

CH352 Mid Term Exam. In class 9:30-11:00 am Thursday, March 6,
2014.

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Q1 Polymer expansion and collapse. Figure 1 shows the configurations of a lattice model of a 4 bead polymer with the distinct red terminal group indicated that enables us to distinguish the different configurations. The configurations are divided into 4 classes depending on their internal energy. The linear polymer configuration (Class 1) defines zero internal energy. If a configuration includes a bend in the chain it lowers the internal energy of the configuration by an amount $-\delta$ (with δ a positive constant). If unconnected particles come to within a lattice spacing of each other an intermolecular-like binding interaction is formed, as in the class 4 configuration, and this lowers the energy by an amount $-\epsilon$ (ϵ is some other positive constant).

(i) Construct a table in which the columns are U , S , and $A = U - TS$, and the rows are the four different classes of configurations.

(ii) Make a single plot on which you display A_1 , A_2 , A_3 , and A_4 as functions of T .

(iii) At low temperatures what is the dominant state observed for the polymer? At high temperatures what is the dominant polymer state?

(iv) Compute the temperature, T_0 at which the change of dominant polymer state occurs.

(v) If the polymer solution fills a constant V container compute the heat q that results when the polymer collapses from its dominant expanded state to its dominant collapsed state and decide if the reaction is exothermic or endothermic.

Q2 Consider two systems, A and B. System A has $N_A = 10$ particles and system B has $N_B = 4$ particles. Each particle has two possible energies, $\epsilon = 0$ or $\epsilon = 1$. Suppose that system A starts with $n_A = 2$ particles with $\epsilon = 1$ and $(N_A - n_A)$ particles with $\epsilon = 0$ (so system A internal energy is $U_A = 2$) and system B starts with $n_B = 2$ particles with $\epsilon = 1$ and $(N_B - n_B)$ particles with $\epsilon = 0$ (so system B internal energy is $U_B = 2$ also). This situation is shown in Figure 2b. The two systems are brought in thermal contact and the total internal energy $U = U_A + U_B$ is conserved since the total combined system is isolated from its surroundings.

(i) Let W be the multiplicity of the total system (system A + system B) (ii) Let W_A and W_B be the multiplicities representing systems A and B respectively. (iii) Let p_0 and p_1 be the probabilities of finding particles with energies $\epsilon = 0$ and $\epsilon = 1$ respectively. In general there will be different distributions of these probabilities for systems A and B. Our goal is

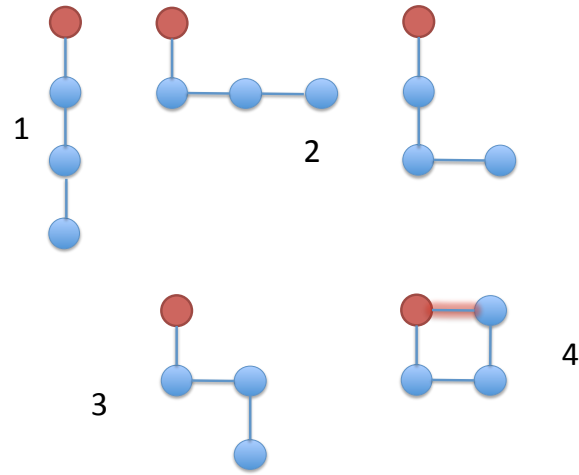


Figure 1: Polymer configurations: **Class 1** has no bends; **Class 2** configurations have one bend; **Class 3** has two bends; and **Class 4** has two bends and an intermolecular-like binding interaction

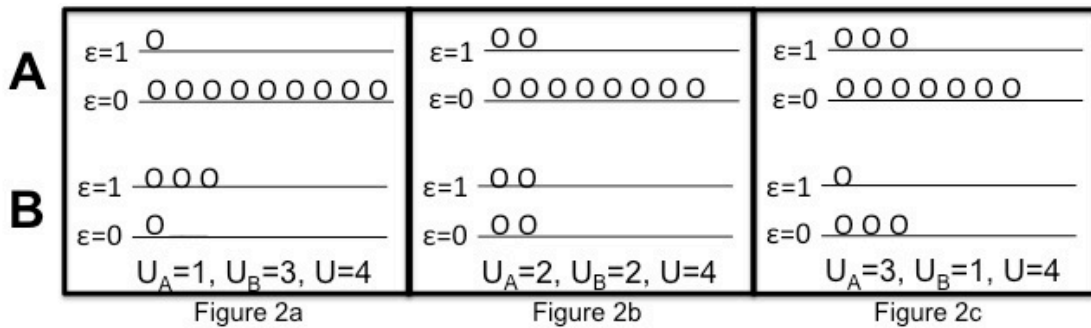


Figure 2: Arrangement of particles in subsystems A and B allowing for different partitioning of the particles between the different energy states. (b) shows the starting distribution of particles between their energy states in which the two subsystems have the same internal energy $U_A = U_B = 2$. (a) Shows the arrangement of particles amongst available states resulting from energy flow from subsystem A to subsystem B from starting configuration in 2(b). (c) Shows arrangement of particles amongst available energy states resulting from energy flow from subsystem B to subsystem A from starting configuration in 2(b).

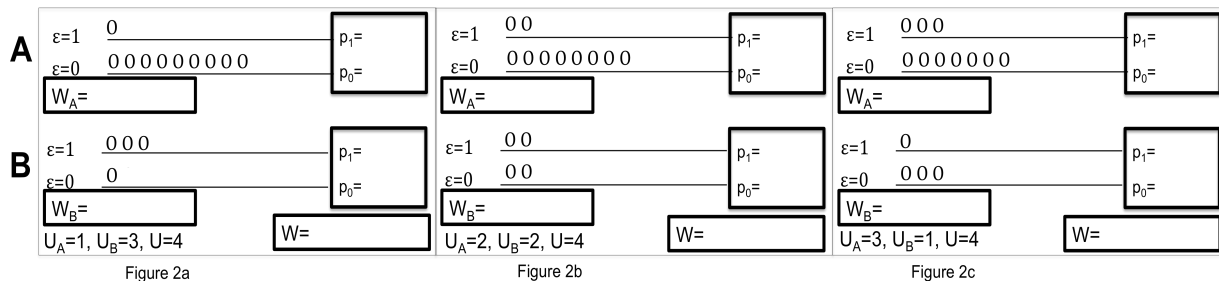


Figure 3: Compute all the required quantities for the different configurations included in this Figure

to understand what happens to these probability distributions when systems A and B are brought into thermal contact with one another but the total energy stays fixed because the total system (A+B) is thermally isolated from its surroundings.

(a) Calculate all the indicated unspecified quantities (displayed *e.g.* as $W_A =$, $p_1 =$, $p_2 =$, *etc.*) in the table presented in Figure 3 for state a (represented by Figure 2a), state b (Figure 2b), and state c (Figure 2c).

(b) What is the total multiplicity of the initial state represented in Figure 2b? Which state would represent the final thermalized state? In this thermalized state, is the energy of system A equal to the energy of system B?

The tendency of heat to flow is not always a tendency to equalize energies. It is a tendency to maximize multiplicity. The tendency toward maximum multiplicity is a tendency toward equal temperatures, not equal energies.

(c) Examine your probability distributions for finding particles of each energy level of all three states. In class we showed that the probability of finding a particle in one of two levels with energies E_i was

$$pE_i = \frac{e^{-\beta E_i}}{e^{-\beta E_0} + e^{-\beta E_1}} \quad (1)$$

So with the energies in this problem $E_0 = 0$ and $E_1 = \epsilon$ we find that $p_0 = 1/(1 + e^{-\beta\epsilon})$ where $\beta = 1/k_B T$. Use this result together with your probabilities to compute the ratio of temperatures T_A/T_B for state b, and for your equilibrium state with maximum multiplicity. You should find that the temperatures of the two subsystems at equilibrium are closest to each other, consistent with thermalization achieving equal temperatures. The temperatures of the subsystems out of equilibrium can be very different from one another.