

9.1: Force and Work

Here we will focus on the stretching and extension behavior of macromolecules. The work done on the system by an external force to extend a chain is

$$w = - \int \vec{f}_{ext} \cdot d\vec{x}$$

Work (w) is a scalar, while force (\vec{f}) and displacement (\vec{x}) are vectors. On extension, the external force is negative, leading to a positive value of w , meaning work was done on the system. Classical mechanics tells us that the force is the negative gradient of the potential one is stretching against ($\vec{f} = -\partial U / \partial \vec{x}$), but we will have to work with free energy and the potential of mean force since the configurational entropy of the chain is important. Since the change in free energy for a process is related to the reversible work needed for that process, we can relate the force along a reversible path to the free energy through

$$\vec{f}_{rev} = - \left(\frac{\partial G}{\partial \vec{x}} \right)_{p,T,N}$$

This describes the reversible process under which the system always remains at equilibrium, although certainly it is uncomfortable relating equilibrium properties (G) to nonequilibrium ones such as pulling a protein apart. For an arbitrary process, $\Delta G \leq w$.

Jarzynski Equality

A formal relationship between the free energy difference between two states and the work required to move the system from initial to final state has been proposed. The Jarzynski equality states

$$e^{-\Delta G/kT} = \langle e^{w/k_B T_{in}} \rangle_{path}$$

Here one averages the Boltzmann-weighted work in the quantity at right over all possible paths connecting the initial and final states, setting T to the initial temperature (T_{in}), and one obtains the Boltzmann weighted exponential in the free energy. This holds for irreversible processes! Further, since one can show that $\langle e^{-w/k_B T} \rangle \geq e^{-(\langle w \rangle)/k_B T}$, we see that the average work done to move the system between two states is related to the free energy through $\langle w \rangle \geq \Delta G$. This reinforces what we know about the macroscopic nature of thermodynamics, but puts an interesting twist on it: Although the average work done to change the system will equal or exceed the free energy difference, for any one microscopic trajectory, the work may be less than the free energy difference. This has been verified by single molecule force/extension experiments.

Statistical Mechanics of Work

Let's relate work and the action of a force to changes in statistical thermodynamic variables.¹ The internal energy is

$$U = \langle E \rangle = \sum_j P_j E_j$$

and therefore, the change in energy in a thermodynamic process is

$$dU = d\langle E \rangle = \sum_j E_j dP_j + \sum_j P_j dE_j$$

Note the close relationship between this expression and the First Law:

$$dU = \delta w + \delta q$$

We can draw parallels between the two terms in these expressions:

$$\begin{aligned} \delta q_{rev} = T dS & \longleftrightarrow \sum_j E_j dP_j \\ \delta w \cong p dV \text{ or } \vec{f} d\vec{x} & \longleftrightarrow \sum_j P_j dE_j \end{aligned}$$

Heat is related to the ability to change populations of energetically different states, whereas work is related to the ability to change the energy levels with an external force.

1. T. L. Hill, An Introduction to Statistical Thermodynamics. (Addison-Wesley, Reading, MA, 1960), pp. 11–13, 66–77.

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