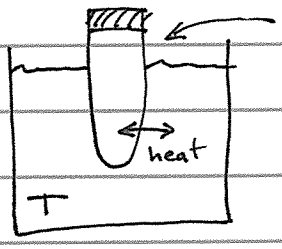
Laboratory Conditions & Free Energy

So far we have focused on problems with U, V, N as independent variables.

- In fact most of stat. mech. is an exercise in maximizing $S(U, V, N)$ subject to constraints in total energy U, total volume V, and particle number N.

When intensive variables, such as T, P & μ are controlled, the extensive pairs to these become unknown.

Example



natural variables for a sealed test tube in a heat bath are T, V, N

- We can use the 1st & 2nd laws to find conditions for equilibrium in terms of changes in the test tube.

- In the combined system (tube + bath) (and assuming these are isolated from the surroundings) equilibrium still maximizes $S(U, V, N)$

- Any change towards equilibrium must raise the entropy of the combined system:

$$dS_{combined} \geq 0$$

$$dS_{combined} = dS_{system} + dS_{bath} \geq 0 \quad \leftarrow 2^{nd} \text{ law}$$

$$dU_{system} + dU_{bath} = 0 \quad \leftarrow 1^{st} \text{ law}$$

Since $S(U,V,N)$, $dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$

We know from statistical mechanics that these partials are related to observables: $\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$, $\left(\frac{\partial S}{\partial V}\right) = \frac{P}{T}$ and $\left(\frac{\partial S}{\partial N}\right) = \frac{-\mu}{T}$

Applying this to the system-bath problem:

$$dS_{bath} = \frac{1}{T} dU_{bath} + \frac{P}{T} dV_{bath} - \frac{\mu}{T} dN_{bath}$$

Assuming the bath is large: $dV_{bath} \approx dN_{bath} \approx 0$

$$dS_{bath} = \frac{1}{T} dU_{bath}$$

$$dS_{bath} = -\frac{dU_{system}}{T}$$

$$dS_{system} - \frac{dU_{system}}{T} \geq 0 \rightarrow dU_{system} - T dS_{system} \geq 0$$

Let's define a function that captures this:

$$F \equiv U - TS$$

Σ Helmholtz free energy

$$dF = dU - T dS - S dT = dU - T dS \quad @ \text{ constant } T$$

What did we just show?

For a system in which T, V, N are constant,

$F(T,V,N)$ is a minimum @ equilibrium

natural variables for F

F is a balance between U & S, and the position of the balance is determined by T.

The system will tend toward high S & low U in order to minimize F.

at high T, S dominates

at low T, U dominates

Here's a neat example model for dimerization to illustrate:

$U = -\varepsilon$

dimer = good energy, bad entropy

$U = 0$

dissociated = bad energy, good entropy.

$W_{dimer} = V - 1$ if there are V sites

$\approx V$ for a large lattice

$S_{dimer} = k \ln W_{dimer}$

$F_{dimer} = U_{dimer} - TS_{dimer} = -\varepsilon - kT \ln V$

total permutations of 2 objects in V boxes

$$W_{monomer} = W_{total} - W_{dimer}$$

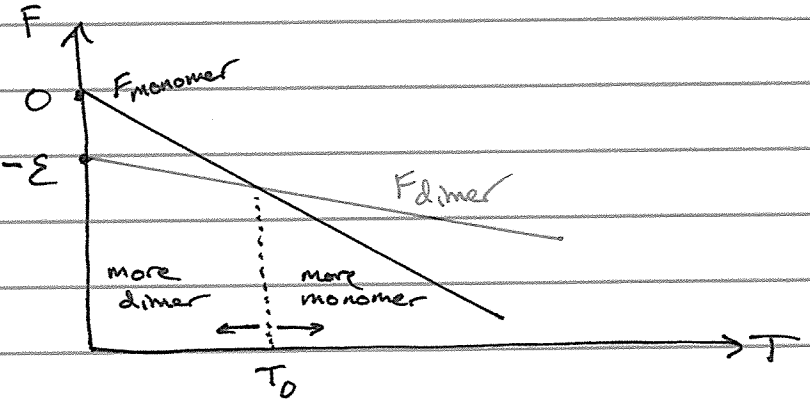
$$= \frac{V!}{2!(V-2)!} - (V-1)$$

$$= \frac{V\cdot(V-1)}{2} - V + 1 = \frac{V^2}{2} - \frac{V}{2} - V + 1$$

$$= \frac{V^2}{2} - \frac{3V}{2} + 1 \approx \frac{V^2}{2} \quad \text{for a large lattice}$$

$$F_{monomer} = U_{monomer} - TS_{monomer}$$

$$= 0 - kT\ln\left(\frac{V^2}{2}\right)$$



At equilibrium T_0 $\quad F_{dimer} = F_{monomer}$

$$-\varepsilon - kT_0 \ln V = -kT_0 \ln\frac{V^2}{2}$$

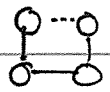
$$\varepsilon = kT_0\ln\left(\frac{V^2}{2}\right) - kT_0\ln(V)$$

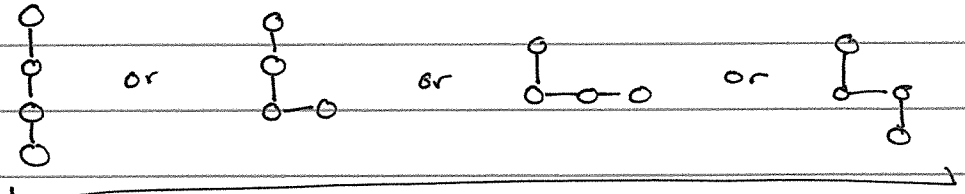
$$= kT_0\ln\left(\frac{V^2}{2V}\right) = kT_0\ln\left(\frac{V}{2}\right)$$

$$T_0 = \frac{\varepsilon}{k\ln(V/2)}$$

- The stronger the particle attraction, ε, the higher the dissociation temperature required to break the bond.

Another example, the cartoon model of protein folding

folded:  $U = -\varepsilon$

unfolded: 

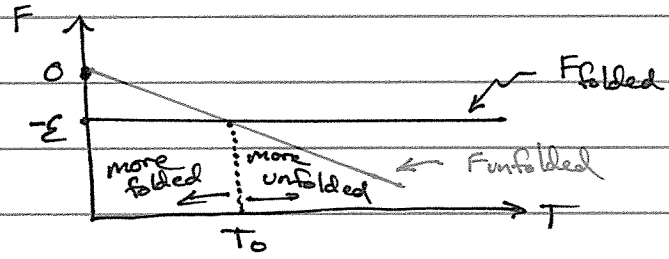
all with $U = 0$

only 1 microstate is folded

$$F_{folded} = -\varepsilon - kT\ln(1) = -\varepsilon$$

four "open" states of this chain

$$F_{unfolded} = 0 - kT\ln(4)$$



$$T_0 = \frac{\varepsilon}{k\ln 4}$$

Consider the folding process

$$\Delta F_{folding} = F_{folded}(T) - F_{unfolded}(T) = -\varepsilon + kT\ln 4$$

$$\Delta U - T\Delta S$$

$$\Delta U_{folding} = -\varepsilon$$

$$\Delta S_{folding} = -k\ln 4$$

The process is exothermic - heat flows from the test tube and into the bath at all T because $\Delta U = \delta q = -\varepsilon < 0$

$$F = U - TS$$

$$dF = dU - T\,dS - S\,dT$$

$$dU = T\,dS - p\,dV + \mu\,dN$$

$$dF = \cancel{T\,dS} - p\,dV + \mu\,dN \cancel{- T\,dS} - S\,dT$$

$$= -S\,dT - p\,dV + \mu\,dN$$

Mathematically:

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

$$\therefore \quad -S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad -p = \left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

Summary: we now have 3 fundamental functions for a system with fixed N & V:

$S(U, V, N) \rightarrow$ U is controlled as boundary condition
S is maximized

$U(S, V, N) \rightarrow$ S is controlled as a boundary condition
U is minimized

$F(T, V, N) \rightarrow$ T is controlled as a boundary condition
F is minimized

Next time: Enthalpy & Gibbs Free energy