Today's goal:

Part A • free energy of a subspace ← *This lecture note only addresses Part A.

Part B • generalization of 1D Ising model ← Notes for part B can be found in Handout 12 "Ising Model".

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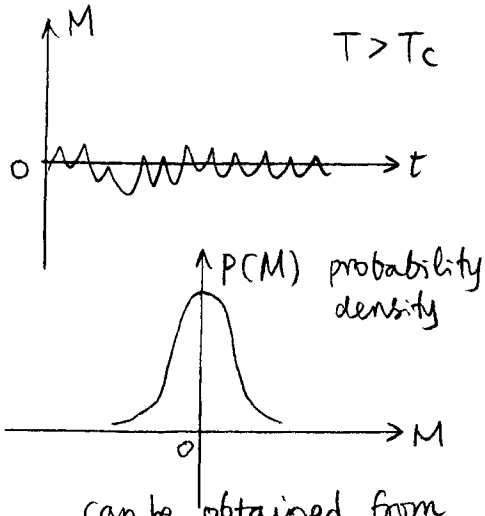
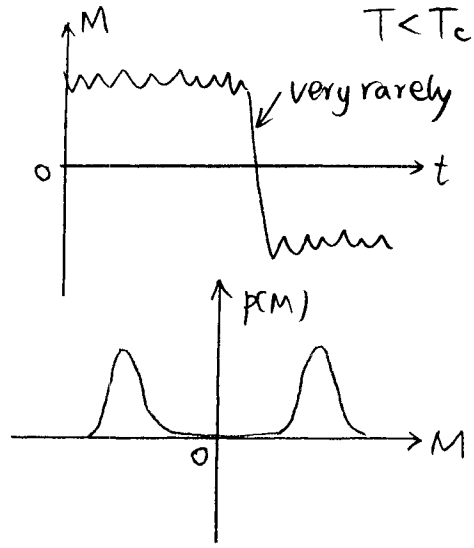
1. Motivation

HW8.3 2D Ising model, instantaneous magnetization $M = \frac{1}{N}\sum_i S_i$

observations from Monte Carlo simulations

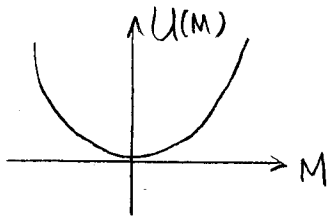


can be obtained from histogram with proper normalization: $\int_{-1}^{1} p(M)\,dM = 1$



Suppose we want to develop a coarse-grained model for M

e.g. $\ddot{M} = -k\frac{\partial U(M)}{\partial M} - \gamma\dot{M} + f^{rand}(t)$



We may consider M(t) as motion inside a one-dimensional potential U(M) subjected to random noise

For consistency, at thermal equilibrium, the probability density of observing a particular value of M is

$$p(M) = \frac{1}{Z} e^{-\beta U(M)}$$

U(M): effective potential, or potential of mean force

We will show that it is the same as the free energy A(M) defined below.

We can obtain $U(M)$ (up to a constant) from $p(M)$:

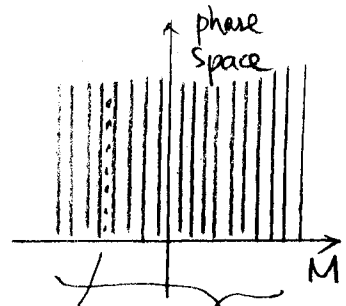
$$U(M) = -k_B T \ln p(M) \underbrace{- k_B T \ln \hat{Z}}_{\text{unknown constant}}$$

2. Ising Model with a constraint

with constraint

$$Z(M,T) = \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \frac{1}{N}\sum_i S_i = M}} e^{-\beta \mathcal{H}(\{S_i\})}$$

(note the phase space is partitioned into many slices. Perhaps this is why Z is called the partition function.)



Summing over one slice

Summing over entire phase space

without constraint

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

$$= \sum_M \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \frac{1}{N}\sum_i S_i = M}} e^{-\beta \mathcal{H}(\{S_i\})}$$

$$= \sum_M Z(M,T)$$

$$e^{-\beta A(M,T)} = Z(M,T)$$

$A(M,T) = -k_B T \ln Z(M,T)$ is the Helmholtz free energy of the Ising model under constraint M.

$$e^{-\beta A(T)} = Z(T)$$

$A(T) = -k_B T \ln Z(T)$ is the Helmholtz free energy of the unconstrained Ising model

note: $Z(M,T) < Z(T)$

$A(M,T) > A(T)$, $\quad e^{-\beta A(T)} = \sum_M e^{-\beta A(M,T)}$

All other thermodynamic quantities are similarly defined in the constrained and unconstrained Ising model, e.g.

$$E(M,T) = -\frac{\partial}{\partial \beta} \ln Z(M,T) \qquad E(T) = -\frac{\partial}{\partial \beta} \ln Z(T)$$

$$S(M,T) = \frac{1}{T}[E(M,T) - A(M,T)] \qquad S(T) = \frac{1}{T}[E(T) - A(T)]$$

$A(M,T)$ is also called the free energy landscape.

3. Proof of $U(M) = A(M,T)$

i.e. the "effective potential" is the same as the "free energy land scape", and as such, should in general depend on temperature.

Recall that

$U(M)$ is defined through:

$$p(M) = \frac{1}{\hat{Z}} e^{-\beta U(M)}$$

↑ probability of observing M in unconstrained model

$A(M,T)$ is defined through:

$$Z(M,T) = e^{-\beta A(M,T)}$$

↑ partition function of a constrained model

For the unconstrained model, the probability of observing a particular spin configuration (one point in phase space) is

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

The probability of observing a specific value of M is

$$p(M) = \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \frac{1}{N}\sum_i S_i = M}} p(\{S_i\}) = \frac{1}{Z(T)} \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \frac{1}{N}\sum_i S_i = M}} e^{-\beta \mathcal{H}(\{S_i\})} = \frac{Z(M,T)}{Z(T)} = \frac{e^{-\beta A(M,T)}}{e^{-\beta A(T)}}$$

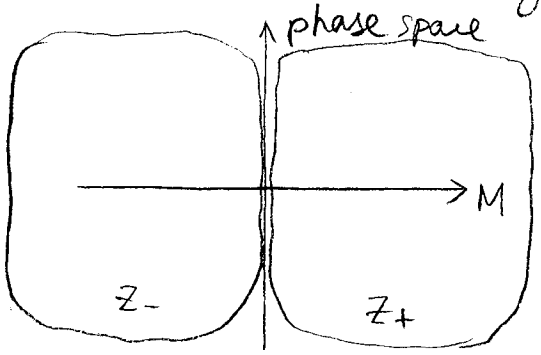
The ratio of the probabilities of observing two values of M is

$$\frac{p(M_1)}{p(M_2)} = \frac{e^{-\beta A(M_1,T)}}{e^{-\beta A(M_2,T)}} = \exp\left[-\beta\left(A(M_1,T) - A(M_2,T)\right)\right]$$

The above results can be generalized into many other situations.

First, we do not have to divide the phase space into infinite number of slices.

e.g. we can divide it into two parts for the Ising model which naturally corresponds to the two phases at low T.



$$Z_+(T) = \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \sum_i S_i > 0}} e^{-\beta \mathcal{H}(\{S_i\})}, \quad A_+(T) = -k_B T \ln Z_+(T)$$

$$Z_-(T) = \sum_{\substack{\{S_i\} \\ \text{s.t.} \\ \sum_i S_i < 0}} e^{-\beta \mathcal{H}(\{S_i\})}, \quad A_-(T) = -k_B T \ln Z_-(T)$$

$$A_+(T) = A_-(T) \quad \text{if } h = 0$$

$$A_+(T) < A_-(T) \quad \text{if } h > 0$$

We can also talk about the free energy of different states of a protein

natural (folded) state

denaturalized (unfolded) state

$$A_n(T) = -k_B T \ln Z_n(T)$$

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

phase space region for the folded state

$$A_d(T) = -k_B T \ln Z_d(T)$$

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

phase space region for the unfolded state

When we compare the free energies of the solid phase and the liquid phase, they are again defined through partition functions that are integrated over subspaces of the entire phase space.