Lecture 7:
Boltzmann distribution & Thermodynamics of mixing

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1 Suggested reading

- *Molecular Driving Forces* – Dill and Bromberg: Chapters 10, 15

2 Boltzmann distribution

Before continuing with the thermodynamics of polymer solutions, we will briefly discuss the Boltzmann distribution that we have used occassionally already in the course and will continue to assume a working knowledge of for future derivations. We introduced **statistical mechanics** earlier in the course, showing how a probabilistic view of systems can predict macroscale observable behavior from the structures of the atoms and molecules that compose them. At the core, we model probability distributions and relate them to thermodynamic equilibria. We discussed macrostates, microstates, ensembles, ergodicity, and the microcanonical ensemble and used these to predict the driving forces of systems as they move toward equilibrium or maximum entropy. In the beginning section of the course, we discussed ideal behavior meaning that we assumed there was no energetic contribution from interactions between atoms and molecules in our systems. In general, we are interested in modeling the behavior of real (non-ideal) systems that accounts for energetic interactions between species of the system. Here, we build on the introduction of statistical mechanics, as presented in Lecture 2, to consider how we can develop mathematical tools that account for these energetic interactions in real systems. The central result is the **Boltzmann distribution**, which provides probability distributions based on the underlying energy levels of the system.

In this approach, we now want to consider simple models (often lattice models) that allow us to count microstates but also assign an energy E_i for each microstate. We then use this information to calculate a probability distribution for the likelihood that the macrostate assumes the proposed mircostates at equilibrium. As an example we could consider the example below of a model, four-monomer 'polymer' chain constrained to two-dimensional space that has four open conformations and one compact conformation.
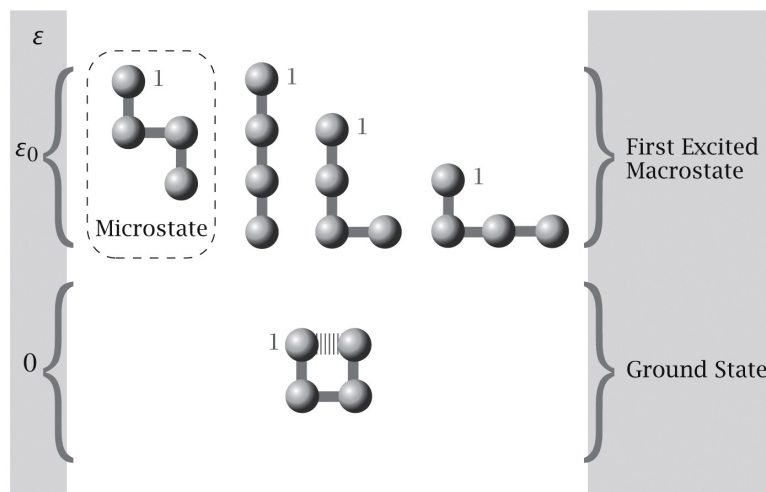

Figure 10.1 Molecular Driving Forces 2/e (© Garland Science 2011)

To start, we must define the system and the associated **energy levels**. The system is a four-monomer chain with two energy levels, where each energy level coresponds to the number of monomer–monomer interactions that the chain can make. We will often take zero as the lowest energy state and refer to this as the **ground state**. Disrupting the contact increases the energy of the system by $\epsilon = \epsilon_0 > 0$. As an aside, we will use ϵ for intermolecular energies and E for macrostate energies, which are equivalent in this case but this is not the case as we consider more complex systems. We refer to states other than the ground state as **excited states**. A microstate refers to a specific conformation and each ground or excited state can be achieved by one or more microstates. We thus seek to compute the set of proabilities $\{p_i\} = p_1, \ p_2, \ldots$ that the model chain adopts

the various possible conformations. We will come back to this example briefly after we derive the Boltzmann distribution law below.

For this derivation we introduce the **Canonical Ensemble**, which assumes constant temperature T, volume V, and components $\{N_i\}$. As before each system has many accessible microstates and observable macrostates. The number of microstates in macrostate i is given as n_i and with N total microstates we can write the probability $p_i = \frac{n_i}{N}$. From Lecture 2 Eq. 8, we know that:

$$\frac{S}{k_B} = -\sum_i p_i \ln p_i. \tag{1}$$

As before, we are interested in predicting the macrostate at equilibrium, which we will determine when the **entropy is maximized**. Stating this mathematically, we want to find the set of probabilities $\{p_i\}$ such that $dS = 0$ with the following constraints:

$$\sum_i p_i = 1 \tag{2}$$

$$\sum_i p_i E_i = \langle E \rangle = \bar{E} \tag{3}$$

We can then use the method of Lagrange multipliers to solve for $dS = 0$ from Eq. 1 and the constraints in Eqs. 2 and 3.

$$\frac{dS}{k_B} = -\sum_i \left[\ln p_i + 1\right] dp_i = -\sum_i \left[\ln p_i\right] dp_i, \tag{4}$$

$$\sum_i dp_i = 0, \tag{5}$$

$$\sum_i \left[p_i dE_i + E_i dp_i\right] = 0. \tag{6}$$

In Eq. 6 the first term goes away as $dE_i \approx 0$, assuming that the energy levels have little dependence on T, V, $\{N_i\}$. Therefore, we can solve the set of equations with the Lagrange multiplier approach as follows:

$$\sum_i \left[-\ln p_i - \alpha - \beta E_i\right] = 0. \tag{7}$$

At the global maximum, each term in the sum in Eq. 7 must be equal to zero so we have:

$$\ln p_i = -\alpha - \beta E_i, \tag{8}$$

$$p_i = e^{-\alpha} e^{-\beta E_i}. \tag{9}$$

Next, we can determine α with a normalization constraint by dividing by $1 = \sum_i p_i$:

$$p_i = \frac{e^{-\alpha} e^{-\beta E_i}}{\sum_i e^{-\alpha} e^{-\beta E_i}} \tag{10}$$

$$= \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{e^{-\beta E_i}}{Q}, \tag{11}$$

where $Q \equiv \sum_i e^{-\beta E_i}$ is defined as the **partition function**. Additionally, we can define β with the constraint that $\sum_i p_i E_i = \bar{E}$.

$$d\bar{E} = \sum_i [E_i dp_i + p_i dE_i] \tag{12}$$

$$dS = -k_B \sum_i \ln p_i dp_i \tag{13}$$

$$= -k_B \sum_i dp_i [-\beta E_i - \ln Q] \tag{14}$$

$$= \beta k_B \sum_i E_i dp_i \tag{15}$$

$$= \beta k_B d\bar{E} \tag{16}$$

Therfore, we can connect with what we have shown about thermodynamic driving forces, namely:

$$\left(\frac{\partial S}{\partial U}\right)_{T,V,\{N_i\}} = \frac{1}{T} \quad \therefore \quad \frac{dS}{d\bar{E}} = \beta k_B \quad \Rightarrow \quad \beta = \frac{1}{k_B T}. \tag{17}$$

This brings us to the common expression of the Boltzmann distribution law:

$$\boxed{p_i = \frac{e^{-E_i/k_B T}}{Q}}. \tag{18}$$

As before, this distribution was calculated by maximizing entropy!

We return briefly to the model chain presented before. We can calulate the partition function as $Q = 1 + 4e^{-\epsilon_0/k_B T}$ and the probabilities as $p_c = \frac{1}{Q}$ and $p_o = \frac{4e^{-\epsilon_0/k_B T}}{Q}$. What is expected to occur at high and low T?

3   Thermodynamics of solution

As we move toward considering materials constructed from polymer chains, including solvent swollen **networks** or **gels**, we need to consider how single polymer chains behave in **solution**. This can be polymer chains in a 'solution' of polymer chains or a more classic view of solution with polymer chains in a solvent. The approach, as before in this course, will be to develop simple models that allow us to calculate the thermodynamics of polymer solutions and, today, we start with simple solutions as we build toward this end.

To do this, we will use the Canonical Ensemble discussed above (constant T, V, $\{N_i\}$) and calculate the Helmholtz free energy $F = U - TS$ on a lattice model where S is the entropy of solution and U accounts for the interaction energies between molecules on the lattice. Here, we will consider a lattice with N sites and n_A molecules of type A and n_B molecules of type B. As before molecules A and B are equivalent in size and each occupies one lattice site. We can visualize the problem as below:
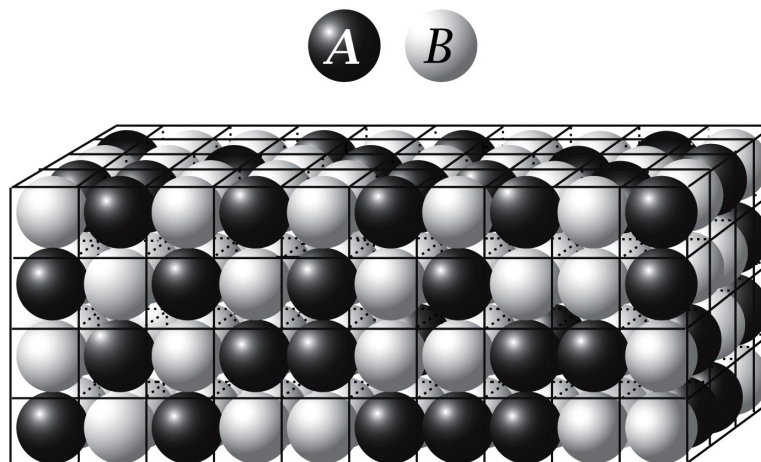

Figure 15.1 Molecular Driving Forces 2/e (© Garland Science 2011)

First, we can calculate the entropy of solution as before by calculating the multiplicity as the total number of spatial arrangements of the system $W = \frac{N!}{n_A! n_B!}$. Therefore, we can use the Boltzmann equation (Lecture 2) and Stirling's approximation:

$$\Delta S_{\text{sol}} = k_B(N \ln N - N - n_A \ln n_A + n_A - n_B \ln n_B + n_B) \tag{19}$$

$$= k_B(n_A \ln N + n_B \ln N - n_A \ln n_A - n_B \ln n_B) \tag{20}$$

$$= -N k_B \left[\frac{n_A}{N} \ln \frac{n_A}{N} + \frac{n_B}{N} \ln \frac{n_B}{N} \right] \tag{21}$$

$$= -k_B(n_A \ln x_A + n_B \ln x_B). \tag{22}$$

where $x_A = n_A/N$ and $x_B = n_B/N$. This can also be written with the mole fraction of one species, say $x = x_A$:

$$\boxed{\frac{\Delta S_{\text{sol}}}{N k_B} = -x \ln x - (1 - x) \ln(1 - x)}. \tag{23}$$

We can then calculate the energy of solution. In our lattice model, this involves counting the sum of the contact interactions between all of the nearest neighbors in the solution. In the system described above, we can consider three types of interactions: AA, BB, and AB.
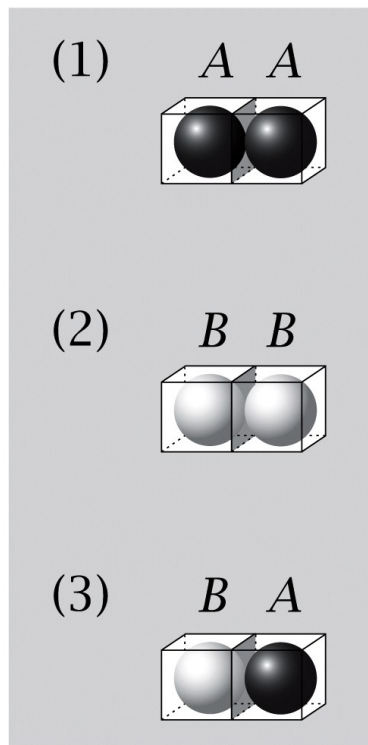

Figure 15.4 Molecular Driving Forces 2/e (© Garland Science

The total energy of the system is then:

$$U = m_{AA} w_{AA} + m_{BB} w_{BB} + m_{AB} w_{AB}, \tag{24}$$

where m_{AA}, m_{BB}, and m_{AB} are the number of AA, BB, and AB interactions, respectively, and w_{AA}, w_{BB}, and w_{AB} are the interaction energies with the associated contacts. For this, we take the interaction energies to be negative.

We then need to count the number of AA, BB, and AB interactions, which are not known in general. A convenient approach is to express these in terms of n_A and n_B. Additionally, each lattice site has z contacts available. Therefore,

$$z n_A = 2 m_{AA} + m_{AB}, \tag{25}$$

and similarly

$$z n_B = 2 m_{BB} + m_{AB}. \tag{26}$$

We can rearrange Eqs. 25 and 26 to solve for m_{AA} and m_{BB}:

$$m_{AA} = \frac{zn_A - m_{AB}}{2}, \tag{27}$$

$$m_{BB} = \frac{zn_B - m_{AB}}{2}. \tag{28}$$

We can combine these results with Eq. 24 to arrive at:

$$U = \left(\frac{zn_A - m_{AB}}{2}\right) w_{AA} + \left(\frac{zn_B - m_{AB}}{2}\right) w_{BB} + m_{AB} w_{AB} \tag{29}$$

$$= \left(\frac{zw_{AA}}{2}\right) n_A + \left(\frac{zw_{BB}}{2}\right) n_B + \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2}\right) m_{AB} \tag{30}$$

To compute U, we still need to calculate m_{AB} and to do this we will employ a *mean-field* approximation as before. We make the assumption that for any number of molecules the system is random and uniformly dispersed, this allows us to more easily estimate m_{AB}.

To do this, we consider a specific site on the lattic next to an A molecule. The probability that a B molecule occupies the neighboring site can be calculated by assuming that B molecules are distributed randomly across the lattice. Therefore, the probability that a given site is occupied by a B molecule p_B is given by:

$$p_B = \frac{n_B}{N} = x_B = 1 - x. \tag{31}$$

On this lattice, there are z nearest-neighbors so on average for each A molecule so the average number of AB contacts on each A molecule is $zn_B/N = z(1-x)$. There are a total of n_A A molecules, so

$$m_{AB} \approx \frac{zn_A n_B}{N} = zNx(1-x). \tag{32}$$

Therefore the total contact energy of the solution in terms of n_A and n_B can be written as:

$$U = \left(\frac{zw_{AA}}{2}\right) n_A + \left(\frac{zw_{BB}}{2}\right) n_B + z\left(w_{AB} - \frac{w_{AA} + w_{BB}}{2}\right) Nx(1-x) \tag{33}$$

$$= \left(\frac{zw_{AA}}{2}\right) n_A + \left(\frac{zw_{BB}}{2}\right) n_B + k_B T \chi_{AB} Nx(1-x) \tag{34}$$

where we define a dimensionless parameter $\chi_{AB} = \frac{z}{k_B T}\left(w_{AB} - \frac{w_{AA} + w_{BB}}{2}\right)$ called the **interaction parameter**.

Then we can compute the full free energy of solution:

$$\frac{F(n_A, n_B)}{k_B T} = n_A \ln \frac{n_A}{N} + n_B \ln \frac{n_B}{N} + \frac{zw_{AA}}{2k_B T} n_A + \frac{zw_{BB}}{2k_B T} n_B + \chi_{AB} Nx(1-x). \tag{35}$$

In practice, we are most interested in computing a free energy difference between the solution and the initial pure states of A and B:

$$\Delta F_{\text{sol}} = F(n_A, n_B) - F(n_A, 0) - F(0, n_B). \tag{36}$$

Thus, we arrive at the full free energy difference as a function of the mole fraction x and the interaction parameter χ_{AB}:

$$\boxed{\frac{\Delta F_{\text{sol}}}{N k_B T} = x \ln x + (1-x) \ln(1-x) + \chi_{AB} x(1-x)}. \tag{37}$$

This is the **regular solution model** originally developed by Hildebrand and demonstrates that while ideal solutions are driven purely by entropy, we must also consider the interactions of molecules when computing the free energies of real solutions. We will build on this in the next lecture as we work toward an understanding of the thermodynamics of a polymer in solution, where one species in many times larger than the other species around it.