Entropy and entropic forces

Focus question

- Biological question: if energy is always conserved, how can some devices be more efficient than others?
- Physical idea: Order controls when energy can do useful work. Order is not conserved.

Recap thermal physics

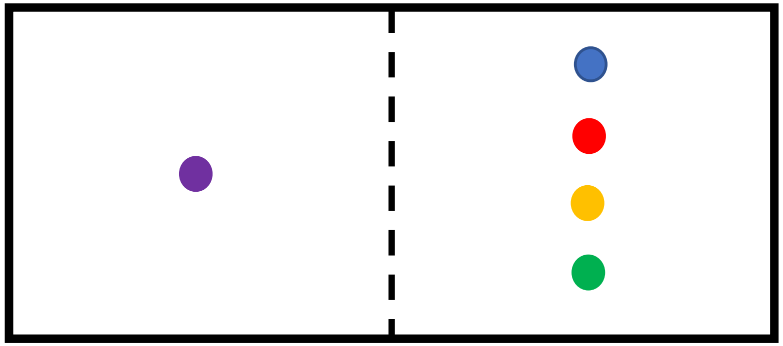
- Micro- and macro states
- Multiplicity
- Fundamental assumption of statistical mechanics
- Equilibrium from probability
- Entropy and equilibrium conditions
- Thermodynamic identity
- Mixtures and chemical potential
- Helmholtz and Gibbs free energy
- Boltzmann statistics
- ---
- Biological examples
- Quiz

Microstates and macrostates

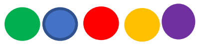
- What is the most likely outcome of tossing 3 coins?
- Microstates: state of all coins
  - heads: si=1, tails: si=0
  - all microstates are equally likely
- Macrostate: sum of states
  - $n=\Sigma_i s_i$ (= 0,1,2,3)
- Which is the most likely macrostate
  - 8 = 2^3 possible microstates
  - Probabilities: n=0: P=1/8
    n=1: P=4/8
    n=2: P=4/8
    n=3: P=1/8

i: 1	2	3	n
0	0	0	0
1	0	0	1
0	1	0	1
0	0	1	1
1	1	0	2
1	0	1	2
0	1	1	2
1	1	1	3

Microstates and macrostates



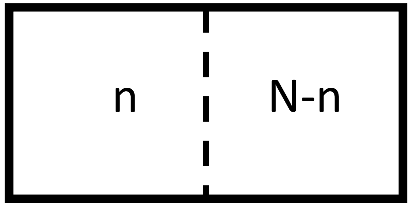
- Box with left and right side
- Example: $N = 5$
- Particles can be distinguished (i=1, 2,.. 5)
- Particle state s_i:
  - left: $s_i=1$
  - right: $s_i=0$
- Macrostates $n=\Sigma_i s_i$ (= 0,1,2, ..5)
- List the possible microstates of macrostate n=1



- 00001
- 00010
- 00100
- 01000
- 10000

5 microstates => multiplicity $\boldsymbol{\Omega}(n,N)$ of macrostate n=1 is $\boldsymbol{\Omega}(1,5) = 5$

Multiplicity of macrostates



n=0	n=1	n=2	n=3	n=4	n=5
00000	00001	00011	11100	11110	11111
	00010	00101	11010	11101	
	00100	01001	10110	11011	
	01000	10001	01110	10111	
	10000	00110	11001	01111	
		01010	10101		
		01100	10011		
		10010	01101		
		10100	01011		
		11000	00111		
Ω(0,5)=1	**Ω**(0,5)=5	**Ω**(0,5)=10	**Ω**(0,5)=10	**Ω**(4,5)=5	**Ω**(5,5)=1

General formula for multiplicity: $\Omega(n,N)=\frac{N!}{(N-n)!n!}$ $\Omega(2,5)=\frac{5!}{3!2!}=10$

Number of possible microstates: $\Omega_t=\sum_{n=0}^{5}\Omega(n)=32(=2^5)$

Probability of macrostates: $\mathrm{P(n,N)}=\Omega(n,N)/2^N=\frac{2^{-N}N!}{(N-n)!n!}$

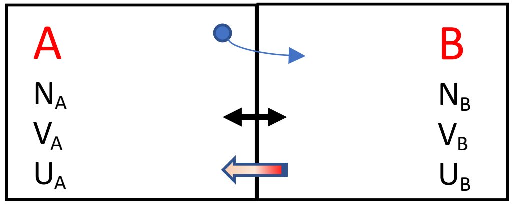
Fundament of statistical mechanics

Fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all accessible microstates are equally probable.

An isolated system will evolve towards the most probable state = macrostate with the highest multiplicity. We call this the equilibrium state.

Equilibrium between two systems

- $N=N_A+N_B$, $V=V_A+V_B$, $U=U_A+U_B$, all (N,V,U) constant
- Can vary one of the three $\alpha \in (N, V, U)$,
  - keeping the other 2 constant
  - keep total constant: $\alpha = \alpha_A + \alpha_B = \text{const.}$
- Multiplicity $\Omega_{tot} = \Omega_A \Omega_B$ is maximum
  - = most likely state
  - = equilibrium state



System: can contain “anything”

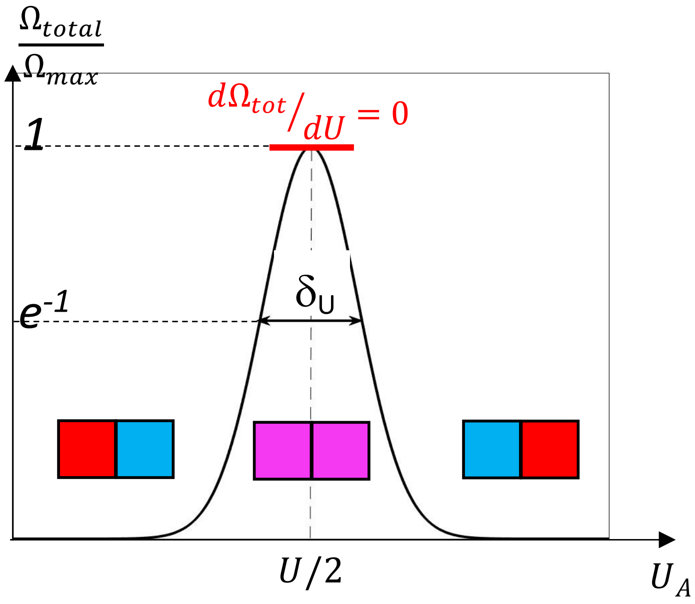
maximum when $\frac{\partial \Omega_{tot}}{\partial \alpha_A} = 0$

$$\frac{\partial(\Omega_A\Omega_B)}{\partial \alpha_A} = \Omega_A \frac{\partial \Omega_B}{\partial \alpha_A} + \Omega_B \frac{\partial \Omega_A}{\partial \alpha_A} = 0$$

$d\alpha_A = -d\alpha_B$

$$\frac{-1}{\Omega_B}\frac{\partial \Omega_B}{\partial \alpha_B} + \frac{1}{\Omega_A}\frac{\partial \Omega_A}{\partial \alpha_A} = 0$$

Equilibrium condition: $$\frac{\partial \ln \Omega_B}{\partial \alpha_B} = \frac{\partial \ln \Omega_A}{\partial \alpha_A}$$



Boltzmann’s Entropy

$$S = k \ln \Omega$$

Relates

- the number of **microstates** (multiplicity) and
- the thermodynamic (**macroscopic**) state of the system

Equilibrium condition: $$\frac{\partial \ln \Omega_B}{\partial q_B} = \frac{\partial \ln \Omega_A}{\partial q_A}$$

$$\frac{\partial S_A}{\partial q_A} = \frac{\partial S_B}{\partial q_B}$$

All systems move towards most probable states = equilibrium

$$\Delta S = k \ln \frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}}$$

Second law of thermodynamics: $\Delta S_{\text{tot}} \geq 0$

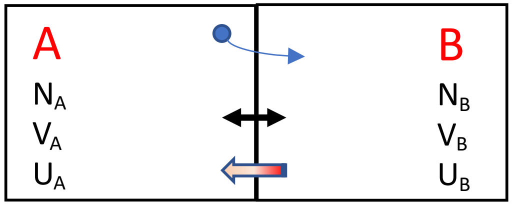
All real processes are irreversible

Equilibrium between two systems

- $N=N_A+N_B$, $V=V_A+V_B$, $U=U_A+U_B$, all (N,V,U) constant
- Can vary one of the three $\alpha \in (N,V,U)$,
  - keeping the other 2 constant
  - keep total constant: $\alpha = \alpha_A + \alpha_B =$ const.
- $S_{tot} = S_A + S_B$ is maximum in equilibrium

Equilibrium criterium:

$$\frac{\partial S_B}{\partial \alpha_B} = \frac{\partial S_A}{\partial \alpha_A}$$



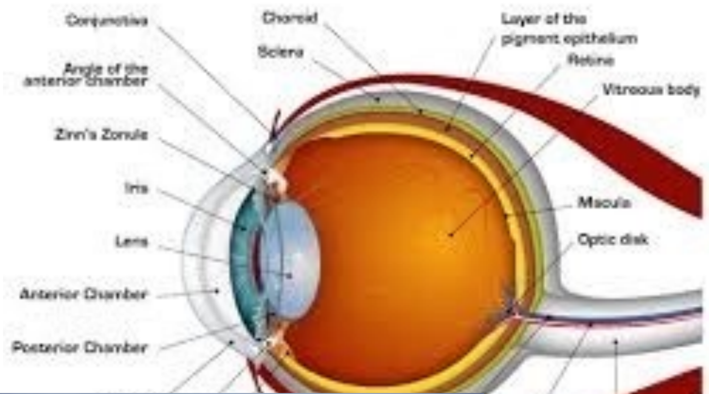
Entropy: $S = k \ln \Omega(N,V,U)$

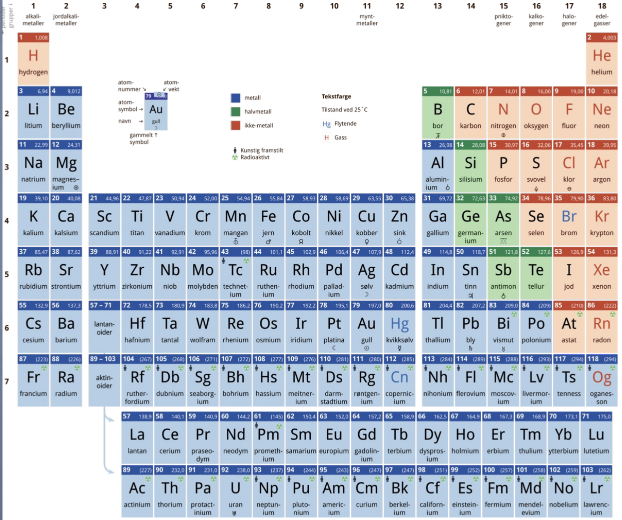
Thermal equilibrium: $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$, $\quad \frac{1}{T} \equiv (\frac{\partial S}{\partial U})_{N,V}$, $\quad \frac{[S]}{[U]} = \frac{J\,K^{-1}}{J}$

Mechanical equilibrium: $\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$, $\quad P \equiv T(\frac{\partial S}{\partial V})_{N,U}$, $\quad \frac{[P]}{[T]} = \frac{J}{m^3 K}$

Chemical equilibrium: $\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$, $\quad \mu \equiv -T(\frac{\partial S}{\partial N})_{U,V}$ $\quad \frac{[\mu]}{[T]} = \frac{J}{K}$

Why do your eyes hurt in fresh water?





	1 alkalimetaller	2 jordalkalimetaller	3	4	5	6	7	8	9	10	11 myntmetaller	12	13	14	15 pniktogener	16 kalkogener	17 halogener	18 edelgasser
1	1 1,008 H hydrogen																	2 4,003 He helium
2	3 6,94 Li litium	4 9,012 Be beryllium											5 10,81 B bor	6 12,01 C karbon	7 14,01 N nitrogen	8 16,00 O oksygen	9 19,00 F fluor	10 20,18 Ne neon
3	11 22,99 Na natrium	12 24,31 Mg magnesium											13 26,98 Al aluminium	14 28,08 Si silisium	15 30,97 P fosfor	16 32,06 S svovel	17 35,45 Cl klor	18 39,95 Ar argon
4	19 39,10 K kalium	20 40,08 Ca kalsium	21 44,96 Sc scandium	22 47,87 Ti titan	23 50,94 V vanadium	24 52,00 Cr krom	25 54,94 Mn mangan	26 55,84 Fe jern	27 58,93 Co kobolt	28 58,69 Ni nikkel	29 63,55 Cu kobber	30 65,38 Zn sink	31 69,72 Ga gallium	32 72,63 Ge germanium	33 74,92 As arsen	34 78,96 Se selen	35 79,90 Br brom	36 83,80 Kr krypton
5	37 85,47 Rb rubidium	38 87,62 Sr strontium	39 88,91 Y yttrium	40 91,22 Zr zirkonium	41 92,91 Nb niob	42 95,96 Mo molybden	43 (98) Tc technetium	44 101,1 Ru ruthenium	45 102,9 Rh rhodium	46 106,4 Pd palladium	47 107,9 Ag sølv	48 112,4 Cd kadmium	49 114,8 In indium	50 118,7 Sn tinn	51 121,8 Sb antimon	52 127,6 Te tellur	53 126,9 I jod	54 131,3 Xe xenon
6	55 132,9 Cs cesium	56 137,3 Ba barium	57 – 71 lantanoider	72 178,5 Hf hafnium	73 180,9 Ta tantal	74 183,8 W wolfram	75 186,2 Re rhenium	76 190,2 Os osmium	77 192,2 Ir iridium	78 195,1 Pt platina	79 197,0 Au gull	80 200,6 Hg kvikksølv	81 204,4 Tl thallium	82 207,2 Pb bly	83 209,0 Bi vismut	84 (209) Po polonium	85 (210) At astat	86 (222) Rn radon
7	87 (223) Fr francium	88 (226) Ra radium	89 – 103 aktinoider	104 (267) Rf rutherfordium	105 (268) Db dubnium	106 (271) Sg seaborgium	107 (272) Bh bohrium	108 (277) Hs hassium	109 (276) Mt meitnerium	110 (281) Ds darmstadtium	111 (280) Rg røntgenium	112 (285) Cn copernicium	113 (284) Nh nihonium	114 (289) Fl flerovium	115 (288) Mc moscovium	116 (293) Lv livermorium	117 (294) Ts tenness	118 (294) Og oganesson
				57 138,9 La lantan	58 140,1 Ce cerium	59 140,9 Pr praseodym	60 144,2 Nd neodym	61 (145) Pm promethium	62 150,4 Sm samarium	63 152,0 Eu europium	64 157,2 Gd gadolinium	65 158,9 Tb terbium	66 162,5 Dy dysprosium	67 164,9 Ho holmium	68 167,3 Er erbium	69 168,9 Tm thulium	70 173,1 Yb ytterbium	71 175,0 Lu lutetium
				89 (227) Ac actinium	90 232,0 Th thorium	91 231,0 Pa protactinium	92 238,0 U uran	93 (237) Np neptunium	94 (244) Pu plutonium	95 (243) Am americium	96 (247) Cm curium	97 (247) Bk berkelium	98 (251) Cf californium	99 (252) Es einsteinium	100 (257) Fm fermium	101 (258) Md mendelevium	102 (259) No nobelium	103 (262) Lr lawrencium

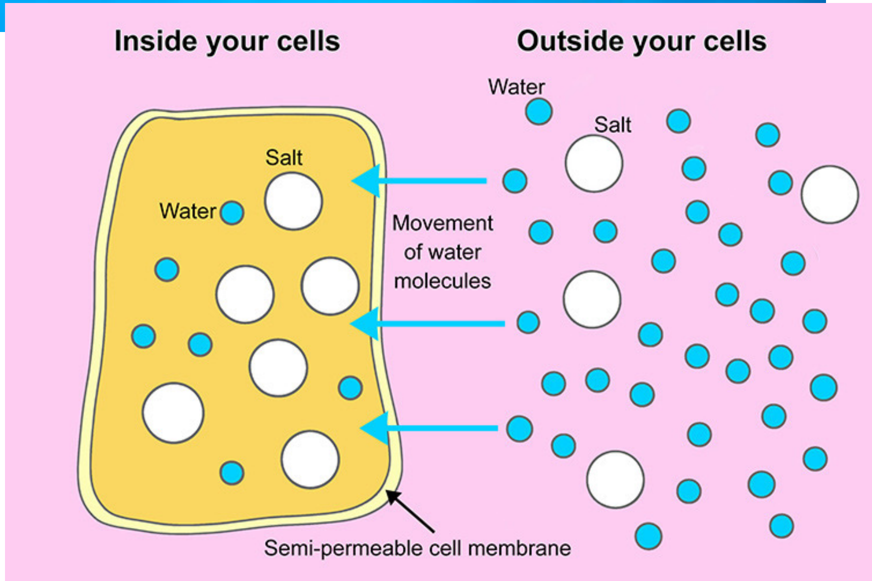
grupper → perioder ↓

atomnummer ↘ 79 ↙ atomvekt
atomsymbol → Au
navn → gull
gammelt ↑ symbol

🟦 metall
🟩 halvmetall
🟥 ikke-metall

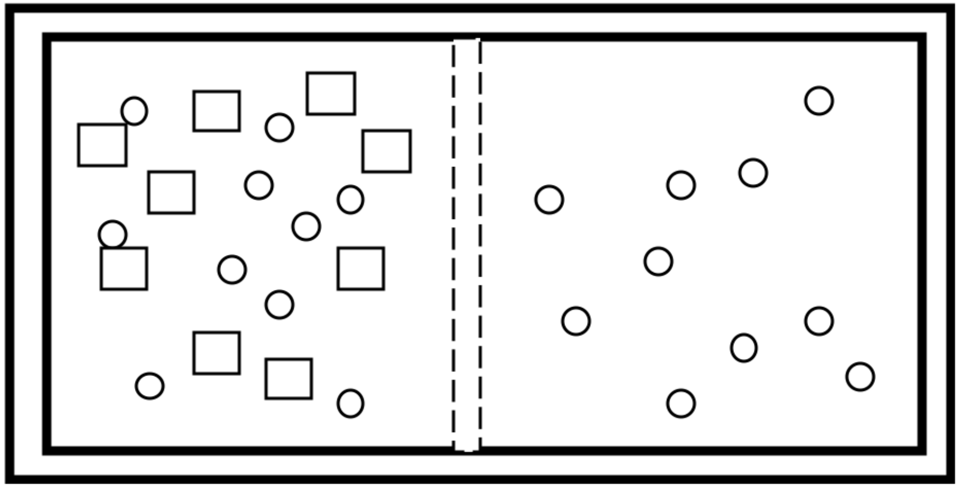
Kunstig framstilt
Radioaktivt

Tekstfarge
Tilstand ved 25 ˚C
Hg Flytende
H Gass



Chemical equilibrium

The two halves of a sealed container are separated by a fixed semi-permeable membrane. There are two species of molecules in the container, C (cubes) and D(disks). The membrane is permeable to the disks only. Each half of this system has two different chemical potentials, one for disks and one for cubes: μ_D and μ_C.

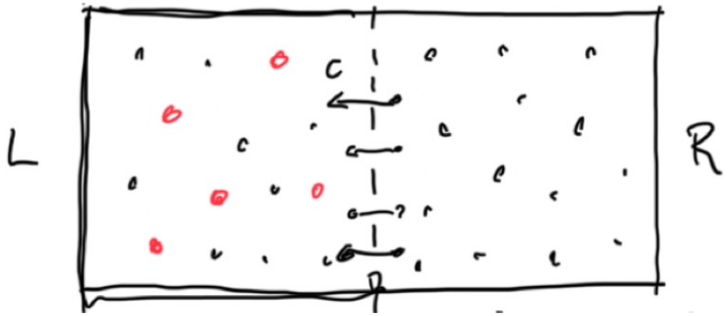


Given the constraints imposed, does this system appear to be in equilibrium? (Hint: How do the μ_C's on the right and left compare? What about the μ_D's?)

A) Yes, it looks close to equilibrium

B) No, it is obviously way out of equilibrium, so the system will look different a short time later.

Osmosis: ideal gas model

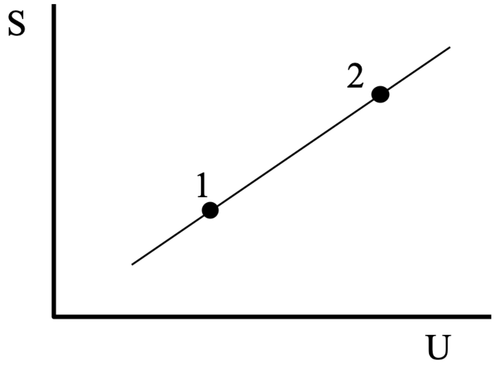


- Fixed volume V, $V_L=V_R=V/2$
- Semipermeable membrane separates volumes
- Black (1, solvent, water) can penetrate
- Red (2, solute) stuck
- $N_2 \ll N_1$

- How will water particles distribute?
  - Type 1: Ω max when $N_{1,L}=N_{1,R}$
  - dilute: ideal solution => $P_{1,L}=P_{1,R}$
- What is the effect of N_2 excess particles on right side?
  - Dilute: red particles do not interact => Ideal gas
  - Solute ideal gas: $P_2V_L=N_2kT$
  - $\Delta P = P_L - P_R = P_2 = \frac{N_2}{V_L} kT$
- Counting: N_2 is the number of free, ideal gas particles
  - $\Delta P = \frac{iN_2'}{V_L} kT = ic_2RT$
    - i = dissociation factor
    - N_2' = number of dry substance particles

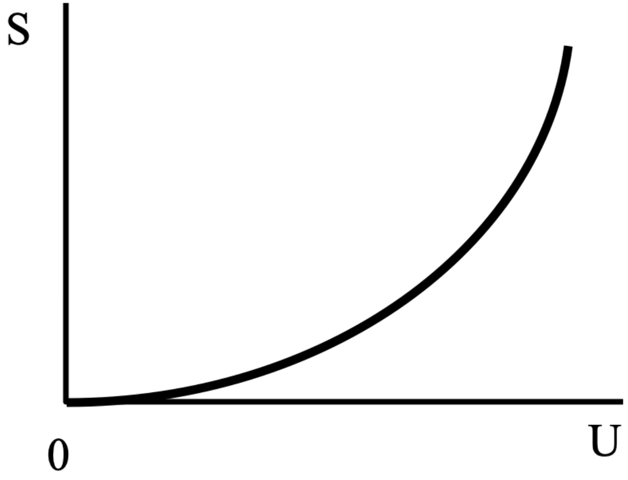
Temperature

Consider the following graph of entropy S vs. energy U for a particular system. How does the temperature at point 1 compare to the temperature at point 2?



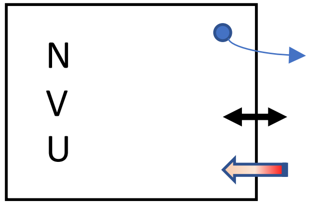
A) $T_1 = T_2$ B) $T_1 > T_2$ C) $T_1 < T_2$

According to the following graph of entropy vs. energy, the temperature of the system, in the limit U → 0, is approaching…



A) zero B) a non-zero, finite constant
C) infinity D) a negative value(!)

Thermodynamic identity



- Change in entropy due to *energy, volume, particle number*

  has a total differential:

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

- Use definitions: $\frac{1}{T} \equiv (\frac{\partial S}{\partial U})_{N,V}$, $P \equiv T(\frac{\partial S}{\partial V})_{N,U}$, $\mu \equiv -T(\frac{\partial S}{\partial N})_{U,V}$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

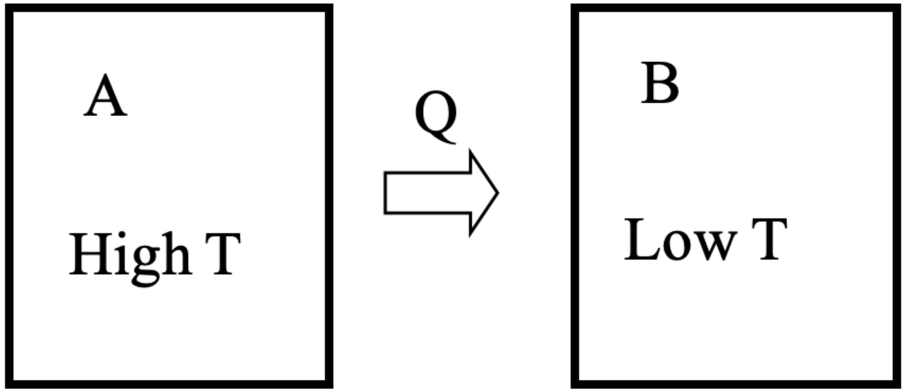
- => Thermodynamic identity for $U(S,V,N)$

$$dU = TdS - PdV + \mu dN$$

- The *thermodynamic identity* holds *true* for any infinitesimal change in a system

Entropy and heat

Two systems, A and B, initially at different temperatures with $T_A > T_B$, are brought into thermal contact. It is observed that some amount of heat flows from a system A to system B.



What happened to $S_{tot} = S_A + S_B$ as a result of the heat transfer?

A) S_{tot} increased B) S_{tot} decreased C) S_{tot} remained constant

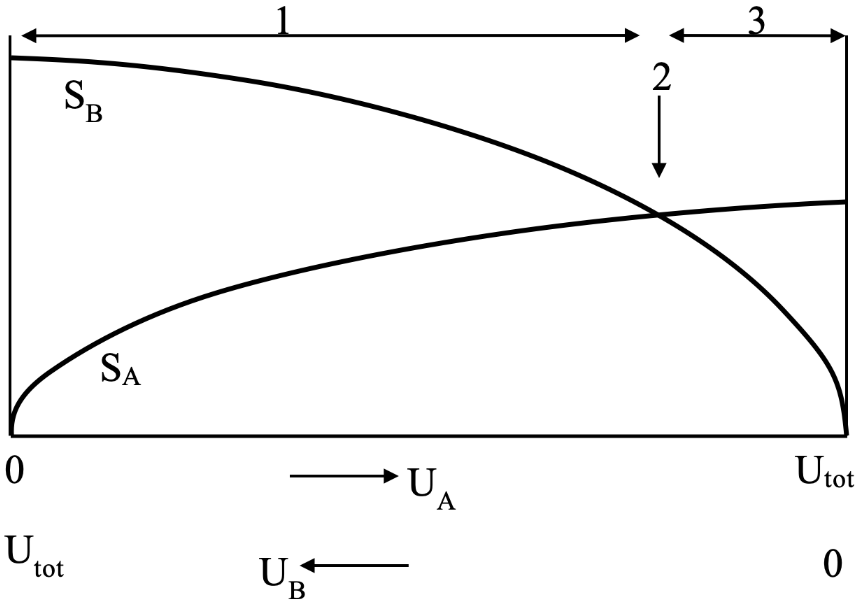
As a result of this heat flow, which is larger, $|\Delta S_A|$ or $|\Delta S_B|$?

A) $|\Delta S_A|$ B) $|\Delta S_B|$ C) Neither, $|\Delta S_A|=|\Delta S_B|$

$$dU = dQ + dW = TdS - PdV, \quad dS=dQ/T$$

Entropy and internal energy

The entropies vs. energy for two systems in thermal contact are shown in the graph. $U_A + U_B = U_{tot}$ =fixed



Where on the graph is the equilibrium of U_A?

A) somewhere in region 1

B) at point 2, where the curves cross

C) somewhere in region 2

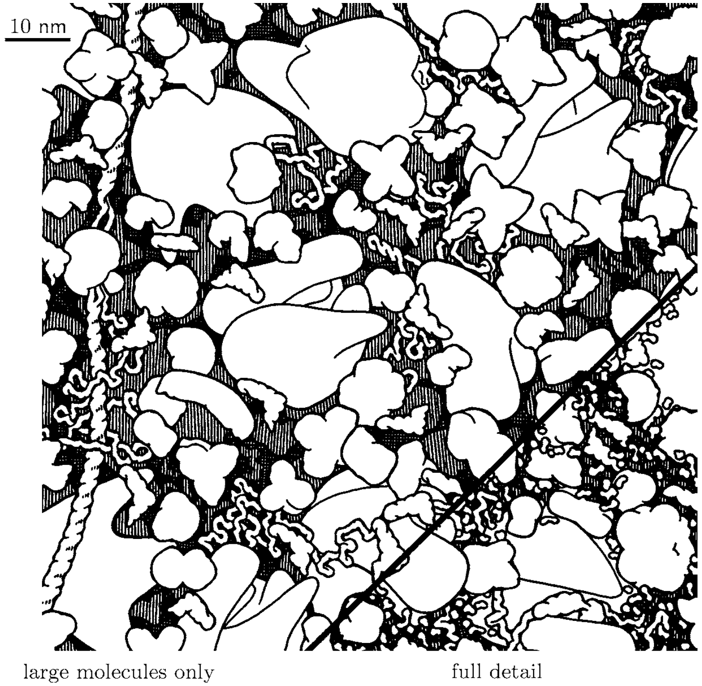
In region 3, which system is hotter?

A) System A is hotter.

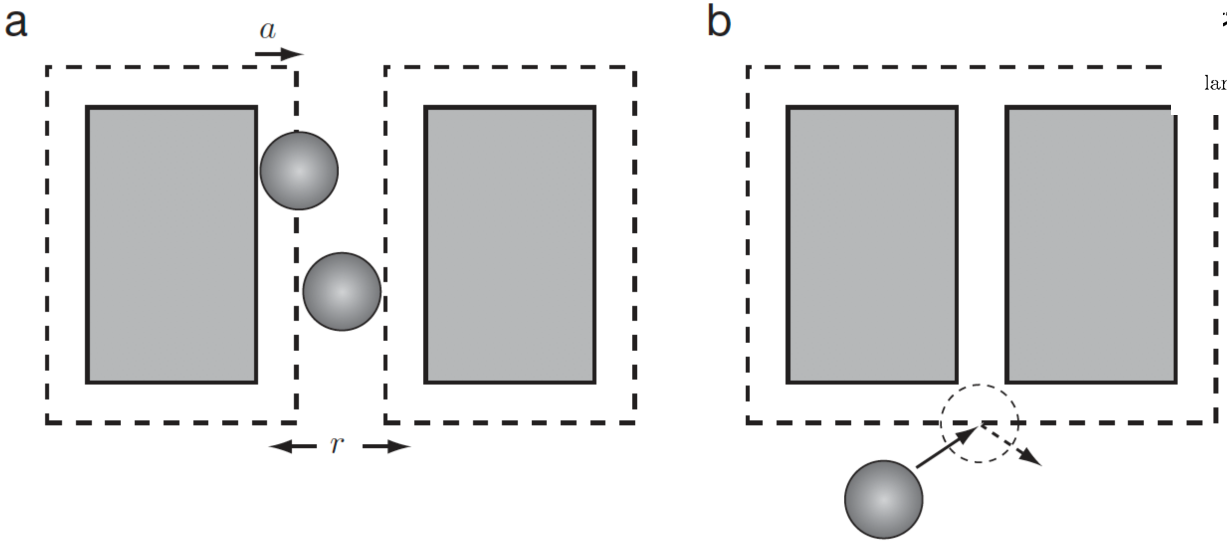
B) System B is hotter.

C) Impossible to tell.

Depletion pressure



“...eliminating the depletion zone would increase the entropy and lower the free energy.”



particles into contact. The pressure is the change of free energy per change of volume (Equation 7.2). As we bring the surfaces into contact, the volume of the depletion zone between them shrinks from $2aA$ to zero. Multiplying this change by the pressure drop $ck_\mathrm{B}T$ in the zone gives

$$(\Delta F)/A = ck_\mathrm{B}T \times 2a. \tag{7.10}$$

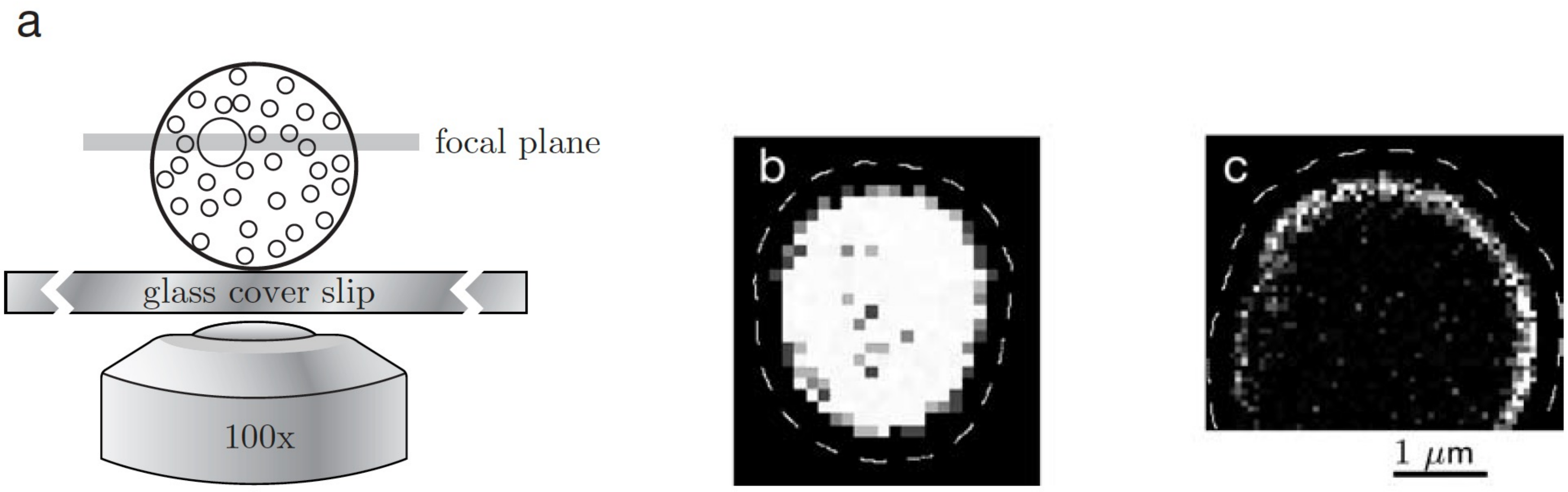


Figure 7.4: (Schematic; experimental data.) (a) Experimental setup of an experiment to measure depletion interactions. A microscope looks at the central plane of a rigid vesicle containing a polystyrene sphere (the "sheep") of radius 0.237 μm. (b) Histogram of the measured location of the large sphere's center over 2000 observations. The solvent in this case contained no smaller objects. Instead of displaying frequencies by the height of bars, the figure instead shows how often the sphere was found in each location by the color of the spot at that position; lighter colors denote places where the sphere was more often found. The dashed line represents the actual edge of the vesicle; the sphere can come no closer than its radius. (c) As (b), but this time the vesicle contained a suspension of smaller, 0.04 μm spheres ("sheepdogs") with volume fraction about 30%. Though the "sheepdogs" are not optically visible, they cause the "sheep" to spend most of its time clinging to the wall of the chamber. [Digital image kindly supplied by A. Dinsmore; see Dinsmore et al., 1998.]

Interpretation and use of the potentials, “free energy”

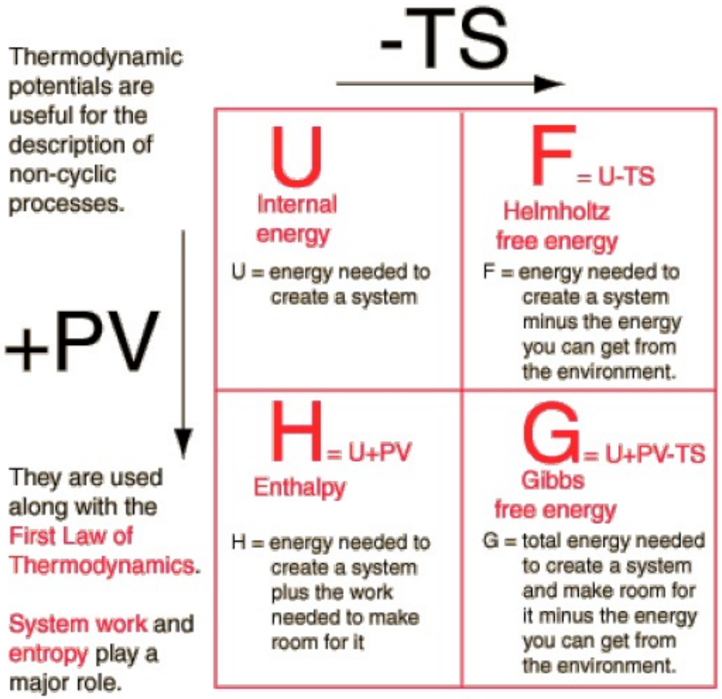
The potentials represent the energy necessary to create the system from nothing, keeping the natural variables (of that potential) constant.

Or, conversely: The energy that is “free” to be used when the system is annihilated.

- V constant: U – energy to create a system
- P constant: H – energy to create a system and the work to make space for it
  - Normal conditions in a lab
  - Enthalpy of reaction, formation, melting, vaporization, mixing...
  - Measured and tabulated for most substances!
- T constant: F – energy to create a system minus the heat from the surroundings.
- P, T constant: G – energy to create a system and the work to make space for it minus the heat from the surroundings.
  - Measured and tabulated for many substances!
  - A process is spontaneous when the Gibbs free energy of the reactants is larger than that of the products.

Thermodynamic potentials

- Internal energy: $U = U(S, V, N)$
- Enthalpy: $H \equiv U + PV = H(S, P, N)$
- Helmholtz: $F \equiv U - TS = F(T, V, N)$
- Gibbs: $G \equiv U - TS + PV = G(T, P, N)$
- Grand: $\Phi \equiv U - TS - \mu N = \phi(V, T, \mu)$



Thermodynamic potentials are useful for the description of non-cyclic processes.

They are used along with the First Law of Thermodynamics.

System work and entropy play a major role.

U = energy needed to create a system

F = energy needed to create a system minus the energy you can get from the environment.

H = energy needed to create a system plus the work needed to make room for it

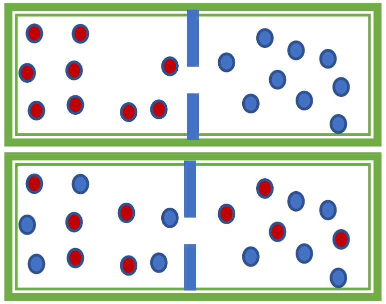
G = total energy needed to create a system and make room for it minus the energy you can get from the environment.

What are the fundamental principles of equilibrium?

Mechanics
$\Sigma_i F_i = -\Sigma_i \nabla U_i = 0$
minimize energy

Thermodynamics
maximize entropy
(minimize F or G)

particle number



identical, coloured, *dU=0*

dS>0, $\mu_1 = \mu_2$

The two principles are related by TDI

$$dU = TdS - PdV + \mu dN$$
$$dH = TdS + VdP + \mu dN$$
$$dF = -SdT - PdV + \mu dN$$
$$dG = -SdT + VdP + \mu dN$$
$$S = -\left(\frac{\partial G}{\partial T}\right)_{N,P} = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$

What is the chemical potential?

From

$$dU = TdS - PdV + \mu dN$$
$$dH = TdS + VdP + \mu dN$$
$$dF = -SdT - PdV + \mu dN$$
$$dG = -SdT + VdP + \mu dN$$

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial H}{\partial N}\right)_{S,P} = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Most useful definitions

F=U-TS	energy to create a system minus the energy from the environment
G=U+PV-TS	energy to create a system and make room for it minus the energy from the environment

OK, but how do we calculate or measure this?

Chemical potential of ideal gas

(thermodynamics)

Ideal gas: $PV = NkT$

expression for μ: $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

We need some relation between energies, *G* or *F* and *P,V,N,T*

TDI (*F*): $dF = -SdT - PdV + \mu dN$

TDI (*G*): $dG = -SdT + VdP + \mu dN$

=> at constant T & N: $dG = VdP, \quad dF = -PdV$

$$dG = VdP = \frac{NkT}{P}dP$$

$$\int dG = G - G_0 = NkT\int\frac{dP}{P} = NkTln\frac{P}{P_0}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \mu_0 + kTln\frac{P}{P_0}$$

$$dF = -PdV = \frac{NkT}{V}dV$$

$$\int dF = F - F_0 = -NkT\int\frac{dV}{V} = -NkTln\frac{V}{V_0}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu_0 - kTln\frac{V}{V_0} = \mu_0 + kTln\frac{P}{P_0},$$

$$\left(\frac{V}{V_0} = \frac{P_0}{P}\right)$$

Chemical potential of ideal gas

(stat. mech. of quantum ideal gas)

Helmholtz free energy of quantum ideal gas:

$$F_N(T,V) = -NkT\left[ln\left(\frac{V}{Nv_Q}\right)+1\right]$$

The chemical potential $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT\left[ln\left(\frac{V}{Nv_Q}\right)+1\right] + NkT\left[\frac{dlnN}{dN}\right]$$

$$\mu = -kTln\left(\frac{V}{V_0}\right),\ V_0 = Nv_Q, \qquad n_Q = v_Q^{-1}$$

$$\mu = kTln\left(\frac{n}{n_Q}\right), \quad n = \frac{N}{V}$$

$$\mu = kTln\left(\frac{P}{P_0}\right), \quad P_0 = n_QkT$$

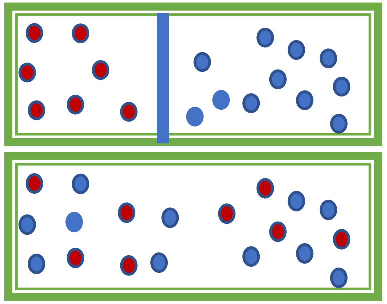
Chemical potential of ideal mixtures

$V_1 \qquad V_2$

$N_1 \qquad N_2$

$T_1 = T_2$

$P_1 = P_2 \quad \Rightarrow \quad \mu_1^0(P,T) = \mu_2^0(P,T)$



$$\mu = \mu_0 - kTln\frac{V}{V_0}$$

Remove wall: $V=V_1+V_2$

Ideal mixture:

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1+N_2}{V_1+V_2}$$

is independent of mixture composition

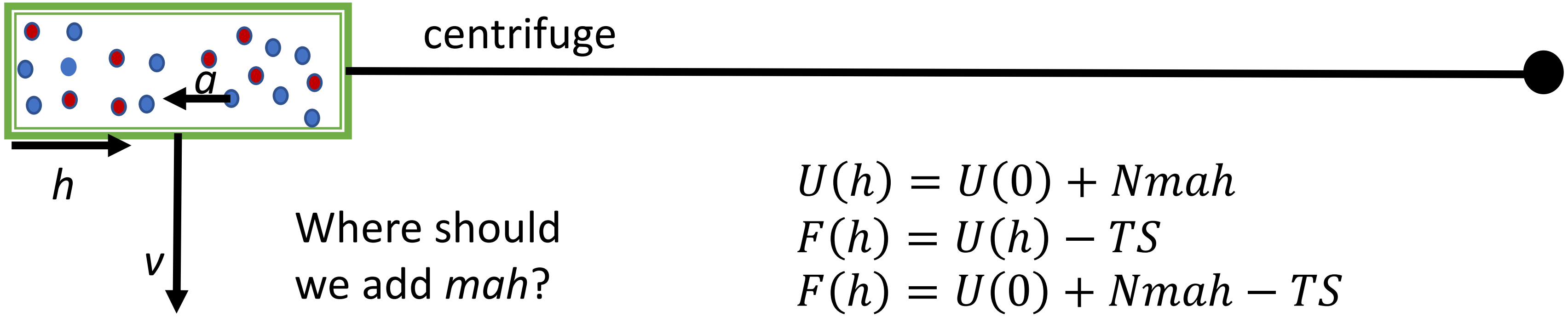
$$\Delta\mu_1 = -kTln\frac{V_1+V_2}{V_1}$$

$$\frac{V_1+V_2}{V_1} = \frac{N_1+N_2}{N_1} = \frac{1}{x_1}$$

$$\Delta\mu_1 = kTlnx_1$$

$$\mu_i(P,T,x_i) = \mu_i^0(P,T) + kTlnx_i$$

Potential energy and the chemical potential



Where should we add *mah*?

$$U(h) = U(0) + Nmah$$
$$F(h) = U(h) - TS$$
$$F(h) = U(0) + Nmah - TS$$
$$F(h) = F(0) + Nmah$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu(0) + mah$$
$$\mu_{tot} = \mu_{int} + \mu_{ext}$$

Barometric pressure: Can we use this to calculate *p(z)*?

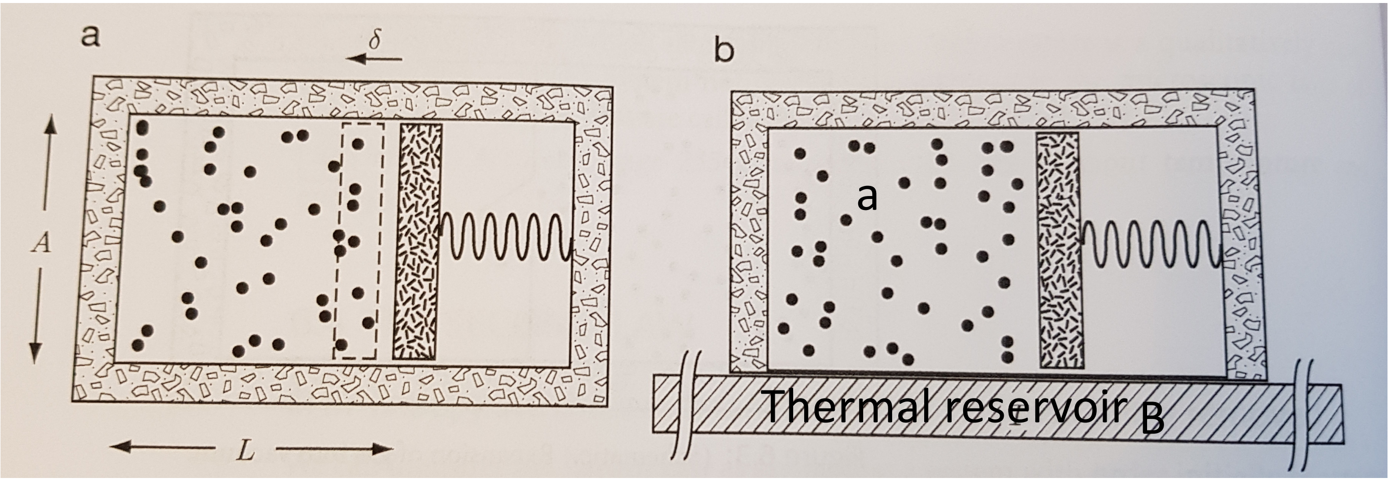
equilibrium: $\mu(z) = \mu_0 = \mu_0 + kTln\frac{P(z)}{P_0} + mgz$

=> $\frac{P(z)}{P_0} = e^{-mgz/kT} = e^{-z/z_c}$

$z_c = kT/mg$

Nitrogen (*m*=28) z_c=8.5km, Oxygen (*m*=32) z_c = 7.4 km, Mount Everest: *P = 0.37 P(0)*

Open systems



Isolated system (left)

First law $\Delta U = Q + W = T\Delta S - P\Delta V$

Adiabatic compression: $Q = 0$

$\Delta V < 0, \quad \Delta N = 0, \quad \Delta U = ?$

Heat: $Q = T\Delta S = 0$

$$S(U,V,N) = k\left[N\ln V + \frac{3N}{2}\ln U + f(N)\right]$$

Entropy: $\Delta S = k\left[N\ln\frac{V_2}{V_1} + \frac{3N}{2}\ln\frac{U_2}{U_1}\right] = 0$

$$\frac{3}{2}\ln\frac{U_2}{U_1} = -\ln\frac{V_2}{V_1}$$

$\frac{U_2}{U_1} = \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{2/3} > 1$ => **heating**

With thermal reservoir:

(NVT) constant instead of (NVU) constant

$T_2 = T_1$ => $Q = T\Delta S < 0$

how can $\Delta S < 0$?

2nd law: $\Delta S_{tot} = \Delta S + \Delta S_R \geq 0$

$\Delta S_R = ?$

TDI $dU = TdS - PdV + \mu dN$

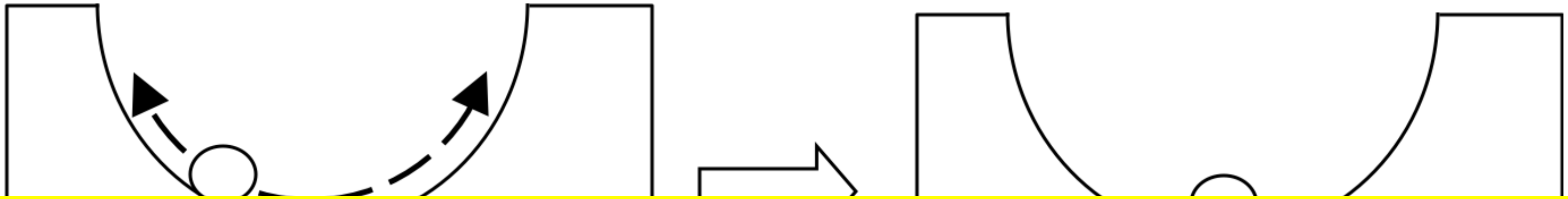
=> $dS_R = \frac{1}{T}dU_R = \frac{1}{T}\mathrm{dU}$

$dS_{tot} = \frac{1}{T}(TdS - dU) \geq 0$

$F = U - TS, \; dF = dU - TdS - \cancel{SdT}$

=> 2nd law using only system variables: $\mathbf{dF \leq 0}$

A ball is rolling back and forth in a valley, which is part of the (infinitely massive) earth. Everything starts at temperature T. Eventually, the ball rolls to a stop and reaches equilibrium with the Earth.



Moral: The reason that balls always roll to a stop (instead of speeding up from rest) is that this minimizes the free energy
(F=U–TS) which is the same as maximizing the entropy of the universe.

The temperature of the ball

A) increased B) decreased C) stayed the same

Answer: stayed the same

The entropy of the earth

A) increased B) decreased C) stayed the same

answer: increased [ΔS = Q/T, and the earth received a non-zero Q. The heat Q came from the (KE+PE) of the ball.]

The entropy of the ball

A) increased B) decreased C) stayed the same

answer: stayed the same. Same ball, same temperature.

The free energy (F = U-TS) of the ball

A) increased B) decreased C) stayed the same

answer: decreased. U decreased since the ball lost its mechanical energy, but T and S remained constant.

2. law for other natural variables than (N,V,U)

When a system is not isolated the entropy of the surroundings (reservoir) must be accounted for: $\boxed{dS_{tot} = dS + dS_R \geq 0}$

- $dS_R = dU_R/T_R + P_R dV_R/T_R - \mu_R dN_R/T_R$ (TDI)
- (NVT) constant:
  - $dS_R = dU_R/T_R = -dU/T$ $T_R = T,\ dU_R = -dU$
  - $dS_{tot} = dS - dU/T = (TdS - dU)/T$
  - $dS_{tot} = -dF/T$
  - 2. law for (NVT) constant: $\Delta F \leq 0$
- (NPT) constant:
  - $dS_R = dU_R/T_R - P_R dV_R/T_R = -dU/T - PdV/T$
  - $T_R = T,\ P_R = P\ dU_R = -dU$
  - $dS_{tot} = (TdS - dU - PdV)/T$
  - $dG = dU - TdS - SdT + PdV + VdP,$ $dT = 0, dP = 0$
  - $dS_{tot} = -dG/T$
  - 2. law for (NPT) constant: $\Delta G \leq 0$
  - Spontaneous prosesses go from high to low Gibbs energy

Thermodynamic potentials and identities

Internal energy

- $dU = TdS - PdV + \mu dN$

Gibbs free energy

- $G \equiv U + PV - TS = H - TS$
- $dG = dU + PdV + VdP - TdS - SdT$
- Thermodynamic identity for G: $dG = VdP - SdT + \mu dN$
- $dG = \left(\frac{\partial G}{\partial P}\right)_{N,T} dP + \left(\frac{\partial G}{\partial T}\right)_{N,P} dT + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN$
- $V = \left(\frac{\partial G}{\partial P}\right)_{N,T}$, $S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}$, $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$

Boltzman probabilities: The probability for a system S described by N, V, T, to be in a state i with energy ϵ_i is given as

$$P(\epsilon_i) = \frac{1}{Z} e^{-\epsilon_i/kT} \ , \tag{7.17}$$

where the system is *in equilibrium*.

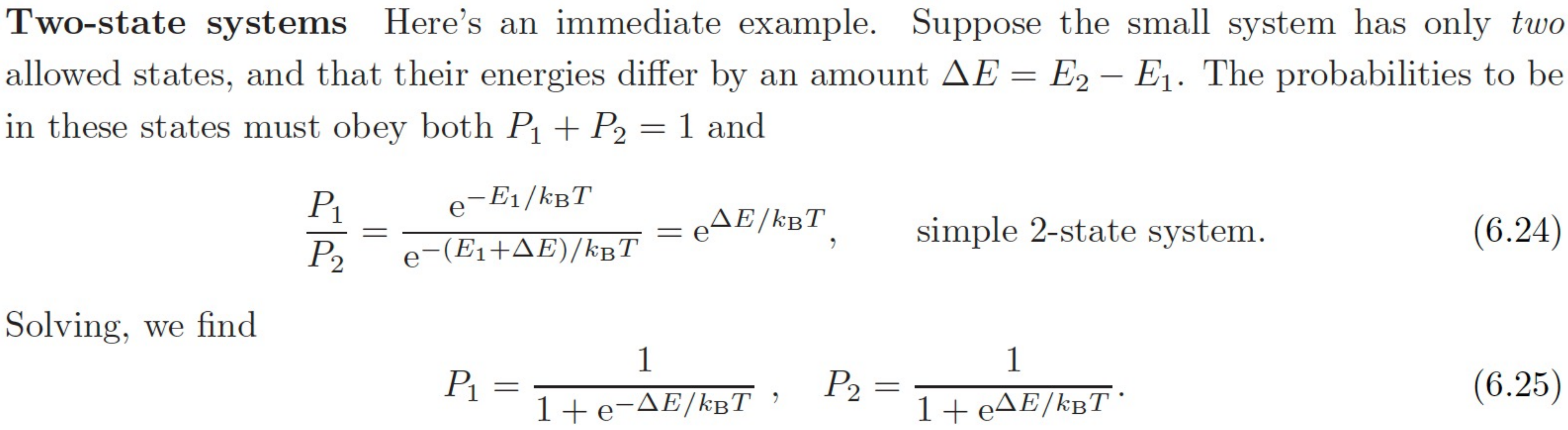
Partition function: The sum $Z = Z(N, V, T)$ is called the partition function. The sum is over *all the states i* of the system:

$$Z(N, V, T) = \sum_i e^{-\epsilon_i/kT} \ . \tag{7.18}$$

The **average** of a quantity Q_i, which depends on the state i of a canonical system with given N, V, T, is:

$$\overline{Q}_i = \sum_i P(i)\, Q_i = (1/Z) \sum_i Q_i\, e^{-\epsilon_i/kT} \tag{7.20}$$

Two-state system



Two-state systems Here's an immediate example. Suppose the small system has only *two* allowed states, and that their energies differ by an amount $\Delta E = E_2 - E_1$. The probabilities to be in these states must obey both $P_1 + P_2 = 1$ and

$$\frac{P_1}{P_2} = \frac{\mathrm{e}^{-E_1/k_{\mathrm{B}}T}}{\mathrm{e}^{-(E_1+\Delta E)/k_{\mathrm{B}}T}} = \mathrm{e}^{\Delta E/k_{\mathrm{B}}T}, \qquad \text{simple 2-state system.} \tag{6.24}$$

Solving, we find

$$P_1 = \frac{1}{1+\mathrm{e}^{-\Delta E/k_{\mathrm{B}}T}}\ , \quad P_2 = \frac{1}{1+\mathrm{e}^{\Delta E/k_{\mathrm{B}}T}}. \tag{6.25}$$

Protein folding

REPORT

Reversible Unfolding of Single RNA Molecules by Mechanical Force

Jan Liphardt[1,*], Bibiana Onoa[1], Steven B. Smith[2], Ignacio Tinoco Jr.[1], Carlos Bustamante[1,2,*]

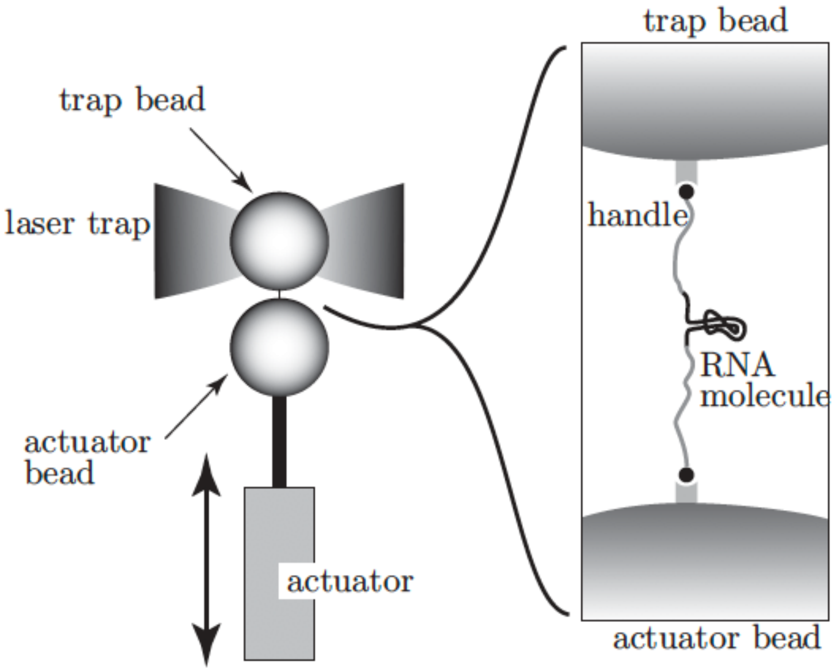
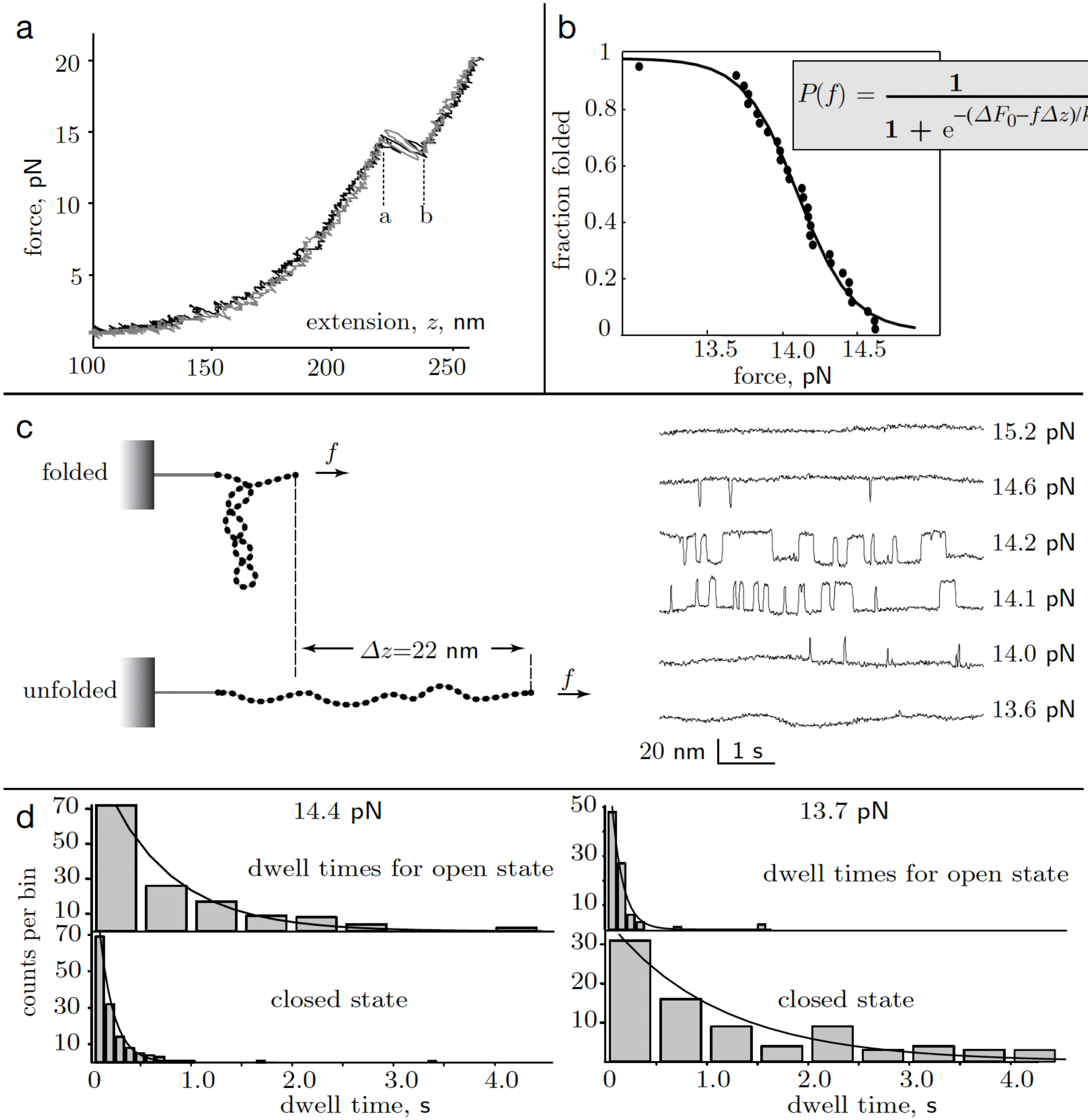
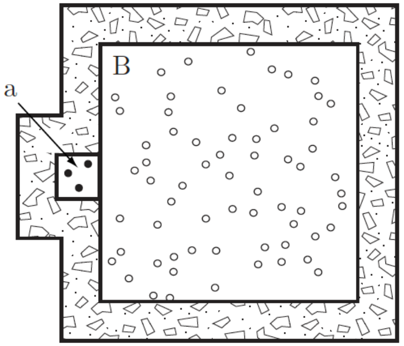


Figure 6.9: (Schematic.) Optical tweezer apparatus. A piezo-electric actuator controls the position of the bottom bead. The top bead is captured in an optical trap formed by two opposing lasers, and the force exterted on the polymer connecting the two beads is measured from the change in momentum of light that exits the optical trap. Molecules are stretched by moving the bottom bead vertically. The end-to-end length of the molecule is obtained as the difference of the position of the bottom bead and the top bead. *Inset:* The RNA molecule of interest is coupled to the two beads via molecular "handles." The handles end in chemical groups that stick to complementary groups on the bead. Compared to the diameter of the beads (≈ 3000 nm), the RNA is tiny (≈ 20 nm). [Figure kindly supplied by J. Liphardt.]





small system in thermal equilibrium with large
$\Rightarrow$ (NVT) => F

What is the most important information to arrive to figure b?

Pressure and diffusion

The thermodynamic identity is $dU = T\,dS - p\,dV$, which implies that $U = U(S,V)$ (N is assumed fixed.) What is the relationship between pressure p and energy U?

A) $P=-(dU/dV)_S$ B) $P=-(dU/dS)_V$ C) Neither of these is correct.

The diameter of a room is doubled (at constant temperature, constant pressure). What happens to the (average) time required for a molecule to diffuse across the room?

A: time doubles B: time increases by factor of 4 C: some other answer

The diameter of a room is doubled (at constant temperature, constant NUMBER OF PARTICLES). What happens to the (average) time required for a molecule to diffuse across the room?

A: time doubles B: time increases by factor of 4 C: some other answer

The "cool-down time" of a building is how long it takes for the temperature difference between inside and outside to fall to (1/e) of its initial value once the heat goes off. (Assume it's winter.) Mean heat flow I_Q= (energy change ΔU)/(time Δt) so $\Delta t = \Delta U/I_Q$. Consider a cubical building. If the edge length L is decreased by a factor of 2. What happens to the cool-down time?

A) increases by 2 (takes longer to cool) B) decreases by 2 (cools faster) C) decreases by 4 D) increases by 4 E) some other answer

The thickness of the insulation in the walls/roof of a building is doubled. What happens to the cool-down time?

A) increases by 2 B) increases by 4 C) increases by 8 D) increases by 16 E) some other answer