Today's goal:

**Part A**: free energy of a subspace

**Part B**: generalization of 1D Ising model

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1. Motivation

**HW 8.3**: 2D Ising model, instantaneous magnetization $M = \frac{1}{N} \sum_i^N \sigma_i$

Observations from Monte Carlo simulations

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

\[ \dot{M} = -k \frac{\partial U(M)}{\partial M} - \gamma M + f_{\text{rand}}(t) \]

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 \( p(M) \):
\[
U(M) = -k_B T \ln p(M) - \frac{k_B T \ln \hat{Z}}{\text{unknown constant}}
\]

2. Ising model with a constraint

With constraint
\[
Z(M,T) = \sum_{\{s_i\}} e^{-\beta H(\{s_i\})}
\]

\(\text{st. } \frac{1}{N} \sum s_i = M\)

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

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

\[A(M,T) = -k_B T \ln Z(M,T)\]

is the Helmholtz free energy of the Ising model under constraint \( M \).

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.

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

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

\[E(T) = -\frac{\partial}{\partial \beta} \ln Z(T)\]

\[S(T) = \frac{1}{T} [E(T) - A(T)]\]

\(A(M,T)\) 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 landscape", and as such, should in general depend on temperature.

Recall that

$U(M)$ is defined through:
\[ p(M) = \frac{1}{Z} e^{-\beta U(M)} \]

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

\[ p(f_{Si}) = \frac{1}{Z(T)} e^{-\beta \tilde{H}(f_{Si})} \]

The probability of observing a specific value of $M$ is

\[ p(M) = \sum_{\{f_{Si}\}} p(f_{Si}) = \frac{1}{Z(T)} \sum_{\{f_{Si}\}} e^{-\beta \tilde{H}(f_{Si})} = \frac{Z(M, T)}{Z(T)} = \frac{e^{-\beta A(M, T)}}{e^{-\beta A(M, T)}} \]

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

\[ \frac{p(M_1)}{p(M_2)} = \frac{e^{-\beta A(M_1, T)}}{e^{-\beta A(M_2, T)}} = \exp \left[ -\beta (A(M_1, T) - A(M_2, T)) \right] \]
The above results can be generalized into many other situations.

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

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

\[ Z_+^{ST} = \sum_{\{S_i\}} e^{-\beta H(S_i)} \]
\[ A_+(T) = -k_B T \ln Z_+(T) \]
\[ Z_-(T) = \sum_{\{S_i\} \text{ s.t. } \sum_i S_i < 0} e^{-\beta H(S_i)} \]
\[ A_-(T) = -k_B T \ln Z_-(T) \]

\[ A_+(T) = A_-(T) \text{ if } h = 0 \]
\[ A_+(T) < A_-(T) \text{ if } h > 0 \]

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

\( A_n(T) = -k_B T \ln Z_n(T) \)
\( Z_n(T) = \int_{\text{phase space region for the folded state}} dp_1 dp_2 \ldots e^{-\beta H(p_1, p_2, \ldots)} \)

\( A_d(T) = -k_B T \ln Z_d(T) \)
\( Z_d(T) = \int_{\text{phase space region for the unfolded state}} dp_1 dp_2 \ldots e^{-\beta H(p_1, p_2, \ldots)} \)

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.