Free energy difference as integral of generalized force

Define generalized force on parameter λ

$$f_\lambda \equiv -\frac{\partial H(\{r_i\},\{p_i\},\lambda)}{\partial \lambda}$$

Ensemble average of the generalized force

$$-\frac{\partial F}{\partial \lambda} = \langle f_\lambda \rangle_\lambda = \frac{\int \prod_{i=1}^{3N} dq_i dp_i \, e^{-\beta H(q_i,p_i,\lambda)} f_\lambda(q_i,p_i,\lambda)}{\int \prod_{i=1}^{3N} dq_i dp_i \, e^{-\beta H(q_i,p_i,\lambda)}}$$

Free energy difference can be obtained by integrating ensemble averages f_λ

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

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Thermodynamic Integration (TI)

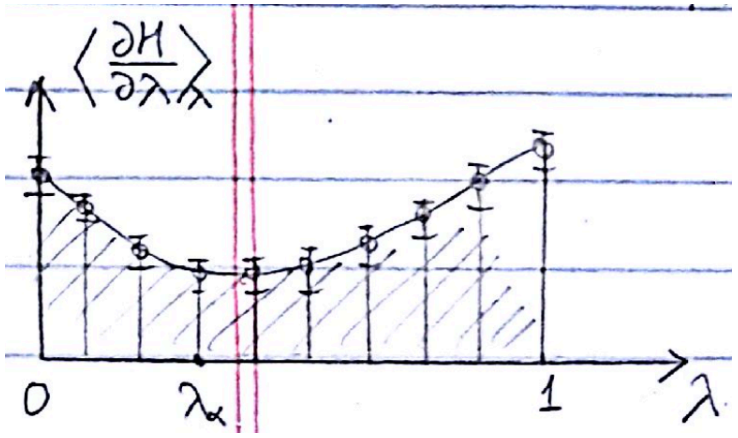
$\lambda = 1$: $H(\{S_i\}, \lambda) = H_1(\{S_i\}) = -J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i$ is the system of interest

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

Reference free energy $F_0 = -k_B T \ln Z_0$ is known analytically

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

$$F_0 = -k_B T \ln \left(2\cosh \beta h\right)^N = -N k_B T \ln (2\cosh \beta h)$$



Perform Monte Carlo simulation at different λ_α and compute ensemble (time) average

$$\left\langle \frac{\partial H(\{S_i\}, \lambda)}{\partial \lambda} \right\rangle_\lambda = \left\langle -J \sum_{\langle i,j \rangle} S_i S_j \right\rangle_\lambda$$

Thermodynamic Integration (TI)

Algorithm 1 (TI)

1. Choose number of subdivision points N_s. define $\lambda_\alpha = \frac{\alpha}{N_s}$, $\alpha = 0, 1, \cdots, N_s$.
2. For each λ_α, perform Monte Carlo simulation using Hamiltonian
   $$H(\{S_i\}, \lambda_\alpha) = -\lambda_\alpha J \sum_{<ij>} S_i S_j - h \sum_i S_i$$
3. For each Monte Carlo simulation using λ_α. Compute time average of $-J \sum_{<ij>} S_i S_j$
   the result is called $\langle -J \sum_{<ij>} S_i S_j \rangle_{\lambda_\alpha}$
4. Numerically integrate $\frac{\partial F}{\partial \lambda}$ (trapezoid rule)

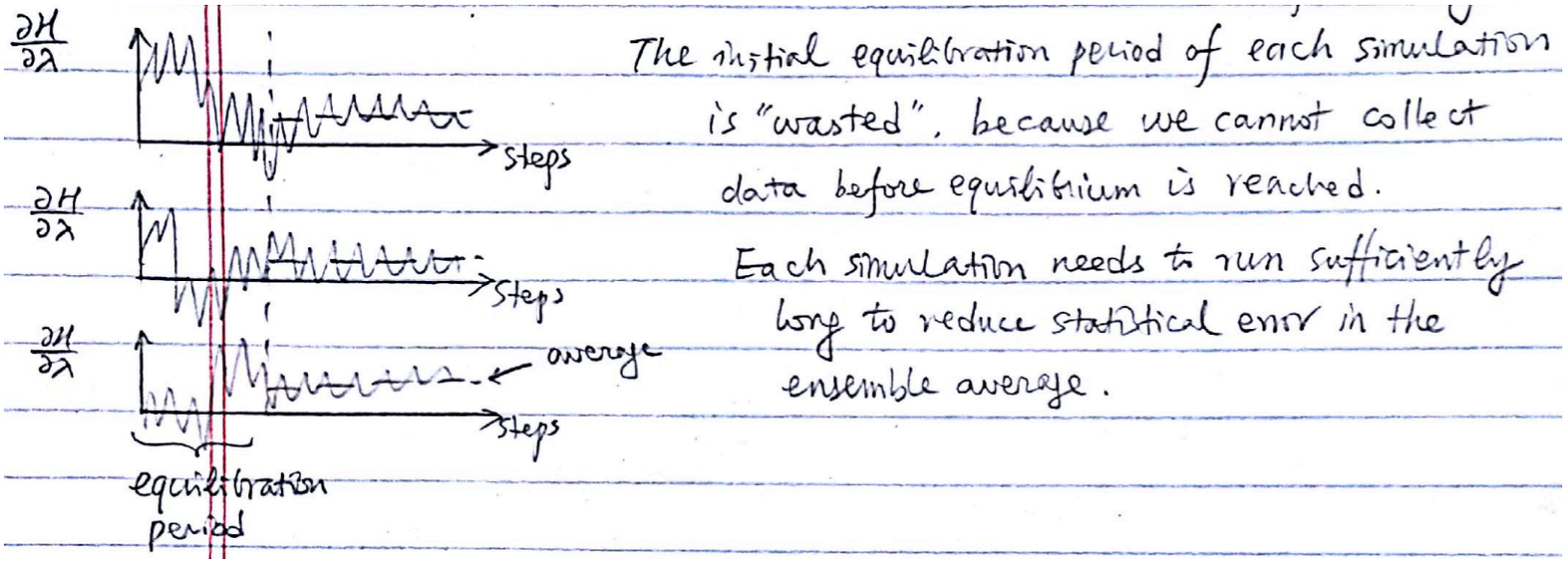
$$F_1 - F_0 = \left(\frac{1}{2} \left\langle -J \sum_{<i,j>} s_i s_j \right\rangle_{\lambda_0} + \sum_{\alpha=1}^{N_s - 1} \left\langle -J \sum_{<i,j>} s_i s_j \right\rangle_{\lambda_a} + \frac{1}{2} \left\langle -J \sum_{<i,j>} s_i s_j \right\rangle_{\lambda_0} \right) \cdot \frac{1}{N_s}$$

(please fix typos on lecture notes)

Problems with the TI Method

a. Not sure how to choose number of subdivision points N_s optimally
   too small Ns leads to discretization error in numerical integration
   too large Ns leads to high computational cost

b. Each Monte Carlo simulation with different λ_α runs independently



c. Not sure if we should run fewer long simulations (small statistical error)
   or more shorter simulations (small discretization error)

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Method of Adiabatic Switching (AS)

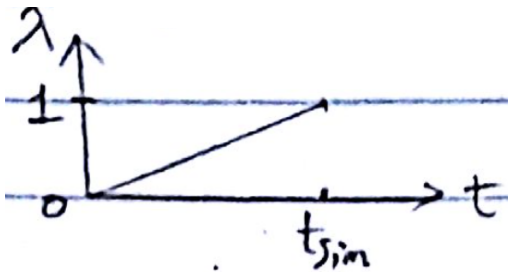
Idea: A long Monte Carlo simulation in which λ changes gradually from 0 to 1

If λ changes sufficiently slowly, the system is always close to the equilibrium distribution corresponding to the instantaneous λ value.

Define 'dynamic work' (assuming each Monte Carlo step takes 1 unit of 'time')

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

Simplest switching function:



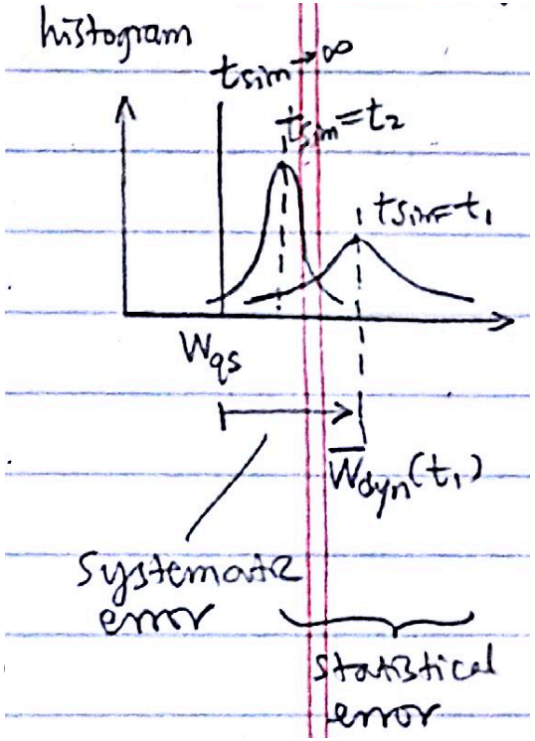
$$\lambda(t) = 1 - \frac{t}{t_{\text{sim}}}$$

Dynamic work in quasi-static limit

In the limit of $t_{sim} \rightarrow \infty$, we go to the quasi-static (qs) limit, and the dynamic work equals the free energy difference.

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

In practice, t_{sim} is always finite. W_{dyn} is different from W_{qs} by a random number.



$t_1 < t_2 < \infty$

Both systematic error and
decreases with increasing switching time t_{sim}.

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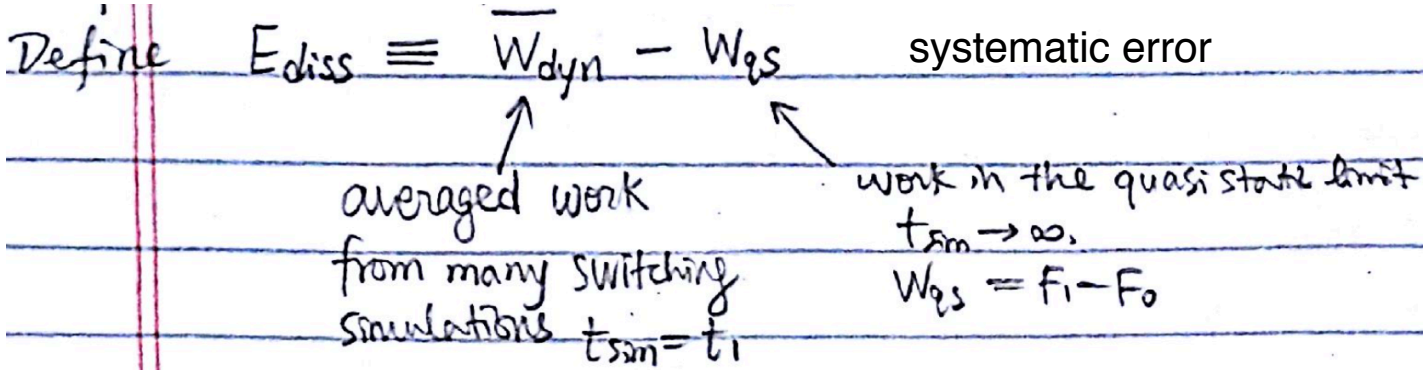
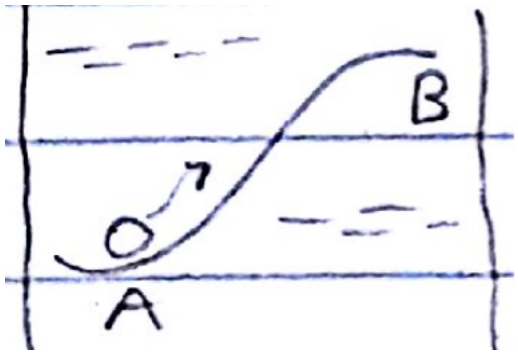
Dissipation in Adiabatic Switching



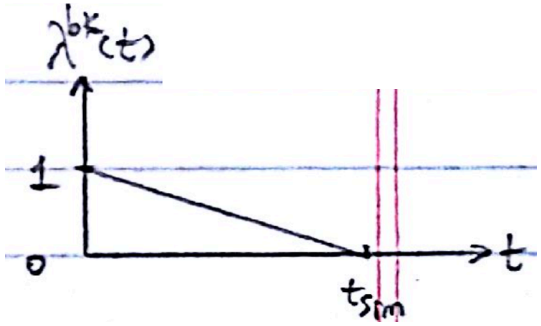


Imagine dragging a ball up a slope beneath water.

Dissipation is always positive

$$E_{\text{diss}} > 0$$

Dissipation in Adiabatic Switching

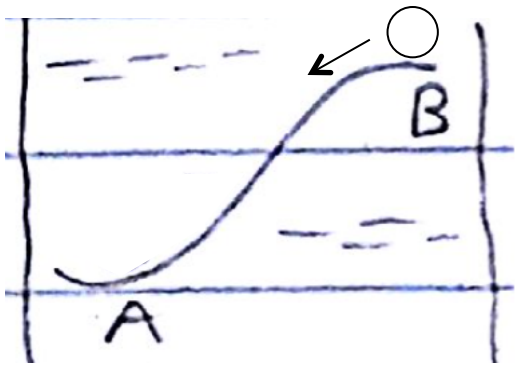


Consider backward switching. The dynamic work is

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

In the quasi-static limit,

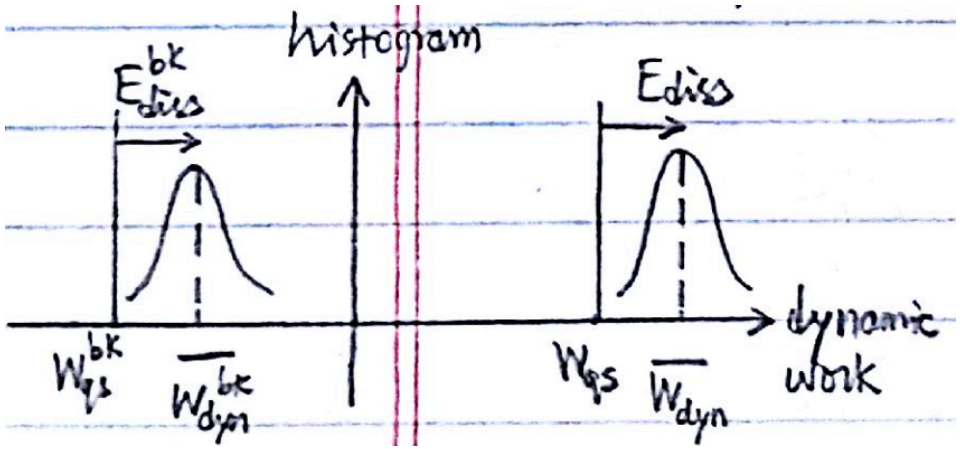
$$\lim_{t_{sim}\to\infty} W_{dyn}^{bk} = W_{qs}^{bk} = -W_{qs} = F_0 - F_1$$



Imagine dragging a ball down a slope beneath water.

Dissipation is still positive

$$E_{\text{diss}}^{\text{bk}} = \bar{W}_{\text{dyn}}^{\text{bk}} - W_{\text{qs}}^{\text{bk}} > 0$$



Estimating Dissipation in Adiabatic Switching

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

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

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

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

This is a better estimate for the free energy difference F_1-F_0

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

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

To reduce systematic error, increase switching time t_{sim}.

To reduce , repeat simulation and compute average.

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Choice of Switching Function

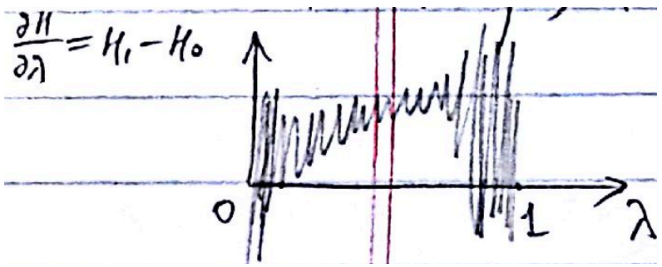
In principle, any continuous, monotonic function that satisfies

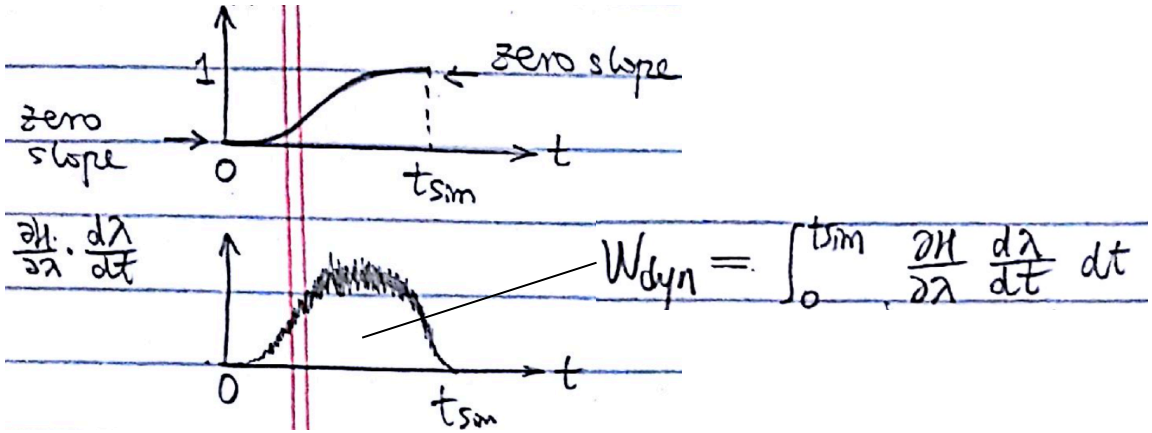
$$\begin{cases} \lambda(t=0)=0 \\ \lambda(t=t_{sim})=1 \end{cases}$$

can be used as a switching function.

But some switching functions are better than others
(application dependent)

For example, if $\partial H/\partial\lambda$ has large fluctuation near $\lambda=0$ and $\lambda=1$,
then it is better to use a switching function with zero slope at two ends.





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Switching along Temperature Axis

We often need to compute $F(T)$, e.g. for calculating melting points.

For simplicity, if we consider $\mathrm{h} = 0$ (no magnetic field)

$$H_1(\{S_i\}) = -J \sum_{\langle ij \rangle} S_i S_j \qquad F_1(T) = -k_B T \ln \left(\sum_{\{S_i\}} e^{\beta J \sum_{\langle ij \rangle} S_i S_j} \right)$$

Parameterized Hamiltonian

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

$$F(T, \lambda) = \lambda F_1(T / \lambda)$$

$$F_1(T_0 / \lambda) = \frac{1}{\lambda} F(T_0, \lambda) = \frac{1}{\lambda} \left(F(T_0, 1) + \int_1^{\lambda} \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_{\lambda} d\lambda \right)$$

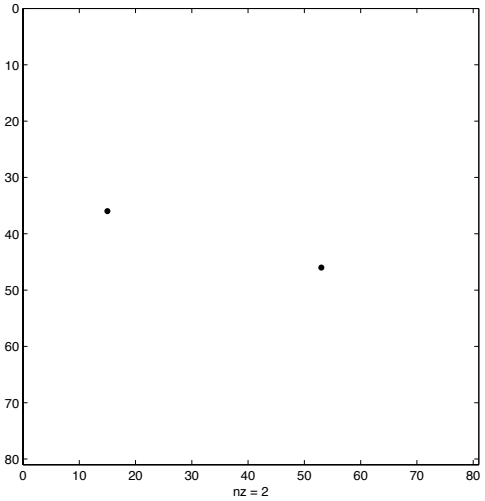
(please fix typos on lecture notes)

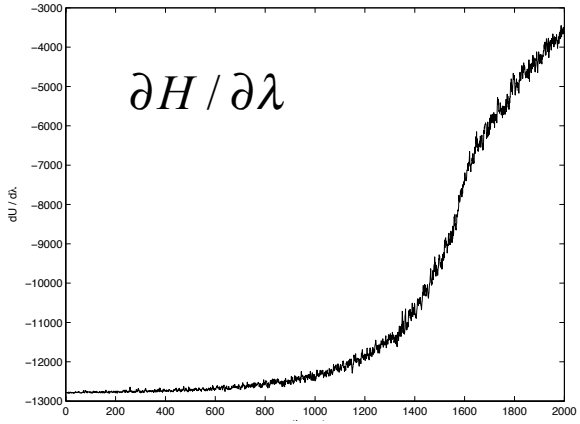
Ising Model Test Case – Adiabatic Switching

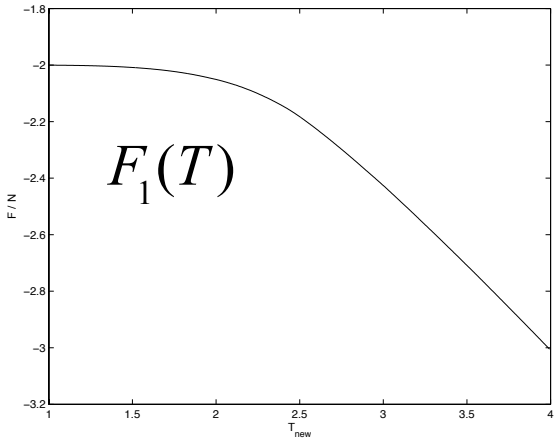
Matlab: `ising2d_switch.m`

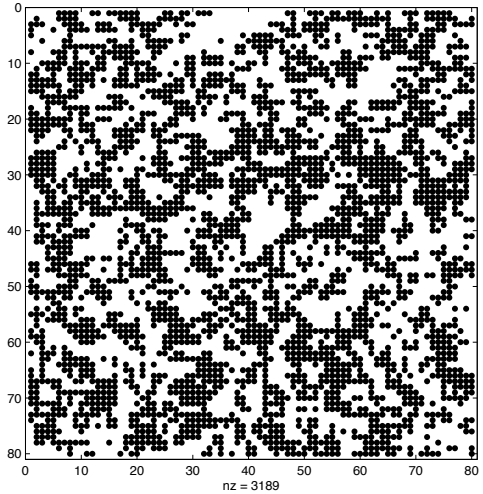
$k_B T_0 = 1.0$

$\lambda = 1.0$ → $\lambda = 0.25$









Extra Reading: *Comput. Sci. Eng.* 2, 88 (2000) PDF available on web site.

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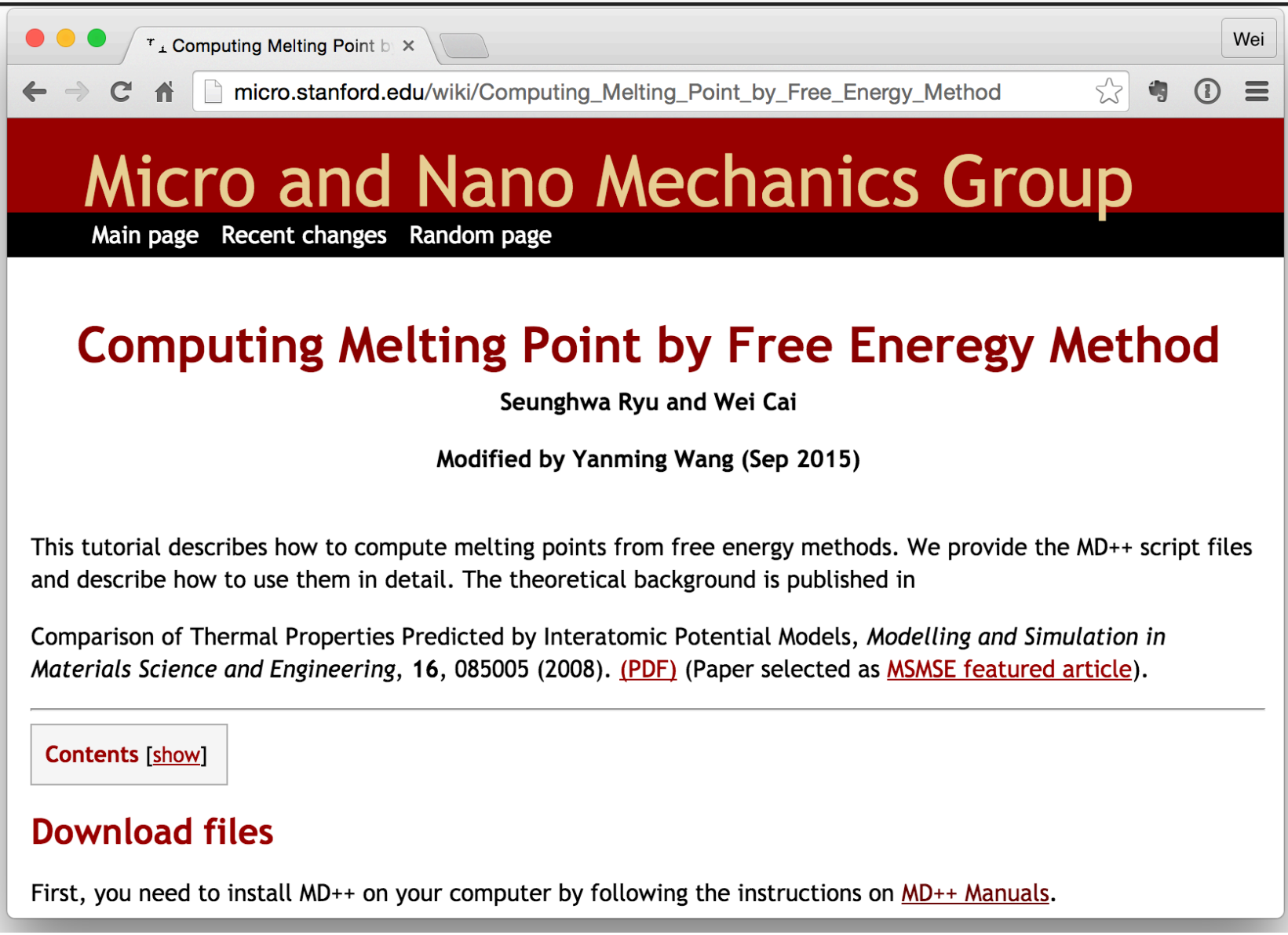


Computing Melting Point by Free Energy Method

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

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

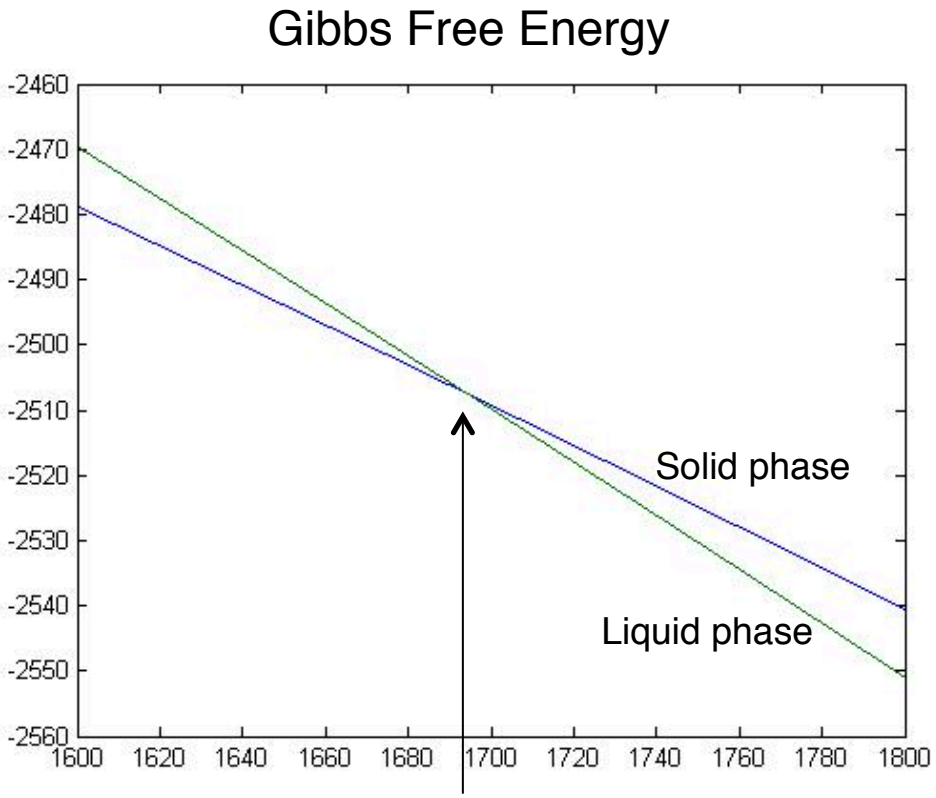
$\omega_i = \sqrt{\frac{K_i}{m}}$ is vibrational frequency.

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

Ideal gas (N atoms in volume V)

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

Test Case: Silicon



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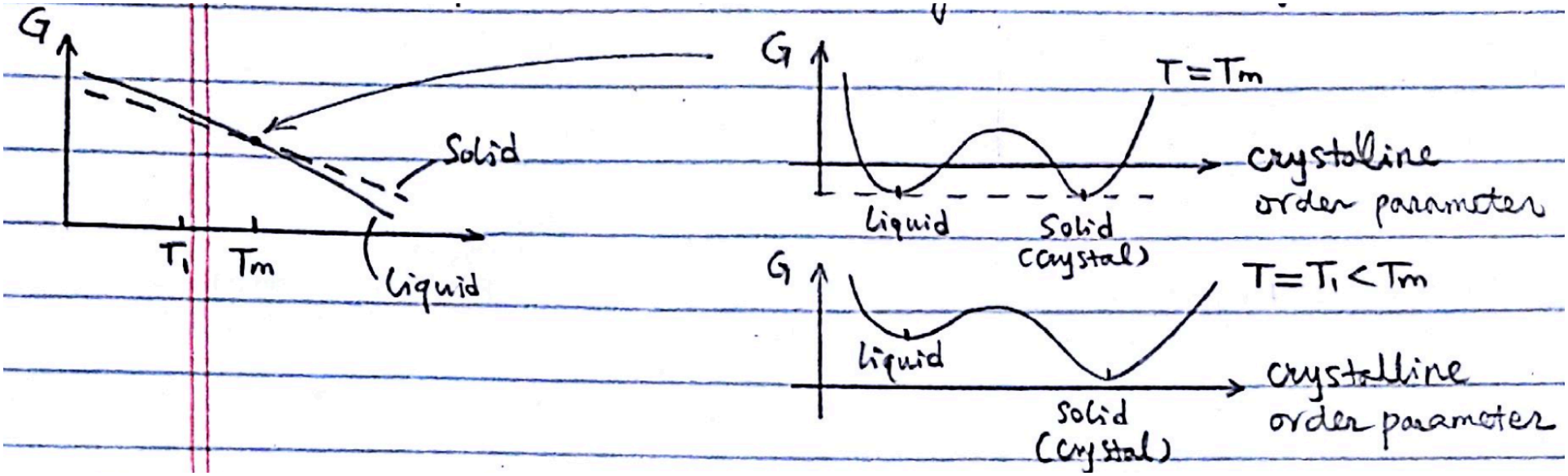
Supercooled Water Experiments – Youtube Videos

http://www.youtube.com/watch?v=pTdiTe3x0Bo&feature=fvw

http://www.youtube.com/watch?v=fSPzMva9_CE

Supercooled Water



At $T = T_1 < T_m$, liquid has higher free energy than solid (crystal).

But to turn liquid to crystal requires the nucleation of a crystal nucleus.

At low temperature, the rate of nucleation can be so low that water can be kept in liquid form below 0°C for a long time, i.e. in the supercooled state.

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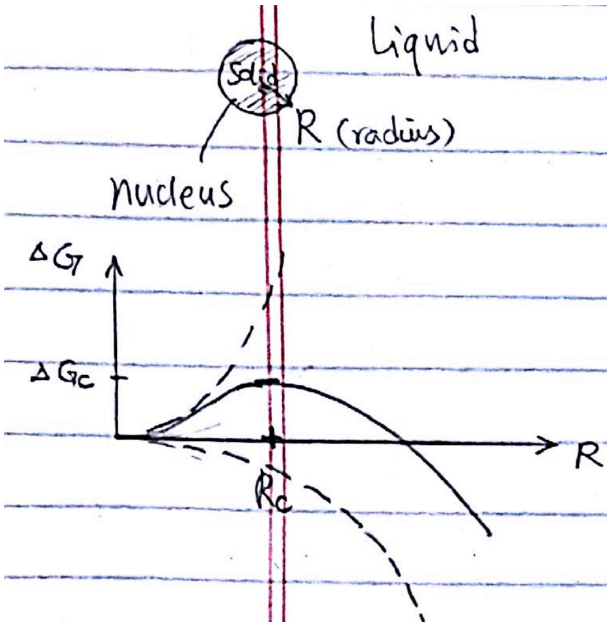
Classical Nucleation Theory (CNT)



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

A small nucleus (radius R) of solid phase can form by thermal fluctuation within the liquid phase.

Free energy change by forming the nucleus

$$\Delta G \cong -\Delta\mu \cdot \frac{4}{3}\pi R^3 + \gamma_{LS} \cdot 4\pi R^2$$

$\Delta\mu$: chemical potential difference between liquid and solid ($\Delta g_L - \Delta g_S$)

$\frac{4}{3}\pi R^3$: Volume

γ_{LS}: surface energy

$4\pi R^2$: surface area

ΔG reaches maximum (ΔG_c) at $R = R_c$ (critical radius).

The probability of finding a nucleus at $R = R_c$ is ~ $\exp(-\Delta G_c / k_B T)$

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

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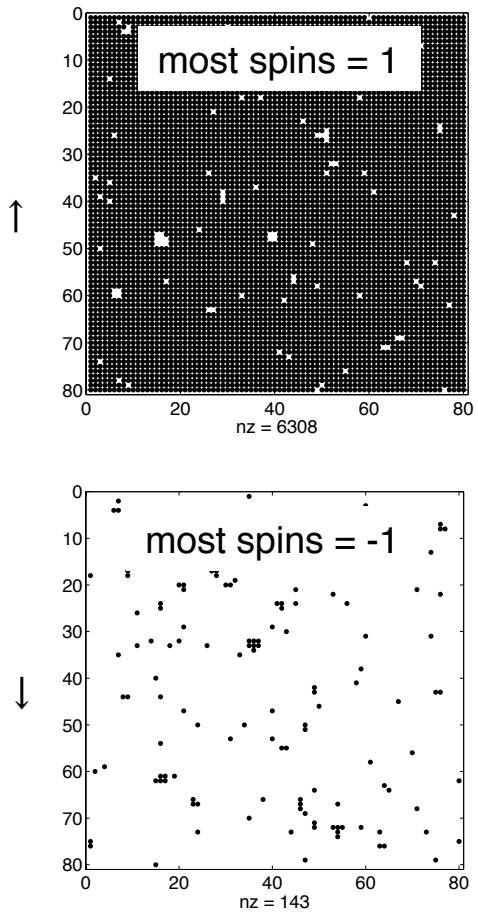
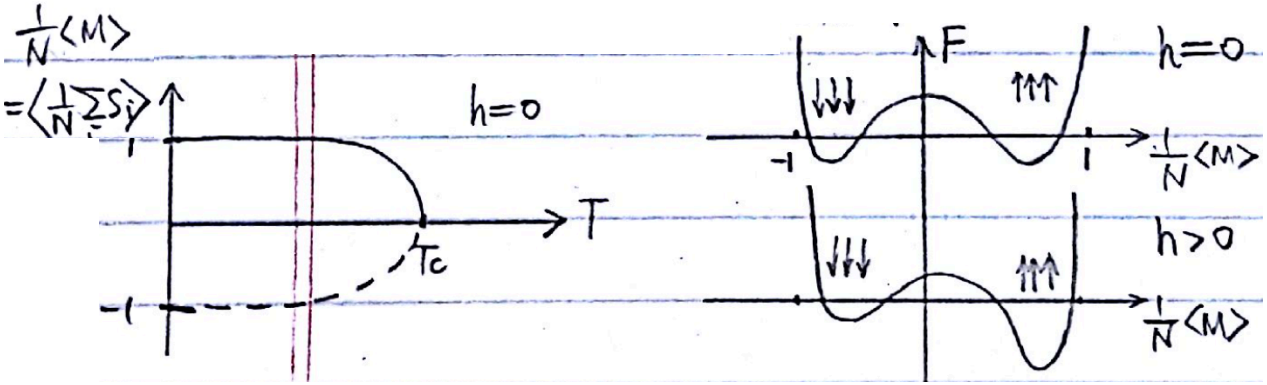
Nucleation in Ising Model

Two ferromagnetic phases at $T < T_c$.



If $h = 0$, the two phases are equally probable.

If $h > 0$, the spin ↑ state has lower free energy than the spin ↓ state.

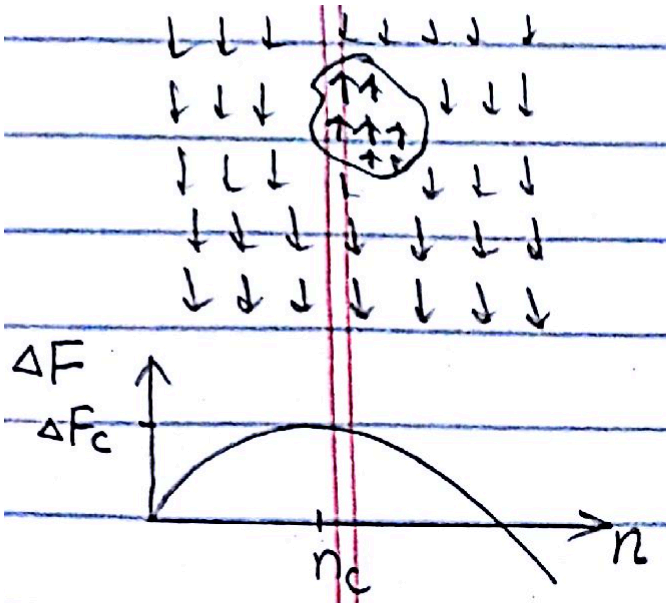


But if the system is initially prepared in the spin ↓ state, it may stay there for a long time.

Eventually, the system transforms into the spin ↑ state by nucleation and growth.

Nucleation in Ising Model

The nucleus is a cluster of spin ↑ in a sea of spin ↓ .



This approximation

Size of nucleus = number (n) of spins in cluster

In 2D, assume cluster is a circle of radius R.

$$\pi R^2 = n \qquad R = \sqrt{n/\pi}$$

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

Free energy change by forming the nucleus

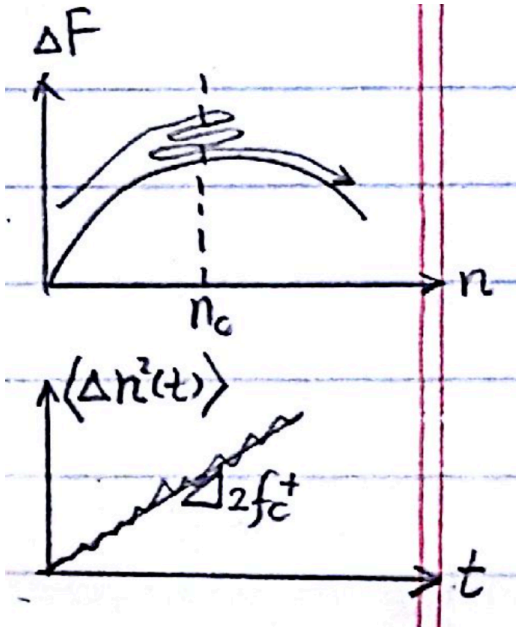
$$\Delta f \cong -2h \cdot n + \gamma \cdot 2\sqrt{\pi n}$$

energy difference between ↓ and ↑

'surface' energy between spin ↑ and spin ↓ phases

Nucleation Rate by Becker-Döring Theory

Goal: compute $\Delta F(n)$ by Monte Carlo without approximations.



Given $\Delta F(n)$, the nucleation rate I can be predicted by Becker-Döring theory.

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

ΔF_c : maximum of $\Delta F(n)$

$\Gamma \equiv \left(\frac{\eta}{2\pi k_B T} \right)^{1/2}$: Zeldovich factor
(to account for multiple crossing)

$\eta = -\frac{\partial^2 \Delta F(n)}{\partial^2 n}$

$2 f_c^+$: slope of 'mean square displacement' curve of size fluctuation starting from n_c

Extra Reading: *Phys. Rev. E. (rapid comm)* 81, 030601(R), 2010 PDF available on web site.

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2. Significance of Free Energy
3. Definition of **Free Energy**
4. Derivative of free energy as Ensemble Average
5. Method of Thermodynamic Integration (**TI**)
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Free Energy as Function of Cluster Size

Free energy of Ising model

$$F = -k_{\mathrm{B}} T \ln Z$$

Partition Function

$$Z = \sum_{\{s_i\}} e^{-\beta H(\{s_i\})} \qquad \beta = \frac{1}{k_{\mathrm{B}} T}$$

sum over all spin configurations

Q: What is the meaning of free energy of cluster size n, F(n) ?

$$F(n) = -k_{\mathrm{B}} T \ln \hat{Z}(n)$$

$$\hat{Z}(n) = \sum_{\{s_i\}} e^{-\beta H(\{s_i\})}$$

s.t. largest cluster size = n

Note:

$$Z = \sum_{n=0}^{\infty} \hat{Z}(n)$$

Why define free energy of cluster as this?

Probability of a specific spin configuration (microstate)

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

Probability of finding a largest cluster of size n (macrostate)

$$p(n) = \sum_{\{s_i\}} p(\{s_i\}) = \frac{1}{Z} \sum_{\{s_i\}} e^{-\beta H(\{s_i\})} = \frac{\hat{Z}(n)}{Z} = \frac{1}{Z} e^{-\beta F(n)}$$

s.t. largest cluster size = n

s.t. largest cluster size = n

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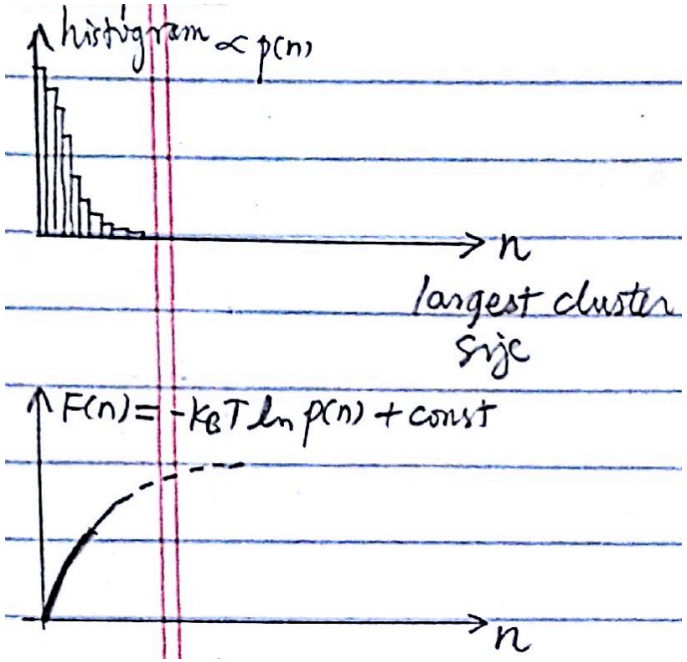
Computing Free Energy from Probability

Given $p(n) = \frac{1}{Z} e^{-\beta F(n)}$, we can obtain F(n) (up to a constant)

$$F(n) = -k_{\mathrm{B}} T \ln p(n) + (\text{unknown constant})$$

we do not know Z



Do Monte Carlo simulation as usual

Compute largest cluster size n periodically

Construct histogram of n

Take logarithm of histogram, multiply -$k_{\mathrm{B}}T$

Problem: at large n,

for $F(n)$ for large n.

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Monte Carlo Simulation with Bias Potential

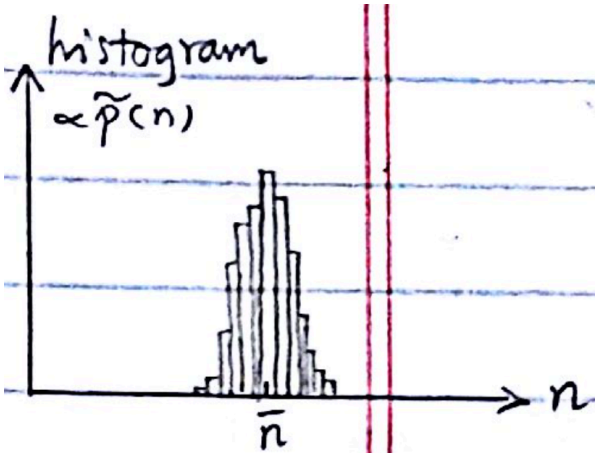
Induce sampling of large clusters by adding a

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

(K, $\bar{n}$: constants)

new Hamiltonian

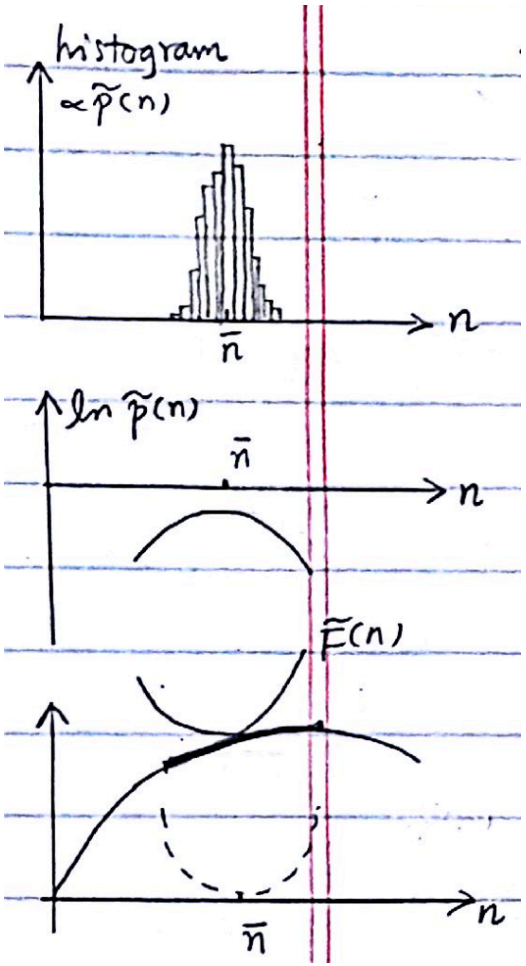
$n(\{s_i\})$ is the largest cluster size of configuration $\{s_i\}$



The only modification to the Monte Carlo algorithm is in the calculation of energy change for spin flip

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

Recover F(n) of Original Ising Model



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

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

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

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

The free energy function of the original system is obtained as

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

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.

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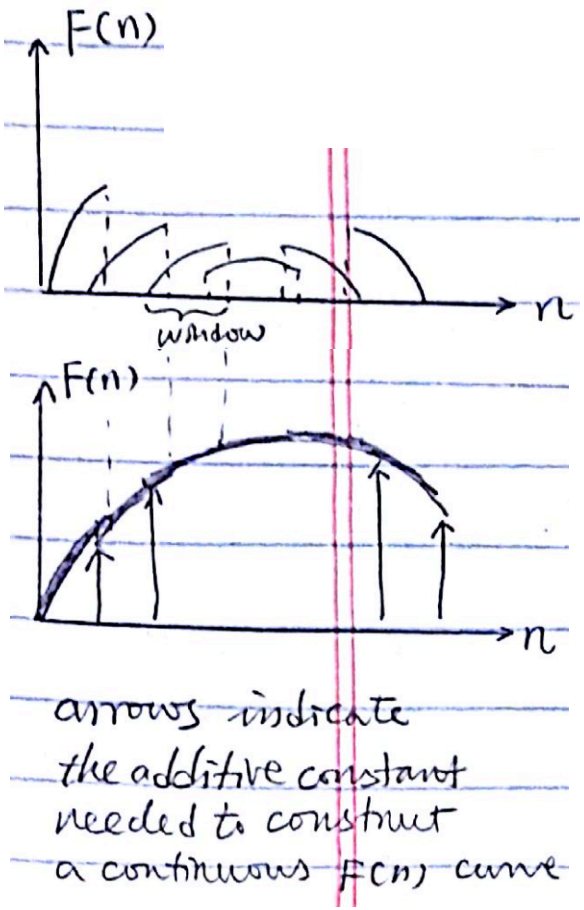
Overlapping Windows (Umbrellas)



So far we only know F(n) in each window up to a constant – because we do not know how much the bias potential changes the partition function Z.

Need to add appropriate constants to each piece of the $F(n)$ curve to get a continuous curve.

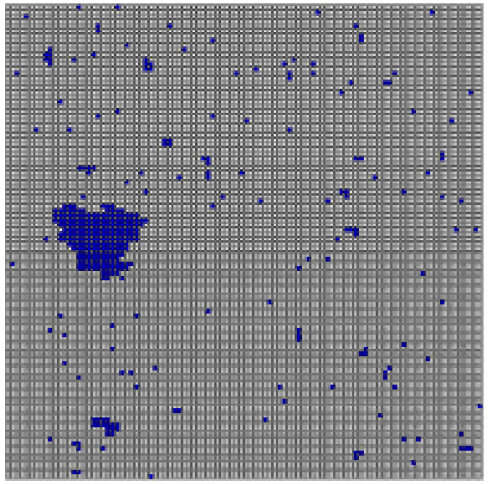
This is possible if there are sufficient overlap between neighboring windows.

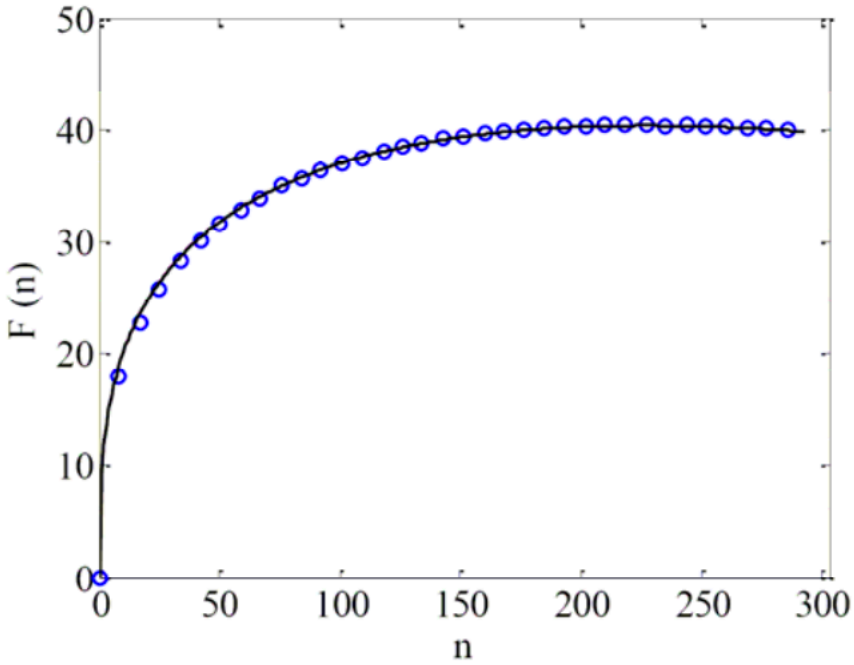
This is like having enough umbrellas to completely cover a street – hence the name umbrella sampling.

The self-consistent histogram method can be used to determine the optimal shift constants [Frenkel and Smit, Understanding Molecular Simulations, 2nd ed. p.179-196].

Ising Model Test Case – Umbrella Sampling

MD++: `Ising Model - Numerical Demonstrations.pdf`
(available on web site)





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Potential research directions:

Atomistic simulations applied to

`Nucleation of crystallization from liquid`

`Nucleation of dislocations in crystals`

`Deformation of metallic glass`

Backup Slides

Ising Model - Numerical Results

2D Ising Model

3D Ising Model

More details can be found at:

Seunghwa Ryu and Wei Cai, "The Validity of Classical Nucleation Theory for Ising Models", *Physical Review E* (*Rapid Communications*), 81, 030601 (R) (2010).

Seunghwa Ryu and Wei Cai, "Numerical Tests of Nucleation Theories for the Ising Models", *Physical Review E*, 82, 011603 (2010).

http://www.stanford.edu/~caiwei/papers.html

Numerical demonstration of MD++, by Seunghwa Ryu, after lunch

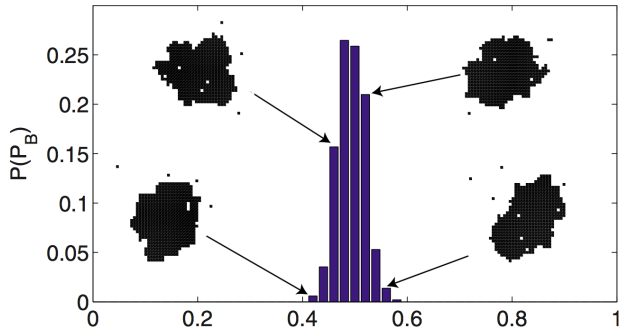
Outline

Advantages of MD:

- Full atomistic detail

Disadvantages of MD:

- High computational cost
- Limited time scale (nanosecond)



Nucleation in Supercooled Water

Refrigerator in my office --- Wait overnight …

Nucleation of Ice by Mechanical Disturbance