Thermodynamics and an Introduction to Thermostatistics, 2nd ed.
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Statistical Mechanics

1/11/06

Outline:

- Goals of statistical mechanics
- Formalism ⇒ Analytical engine
- Examples
  - force-extension for DNA
  - DNA binding proteins + gene regulation
  - Hemoglobin & Oxygen

[Biophysics Lecture Series Talk
Jan. 23 - Steve Block]

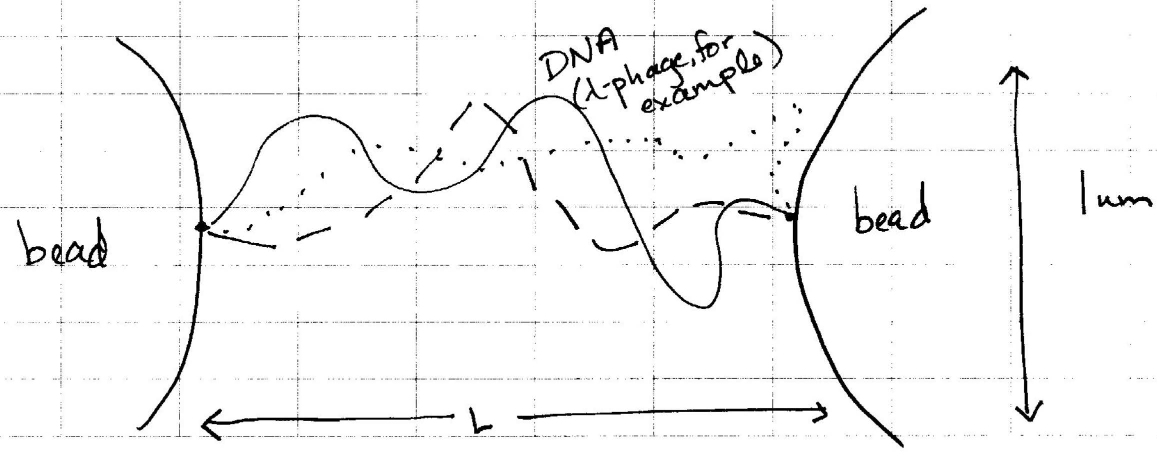
Thermodynamics ⇔ Statistical Mechanics
(Macroscopic) (Microscopic)

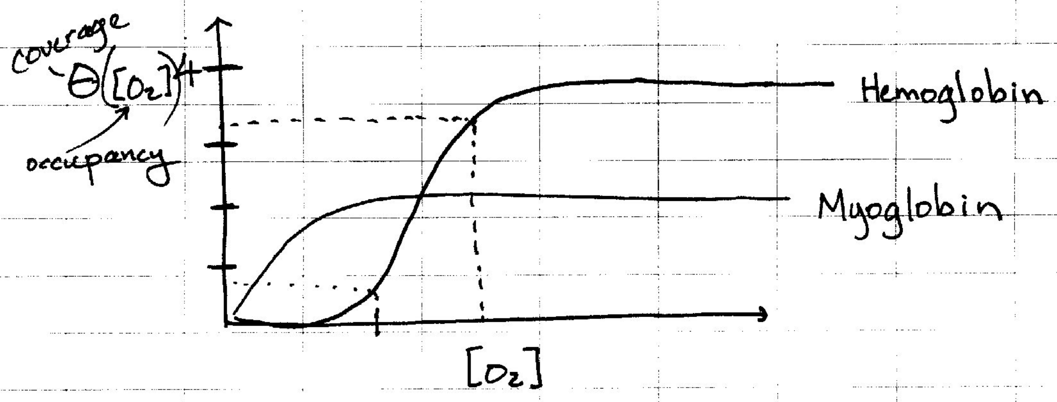
↓ .... elaboration ... ↓

Macrostates (P, V, T)

Microstates → $\{p_i, q_i\}$
(example: all coordinates and momenta of all the microscopic particles)

$$\{p_i, q_i\} = (\underset{\text{momentum of molecule 1}}{p_1}, p_2, \cdots \underset{\text{momentum of molecule N}}{p_N}; q_1, \underset{\text{position of molecule 2}}{q_2}, \cdots, q_N)$$





A "Goal" of Statistical Mechanics
- find the probability of the microstates
  $\Rightarrow$ prob(microstates)
  e.g. gas: $p(\{p_i, q_i\})$

More formally:
let's label our microstates by their energies, E_n

$p(E_n) \equiv$ probability of microstate with energy, E_n

Compute averages:

e.g. $\langle E \rangle = \sum_n E_n p(E_n)$

$\rightarrow$ Example of a polymer

$$\langle \text{Length} \rangle = \sum_{\text{configurations}} p(\text{config}, \underbrace{f}_{\text{force}})\, l(\text{config})$$

Notion of Entropy

- Fundamental idea of thermodynamics + statistical mechanics

$$\underset{\text{macroscopic}}{\underset{\uparrow}{S(E)}} = k_B \ln \underset{\text{microscopic}}{\underset{\uparrow}{\Omega(E)}}$$ (Boltzmann's Law)

$\Omega(E) \equiv$ # of microstates of energy E

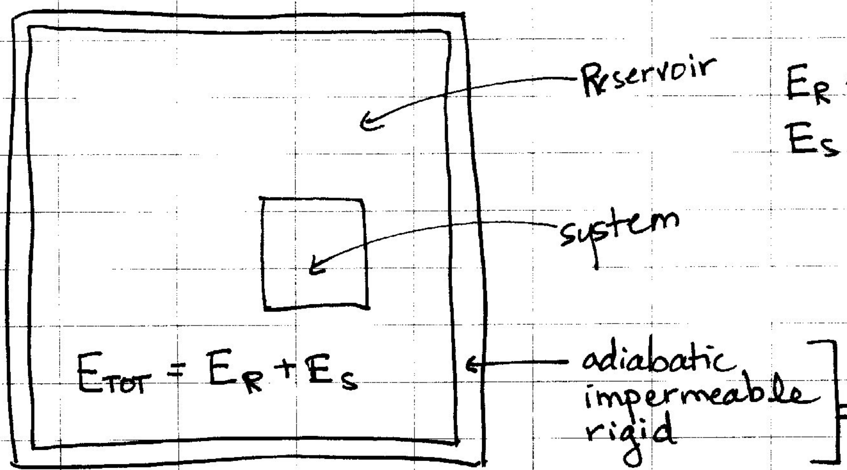
2nd Law of Thermodynamics:
A closed system will reach the terminal privileged state of maximum entropy.

Josiah Willards Gibbs - translated the 2nd law of thermo. into mathematical calculations using ΔS.

State of maximum entropy is when $d\underset{\text{equilibrium}}{\underset{\uparrow}{S_{TOT}}} = 0$ (Energy of system is constant)

✱ Boltzmann Distribution: $p(E_n) = \dfrac{e^{-E_n/k_BT}}{Z}$

$Z \equiv \sum_n e^{-E_n/k_BT} \equiv$ partition function
("analytical engine of statistical mechanics")



= the universe is isolated

E_R = energy of reservoir
E_s = energy of system

$$S_{TOT}(E_{TOT}) = S_R(E_R) + S_s(E_s)$$

$$p(E_j) = \frac{\Omega_{Res}(E_{TOT} - E_j)}{\Omega_{TOT}(E_{TOT})}$$

$\Omega_{Res}(E_{TOT} - E_j)$ ← # of states where the reservoir has energy of $E_{TOT} - E_j$

$\Omega_{TOT}(E_{TOT})$ ← total # of microstates available in the system + Reservoir

$$= \frac{e^{\ln \Omega_{Res}(E_{TOT} - E_j)}}{e^{\ln \Omega_{TOT}(E_{TOT})}}$$

$$= \frac{e^{S_{Res}(E_{TOT} - E_j)/k_B}}{e^{S_{TOT}(E_{TOT})/k_B}}$$

Aside #1:

$$S_{Res}(E_{TOT} - E_j) = S_{Res}(E_{TOT} - \langle E \rangle + \langle E \rangle - E_j)$$

$\langle E \rangle$: average energy of system

Taylor expansion

$$\simeq S_{Res}(E_{TOT} - \langle E \rangle) + \frac{dS}{dE}\underbrace{(\langle E \rangle - E_j)}_{\text{small parameter}}$$

Aside #2:

$$\frac{1}{T} = \frac{dS}{dT}$$

$$p(E_j) = \frac{e^{S_{Res}(E_{TOT} - \langle E \rangle)/k_B}\, e^{\frac{1}{k_B T}(\langle E \rangle - E_j)}}{e^{S_{Res}(E_{TOT} - \langle E \rangle)/k_B}\, e^{S_{sys}(\langle E \rangle)/k_B}}$$

$$S_{TOT}(E_{TOT}) = S_{Res}(E_{TOT} - \langle E \rangle) + S_{sys}(\langle E \rangle)$$

$$\Rightarrow p(E_j) = \text{const.}\, e^{-E_j/k_BT} = e^{-E_j/k_BT} e^{\frac{1}{k_BT}(\langle E\rangle - S_{sys}(\langle E\rangle)T)}$$

$$= e^{-E_j/k_BT} e^{F/k_BT}$$

Normalization : $\sum_n p(E_n) = 1$

$$\sum_j e^{\beta F} e^{-\beta E_j} = 1 \Rightarrow e^{\beta F} \sum_j e^{-\beta E_j} = 1$$

$$e^{\beta F} = \frac{1}{\sum_j e^{-\beta E_j}} = \frac{1}{Z}$$

$$\Rightarrow Z = \sum_j e^{-\beta E_j} \qquad \leftarrow \quad \beta = \frac{1}{k_BT}$$

Know these:

(1) $p(E_j) = \frac{1}{Z} e^{-\beta E_j}$ Boltzmann Distribution

(2) $Z \equiv \sum_j e^{-E_j/k_BT}$ Partition Function