Statistical Mechanics Assignment 6 Solutions

1. The structures I found, along with the hydrophobic-solvent contact counts, are shown in table 1. Depending on what operations you allow on the lattice, you can come to a different count. I decided that two structures were the same if I could rotate or flip them into the same orientation. You always have to look for rotational symmetries, but the flip is an out-of-plane operation, so you could legitimately exclude it. This makes many of the structures chiral. Table 2 shows the extra structures you would get if you don't allow flips.

Table 1: Structures of the 1001 lattice protein. The second column of the table gives the number of hydrophobic-solvent contacts.

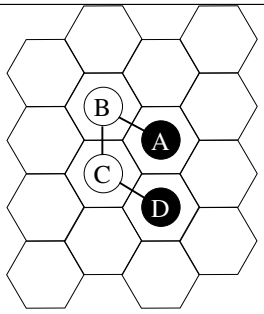
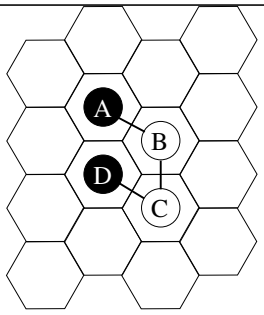
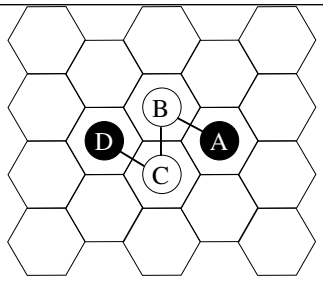
Structure	$\epsilon_i/\Delta\epsilon$
	7
	7
	8

Table 1: Structures of the 1001 lattice protein (continued)

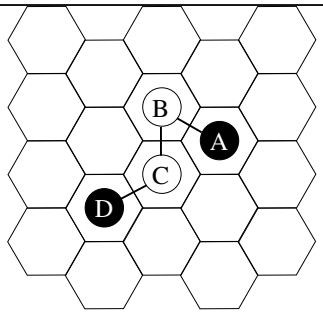
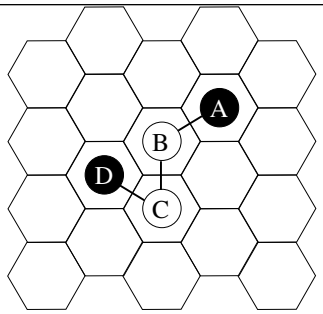
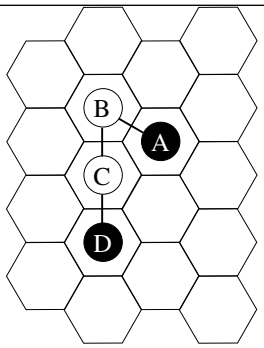
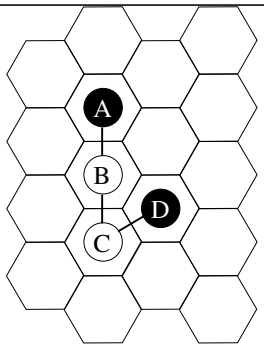
Structure	$\epsilon_i/\Delta\epsilon$
	9
	9
	9
	9

Table 1: Structures of the 1001 lattice protein (continued)

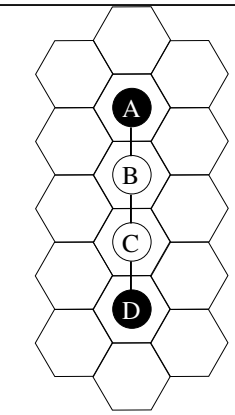
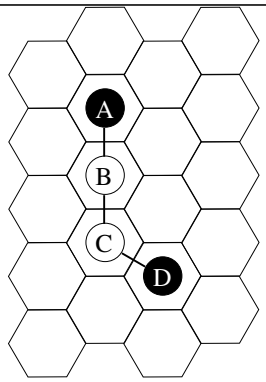
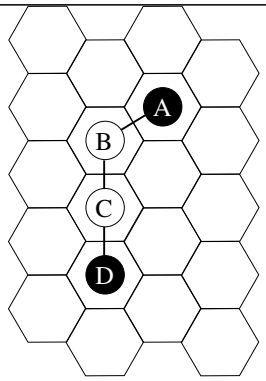
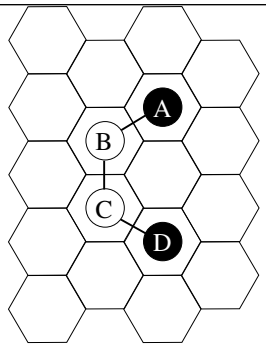
Structure	$\epsilon_i/\Delta\epsilon$
	10
	10
	10
	10

Table 1: Structures of the 1001 lattice protein (continued)

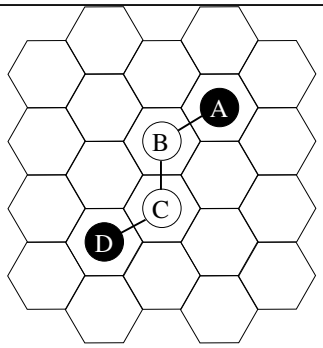
Structure	$\epsilon_i/\Delta\epsilon$
	10

Table 2: "Enantiomers" of the 1001 lattice protein. The second column of the table gives the number of hydrophobic-solvent contacts.

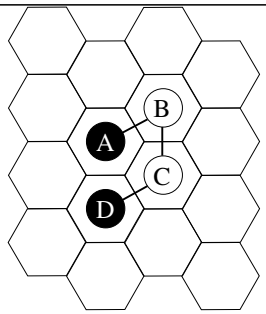
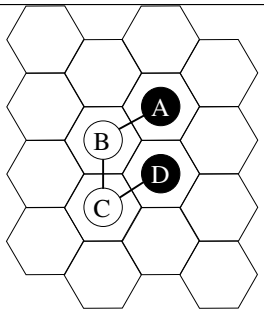
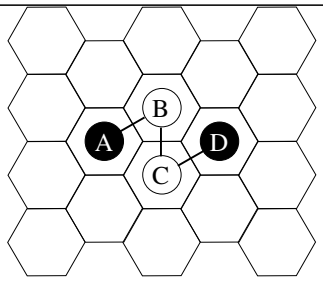
Structure	$\epsilon_i/\Delta\epsilon$
	7
	7
	8

Table 2: "Enantiomers" of the 1001 lattice protein (continued)

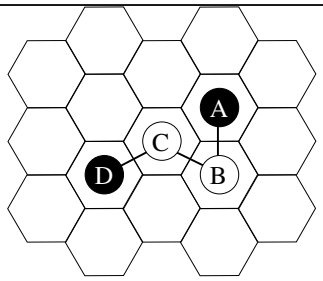
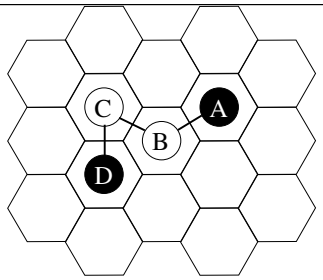
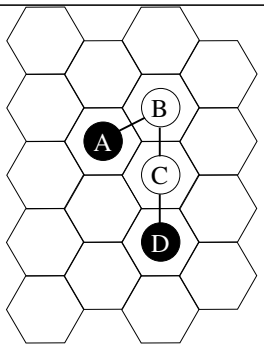
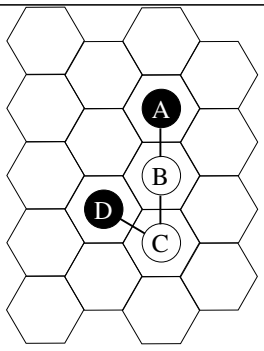
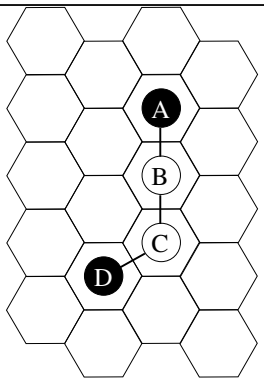
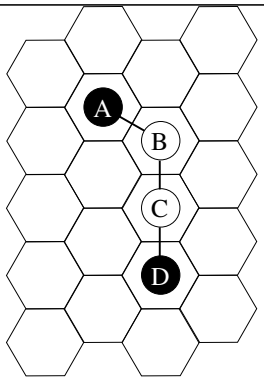
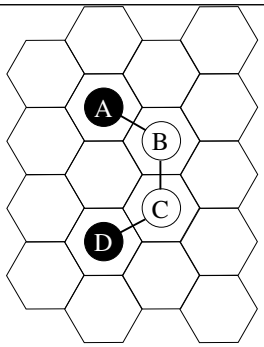
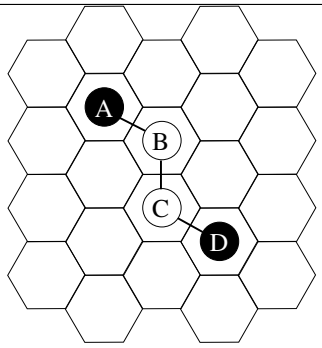
Structure	$\epsilon_i/\Delta\epsilon$
	9
	9
	9
	9

Table 2: "Enantiomers" of the 1001 lattice protein (continued)

Structure	$\epsilon_i/\Delta\epsilon$
	10
	10
	10
	10

The ground state is degenerate. The two ground-state structures may look superficially

i	$\epsilon_i/\Delta\epsilon$	g_i	g_i'
1	7	2	4
2	8	1	2
3	9	4	8
4	10	5	9

Table 3: Energy levels and degeneracies of the 1001 lattice protein. g_i is the degeneracy if we allow flips as a symmetry operation, and g_i' is the degeneracy if flips are not allowed.

similar, but counting the number of solvent contacts of the two end amino acids shows that they are in fact different.

2. Table 3 gives the energies and degeneracies, both with and without flips.

3. The partition function is

$$q = \sum_{i=1}^{4} g_i e^{-\epsilon_i/(kT)}.$$

If we assume that all of the degenerate $i = 1$ structures are biologically active (which may not be the case), then the denaturation curve is just a plot of p_1 vs T, where

$$p_1 = g_1 e^{-\epsilon_1/(kT)}/q.$$

Figure 1 shows the denaturation curves both if we do and don't allow flips as a symmetry operation. These curves are actually very similar to the one we computed for the square lattice, give or take some relatively small quantitative differences.

Comparing the two curves to each other, we see that p_1 decreases slightly more slowly if flips are not allowed as a symmetry operation. In fact, it is easy to see that it tends to a slightly different limit, basically because g_4' is slightly less than twice as large as g_4, whereas all the other degeneracies exactly double between one model variant and the other.

If only one of the conformations is biologically active, then instead of p_1 we should plot

$$p_a = e^{-\epsilon_1/(kT)}/q,$$

which of course is smaller than p_1 by a factor of g_1.

4. We must first calculate the internal energy:

$$U_m = RT^2 \left.\frac{\partial \ln q}{\partial T}\right|_V = \frac{1}{q}\sum_{i=1}^{4} g_i \epsilon_{i,m} e^{-\epsilon_i/(kT)}.$$

The heat capacity is then

$$C_{V,m} = \left.\frac{\partial U}{\partial T}\right|_V = \frac{q\sum_{i=1}^{4} g_i \epsilon_{i,m}^2 e^{-\epsilon_i/(kT)} - \left(\sum_{i=1}^{4} g_i \epsilon_{i,m} e^{-\epsilon_i/(kT)}\right)^2}{RT^2 q^2},$$

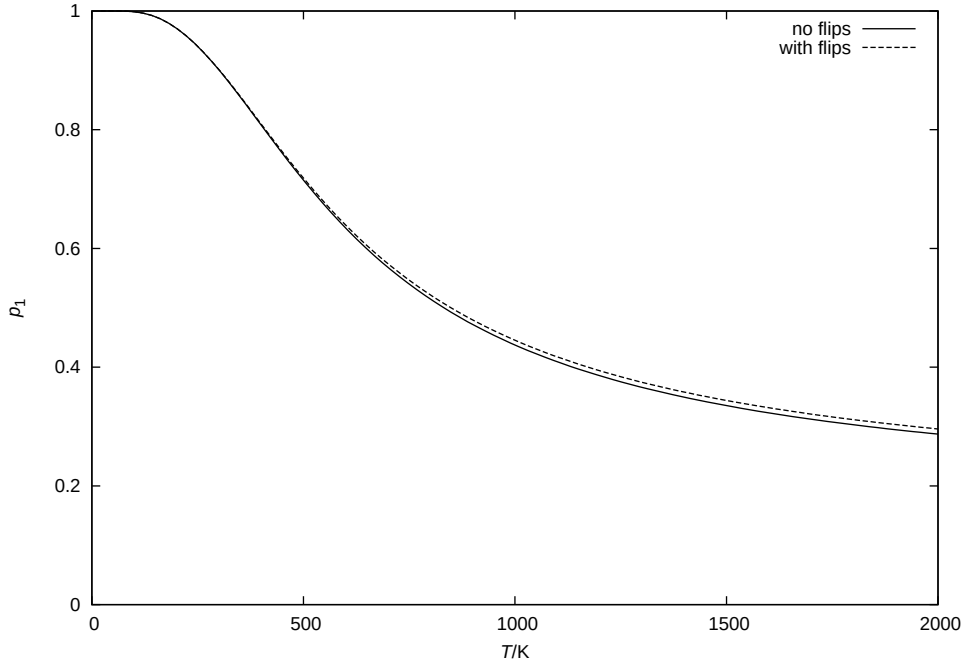


Figure 1: Thermal denaturation curves

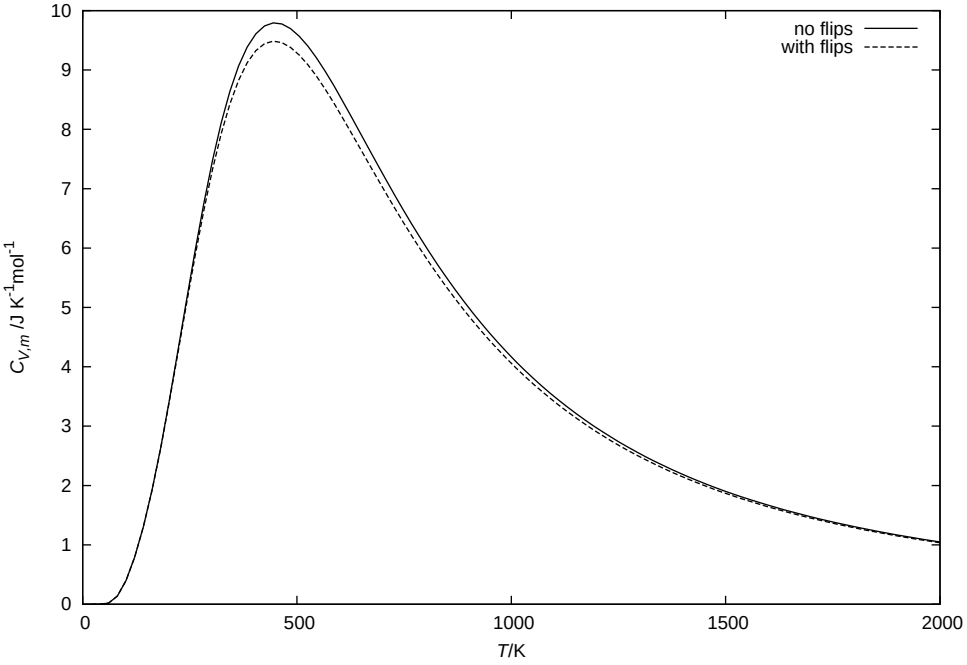


Figure 2: Heat capacity as a function of temperature

where $\epsilon_{i,m}$ is the molar value of ϵ_i. Figure 2 shows the heat capacity as a function of temperature for both model variants. Again, the differences between this model and the square lattice model are pretty small. The differences between the two models are again due to the slightly smaller relative degeneracy of ϵ_4: As the temperature increases, there is a smaller number of excited states to populate relative to the ground state, so the heat capacity reaches a smaller maximum value.