STATISTICAL MECHANICS

BEH.410 Tutorial

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Why Statistical Mechanics?

Understand & predict the physical properties of macroscopic systems from the properties of their constituents

Deterministic approach $ma = F$

- need of *6N* coordinates at t_o: r_i and v_i

- but typically $N \equiv$ moles (10^{23}) !

"Ensemble" rather than microscopic detail

… and its surroundings

➢ microcanonical, canonical, grand canonical

What With Statistical Mechanics?

Averages, distributions, deviation estimates…

… of <u>microstates</u>: specification of the complete set of positions and momenta at any given time (points on the constant energy hypersurface for Hamiltonian dynamics)

Ensemble average & ergodic hypothesis:

$$A = \langle a \rangle_{ensemble} = \frac{1}{N}\sum_{i=1}^{N} a(x_i) = \lim \frac{1}{T}\int_0^T a(x(t))dt$$

A system that is ergodic is one which, given an infinite amount of time, will visit all possible microscopic states available to it.

The First Law – Work

Work, heat & energy = basic concepts
Energy of a system = capacity to do work

- At the molecular level, difference in the surroundings

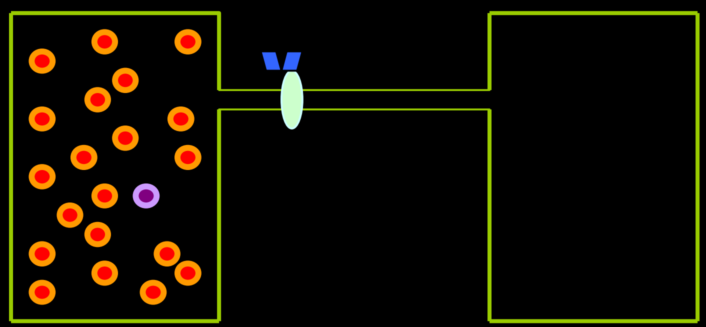
	Energy transfer that makes use of…
Heat	… chaotic molecular motion
Work	… organized molecular motion

$$\Delta U = q + w$$

state function – independent of how state was reached

Second Law – Gibbs

- Spontaneous processes increase the overall "disorder" of the universe



❖ Reasoning through an example

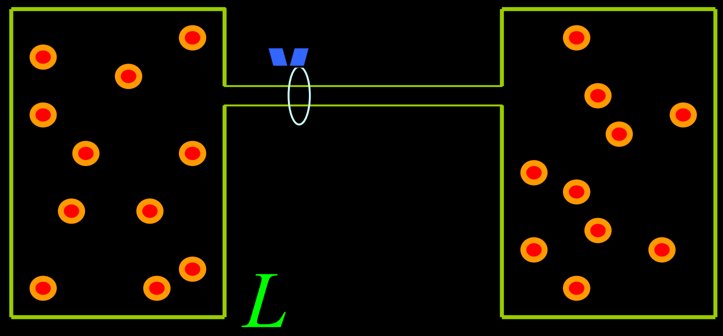
- microstates to achieve macrostate

<u>Gibbs postulate</u>: for an isolated system, all microstates compatible with the given constraints of the macrostate (here E, V and N) are equally likely to occur

- Here 2^N ways to distribute N molecules into 2 bulbs

Second Law - Probability

- Number of (indistinguishable) ways of placing L of the N molecules in the left bulb:



$$W_L = \frac{N!}{L!(N-L)!}$$

- Probability $W_L / 2^N$ maximum if $L = N / 2$
  - ✓ With $N = 10^{23}$, $p\,(L = R \pm 10^{-10}) = 10^{-434}$ possible but extremely unlikely

Second Law - Entropy

$$S = k \ln W$$

$$\frac{S}{k} = -\sum_{i=1}^{t} p_i \ln\, p_i$$

Boltzmann's constant

k = 1.38 x 10^{-23} J.K^{-1}

- Principle of Fair Apportionment

$$W = \frac{N!}{n_1!\, n_2! \ldots n_t!}$$

Multiplicity of outcomes

$$= \frac{\left(\frac{N}{e}\right)^N}{\left(\frac{n_1}{e}\right)^{n_1}\left(\frac{n_2}{e}\right)^{n_2}\ldots\left(\frac{n_t}{e}\right)^{n_t}} = \frac{N^N}{n_1^{n_1} n_2^{n_2} \ldots n_t^{n_t}} = \frac{1}{p_1^{n_1} p_2^{n_2} \ldots p_t^{n_t}}$$

Second Law - Entropy

$$S = k \ln W$$

$$\frac{S}{k} = -\sum_{i=1}^{t} p_i \ln p_i$$

$$\ln W = -\sum_{i=1}^{t} n_i \ln p_i$$

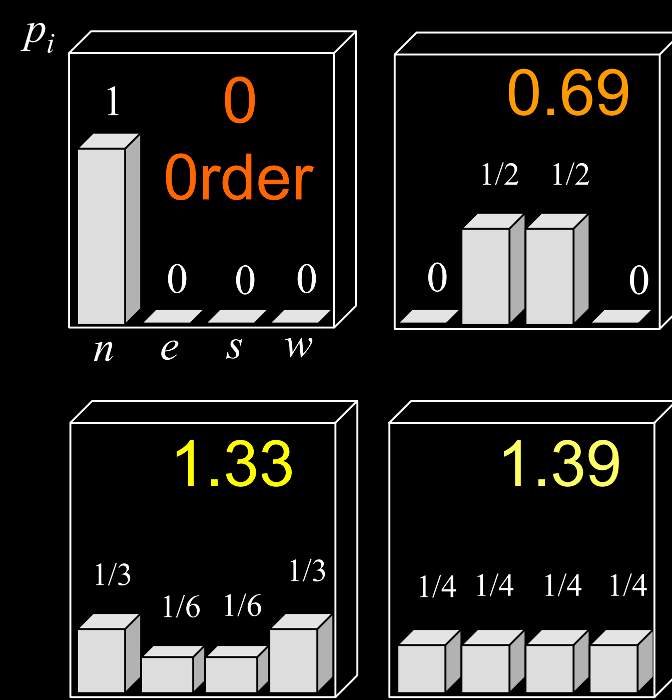
$$\frac{S}{k} = \frac{S_N}{Nk} = \frac{1}{N} \ln W = -\sum_{i=1}^{t} p_i \ln p_i$$

The absolute entropy is never negative

$$S \geq 0$$

S max at equilibrium

Flat distribution ≡ high *S*



The Boltzmann Distribution Law

E_3

E_2

E_1

- Maximum entropy principle + constraints

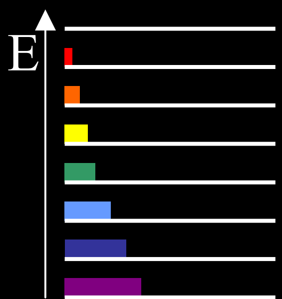
$$\frac{S}{k} = -\sum_{i=1}^{t} p_i \ln p_i \qquad \begin{cases} \langle U \rangle = \dfrac{E}{N} = \displaystyle\sum_{i=1}^{t} p_i E_i \\ \displaystyle\sum_{i=1}^{t} p_i = 1 \end{cases}$$

$\Rightarrow$ exponential distribution

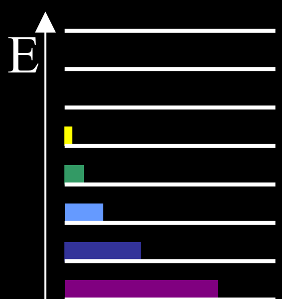
$$p_i^* = \frac{p_i^*}{\sum_{i=1}^{t} p_i^*} = \frac{\exp\left(-\dfrac{E_i}{kT}\right)}{Q}$$

Partition function $\quad Q = \sum_{i=1}^{t} \exp\left(-\dfrac{E_i}{kT}\right)$

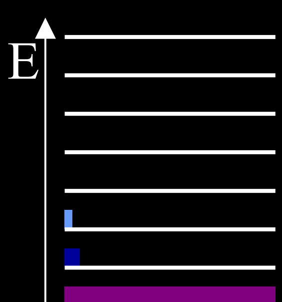
The Boltzmann Distribution Law (2)



high T



medium T



low T

- More particles have low energy: more arrangements that way

$$p_i^* = \frac{\exp\left(-\frac{E_i}{kT}\right)}{Q}$$

- $Q \equiv$ connection between microscopic models & macroscopic thermodynamic properties

$$U = kT^2\left(\frac{\partial \ln Q}{\partial T}\right) \quad \text{and} \quad S = k\ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)$$

- $Q \equiv$ number of states effectively accessible to system

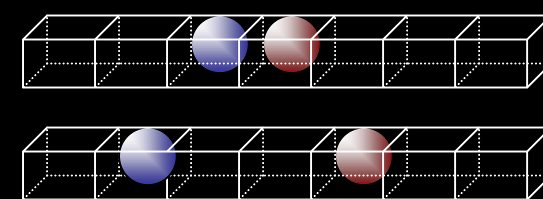
$$Q = \sum_{i=1}^{t}\exp\left(-\frac{E_i}{kT}\right) = 1 + e^{-E_2/kT} + e^{-E_3/kT} + \ldots + e^{-E_t/kT}$$

$$T \to +\infty \Rightarrow \frac{E_i}{kT} \to 0 \Rightarrow Q \to 1+1+1+\ldots+1 = t$$

The Helmholtz Free Energy

- Systems held at constant $T \rightarrow$ minimum free energy ($\neq S_{max}$)
  Equilibrium if $F(T, V, N)$ minimum (T fixed at boundaries)

Internal energy   Entropy   *F = U - TS*

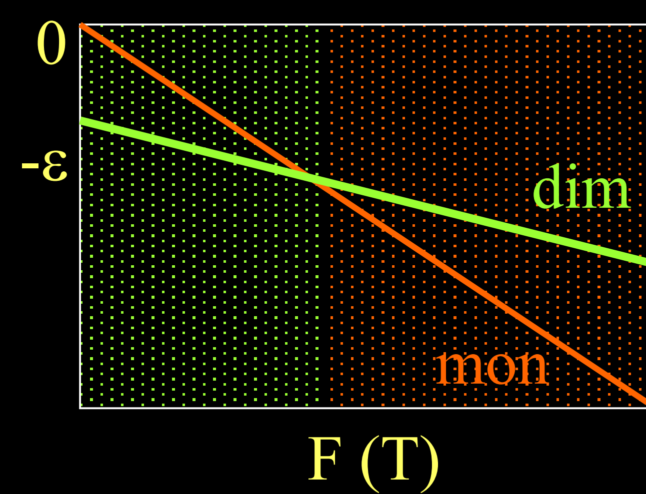


❖ Example of ‘dimerization’

$$F_{\dim} = U_{\dim} - TS_{\dim} = -\varepsilon - kT\ln(V-1)$$

$$W_{mon} = W_{tot} - W_{\dim} = \frac{V!}{(2!)(V-2)!} - (V-1) = \left(\frac{V}{2} - 1\right)(V-1)$$

$$F_{mon} = U_{mon} - TS_{mon} = -kT\ln\left[\left(\frac{V}{2} - 1\right)(V-1)\right]$$



Fundamental Functions

U (S, V, N)	min (S and V at boundaries)	$dU = TdS - pdV + \sum_i \mu_i dN_i$	calorimetry
S (U, V, N)	max (U and V at boundaries)	$dS = \left(\frac{1}{T}\right)dU + \left(\frac{p}{T}\right)dV - \sum_i \left(\frac{\mu_i}{T}\right)dN_i$	cal.
H (S, p, N)	min (S and p at boundaries)	$dH = TdS + Vdp + \sum_i \mu_i dN_i$	calorimetry
F (T, V, N)	min (T and V at boundaries)	$dF = -SdT - pdV + \sum_i \mu_i dN_i$	Internal energy vs.entropy
G (T, p, N)	min (T and p at boundaries)	$dG = -SdT + Vdp + \sum_i \mu_i dN_i$	Enthalpy vs. entropy

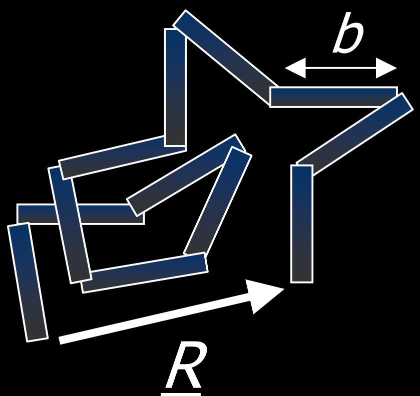
Macromolecular Mechanics

- Why study the mechanics of biological macromolecules?

  - provide structural integrity and shape
  - coupling of geometry & dynamics $\Rightarrow$ what is possible
  - importance of conformation for ion channels, pumps…
  - motility
  - mechanotransduction, signaling

The Gaussian Chain Model (Kuhn)

- Long floppy chain made of N rigid links of length b (free to swivel about joints, overlapping & crossing allowed)
- Valid for small displacements from equilibrium, not large extensions



$$G_g = H - TS = -Tk \ln P(\underline{R}, N)$$

Entropic reasoning ⇒ mechanical spring (straightening out ≡ decrease of entropy)

$$\langle \underline{R} \rangle = 0 = \mu$$

$$\langle \underline{R}^2 \rangle = Nb^2 = \sigma^2$$

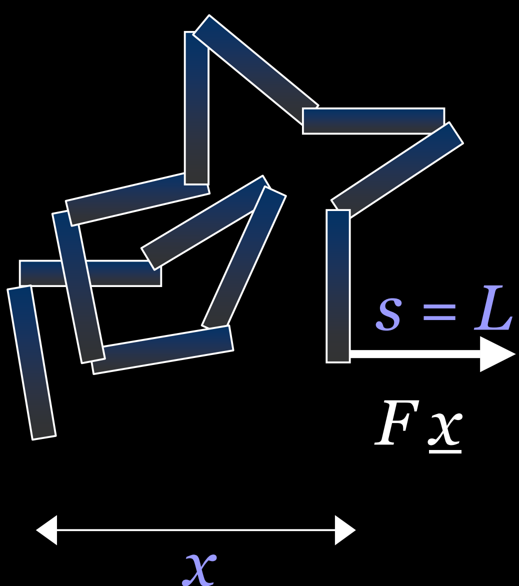
$$P(\underline{R}, N) = \left(\frac{3}{2\pi\sigma^2} \right)^{3/2} \exp\left(-\frac{3}{2} \cdot \frac{(|\underline{R}| - \mu)^2}{\sigma^2} \right)$$

$$G_g = \frac{1}{2} \cdot \frac{3kT}{Nb^2} \cdot |\underline{R}|^2 = \frac{1}{2} \cdot K \cdot (\ell - \ell_0)^2$$

The Worm-like Chain Model

- Self-avoiding linear chains (Flory, 1953)
- Freely-jointed chain model (Grosberg & Khoklov, 1988)

- Worm-like chain model: Bending stiffness of polymer on short length scales



$$E = -\underline{F}\,\underline{x} + \int_0^L \frac{B\kappa^2}{2}\,ds$$ (Kratky-Porod)

$$F = \frac{kT}{16\ell_p}\left(1 - \frac{x}{L}\right)^{-2}$$ (diverges for $x \to L$)

Persistence length $$\ell_p = \frac{YI}{kT}$$

YI ← bending

kT ← thermal

Experimental Validation of Models

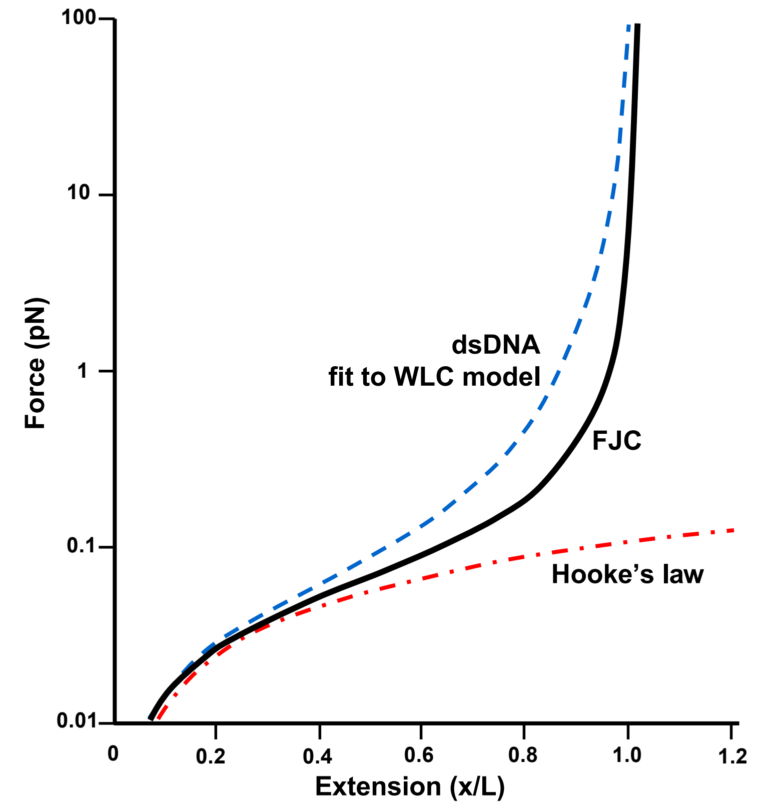
- Single-molecule studies of DNA mechanics:

  Bustamante *et al.* (2000) *Curr. Op. Struct. Biol.*, **10**: 279

- WLC interpolated:

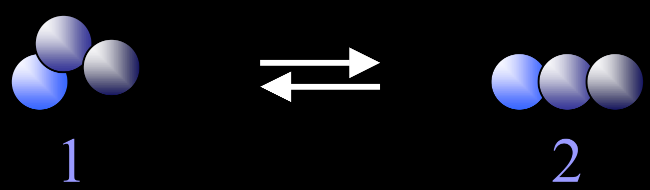
  Marko & Siggia (1995) *Macromolecules*, **28**: 8759

$$F = \frac{kT}{\ell_p}\left[\frac{x}{L} + \frac{1}{16}\left(1 - \frac{x}{L}\right)^{-2} - \frac{1}{16}\right]$$



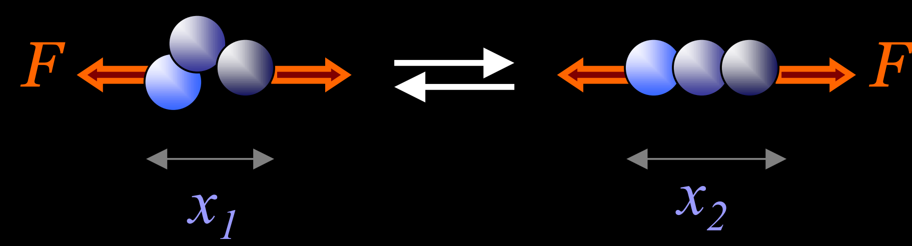
After Bustamante et al., *Current Opinion in Structural Biology*, 2001

Effect of Force on Equilibrium



$$\left.\frac{[1]}{[2]}\right|_{noForce} = \frac{p_1}{p_2} = \frac{\exp\left(-\dfrac{G_1}{kT}\right)}{\exp\left(-\dfrac{G_2}{kT}\right)}$$

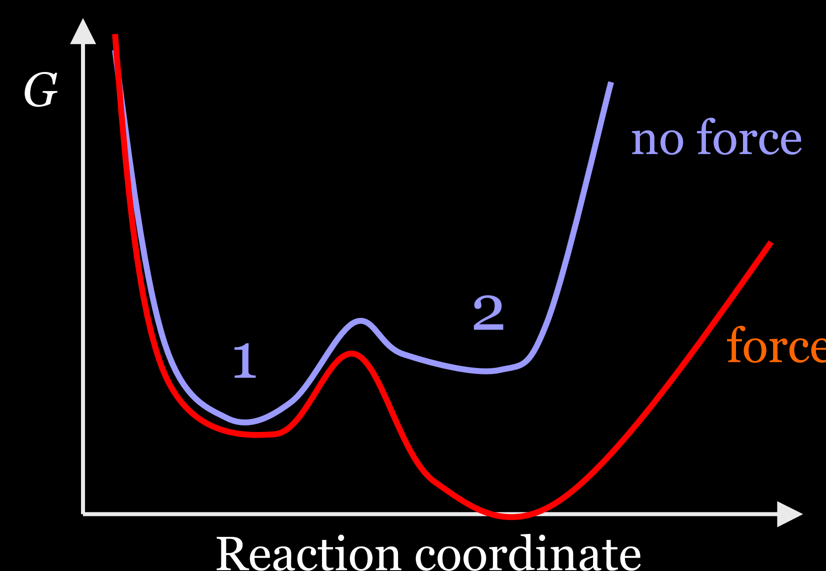
$$= \exp\left(-\frac{\Delta G^0_{noForce}}{kT}\right)$$



$$\left.\frac{[1]}{[2]}\right|_{Force} = \exp\left(-\frac{\Delta G^0_{noForce}}{kT}\right)\exp\left(\frac{\Delta x \cdot F}{kT}\right)$$

- Force tilts energy profile

$\Rightarrow$ favors configuration



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