

EXAM 1 - CHEM 430b/530b
Statistical Methods and Thermodynamics

Exercise 1:

Small synthetic polypeptides of identical aminoacids can undergo a transition from an α -helical state with energy $E_\alpha = -\Delta$ to a coiled state with energy $E_c = \Delta$, as illustrated in Fig. 1 (a). Long polypeptides have multiple helices and coils, as illustrated in Fig 1(b).

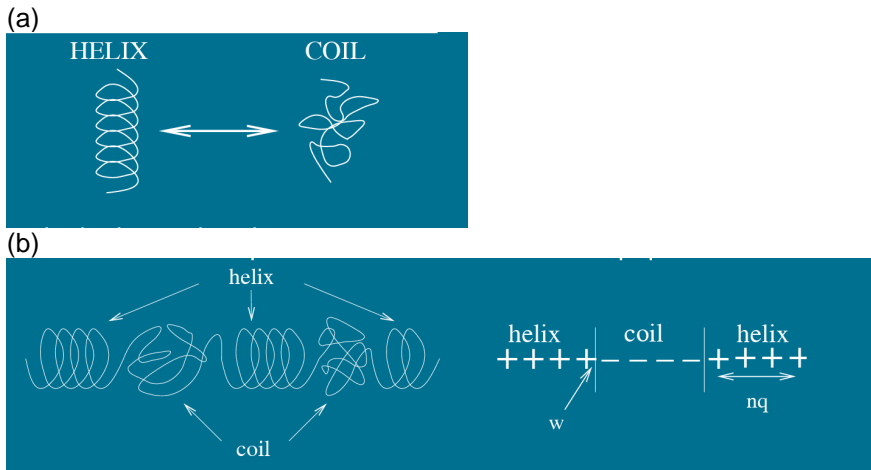


Figure 1. (a) Helix-coil transition in polypeptides; (b) Multiple helices and coils in a long polypeptide.

Consider a polypeptide with a large number N of segments at thermal equilibrium, where each segment can be in the “helix” or “coil” state.

- 1.1. (20 points) Determine the ensemble average internal energy of the polypeptide as a function of temperature.
- 1.2. (20 points) Determine the entropy of the polypeptide as a function of temperature.
- 1.3. (20 points) Determine the ensemble average fraction χ_α of helical segments as a function of temperature.

Exercise 2:

- 2.1. (10 pts) Explain the fundamental principles of Statistical Mechanics and how they are related to the Ergodic Hypothesis.
- 2.2. (10 pts) Explain the correspondence between the density of states of a microcanonical $\Omega(E)$ ensemble and the canonical partition function Z .
- 2.3. (10 pts) Prove that there is a unique mathematical correspondence between the grand canonical partition function Ξ and the canonical partition function Z .
- 2.4. (10 pts) Prove that the density matrix of a canonical ensemble at equilibrium is stationary.

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Answer Key

Exercise (1.1.):

$$\bar{E} = -\frac{\partial \ln Z}{\partial(\beta)} \quad (1)$$

where $Z = \sum_j e^{-\beta E_j}$ is the canonical partition function.

The total energy of the protein in configuration j is

$$E_j = \sum_{k=1}^N n_k^{(j)} \Delta,$$

where $n_k^{(j)} = -1$ if domain k is in the α -helix state and $n_k^{(j)} = +1$ if domain k is in the coiled state. Therefore,

$$Z = \sum_j e^{-\beta \sum_{k=1}^N n_k^{(j)} \Delta} = \prod_{k=1}^N \sum_{n_k=-1}^1 e^{-\beta n_k \Delta} = 2^N \cosh^N(\beta \Delta). \quad (2)$$

Substituting Eq. (2) into Eq. (1), we obtain:

$$\boxed{\bar{E} = -\Delta N \tanh(\beta \Delta)} \quad (3)$$

Exercise (1.2.):

According to the Gibbs definition of entropy,

$$S = -\sum_j p_j \ln p_j, \quad (4)$$

with

$$p_j = Z^{-1} e^{-\beta E_j}. \quad (5)$$

Therefore, substituting Eq. (5) into Eq. (4), we obtain:

$$S = \frac{\bar{E}}{T} + k \ln Z. \quad (6)$$

and, substituting Eqs. (2) and (3) into Eq. (6), we obtain:

$$\boxed{S = -\frac{\Delta N}{T} \tanh(\beta\Delta) + k \ln(2^N \cosh^N(\beta\Delta))} \quad (7)$$

Exercise (1.3.):

The total energy of the protein in configuration j is

$$E_j = N_j^{(\alpha)}(-\Delta) + (N - N_j^{(\alpha)})\Delta.$$

Therefore,

$$Z = \sum_j e^{-\beta E_j} = \sum_j e^{-\beta(N\Delta - 2\Delta N_j^{(\alpha)})}. \quad (8)$$

Note that

$$\frac{\partial \ln Z}{\partial(\beta\Delta)} = 2Z^{-1} \sum_j N_j^{(\alpha)} e^{-\beta E_j} - \frac{N}{Z} \sum_j e^{-\beta E_j} = 2N^{\bar{(\alpha)}} - N. \quad (9)$$

Therefore,

$$\chi^{(\alpha)} = \frac{N^{\bar{(\alpha)}}}{N} = \frac{1}{2} \left(1 + \frac{1}{N} \frac{\partial \ln Z}{\partial(\beta\Delta)} \right), \quad (10)$$

and

$$\boxed{\chi^{(\alpha)} = \frac{1}{2}(1 + \tanh(\beta\Delta))} \quad (11)$$

Exercise (2.1.): See lecture notes p.26-28. Also, see practice exam, p. 31.

Exercise (2.2.): See lecture notes p.15-16. Also, p. 65 of the textbook.

Exercise (2.3.): See lecture notes p.21.

Exercise (2.4.): See lecture notes p.12 (Exercise 6 of homework).