KJM4310 Exercise 2
2D Polymer Lattice Models

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The computations are found at GitHub repository (Aricigil [2022]).

Exercise 1

Given $\alpha > 0$, the exchange parameters $\chi_{HP} > 0$ and $\chi_{HW} > 0$.

$$\chi_{HP} = \frac{z}{KT}\left(w_{HP} - \frac{w_{HH} + w_{PP}}{2}\right) = \frac{z}{KT}\left(\alpha - \frac{0+0}{2}\right) = \frac{z\alpha}{KT} > 0 \tag{1}$$

$$\chi_{HW} = \frac{z}{KT}\left(w_{HP} - \frac{w_{HH} + w_{WW}}{2}\right) = \frac{z}{KT}\left(\alpha - \frac{0+0}{2}\right) = \frac{z\alpha}{KT} > 0 \tag{2}$$

$$\chi_{PW} = \frac{z}{KT}\left(w_{PW} - \frac{w_{PP} + w_{WW}}{2}\right) = \frac{z}{KT}\left(0 - \frac{0+0}{2}\right) = 0 \tag{3}$$

Exercise 2

According to the calculations of both homopolymers HHHHHH and PPPPPP the configuration HHHHHH is the only polymer that yields a three level energy distribution, as shown in Figure 1. This is an expected result due to the non-zero interactions arising between non-polar beads and water. The largest collection of conformations is found at the highest energy level 14α where the polymer adopts more expanded conformations resulting from increased polymer-water interactions.

In contrast, replacing all the non-polar beads with polar beads (PPPPPP) yield only a single energy level that takes a value of zero. This is caused by the zero interaction energies between polar beads and water; the lattice model behaves as though the polymer is not there. This leads to all 71 conformations to occur equally probable such that the conformation adopted by the polymer becomes random.
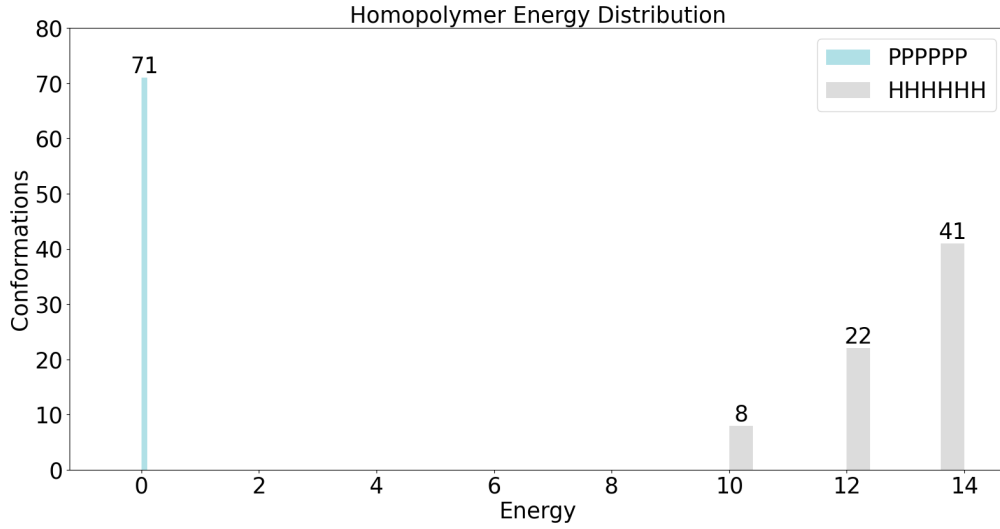
Figure 1: Number of polymer conformations distributed over the three energy levels for homopolymers HHHHHH and PPPPPP.

Exercise 3

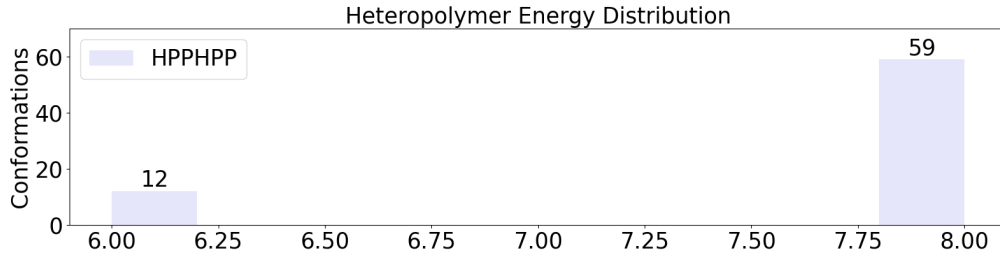A HPPHPP polymer has two energy levels (Figure 2) with degeneracy 12 and 59.

Figure 2: Energy distribution for polymer HPPHPP.

If there were N number polymers organized in a lattice, Q would be given by q^N, where each q corresponded to a polymer in the lattice. In this case however, there is only a single polymer which is why it will be regarded as a whole unit. The partition function is consequently given by

$$q_{polymer} = 12e^{-6\alpha\beta} + 59e^{-8\alpha\beta} \qquad (4)$$

Exercise 4

4.1 Binding Energy

The binding energy is the energy required for the polymer to bind into the cavity. This means that the calculation entails filling the cavity with the polymer and proceeding to subtract the internal energy of the polymer and the energy of the empty cavity from this value. In this particular enzyme pocket only 16 of 71 conformations fit into the cavity. The conformations and their respective binding energies are given in Figure 3.
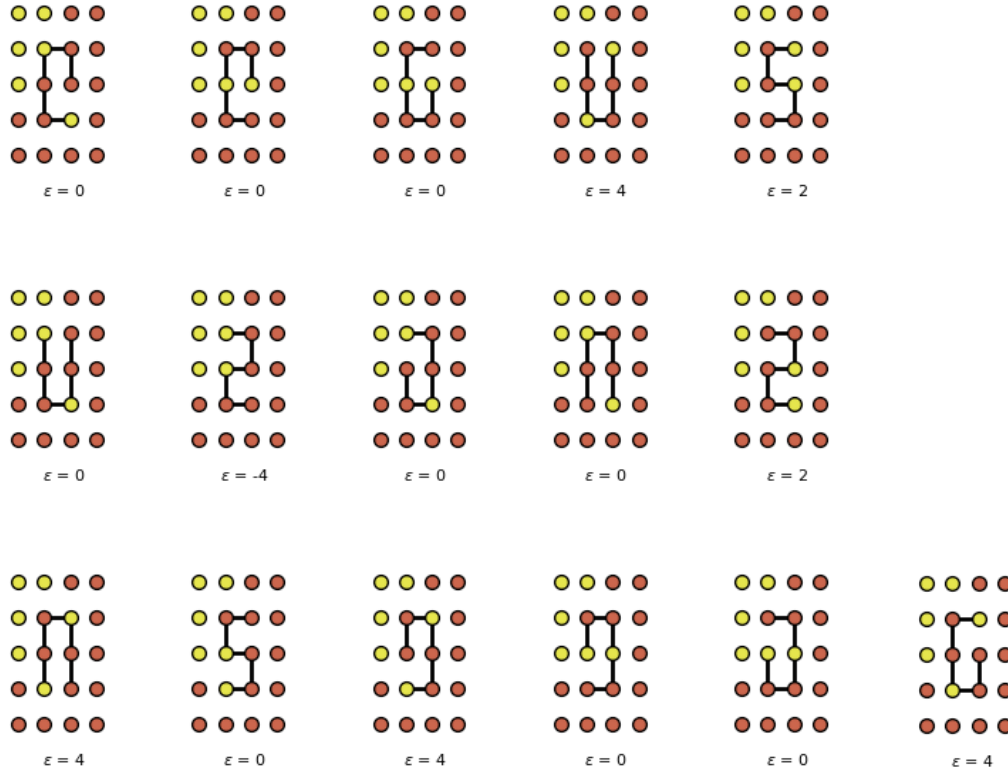

Figure 3: Conformations and their respective binding energies of polymer HPPHPP to the enzyme pocket.

4.2 Entropy

Calculating the change in entropy upon binding requires the definition of the partition function for HPPHPP polymer given in Eq. 4 and another partition function for the polymer in the cavity. The binding energies and their degeneracy given in Figure 3 gives the following partition function for the polymer binding

$$q_{polymer+enzyme} = e^{3\alpha\beta} + 9e^{-1\alpha\beta} + 2e^{-3\alpha\beta} + 4e^{-5\alpha\beta} \tag{5}$$

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Assuming that $\alpha \gg kT$ the entropy expression reduces to $k \ln a$ (Appendix), where a is the degeneracy of the ground state.

$$\begin{aligned} \triangle S_{binding} &= S_{polymer+enzyme} - S_{polymer} \\ &= k \ln 1 - k \ln 12 \\ &= k \ln \frac{1}{12} < 0 \end{aligned} \tag{6}$$

The negative value given in Eq. 6 indicates loss of entropy. Filling the cavity with the polymer displaces the water generating a more ordered lattice.

4.3 Free Energy

The *free energy* expression is given by

$$\begin{aligned} F &= -kT \ln q_{polymer+enzyme} \qquad\qquad\qquad\qquad\qquad (7) \\ &= -kT \ln \left(e^{3\alpha\beta} + 9e^{-1\alpha\beta} + 2e^{-3\alpha\beta} + 4e^{-5\alpha\beta} \right) \\ &= -kT \left(\ln 1 + 3\alpha\beta + \ln 9 - 1\alpha\beta + \ln 2 - 3\alpha\beta + \ln 4 - 5\alpha\beta \right) \\ &= -kT \left(-1\alpha\beta - 5\alpha\beta + \ln 9 + \ln 2 + \ln 4 \right) \\ &= -kT \left(6\alpha\beta + \ln(9 \cdot 2 \cdot 4) \right) \\ &= -kT \left(6\alpha\beta + \ln 72 \right) < 0 \end{aligned}$$
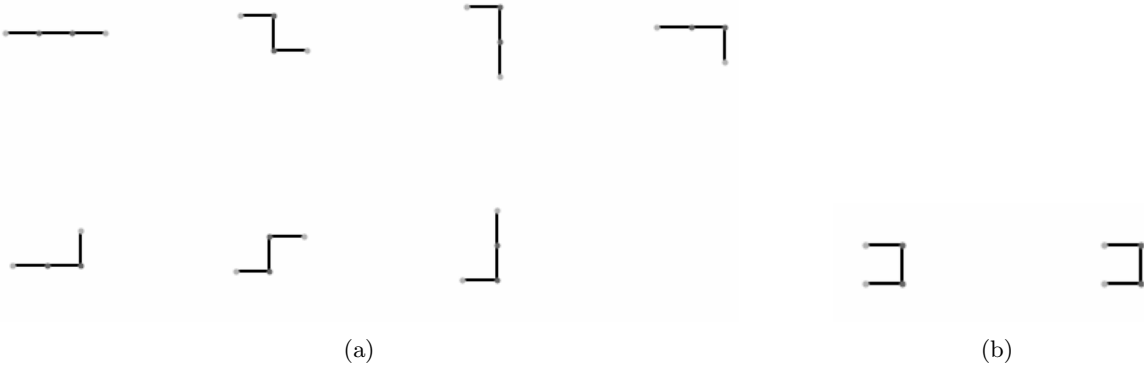
Exercise 5

Figure 4: HPPH and PHHP conformations in a 2D lattice where energies are (a) $\epsilon_{HPPH} = 6\alpha$ and $\epsilon_{PHHP} = 4\alpha$ (b) $\epsilon_{HPPH} = \epsilon_{PHHP} = 4\alpha$

HPPH yields two energy levels; the less stable conformations are given in Figure 4a) while the stable conformations are given in Figure 4b). PHHP has only a single energy level and therefore no energy minimum. The solvation energies are computed in a similiar way to binding energies; the polymer's internal energy is subtracted from the lattice leaving only the polymer-water interactions.

5.1 Global Solvation Free Energy

The global solvation free energy is calculated in the same way as in Eq. 7. The free energy for a HPPH polymer is

$$
\begin{aligned}
F_{HPPH} &= -kT \ln q_{HPPH} \\
&= -kT \ln \left(2e^{-4\alpha\beta} + 7e^{-6\alpha\beta} \right) \\
&= -kT \left(\ln 2 - 4\alpha\beta + \ln 7 - 6\alpha\beta \right) \\
&= -kT \left(-10\alpha\beta + \ln 14 \right) < 0
\end{aligned}
\tag{8}
$$

and for a PHHP polymer is

$$
\begin{aligned}
F_{PHHP} &= -kT \ln q_{PHHP} \\
&= -kT \ln 9e^{-4\alpha\beta} \\
&= -kT \left(-4\alpha\beta + \ln 9 \right) < 0
\end{aligned}
\tag{9}
$$

where a negative free energy value is expected for both polymers since β is a small value, $\ln 14 >> -10\alpha\beta$ and $\ln 9 >> -4\alpha\beta$.

5.2 Entropy

The entropy expression for HPPH ($\alpha >> kT$) is given in Eq. 17.

$$
S_{HPPH} = k \ln 2 \approx 0
\tag{10}
$$

To show that PHHP is temperature independent, it is adequate to look at the general entropy expression given in Eq. 16.

$$
\begin{aligned}
S_{PHHP} &= -\frac{4\alpha}{T} + k \ln 9 + \frac{1}{T} \cdot \frac{\cancel{9} \cdot 4\alpha}{\cancel{9}} \\
&= -\frac{4\cancel{\alpha}}{T} + \frac{4\cancel{\alpha}}{T} + k \ln 9 \\
&= k \ln 9 \approx 0
\end{aligned}
\tag{11}
$$

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By not having to take the limit for $\alpha >> KT$, the entropy expression cancels out the temperature terms proving that PHHP polymer is temperature independent.

Exercise 6

The free energy of transfer for HPPH polymer is given by

$$\triangle\mu = F_{oil,solv} - F_{water,solv} \tag{12}$$

The expression for $F_{water,solv}$ is already given in Eq. 8. To find the free energy of HPPH in oil, the interactions between polymer-water are simply reversed, i.e. hydrophobic beads acts as polar beads and oil acts as water. The results therefore indicate that HPPH in oil has the same partition function as PHHP.

$$\triangle\mu = kT \ln 9e^{-4\alpha\beta} - kT \ln \left(2e^{-2\alpha\beta} + 7e^{-6\alpha\beta}\right)$$

$$= kT \ln \left(\frac{9e^{-4\alpha\beta}}{2e^{-2\alpha\beta} + 7e^{-6\alpha\beta}}\right) \tag{13}$$

To find the partition coefficient K from $\triangle\mu$, the following relation is used

$$\ln K = \frac{\triangle\mu}{kT}$$

$$\ln K = \frac{\cancel{kT} \ln \left(\frac{9e^{-4\alpha\beta}}{2e^{-2\alpha\beta}+7e^{-6\alpha\beta}}\right)}{\cancel{kT}}$$

$$K = \frac{9e^{-4\alpha\beta}}{2e^{-2\alpha\beta} + 7e^{-6\alpha\beta}}$$

One way to study the effect of temperature on the partition coefficient is to let $T \to \infty$ (or alternatively, $\beta \to 0$), and $T \to 0$ ($\beta \to \infty$).

$$\lim_{\beta \to 0} K = \frac{9 \cdot 1}{7 \cdot 1 + 2 \cdot 1} = \frac{9}{9} = 1 \tag{14}$$

$$\lim_{\beta \to \infty} \frac{9e^{-4\alpha\beta}}{2e^{-2\alpha\beta} + 7e^{-6\alpha\beta}} = \lim_{\beta \to \infty} \frac{9}{2 + 7e^{-(6-2)\alpha\beta}} = \lim_{\beta \to \infty} \frac{9}{2 + 7e^{-4\alpha\beta}} = \frac{9}{2 + 7 \cdot 0} = 0 \tag{15}$$

At higher temperatures K will tend to 1 (Eq. 14) which implies that HPPH will partition equally between oil and water phase. Conversely, at lower temperature, HPPH prefers to stay in one phase (Eq. 15); in this case it will be in the water layer since this is where the polymer initially resides before the oil is added.

Appendix

Entropy is derived using $F = -kT \ln q$ and the relation $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$
$$= -\left[-k \ln q + kT \frac{1}{q} \cdot \frac{\partial q}{\partial T}\right]$$

By substituting $\frac{\partial q}{\partial T}$ with $\frac{\partial q}{\partial \beta} \cdot \frac{\partial \beta}{\partial T}$ the partition function q can be expressed as a function of β instead of T allowing simpler calculations.

$$= -\left[-k \ln q + kT \frac{1}{q} \cdot \frac{\partial q}{\partial \beta} \cdot \frac{\partial \beta}{\partial T}\right]$$
$$= -\left[-k \ln q + \cancel{k}\cancel{T} \frac{1}{q} \cdot \frac{\partial q}{\partial \beta} \cdot \left(-\frac{1}{\cancel{k}T^{\cancel{2}}}\right)\right]$$
$$= k \ln q - \frac{1}{qT}\frac{\partial q}{\partial \beta}$$

For a two energy level system $q = ae^{-\epsilon_0 \beta} + be^{-\epsilon_1 \beta}$, the entropy becomes

$$S = k \ln(ae^{-\epsilon_0 \beta} + be^{-\epsilon_1 \beta}) - \frac{1}{T} \cdot \frac{1}{ae^{-\epsilon_0 \beta} + be^{-\epsilon_1 \beta}} \cdot (-a\epsilon_0 e^{-\epsilon_0 \beta} - b\epsilon_1 e^{-\epsilon_1 \beta})$$

The partition function can be alternatively written as $q = ae^{-\epsilon_0 \beta} + be^{-\epsilon_1 \beta} = e^{-\epsilon_0 \beta}\left(a + be^{-\overbrace{(\epsilon_1 - \epsilon_0)}^{\triangle\epsilon}\beta}\right)$

which further simplifies the entropy expression.

$$= k \ln\left[e^{-\epsilon_0 \beta}\left(a + be^{-\epsilon_1 \beta}\right)\right] - \frac{1}{T} \cdot \frac{\cancel{e^{-\epsilon_0 \beta}}\left(-a\epsilon_0 - b\epsilon_1 e^{-\triangle\epsilon\beta}\right)}{\cancel{e^{-\epsilon_0 \beta}}\left(a + be^{-\triangle\epsilon\beta}\right)}$$
$$= k\left[\ln e^{-\epsilon_0 \beta} + \ln\left(a + be^{-\triangle\epsilon\beta}\right)\right] - \frac{1}{T} \cdot \frac{\left(-a\epsilon_0 - b\epsilon_1 e^{-\triangle\epsilon\beta}\right)}{a + be^{-\triangle\epsilon\beta}}$$
$$= \cancel{k}\epsilon_0 \overbrace{\beta}^{\frac{1}{\cancel{k}T}} + k \ln\left(a + be^{-\triangle\epsilon\beta}\right) + \frac{1}{T} \cdot \frac{a\epsilon_0 + b\epsilon_1 e^{-\triangle\epsilon\beta}}{a + be^{-\triangle\epsilon\beta}}$$
$$= -\frac{\epsilon_0}{T} + k \ln\left(a + be^{-\triangle\epsilon\beta}\right) + \frac{1}{T} \cdot \frac{a\epsilon_0 + b\epsilon_1 e^{-\triangle\epsilon\beta}}{a + be^{-\triangle\epsilon\beta}}$$

For any multiple energy level system the equation is generalized as

$$S = -\frac{\epsilon_0}{T} + k \ln \left(a + \sum_{i=b} \iota_i \sum_{j=1} e^{-(\epsilon_j - \epsilon_0)\beta} \right) + \frac{1}{T} \cdot \frac{a\epsilon_0 + \sum_{i=b} \iota_i \sum_{j=1} \epsilon_j e^{-(\epsilon_j - \epsilon_0)\beta}}{a + \sum_{i=b} \iota_i \sum_{j=1} e^{-(\epsilon_j - \epsilon_0)\beta}} \qquad (16)$$

The equation can be further simplified by assuming that $\alpha >> kT$ since $kT \approx 0$ ($T \to 0$ or $\beta \to \infty$).

$$\lim_{\beta \to \infty} -\frac{\epsilon_0}{T} + k \ln \left(a + \sum_{i=b} \iota_i \sum_{j=1} \overbrace{e^{-(\epsilon_j - \epsilon_0)\beta}}^{=0} \right) + \frac{1}{T} \cdot \frac{a\epsilon_0 + \sum_{i=b} \iota_i \sum_{j=1} \epsilon_j \overbrace{e^{-(\epsilon_j - \epsilon_0)\beta}}^{=0}}{a + \sum_{i=b} \iota_i \sum_{j=1} \overbrace{e^{-(\epsilon_j - \epsilon_0)\beta}}^{=0}}$$

$$= -\frac{\epsilon_0}{T} + k \ln \left(a + 0 \right) + \frac{1}{T} \cdot \frac{a\epsilon_0 + 0}{a + 0}$$

$$= -\frac{\epsilon_0}{T} + k \ln a + \frac{1}{T} \cdot \frac{\cancel{a}\epsilon_0}{\cancel{a}}$$

$$= -\frac{\cancel{\epsilon_0}}{T} + k \ln a + \frac{\cancel{\epsilon_0}}{\cancel{T}}$$

$$= k \ln a \qquad (17)$$

References

Derya Aricigil. Physical chemistry 3, assignment 2, 2022. URL https://github.com/deryaaricigil/KJM4310-2.