

The Entropic Force

Christoph Kowitz

March 14, 2008

1 Chain Like Model

Before I can explain the mode of action of the entropic force, I have to explain the models for a chain molecule. This is the freely jointed chain (FJC) model. In this model a polymer chain is simulated by a simple chain, where each monomer is connected by a rigid rod with the Kuhn-length I_K . So the length of the whole polymer $L = I_K N$, where N is the number of monomers. There are no interactions between the monomers, so that is possible, that two monomers can be at the same place.

2 Entropic Force

If we take the simple FJC model, we can see that for every single distance d between the first and the last molecule the chain can have a number of different configurations. It is obvious, that if this $d \rightarrow L$ the chain will have less possibilities to form than if d is much smaller than L . And this is the cause of the entropic force.

Entropy is microcanonical defined as :

$$S = k_B \ln \Omega,$$

where Ω is the number of microstates for this macrostate. In our case the macrostate is the d . Due to the physical law, that every systems tends to go to a state of maximal entropy, that chain in the macrostate d tends to go to a d with a higher entropy. This is the source of the entropic force. It is not a force itself. If one takes a look at a isolated polymer in vacuum, one will not see that force. But a molecule is always exposed to thermal and kinetic fluctuations from its environment (water or air molecules). And this small fluctuation drive the system to a state of maximal entropy and act like a force on the molecule. And the number of states and the entropy of a polymer is much higher for shorter d , leads to a force which leads to a shorter d thus to a coiled up molecule.

3 BLN-model

The FJC model is a purely statistical model of a macromolecule, which does not include any intramolecular interactions between the molecules. So this model is not useful to explore the energylandscape of a protein at all, because we do not have a potential energy funtion, which describes the energy of the protein in every configuration. But the BLN model provides us with such kind of potential.

$$V = \frac{1}{2}K_R \sum_{i=1}^{N-1} (R_{i,i+1} - R_e)^2 \quad (1)$$

$$+ \frac{1}{2}K_\theta \sum_i^{N-2} (\theta_i - \theta_e)^2 \quad (2)$$

$$+ \epsilon \sum_i^{N-3} [A_i(1 + \cos \phi_i) + B_i(1 + \cos 3\phi_i)] \quad (3)$$

$$+ 4\epsilon \sum_{i=1}^{N-2} \sum_{j=i+2}^N C_{ij} \left[\left(\frac{\sigma}{R_{ij}} \right)^{12} - D_{ij} \left(\frac{\sigma}{R_{ij}} \right)^6 \right] \quad (4)$$

In this equation the term (1) is a harmonic potential between the monomers, which are connected to each other. Term (2) is a spring term forcing a bond angle θ_e between three monomers. The next term (3) controls the preferred dihedral angle between 4 monomers. So far the potential just describes a spring chain. To connect this model with the entropical force, it introduces a Lennard Jones interaction in term (4). All the coefficients A, B, C, D depend on the affected monomers. There are three kinds of monomers: hydrophobic (B), hydrophilic (L) and neutral (N). The Lennard Jones attraction does just apply for the hydrophobic monomers, because most of the time the protein will be in a water environment, where the protein has a higher entropy, if the the hydrophobic molecules are less exposed to water by being attracted to each other into the inner part of the molecule. For the hydrophilic monomers only the repelling part of the LJ potential dows apply. In a wet environment the entropy forces lead the hydrophilic monomers out of the molecule to an exposed position. This Lennard Jones potential is has no real physical foundation, it is just there to give us an empirical potential for the entropic force of the protein, which is no "real" interatomic force at all.

So the BLN model already contains the entropic force. But it doesn't have the statistical foundation and just simulates the statistical properties of a FJC.