Lecture 2 Energy + Entropy

Central idea that living things are <u>not</u> in equilibrium. The dissipation of energy is central to keeping away from $\equiv m$ so that there is potential to meet goals:
- driving motors for locomotion
- sorting chemicals, synthesizing new ones.
- maintaing conc. + elect. gradients

1. Food supply.

Higher animals – eating fat, carbohyd, protein
mostly plants, animals, fungi.
Most ecosystems ultimately use sunlight.
→ bacteria or plants
→ photosynthesis.
→ electrical (ion) gradient, like battery.
→ absorb CO_2 synthesize sugars
then everything else.

Forms of energy:
electromagnetic
mechanical
chemical
} can interconvert

all ends with thermal energy which cannot convert back (2nd law thermodynamics)
Equilibrium is mathematically convenient, but when can we apply it?
Key insight: depends on time scale.
Concept of quasiequilibrium = locally valid

2. Energy Landscape.

Energy as a function of system coordinates

But many variables / multi dimensional space
Exploration of landscape is also driven by thermal fluctuations:

Probability of reaching "microstate" with $E = E_{det}$ (some deterministic energy $> k_BT$).

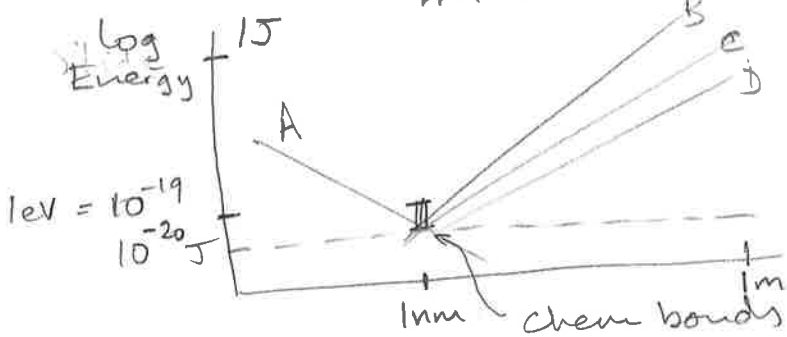
Prob. $\propto e^{-E_{det}/k_BT}$ Boltzmann factor.

T doesn't vary much for living systems:

k_BT = 4.1 pN nm.
0.6 kcal/mol.
2.5 kJ/mol
25 meV.
4.1×10^{-21} J.

A: electron in bose
B: electrostatic energy of protein ball
C: bending of beam

Slide:



Nanometre scale is where thermal energies are important.

Brownian motion is best seen on particles ~500 nm (Perrin) ~30 sec time scale

Compromise btw visibility in light microscope + magnitude of fluctuations.

3. Metabolism

Biochemical pathway for extracting energy from a food source, glucose.

"Glycolytic pathway".

Very common for all life forms that cannot photosynthesize. Up to 30 x ATP's available/gluc.

Glucose (C_6) → 2x pyruvate (C_3) → 6 x CO_2

anaerobic — no oxygen

aerobic — oxygen available

E. coli bacteria can grow either way.

Within the cell, energy is stored as:

ATP: adenosine triphosphate

NADH: nicotinamide adenine dinucleotide (chemical reducing agent) $NAD^+ H^-$ lower en.

slide $P^-O-P^-O-P=O$ is a high energy state because of concentr. charges

→ $P^-O-P=O + PO_4^-$ } lower in energy by $20 k_B T$

ADP + P_i

ATP is almost universal currency of life.

i) $20 bill = convenient amount.

ii) $20 k_B T$ makes reversible process irreversible. by $e^{-20} = 10^{-9}$ Bottzmann factor.

iii) works by phosphorylation of active -OH bonds, often using serine "kinase" common enzyme.

iv) phosphorylated form can undergo otherwise impossible chem. reactions

$k_B T = 4.1 \times 10^{-21}$ J = 0.6 kcal/mole = 2.5 kJ/mole

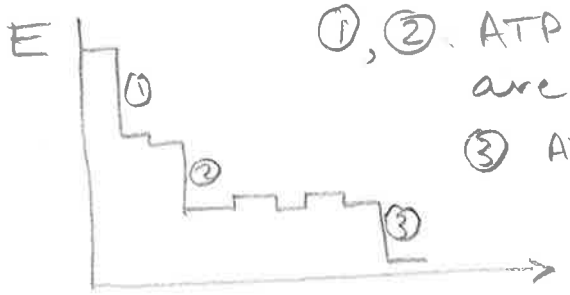
= 25 meV.

4. Electrostatic energy p192.
Stored by voltage difference across cell / organelle membranes. ~ 90 mV typical. ~ 3.5 k_BT.
Important because of ready high-efficiency interconversion to ATP.

ATP synthase. (F_1-F_o ATP synthase)

Reversible enzyme converts 4 × H^+ protons crossing membrane to one ADP + P_i → ATP.
In higher organisms, eukaryotes, this happens in the mitochondria.

5. Glycolysis energy diagram (slide).



①, ② ATP driven steps are essentially irreversible
③ ATP generating step also irrev.

6. Energy to build E. coli?
DNA is 4.6×10^6 bp. Length of genome.
Molecular weight of bp is 600 ~ 50 · C atoms.
⇒ DNA needs 2×10^8 C's.
Number of proteins ≃ 3×10^6 / cell.
300 amino acids each.
4 ATP equivalents for ribosome + tRNA machinery
1.2 ATP equivalents to synthesize (~~table~~) slide

4.5×10^9 ATP equivalents for protein
Other components in table 5.2
2×10^9 glucoses for C atoms
3×10^8 glucoses to provide energy

Total
10^{10} ATPs @ 20 k_BT
$= 8 \times 10^{-10}$ J
≃ 1 nJ

Sunlight = 340 W/m² = 1 W / (5cm)²

[10^9 E coli/s at 1W] / (1mm)³ 1W × 1ns.

7. Entropy (5.5, p219).

Free Energy = Energy − T × entropy : minimised
G. (Enthalpy) TS.

Entropy measures disorder.

Equilibrium state is the one that minimises G.

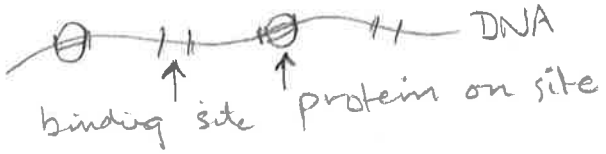
$S = k_B \ln W$ ← Boltzmann definition
number of microstates.

More disorder ↔ more available states of system

Lowest free energy = max entropy
= most disordered state

Statistical definition.

slide ⇒ Specific example



N binding sites
Np occupied.
1st one has N possible sites
2nd ... N−1 ...
} $W = N(N-1)\cdots(N-N_p+1)$

but this ignores the fact that the Np are indistinguishable, so divide by $N_p! = 1\times2\times\cdots N_p$

$$W = \frac{N(N-1)\cdots(N-N_p+1)}{N_p!} = \frac{N!}{N_p!(N-N_p)!} = \binom{N}{N_p}$$

this is the same definition of the binomial coef:

$$(1+x)^3 = 1 + 3x + 3x^2 + x^3.$$

Factorials and logarithms go together: Stirling

$$\ln N! = \underbrace{N\ln N - N}_{\text{2 terms enough here}} + \frac{1}{2}\ln(2\pi N)$$

$$\ln W = N\ln N - \cancel{N} - N_p \ln N_p + \cancel{N_p} - (N-N_p)\ln(N-N_p) \quad \cancel{+N-N_p}$$

$$= N\left[\ln N - \ln(N-N_p)\right] + N_p\left[\ln(N-N_p) - \ln N_p\right]$$

$$= -N\ln\left(1-c\right) + Nc\left[\ln N(1-c) - \ln Nc\right] \qquad c = \frac{N_p}{N}$$

$$= -N\ln(1-c) + Nc\left[\cancel{\ln N} + \ln(1-c) - \cancel{\ln N} - \ln c\right]$$

$$= -N(1-c)\ln(1-c) - Nc\ln c$$

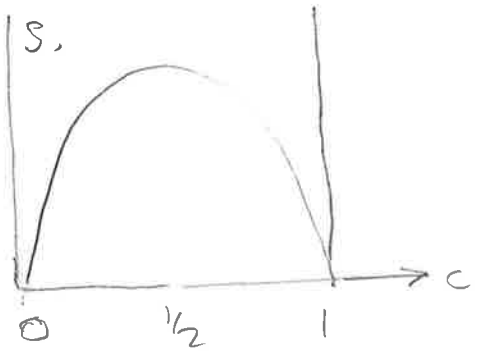
$$\Rightarrow S = -k_B N\left[(1-c)\ln(1-c) + c\ln c\right]$$

This entropy function is already interesting

$c \to 0 \quad S \to 0$

$c \to 1 \quad S \to 0$

$c = 1/2 \quad S = k_B N \ln 2$



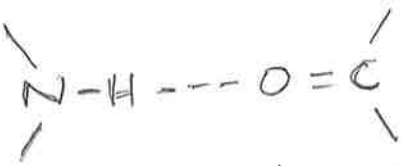
slide 3:35

8. Hydrophobic Effect.

We already saw importance of hydrophobic side chains in folding of proteins. How to account for the energies involved?

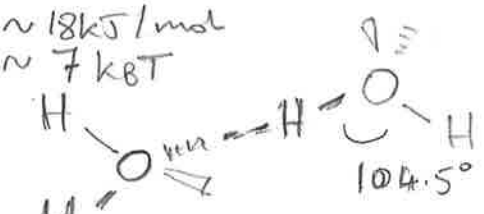
Broken Hydrogen bonds.

~8kJ/mol
~3k_BT



within backbone of protein

~18kJ/mol
~7k_BT



lone-pair orbitals

Because of lone pairs, water molecules are approx tetrahedral shaped and form 4 H bonds following "ice rules" [Pauling 1935]. Structure of H_2O, ice.

104.5° → 109° tetrahedral.

Dill-Bromberg model (p223) coarse-grained

6 ways of placing H_2O in a tetrahedron;

slide Half of them (3/6) eliminated when H_2O placed next to a CH_3 group of an alkane.

Entropy change:

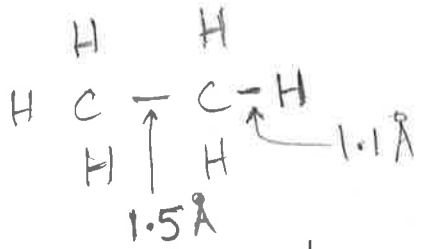
$$\Delta S = k_B \ln 3 - k_B \ln 6 = -k_B \ln 2.$$

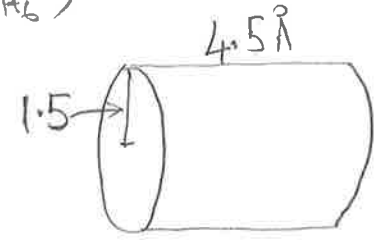
If a side chain is surrounded by n water molecules, its Free Energy changes by

$$\Delta G = -T\Delta S = +nk_BT \ln 2.$$

O-H···O distance is 3Å = 0.3 nm
So area = 0.09 nm², or ~10 H_2Os per (nm)².
$n = 10/nm^2$ $\ln 2 = 0.7$
$\boxed{\Delta G \triangleq 7\ k_BT\ /nm^2}$ of exposed area.

i) Ethane molecule (C_2H_6)





$V = 0.03\ nm^3$
$A = 0.45 + 0.07$
$= 0.52\ nm^3$.

Density = 0.54 g/cc MWt = 30 (2×12+6)
30g is 16.2 cc contains 6×20^{23} molecules
Vol = 2.7×10^{-23} cc = 0.027 nm³.
⇒ $\Delta G = 3.5\ k_BT$ energy to dissolve in H_2O
Boltzmann factor $e^{-3.5} = 0.03$ unlikely
Smaller molecules like O_2 do a bit better.

ii) Octane C_8 : cylinder L = 12Å A = 1.2 nm³
$\Delta G = 8.4\ k_BT$ $e^{-\Delta G/kT} = 2 \times 10^{-4}$ phase separates.

iii) Lipid tail is C_{18} ~~to C_{22}~~
Membrane bilayer = 30 Å (3nm) thick.
L = 1.5 nm A = 1.5 nm² $\Delta G = 10.5 k_BT$ $e^{-10.5} = 3 \times 10^{-5}$
these are safely long enough to avoid dissolution.

HW2

iv) Protein folding. ΔG cost of hydrophobic side chains means they prefer to come together
Oil-water separation drives folding.

movies

[Karplus, Levitt, Warshel : Nobel 2013]

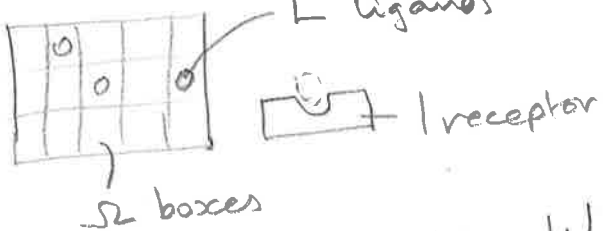
9. Second Law of Thermodynamics

System moves towards equilibrium G min
System moves to maximise entropy. S max.

10. Energy Landscape, again.
300 amino acid protein has many conformations
Too many to explore thermally.
Local folding can be explored, then local regions find each other and pass "funnel"

movie Pande Lab (Stanford). NTL9
Aromatic side chains highlited.

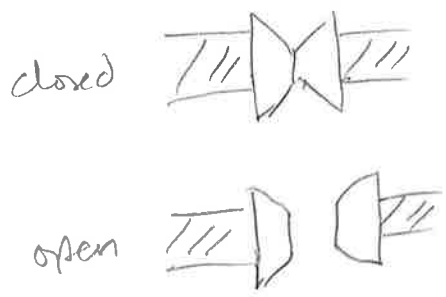
11. Microstates (Ch 6) p 238
slide i) Ligand – Receptor: important common case.
– will derive result a few different ways.



Unbound: no. states $W = \frac{\Omega!}{(\Omega-L)!} \times \frac{1}{L!}$
no of configs. indistinguishable

12. 2-state system with energy change
Ion channel open/closed.

omit?



ε_{closed} $e^{-\varepsilon_{closed}/k_BT}$

ε_{open} $e^{-\varepsilon_{open}/k_BT}$

energy weight

Express as a probability, by normalising.

$$p(\text{open}) = \frac{1}{Z} e^{-\varepsilon_{\text{open}}/kT}$$

$$p(\text{closed}) = \frac{1}{Z} e^{-\varepsilon_{\text{closed}}/kT}$$

Only 2 states, so $p(\text{open}) + p(\text{closed}) = 1$.

$$\Rightarrow Z = e^{-\varepsilon_{\text{open}}/kT} + e^{-\varepsilon_{\text{closed}}/kT}$$

13. In general, set of N states with energies E_i

$$p_i = \frac{1}{Z} e^{-E_i/kT} \qquad \sum_i p_i = 1 = \frac{1}{Z} \sum_{i=1}^{N} e^{-E_i/kT}$$

$$\Rightarrow Z = \sum_{i=1}^{N} e^{-E_i/kT}$$

this is called the Partition Function. (= denominator)

Average energy given by probabilities

$$\langle E \rangle = \sum_{i=1}^{N} E_i p_i = \frac{1}{Z} \sum_{i=1}^{N} E_i e^{-E_i/kT}$$

General trick: write $\beta = 1/k_B T$

$$\langle E \rangle = \frac{-1}{Z} \frac{\partial Z}{\partial \beta} \quad \text{where } Z = \sum_{i=1}^{N} e^{-\beta E_i}$$

$$\frac{\partial Z}{\partial \beta} = \sum_{i=1}^{N} \left(-E_i e^{-\beta E_i} \right) \text{ shows correct.}$$

Boltzmann distribution

14. Ligand Receptor evaluation

One receptor, many ligands L, many boxes Ω

Bound or unbound : 2 states.

Energy

$(L-1)\varepsilon_{sol} + \varepsilon_b$. $L\varepsilon_{sol}$.

Count the microstates, unbound first L into Ω

$$\frac{\Omega!}{(\Omega-L)!} \frac{1}{L!}$$

$(\Omega-L)!$: configs. $L!$: degen

$$\#\text{configs} = \Omega(\Omega-1)(\Omega-2)\cdots(\Omega-L+1) \simeq \Omega^L$$

so long as $\Omega \gg L$ large number of boxes

Adding all parts of partition function:

$$Z = \sum e^{-\beta E_i} = \frac{\Omega^L}{L!} e^{-\beta L \varepsilon_{sol}} + \frac{\Omega^{L-1}}{(L-1)!} e^{-\beta((L-1)\varepsilon_{sol} + \varepsilon_b)}$$

$\Omega^L / L!$: no. of states. unbound. A

$\Omega^{L-1}/(L-1)!$: bound. B.

Probability of ligand being bound:

$$P_{bound} = \frac{B}{Z} = \frac{B}{A+B} = \frac{e^{-\beta(\varepsilon_b - \varepsilon_{sol})}}{\Omega/L + e^{-\beta(\varepsilon_b - \varepsilon_{sol})}}$$

} taking out common factors.

$$= \frac{(c/c_0) e^{-\beta\Delta\varepsilon}}{1 + (c/c_0) e^{-\beta\Delta\varepsilon}}$$ where $\Delta\varepsilon = \varepsilon_b - \varepsilon_{sol}$. $c/c_0 = L/\Omega$

c/c_0 is the concentration of ligand in units of molecules / boxes; more commonly it would be relative to a reference concentration:

$c_0 = 1\,M$ often in chemistry

$c_0 = 1/nm^3$ one box per nm^3 = 'size' of box

Conversion: 1 M is $n_A = 6 \times 10^{23}$ molecules / litre.

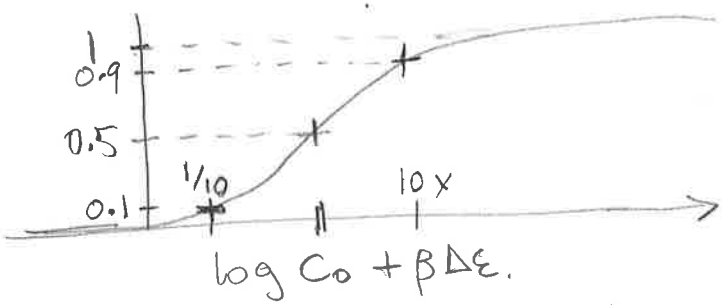
1 litre $= (0.1\,m)^3 = (10^8)^3\, nm^3 = 10^{24}\, nm^3$

$\Rightarrow$ 1 M is 6×10^{23} mols / $10^{24}\, nm^3$ = 0.6 mols / nm^3.

$\Rightarrow c_0 = 1/nm^3$ is 1.6 M similar sized units.

Function $P_{bound}(c)$ is Langmuir Isotherm

slide



$$\frac{c}{c_0} e^{-\beta\Delta\varepsilon} = 1$$

$$c = c_0 e^{+\beta\Delta\varepsilon}$$

$$\log c = \log c_0 + \beta\Delta\varepsilon.$$

Widely occuring "titration" curve. Later we will see other contexts, but recall that 1 pH unit corresponds to 10 x concentration change.

19.02.2015

Ligand - receptor binding is often interesting in the micromolar (μM) range: rare species in cells or drugs finding targets.

50% binding midpoint:

$$c/c_0 = 10^{-6} \qquad c/c_0 e^{-\beta\Delta\varepsilon} = 1$$

$$\Delta\varepsilon = -\ln(10^{-6})\, k_B T = 14\, k_B T$$

This is quite strong binding:
- about 2 H-bonds.
- hydrophobic interaction of an entire C_{18} lipid tail.

- Binding curve represents compromise between entropy and energy (via free energy).
- Note: definition of $\Delta\varepsilon$ and c_0 are coupled by choice of reference state / reservoir.

15. RNA polymerase binding

Seen in central dogma: RNAP

Slides In E. Coli, ~1000 copies, almost all bound to DNA:

Promotor site - specific binding. } $\Delta\varepsilon \sim -2.9 k_B T$

Other sites - inspecific $-8.1 k_B T$ (T7 phage)

Same calculation + binding curve,

$\Delta\varepsilon \sim$ single H-bond, very low level of specificity for sequence of RNAP promotor.

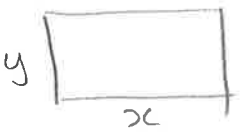
movies Other proteins (promoters etc) are involved.

16. Lagrange Multipliers.

We will use these to understand the Boltzmann distributions.

Mathematical trick to add constraints to an optimisation problem. Example p255.

Maximise area of a rectangle, subject to perimeter = constant:



$A = xy$

$P = 2x + 2y = \text{const.}$

Write $A' = A + \lambda(P - 2x - 2y)$

this has to be optimised wrt the original x, y but also λ, the Lagrange Multiplier.

$$\left.\begin{aligned} \frac{\partial A'}{\partial x} &= y - 2\lambda = 0 \\ \frac{\partial A'}{\partial y} &= x - 2\lambda = 0 \end{aligned}\right\} \quad x = y = 2\lambda.$$

$$\frac{\partial A'}{\partial \lambda} = P - 2x - 2y = 0 = P - 4x \Rightarrow x = y = \frac{P}{4}.$$

17. Shannon Entropy p253

The form of entropy we used before was a derived result: it comes from information theory.

Out of all possible probability distributions, p_i which one is least biased? $\{p_i, E_i, i = 1 \ldots N\}$

$$S = -\sum_1^N p_i \ln p_i \quad \text{Shannon Entropy.}$$

Sometimes called the "Missing Information"

Extremes:

i) p_i all equally likely $p_i = \frac{1}{N}$ $S = \ln N$ max

ii) $p_1 = 1$ $p_2 \cdots p_N = 0$ $S = 0$ min

Case ii) is fully determined, no missing info

iii) $p_1 = 0.5$ $p_2 = 0.5$ $p_3 \cdots p_N = 0$ $S = \ln 2$

To select the least biased prob. dist we need to maximise the entropy.

Constraint I : $\sum_{i=1}^{N} p_i = 1$ normalization

Constraint II : state p_i has energy E_i this is maintained by equilibrium with a reservoir defining the average energy $\langle E \rangle$

$$\sum_{i}^{N} p_i E_i = \langle E \rangle$$

Following Lagrange Multiplier rules λ, β for now are just numbers.

$$S' = -\sum p_i \ln p_i - \lambda\left(\sum p_i - 1\right) - \beta\left(\sum p_i E_i - \langle E \rangle\right)$$

$$\frac{\partial S'}{\partial p_i} = -\ln p_i - \cancel{p_i \frac{1}{p_i}} - \lambda - \beta E_i = 0$$

$$\ln p_i = -1 - \lambda - \beta E_i$$

$$p_i = e^{-1-\lambda-\beta E_i}$$

$$\frac{\partial S'}{\partial \lambda} = \sum_i p_i - 1 = 0 \Rightarrow \sum p_i = 1 = \sum e^{-1-\lambda-\beta E_i}$$

$$\text{So } e^{-1-\lambda} = \frac{1}{\sum_i e^{-\beta E_i}} = \frac{1}{Z}$$

recognise as partition funct (definition)

Substitute into expression for p_i:

$$p_i = e^{-1-\lambda} e^{-\beta E_i} = \frac{e^{-\beta E_i}}{\sum e^{-\beta E_i}}$$

This is the familiar Boltzmann form, except for the detail that β is so far undefined. We will find $\beta = 1/k_B T$ from Constraint II, but we have to look at a known, real system to obtain this : ideal gas.

18. Ideal gas in 1D.

Main result of stat mech. is that the average energy of every degree of freedom is $\frac{1}{2}k_BT$; assuming thermodynamic equilibrium with a reservoir. Ideal gas has no potential energy (non-interacting particles); only degree of freedom is the particle momentum.

Continuum of states, probabability $p(p_x)\,dp_x$.

$$E = \frac{p_x^2}{2m} \qquad p(p_x) = \frac{e^{-\beta(p_x^2/2m)}}{\sum_{\text{states}} e^{-\beta(p_x^2/2m)}}$$

$$\sum_{\text{states}} \rightarrow \int dp_x = \int_{-\infty}^{\infty} e^{-\beta(p_x^2/2m)}\,dp_x = \sqrt{\frac{2m\pi}{\beta}}$$

Connect to stat mech by $\langle E\rangle = \frac{1}{2}k_BT$

$$\langle E\rangle = \int E\,p(p_x)\,p_x = \int \frac{p_x^2}{2m} e^{-\beta(p_x^2/2m)}\,dp_x \Big/ \sqrt{2m\pi/\beta}$$

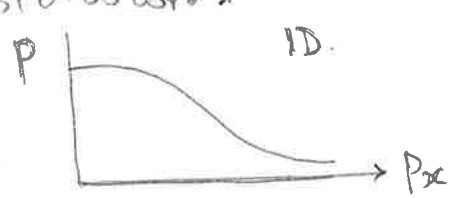
Put $\alpha = \beta/2m$.

$$\langle E\rangle = \alpha/\beta \int p_x^2 e^{-\alpha p_x^2}\,dp_x \Big/ \sqrt{\pi/\alpha}.$$

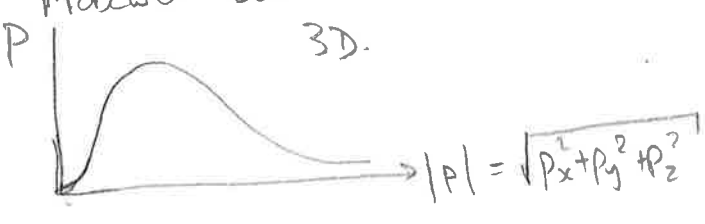
$$= \alpha/\beta \cdot \sqrt{\alpha/\pi}\,\frac{-\partial}{\partial\alpha} \underbrace{\int e^{-\alpha p_x^2}\,dp_x}_{\frac{\partial}{\partial\alpha}\sqrt{\frac{\pi}{\alpha}} = \frac{-1}{2}\sqrt{\pi}\,\alpha^{-3/2}}.$$

$$= \frac{1}{2\beta} = \frac{1}{2}k_BT \quad \Rightarrow \quad \beta = 1/k_BT$$

We have determined the Lagrange multiplier, β. But retain $\beta = 1/k_BT$ as a generally useful substitution.



Maxwell-Boltzmann dist.



19. Ideal Solution

Dilute solution of non-interacting solutes, N_S

slides

$$W = \frac{\Omega!}{N!\,(\Omega - N)!} = \frac{(N_{H_2O} + N_S)!}{N_{H_2O}!\; N_S!}$$ total no. of configurations.

Use Stirling formula, $\ln N! = N \ln N$

$$S_{mix} = k_B \ln W = k_B \Big[(N_{H_2O} + N_S) \ln (N_{H_2O} + N_S) - N_{H_2O} \ln N_{H_2O} - N_S \ln N_S \Big]$$

$$= -k_B \left[N_{H_2O} \ln \frac{N_{H_2O}}{N_{H_2O} + N_S} + N_S \ln \frac{N_S}{N_{H_2O} + N_S} \right]$$

Dilute solution has $N_{H_2O} \gg N_S$:

$$\ln \frac{N_{H_2O}}{N_{H_2O} + N_S} \simeq \ln \left(1 - \frac{N_S}{N_{H_2O}}\right) \approx -\frac{N_S}{N_{H_2O}} \qquad [e^x = 1 + x]$$

$$\Rightarrow S_{mix} = k_B N_S \left[1 - \ln \frac{N_S}{N_{H_2O}} \right] = k_B N_S \left[1 - \ln N_S + \ln N_{H_2O} \right]$$

General expression for free energy of solution:

$$G_{tot} = N_{H_2O}\, \mu^0 + N_S \varepsilon_S - T S_{mix}$$

μ^0: chemical potential of solvent. ε_S: energy to embed each solute.

Hence, chem. pot. of the solute,

$$\mu_S = \left(\frac{\partial G_{tot}}{\partial N_S} \right) = \varepsilon_S - k_B T \left[1 - \ln N_S + \ln N_{H_2O} - N_S \frac{1}{N_S} \right]$$

$$= \varepsilon_S + k_B T \ln \frac{N_S}{N_{H_2O}} = \varepsilon_S + k_B T \ln \frac{C}{C_0}$$

Where C_0 is a reference concentration, eg 1 M.

General result that chem. pot. varies as the logarithm of the concentration

20. Osmotic Pressure

Directly following from above when we consider the H_2O part of the expression for G_{tot}.

Concentrated solutions compete with dilute ones for solvent molecules to increase entropy.

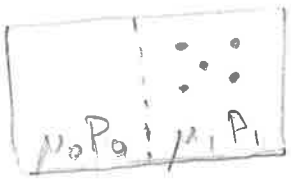
E. coli membrane is permeable to H_2O.

Gut bacteria are excreted into more dilute solution (river; toilet bowl) = osmotic shock.

To maintain integrity (high concentrations of chem species inside cell wall) bacteria actively pump against the "osmotic pressure".

$$\mu_{H_2O} = \frac{\partial G_{tot}}{\partial N_{H_2O}} = \mu^0 - k_B T N_s \frac{1}{N_{H_2O}}$$

If we consider the change in μ^0 to be due to a thermodynamic pressure:



$$\mu_1^0 = \mu_0^0 + \left(\frac{\partial \mu}{\partial P}\right)(P_1 - P_0)$$

$$\| \quad \nu \text{ (volume/molecule) per water}$$

from thermodynamic relation

P and V are conjugate thermo. variables

So we can assign the concentration difference to an effective pressure: put $\mu_{H_2O} = \mu_0^0$

$$\nu (P_1 - P_0) = + k_B T \frac{N_s}{N_{H_2O}} \rightarrow \text{Multi by } N_{H_2O}$$

$$\Rightarrow P_1 - P_0 = k_B T \frac{N_s}{V} \quad N_{H_2O}\nu = \text{volume of container.}$$

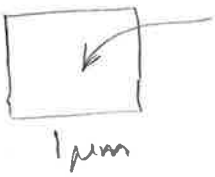
$P_1 - P_0$: osmotic pressure

$\frac{N_s}{V}$: concentration of solute

van't Hoff formula.

21. Examples.

i) O.P. inside an E. coli



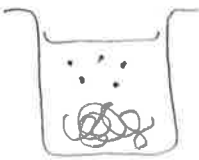
6×10^7 molecules $= N_S$
$V = 1\mu m^3 = 10^9\ nm^3$
$k_B T = 4\ pN \cdot nm$

$\Big\}$ $P = 0.24\ pN/nm^2$

1 atmosphere $\simeq 10^5 \underbrace{N/m^2}_{Pa} = \frac{10^5 \times 10^{12}}{(10^9)^2} = 0.1\ pN/nm^2$

ii) DNA condensation

DNA + polyamine (cation)



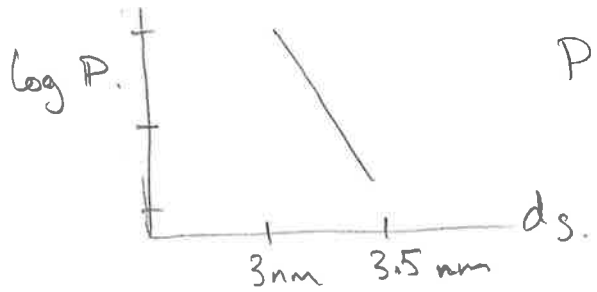
Spermine	$(CH_2)_{10}(NH)_4$
spermidine	$(CH_2)_7(NH)_3$
putrescine	$(CH_2)_4(NH)_2$

condensing agents.

PEG = poly ethylene glycol is a water soluble polymer that does not mix with condensate. But they share the solvent and compete.

Expt: vary: [PEG], hence P_{osm}.
observe: density of condensed DNA.
spacing of helices

slides.



$P \propto e^{-ds/c}$.