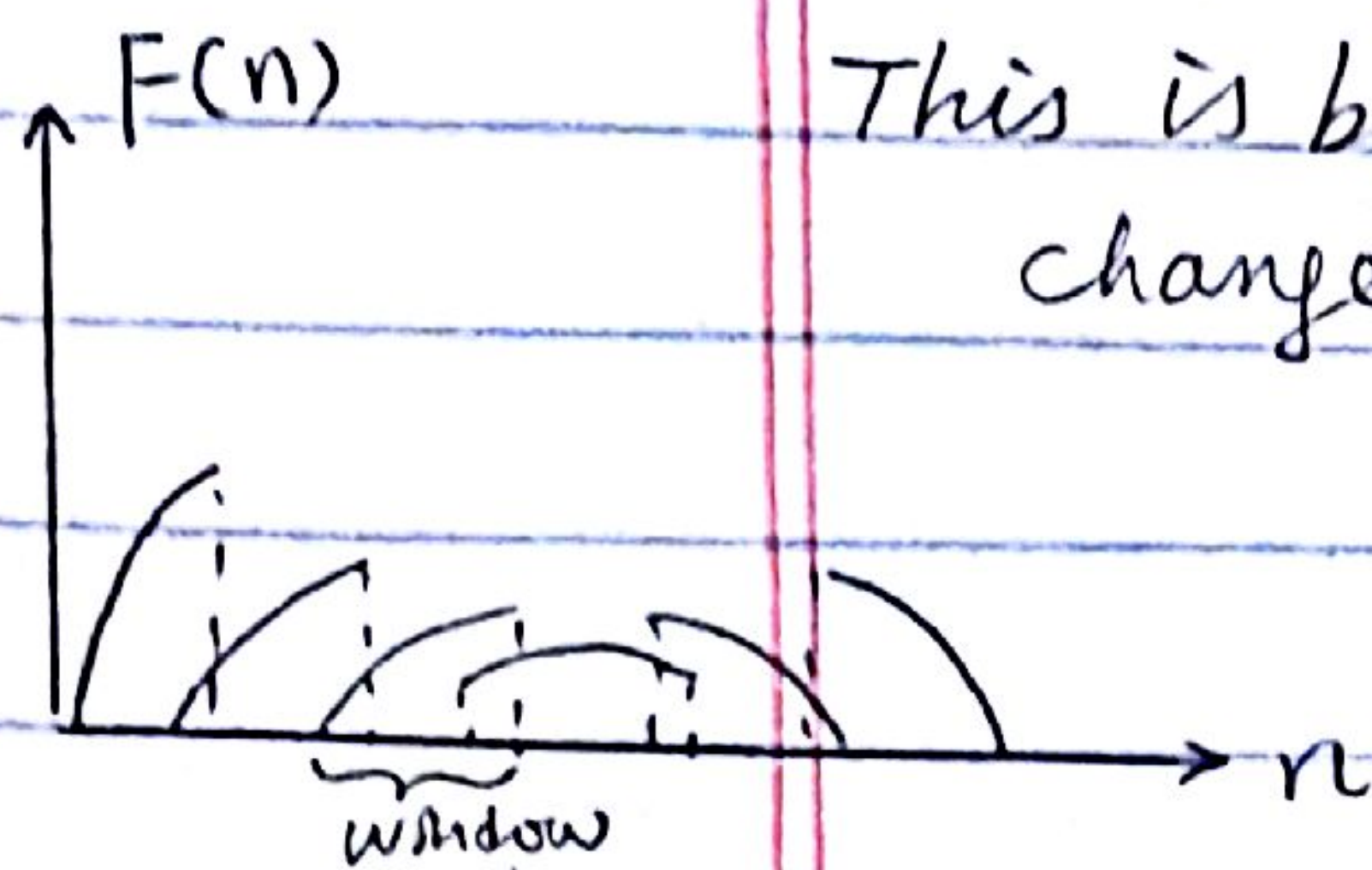
We now have information on  $F(n)$  in a different window centered around  $\bar{n}$ .

We can repeat the above Monte Carlo simulation for different  $\bar{n}$ , giving us the information on  $F(n)$  in different windows, i.e. umbrellas.



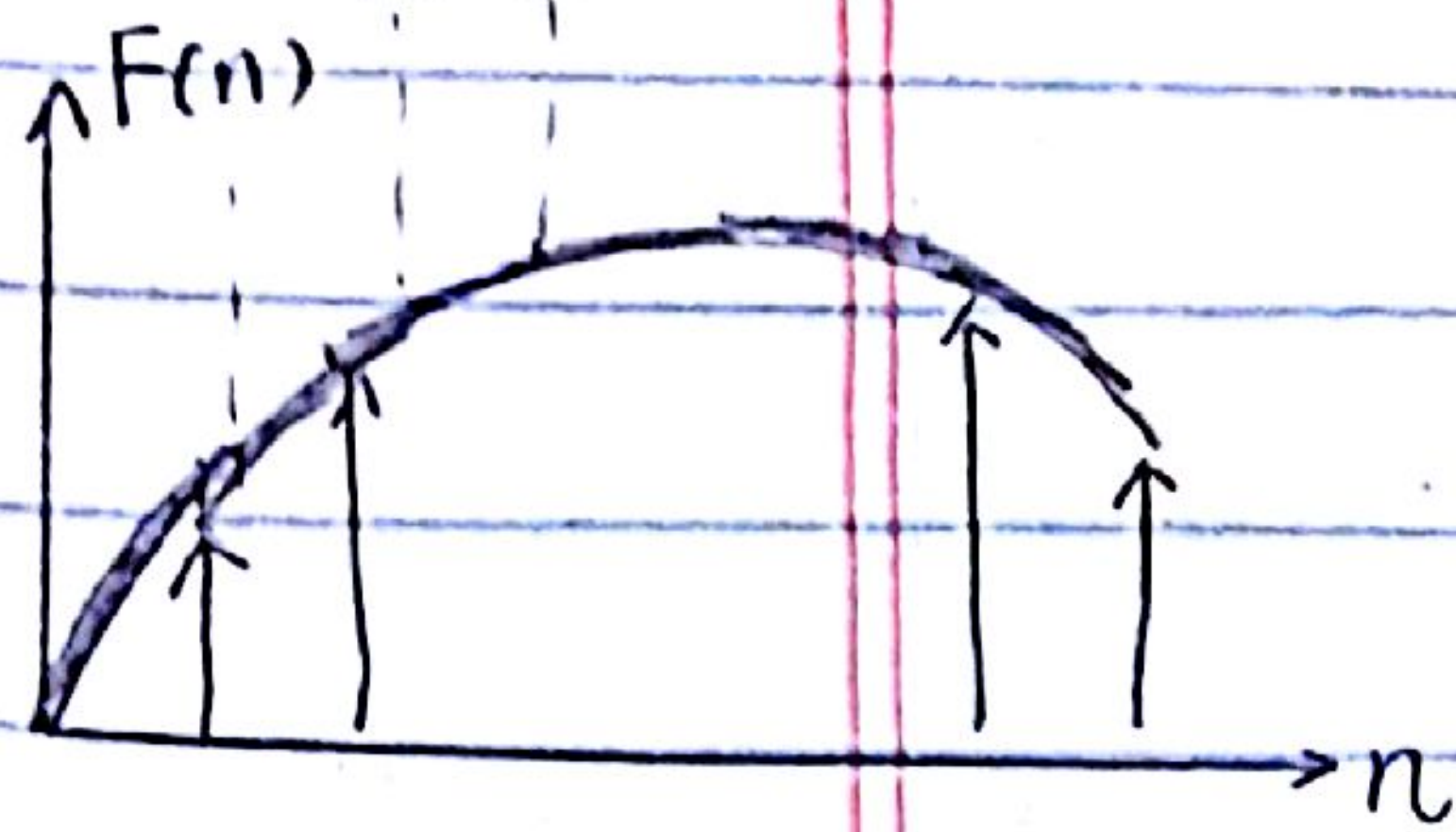
## 7 Overlapping Windows (or umbrellas)

Using the method described above, we obtain  $F(n)$  in different windows on the  $n$ -axis, but in each window we only know  $F(n)$  up to a constant.



This is because we do not know how much does the partition function  $Z$  change when we apply the bias potential.

Therefore, the  $F(n)$  curves obtained in different windows generally do not agree with each other even in overlapping regions.



arrows indicate the additive constant needed to construct a continuous  $F(n)$  curve.

What we need to do is to add appropriate constants to each piece of the  $F(n)$  curve (in different windows) so that we obtain one continuous curve, which is our final answer.

This works if there are sufficient overlap between neighboring windows, so that we can determine how much constant is needed.

This is like having enough umbrellas to completely cover a street so that no one on the street gets wet

— hence the name umbrella sampling.

The self-consistent histogram method can be used to determine the appropriate constants needed to construct the  $F(n)$  curve with least error.

(Ref: Frenkel and Smit, Understanding Molecular Simulations, 2nd ed.)  
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