

Entropy and entropic forces

Focus question

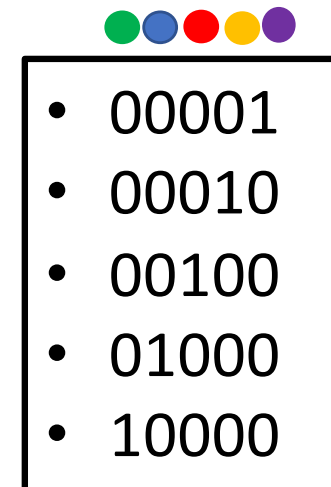
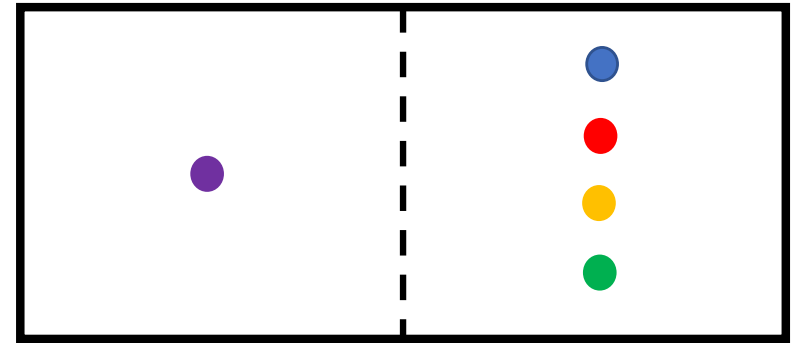
- Biological question: if energy is always conserved, how can some devices be more efficient than others?
- Physical idea: Order controls when energy can do useful work. Order is not conserved.

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
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- Biological examples
- Quiz

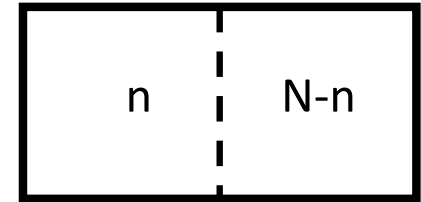
Microstates and macrostates

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



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

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		

$$\Omega(0,5)=1 \quad \Omega(1,5)=5 \quad \Omega(2,5)=10 \quad \Omega(3,5)=10 \quad \Omega(4,5)=5 \quad \Omega(5,5)=1$$

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

Fundament of statistical mechanics

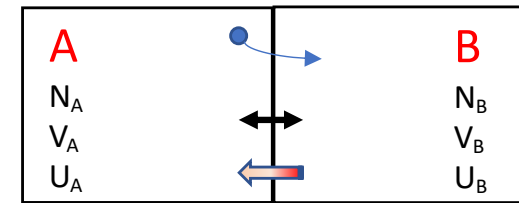
Fundamental assumption of statistical mechanics:

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



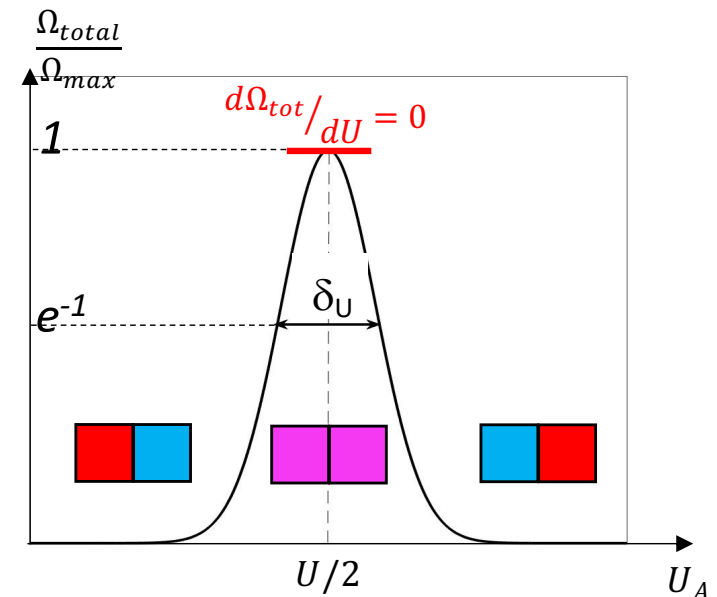
System: can contain "anything"

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

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

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

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

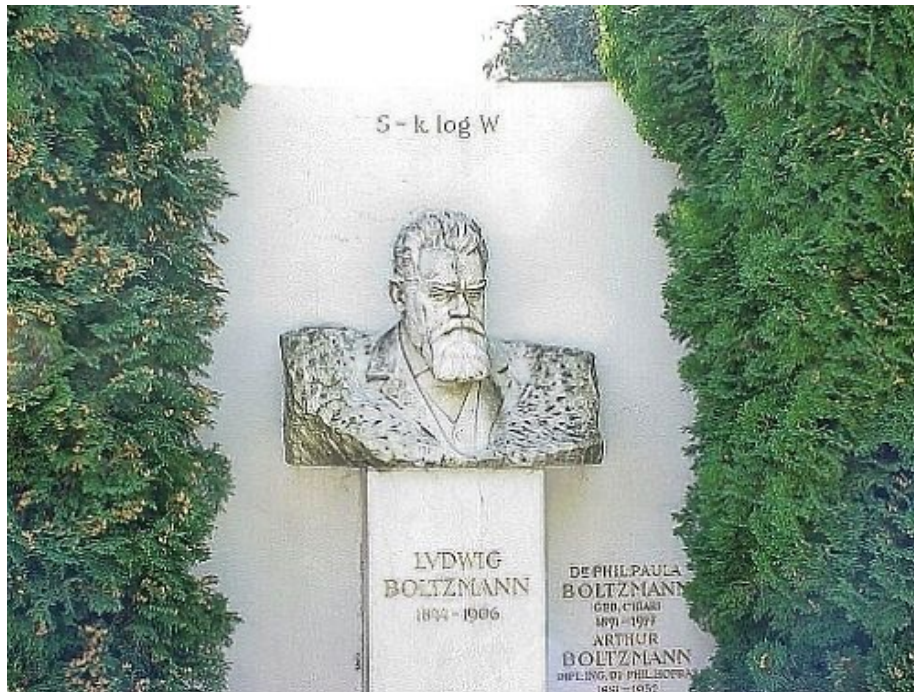


Boltzmann's Entropy

$$S = k \ln \Omega$$

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:

$$\Delta S_{\text{tot}} \geq 0$$

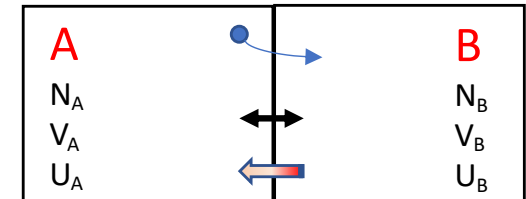
All real processes are irreversible

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: $\alpha = \alpha_A + \alpha_B = \text{const.}$
- $S_{tot} = S_A + S_B$ is maximum in equilibrium

Equilibrium criterium:

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



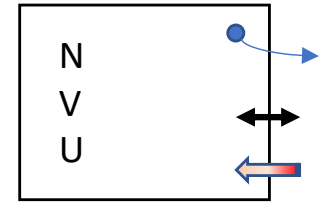
Entropy: $S = k \ln \Omega(N, V, U)$

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

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

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

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

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

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

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

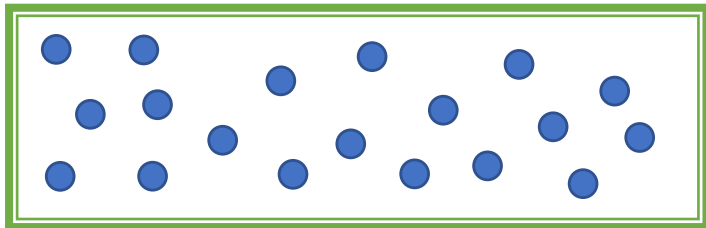
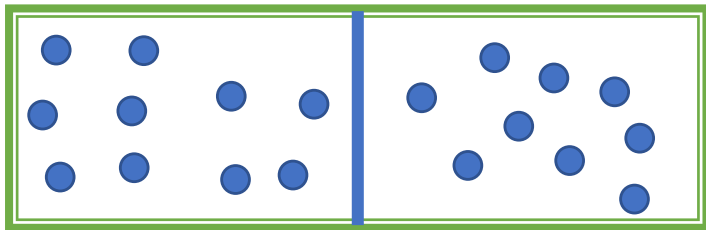
- The *thermodynamic identity* holds *true* for any infinitesimal change in a system

Ideal gas: entropy S and temperature T

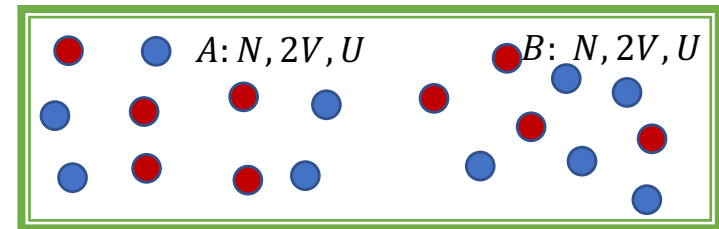
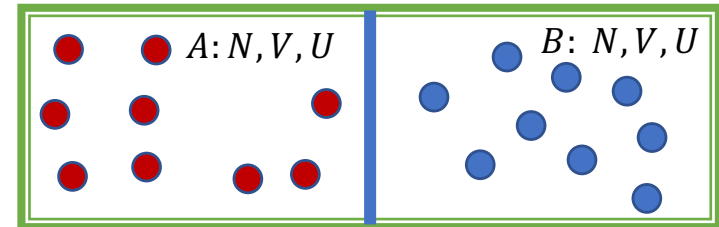
- Sackur-Tetrode Entropy:

$$S(U, V, N) = kN \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]$$

Entropy of mixing



$\Delta S = ?$



$\Delta S = ?$

Entropy of mixing: ΔS

If the gas is **the same** on both sides of the wall

$$S_{initial} = S_A + S_B = 2S(U, V, N)$$

$$\Delta S_{tot} = S(2U, 2V, 2N) - 2S(U, V, U)$$

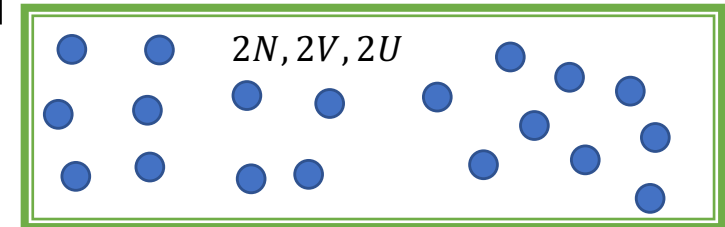
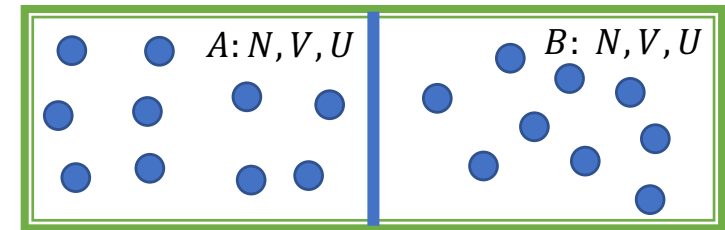
Using Sackur-Tetrode formula

$$S(U, V, N) = kN \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] = kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + const \right]$$

$$\Delta S_t = k2N \left[\ln \frac{2V}{2N} + \frac{3}{2} \ln \frac{2U}{2N} + const \right] - 2kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{U}{N} + const \right]$$

$$\Delta S_t = 0$$

Nothing changes, when we remove the wall!



Entropy of mixing: ΔS

- If the gas is **different (distinguishable)** on both sides of the wall

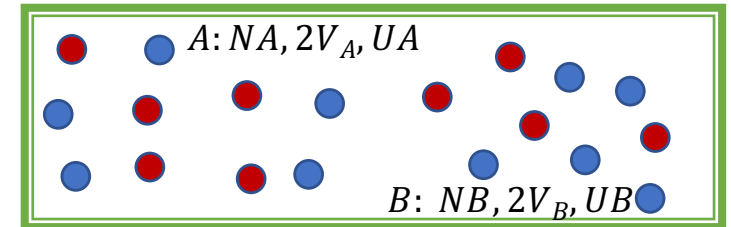
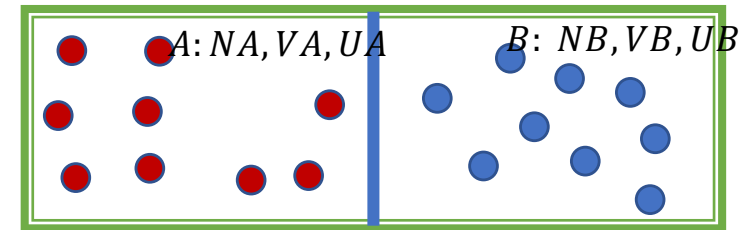
$$\Delta S_t = \Delta S_A + \Delta S_B$$

Using Sackur-Tetrode formula

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

$$\Delta S_t = kN \ln \frac{V_{A,final}}{V_{A,initial}} + kN \ln \frac{V_{B,final}}{V_{B,initial}}$$

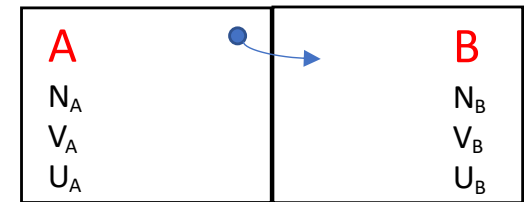
$$\Delta S_t = 2kN \ln 2$$



- ❑ Entropy increases when we mix *different* gases

- ❑ Effectively, the available volume increases upon mixing hence the number of configurations increases

Ideal mixtures



$$\begin{aligned} N &= N_A + N_B \\ V &= V_A + V_B \\ U &= U_A + U_B \end{aligned}$$

Thermal and mechanical equilibrium: $T_A = T_B, P_A = P_B$

Composition: $x_i = \frac{N_i}{N}, i = A, B, \quad x_A + x_B = 1, \quad \rho = \frac{N_A}{V_A} = \frac{N_B}{V_B} = \frac{N}{V}$

Ideal gas and ideal mixture = **U and P are independent of composition:** $U = U_A + U_B = \text{const.}$

Remove wall between A & B: Equilibrium criterium: $\left(\frac{\partial S_A}{\partial N_A}\right)_{U_A, V_A} = \left(\frac{\partial S_B}{\partial N_B}\right)_{U_B, V_B}, U_A, V_A \rightarrow U, V$

Entropy change on mixing $\Delta S_i = kN_i \ln \frac{V}{V_i} = kN \left(\frac{N_i}{N} \ln \frac{N}{N_i}\right) = -kN x_i \ln x_i$

Entropy of mixture $S_i(x_i) = S_{i,0}(x_i = 1) + \Delta S_i(x_i)$

Chemical potential of mixture: $\mu_A \equiv -T \left(\frac{\partial S_A}{\partial N_A}\right)_{U, V, N_B} \quad \frac{\partial x_A}{\partial N_A} = \frac{\partial N_A/N}{\partial N_A} = \frac{1}{N}$

$$\begin{aligned} &= -\frac{T}{N} \left(\frac{\partial S_A}{\partial x_A}\right)_{U, V, N_B} \\ &= -\frac{T}{N} \left(\frac{\partial S_{A,0}}{\partial x_A}\right)_{U, V, N_B} - \frac{T}{N} \left(\frac{\partial \Delta S_A}{\partial x_A}\right)_{U, V, N_B} \\ &= \mu_{A,0} + \frac{T}{N} \left(\frac{\partial kN x_A \ln x_A}{\partial x_A}\right)_{U, V, N_B} = \mu_{A,0} + kT \left(\frac{\partial x_A \ln x_A}{\partial x_A}\right)_{U, V, N_B} \\ &= \mu_{A,0} + kT(\ln x_A + 1) \\ &= \mu_{A,0}^* + kT \ln x_A \end{aligned}$$

Equilibrium criterium: $\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \Rightarrow \mu_A = \mu_B$ ideal mixtures $\Rightarrow \ln x_A = \ln x_B \Rightarrow x_A = x_B$

Why is the chemical potential difficult to grasp?

- We understand what we experience/measure
 - T – radiation or equilibrium with sensor
 - V – lengths
 - P – Equilibrium with liquid columns, bent membranes
 - N – mass, weight
 - Q – known dissipation (for example $P = \frac{dQ}{dt} = RI^2$)
 - $W = P\Delta V$, we feel it when working
 - $C_V = Q/\Delta T$, we feel the difference between plastic and rocks
- Cannot be measured directly
 - U – 1st law: $Q + W, G, H, F$
 - S – needs integration of C_V
 - μ – derivative of $S, G, F...$

What are the fundamental principles of equilibrium?

Mechanics

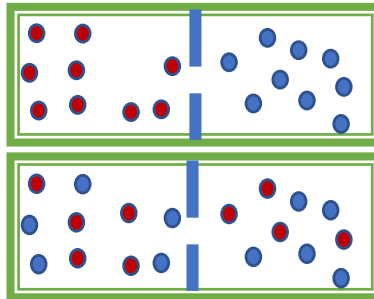
$$\sum_i F_i = -\sum_i \nabla U_i = 0$$

minimize energy

Thermodynamics
maximize entropy
(minimize F or G)

identical, coloured, $dU=0$

particle number



$dS > 0$, $\mu_1 = \mu_2$

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 : $dG = VdP, \quad dF = -PdV$

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

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

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

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

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

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

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

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

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

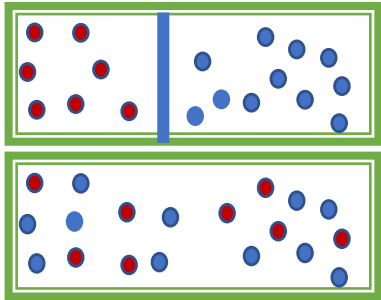
$$\mu = -kT \ln \left(\frac{V}{V_0} \right), \quad V_0 = Nv_Q, \quad n_Q = v_Q^{-1}$$

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

$$\mu = kT \ln \left(\frac{P}{P_0} \right), \quad P_0 = n_Q kT$$

Chemical potential of ideal mixtures

$$\begin{matrix} V_1 & V_2 \\ N_1 & N_2 \\ T_1 & = & T_2 \\ P_1 & = & P_2 \end{matrix} \Rightarrow \mu_1^0(P, T) = \mu_2^0(P, T)$$



Remove wall: $V=V_1+V_2$

$$\mu = \mu_0 - kT \ln \frac{V}{V_0}$$

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

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

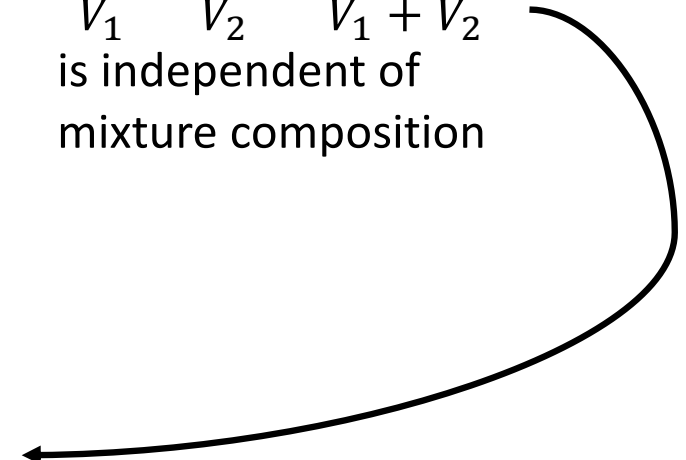
$$\Delta\mu_1 = kT \ln x_1$$

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

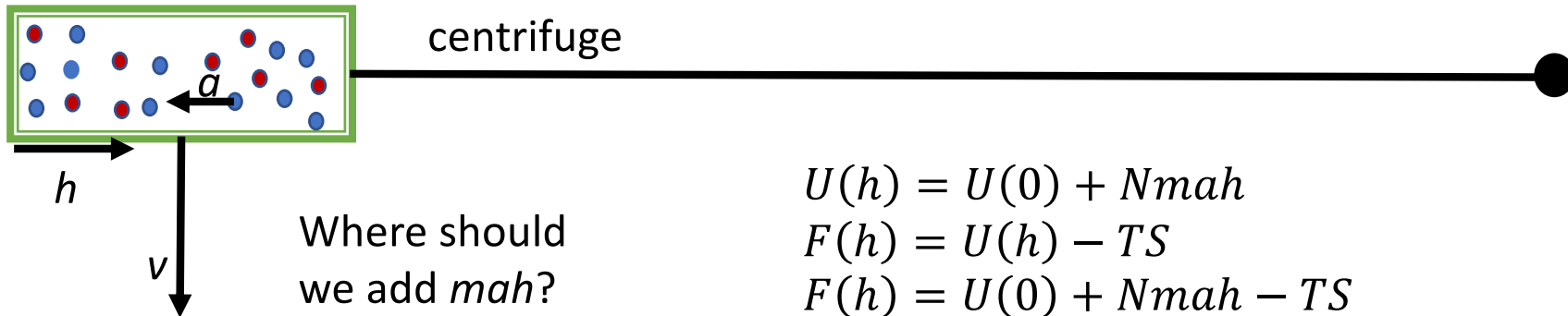
Ideal mixture:

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

is independent of mixture composition



Potential energy and the chemical potential



$$U(h) = U(0) + Nmah$$

$$F(h) = U(h) - TS$$

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

$$F(h) = F(0) + Nmah$$

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

$$\mu_{tot} = \mu_{int} + \mu_{ext}$$

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

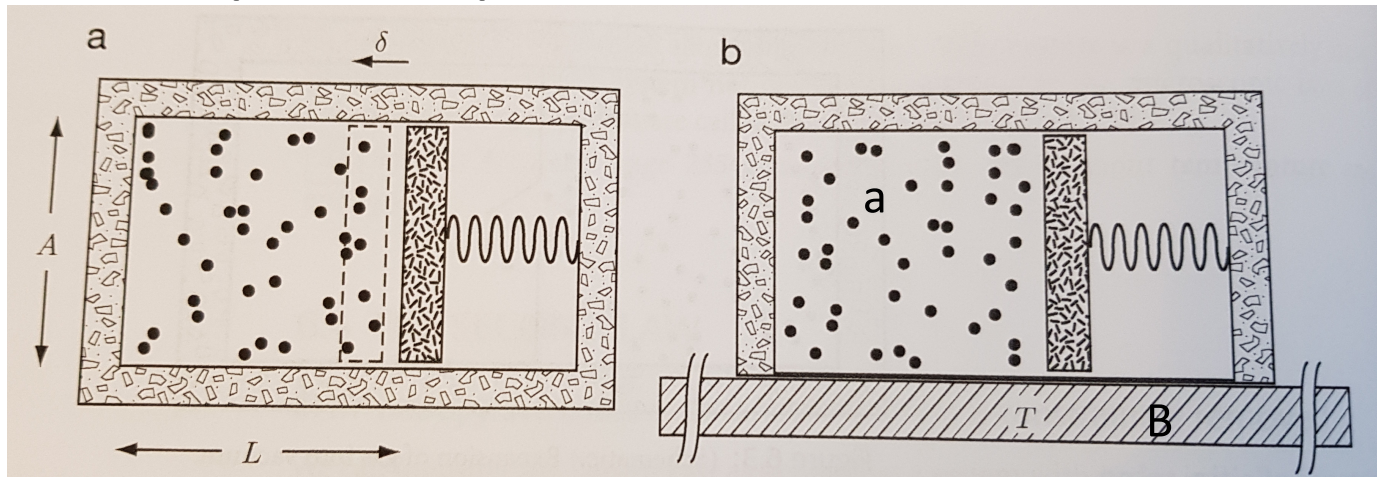
equilibrium: $\mu(z) = \mu_0 = \mu_0 + kT \ln \frac{P(z)}{P_0} + mgz$

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

$$z_c = kT/mg$$

Nitrogen ($m=28$) $z_c=8.5\text{km}$, Oxygen ($m=32$) $z_c = 7.4 \text{ km}$, Mount Everest: $P = 0.37 P(0)$

Open systems



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

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

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

With thermal reservoir:

(NVT) constant instead of (NVU) constant

$T_2 = T_1 \quad \Rightarrow \quad Q = T\Delta S < 0$

how can $\Delta S < 0$?

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

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

$\Rightarrow \quad dS_R = \frac{1}{T} dU_R = \frac{1}{T} dU$

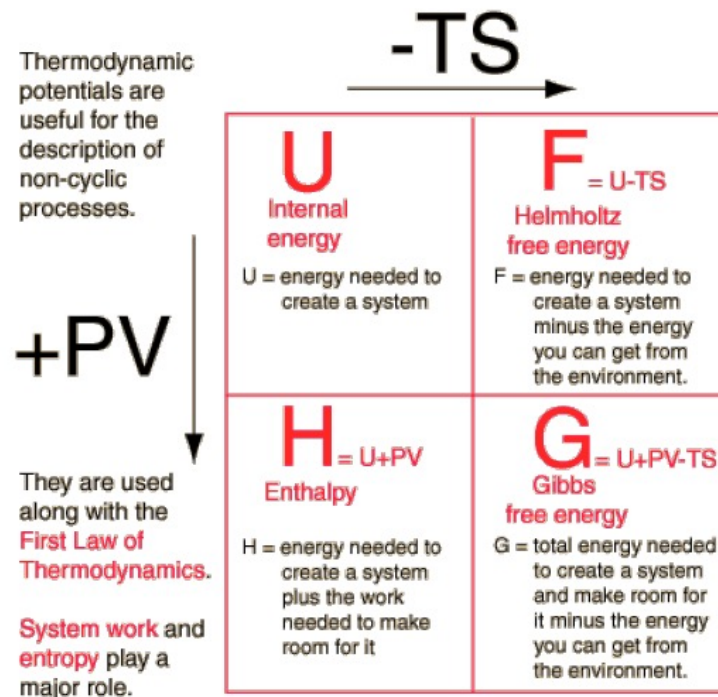
$dS_{tot} = \frac{1}{T} (TdS - dU) \geq 0$

$F = U - TS, \quad dF = dU - TdS - SdT$

\Rightarrow 2nd law using only system variables: **$dF \leq 0$**

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: $\Phi \equiv U - TS - \mu N = \phi(V, T, \mu)$



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.

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: $dS_{tot} = dS + dS_R \geq 0$

▶ $dS_R = dU_R/T_R + P_R dV_R/T_R - \mu_R dN_R/T_R$ (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:

▶ $dS_R = dU_R/T_R - P_R dV_R/T_R = -dU/T - PdV/T$

▶ $T_R = T, P_R = P, dU_R = -dU$

▶ $dS_{tot} = (TdS - dU - PdV)/T$

▶ $dG = dU - TdS - SdT + PdV + VdP, \quad dT = 0, dP = 0$

▶ $dS_{tot} = -dG/T$

▶ 2. law for (NPT) constant: $\Delta G \leq 0$

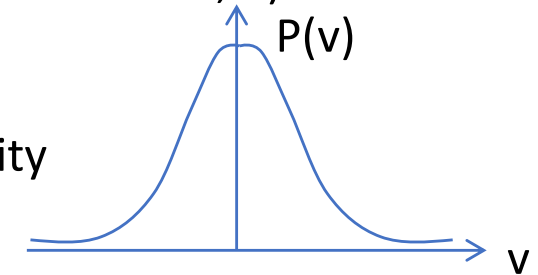
▶ Spontaneous processes go from high to low Gibbs energy

Probability of jumping people



To states: 1) On the floor, 2) on red box

MB velocity
distr.

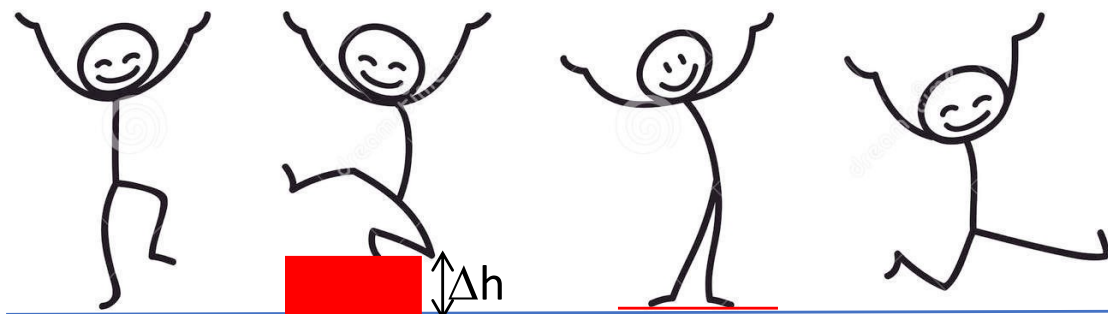


Mean kinetic energy
 $m\langle v^2 \rangle / 2 = kT$

Mean potential energy
 $mg\langle h \rangle = m\langle v^2 \rangle / 2$

Relative probability

$$\begin{aligned} P(2)/P(1) &= \exp(-\Delta h / \langle h \rangle) \\ &= \exp(-mg\Delta h / kT) \\ &= \exp(-\Delta E / kT) \end{aligned}$$



$$\begin{aligned} P(2)/P(1) &= \exp(-E_2/kT) / \exp(-E_1/kT) \\ &= \exp(-(E_2 - E_1)/kT) \end{aligned}$$

Boltzmann-statistics

- Reservoir + small system => NVT for the small
- Probability for a state i , ε_i ; $E_R = E_0 - \varepsilon_i$.
- $P(i) = C \Omega_R(E_0 - \varepsilon_i)$, multiplicity of the reservoir
- $\varepsilon_i \ll E_0$, expand

- $P(i) = \exp(-\varepsilon_i/kT)/Z$ Boltzmannfactor

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

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

where the system is *in equilibrium*.

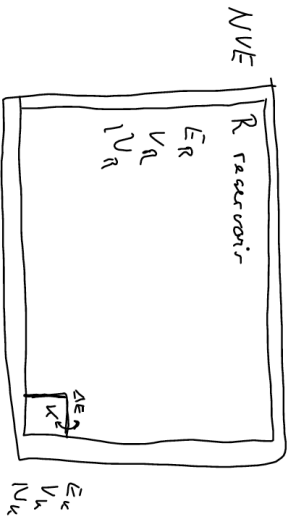
Partition function: The sum $Z = Z(N, V, T)$ is called the partition function. The sum is over *all the states* i of the system:

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

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

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

Til næ NVE, Konst. Temperatur \Rightarrow NVT (Cannonsk system)



R: varer God $E_R, V_R, N_R \gg E_S, V_S, N_S$
 ubetydlig $\Delta E \Rightarrow$ partikel i Ω_R

Likelihood $T_R = T_S$

\Rightarrow K: NVT

$E = E_0 = E_R + E_S$

$V = V_R + V_S$

$N = N_R + N_S$

Mikrotilstand i med $E_i = E_0 - \epsilon_i$ (mange mikrotilst. med ϵ_i) $\Rightarrow \Omega_k = 1$

$$E_R = E_0 - \epsilon_i$$

Hva er sandsynligh. til tilstand i ?

$$P(i) = \frac{\Omega_R \Omega_k}{\sum_R \Omega_R \Omega_k} = C \cdot \Omega_R(E_0 - \epsilon_i)$$

$$\ln P(i) = \ln C + \ln \Omega_R(E_0 - \epsilon_i)$$

$$\ln P(i) = \ln C + \ln \Omega_R(E_0) + \frac{\partial \ln \Omega_R(E)}{\partial E} (-\epsilon_i) + O(\epsilon_i^2)$$

$$= -\ln Z - \frac{\partial S(E)}{\partial E} \cdot \epsilon_i$$

$$S = k_B \ln \Omega$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N, V}$$

$$P(i) = \frac{1}{Z} e^{-\epsilon_i / kT} \quad e^{-\epsilon_i / kT} \text{ Boltzmann-faktor}$$

$$\sum P(i) = 1 = \frac{1}{Z} \sum_i e^{-\epsilon_i / kT}$$

$$Z = \sum_i e^{-\epsilon_i / kT}$$

$$\beta = \frac{1}{kT}$$

Tilstandssummer
 Partitionsfunktion

Sandsynligheden for et system i tilstand i med energi ϵ_i er $P(i) = \frac{e^{-\beta \epsilon_i}}{Z}$

Tilstandssummer (part. funktion) Z er summer over alle tilstande i systemet med N, V, T konst.

$$Z(N, V, T) = \sum_i e^{-\beta \epsilon_i}$$

$$= \sum_{\epsilon_i} g(\epsilon_i) e^{-\beta \epsilon_i}$$

der $g(\epsilon_i)$ er antallet tilstande med energi ϵ_i , (degenerationsgrad)

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

$$\frac{P_1}{P_2} = \frac{e^{-E_1/k_B T}}{e^{-(E_1 + \Delta E)/k_B T}} = e^{\Delta E/k_B T}, \quad \text{simple 2-state system.} \quad (6.24)$$

Solving, we find

$$P_1 = \frac{1}{1 + e^{-\Delta E/k_B T}} \quad , \quad P_2 = \frac{1}{1 + e^{\Delta E/k_B T}}. \quad (6.25)$$

Biological examples

Protein folding

SHARE REPORT



Reversible Unfolding of Single RNA Molecules by Mechanical Force

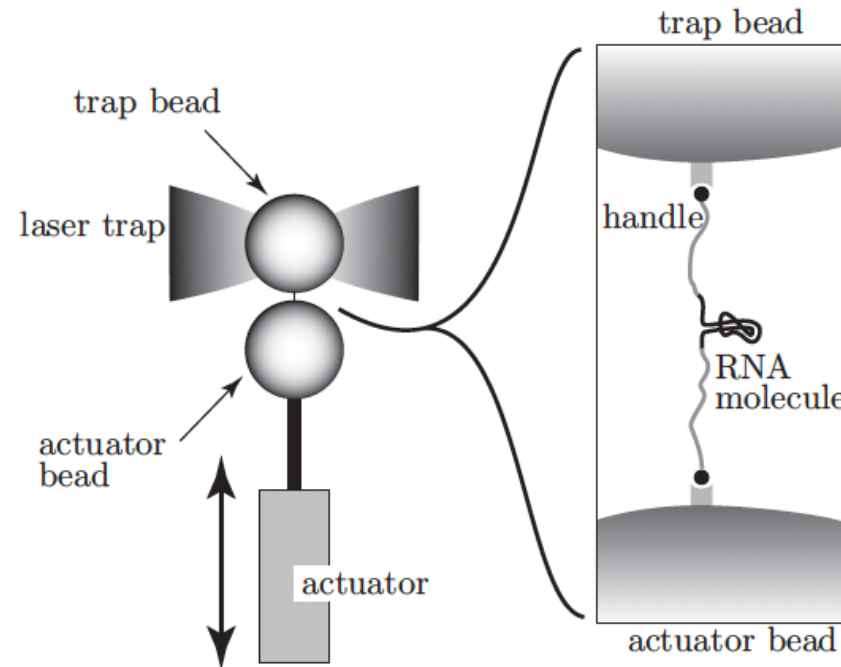
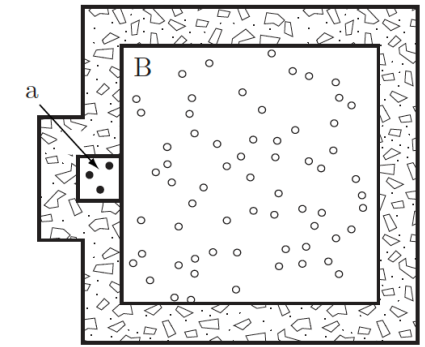
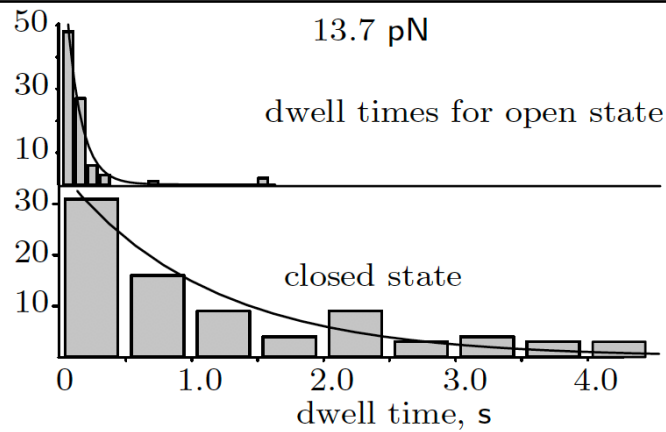
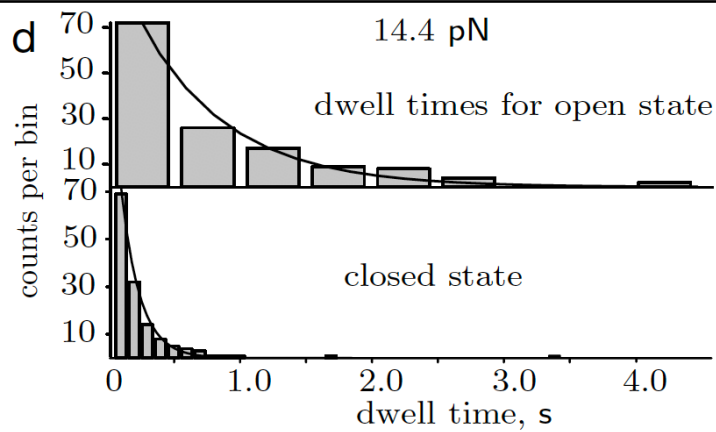
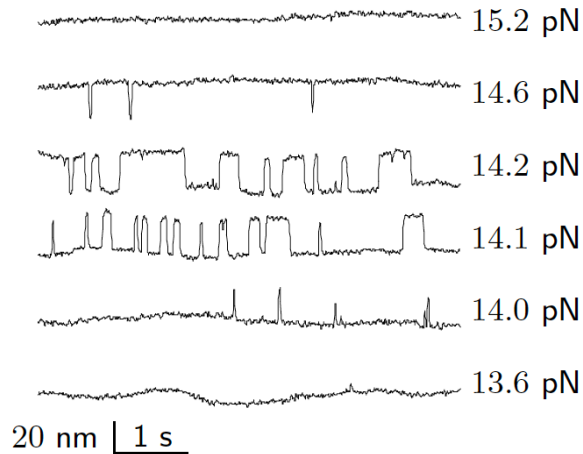
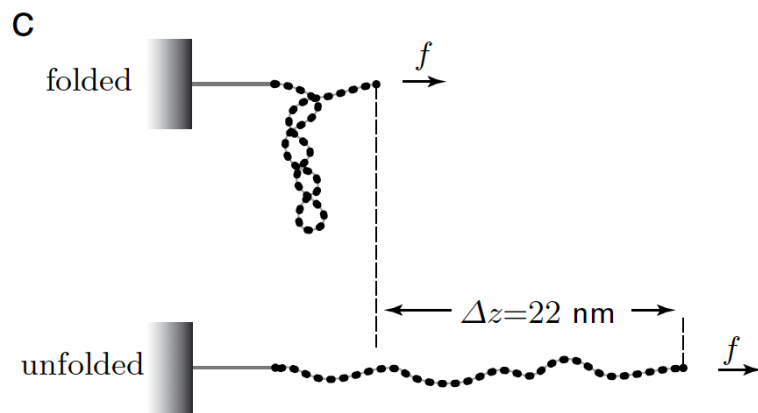
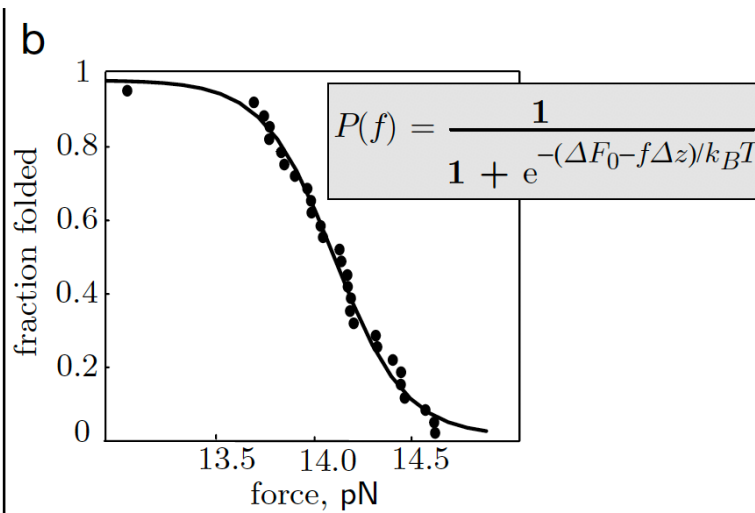
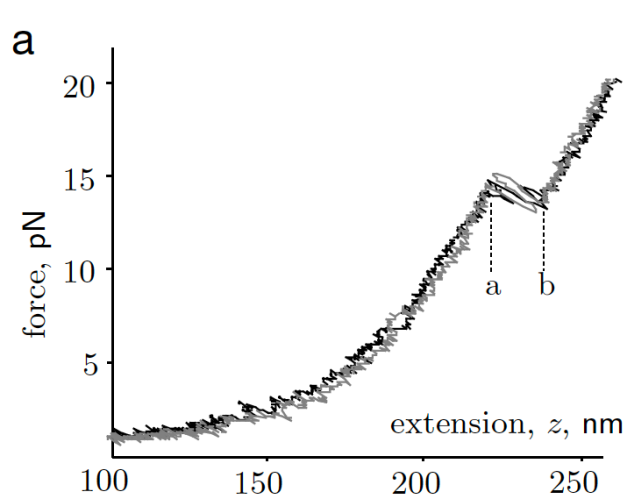
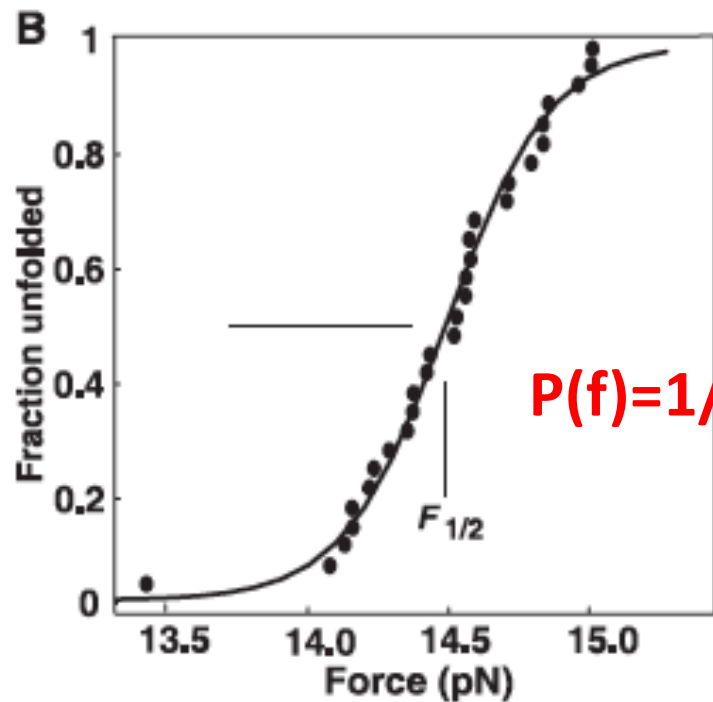
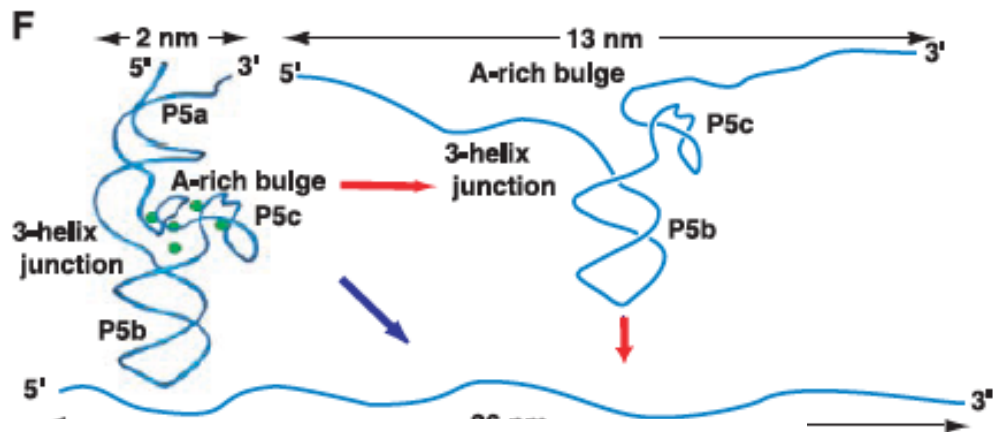
Jan Liphardt^{1,*}, Bibiana Onoa¹, Steven B. Smith², Ignacio Tinoco Jr.¹, Carlos Bustamante^{1,2,*}

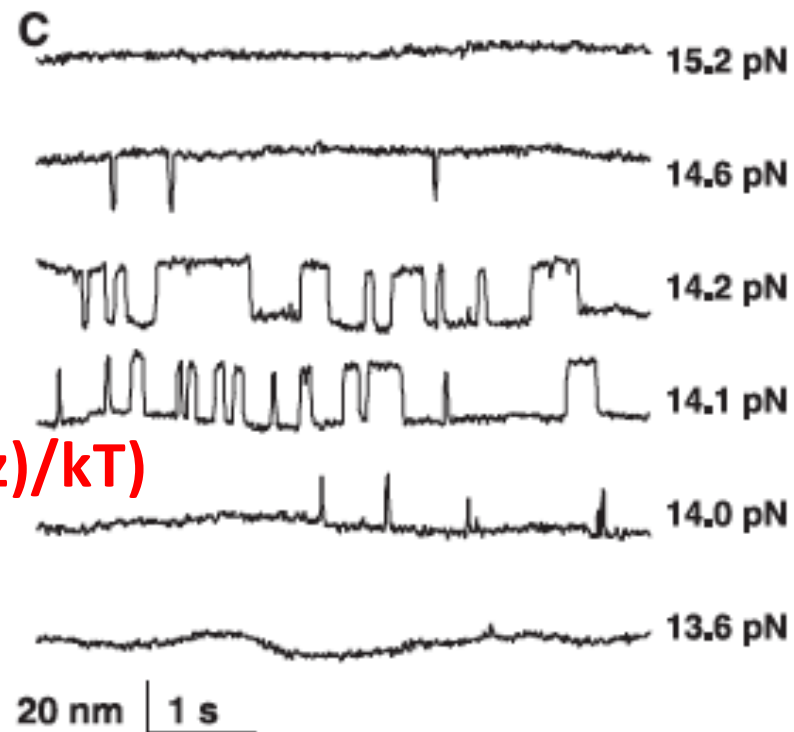
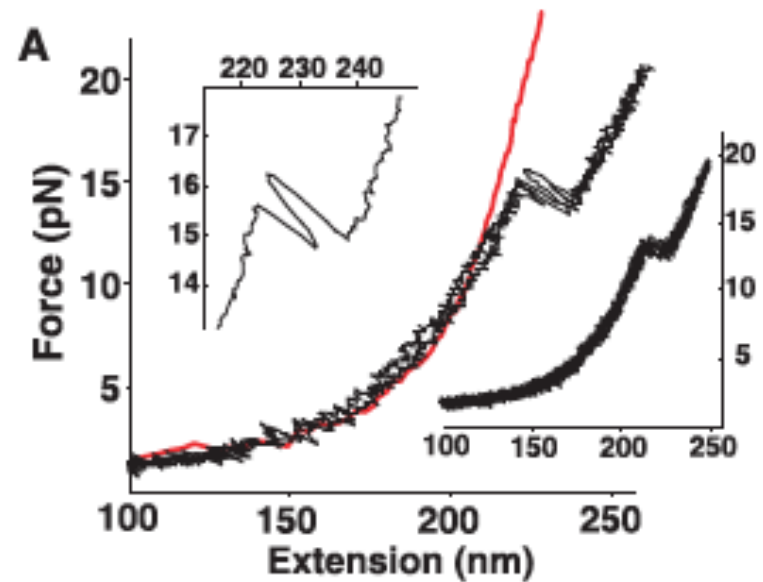
Figure 6.9: (Schematic.) Optical tweezer apparatus. A piezo-electric actuator controls the position of the bottom bead. The top bead is captured in an optical trap formed by two opposing lasers, and the force exerted on the polymer connecting the two beads is measured from the change in momentum of light 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.]



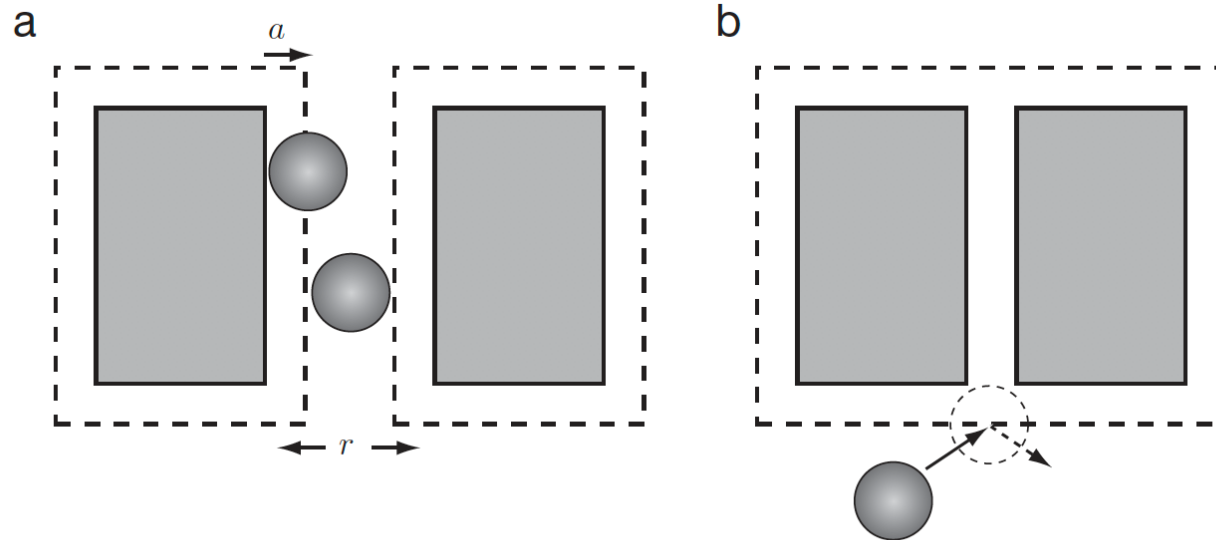
small system in thermal equilibrium with large $\Rightarrow (NVT) \Rightarrow F$



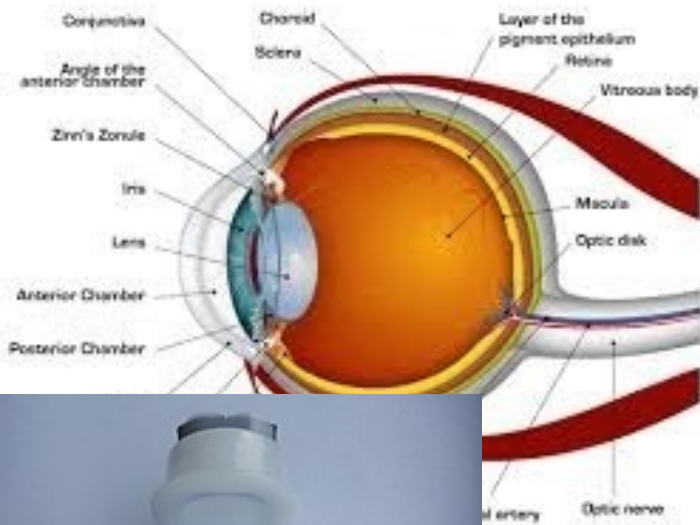
$$P(f) = 1 / (1 + \exp(\Delta E - f\Delta z) / kT)$$



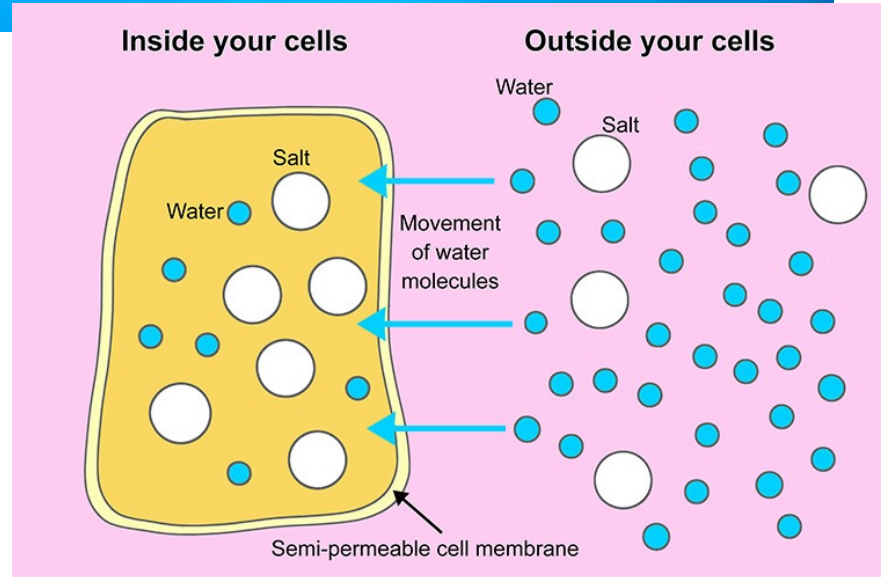
Depletion pressure



Why do your eyes hurt in fresh water?



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1	H																He	
2	Li	Be										B	C	N	O	F	Ne	
3	Na	Mg										Al	Si	P	S	Cl	Ar	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
				La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



Problems

6.6 Polymer mesh

Recently D. Discher studied the mechanical character of the red blood cell cytoskeleton, a polymer network attached to its inner membrane. Discher attached a bead of diameter 40 nm to this network (Figure 6.12a)). The network acts as a spring, constraining the free motion of the bead. He then asked, “What is the stiffness (spring constant) of this spring?”

In the macroworld we’d answer this question by applying a known force to the bead, measuring the displacement Δx in the x direction, and using $f = k\Delta x$. But it’s not easy to apply a known force to such a tiny object. Instead Discher just passively observed the thermal motion of the bead (Figure 6.12b). He found the bead’s root-mean-square deviation from its equilibrium position, at room temperature, to be $\sqrt{\langle(\Delta x)^2\rangle} = 35$ nm, and from this he computed the spring constant k . What value did he find?

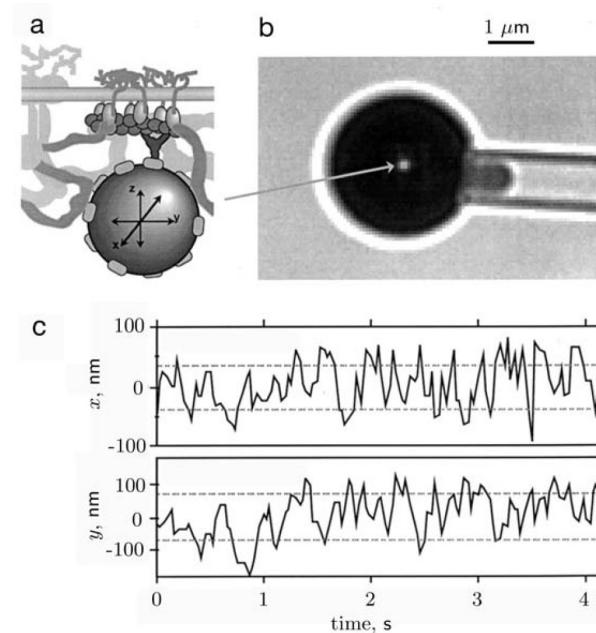
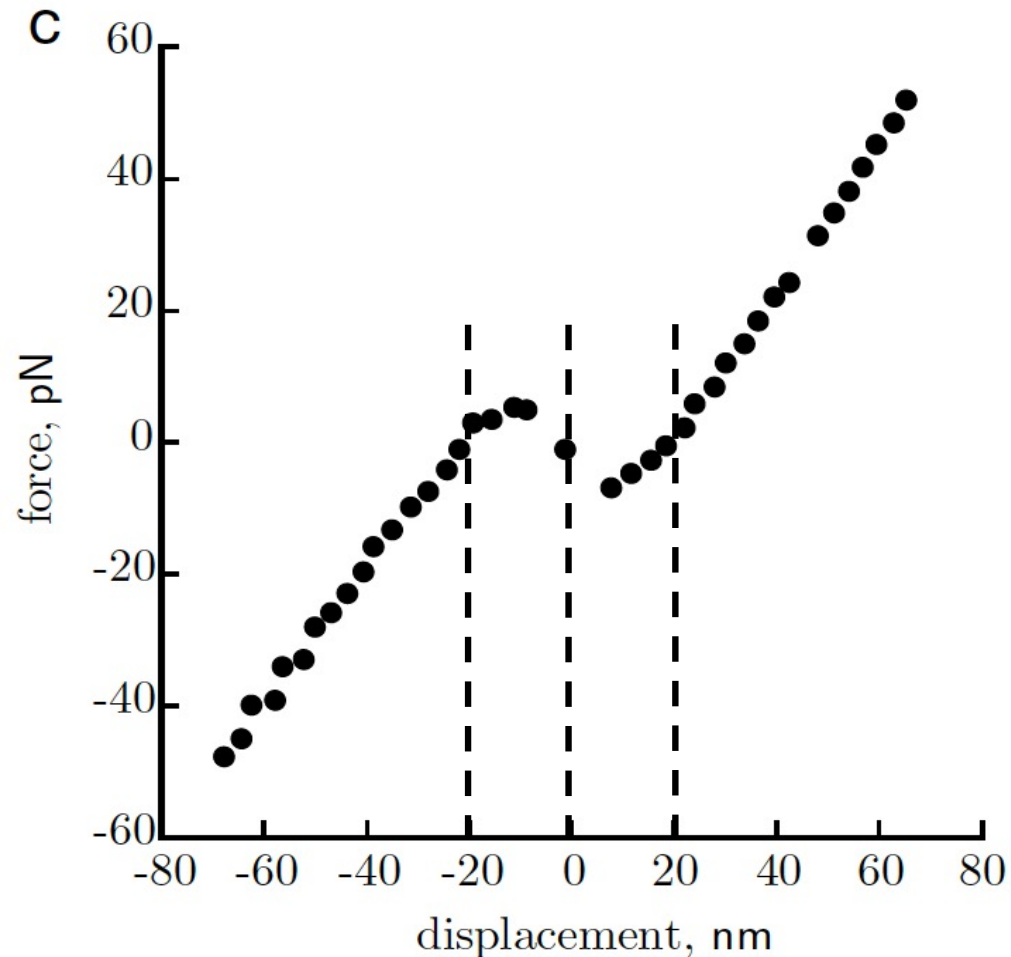


Figure 6.12: (Schematic; optical micrograph; experimental data.) (a) Attachment of a single fluorescent nanoparticle to actin in the red blood cell cortex. (b) The red cell, with attached particle, is immobilized by partially sucking it into a micropipette (right) of diameter $1\ \mu\text{m}$. (c) Tracking of the thermal motion of the nanoparticle gives information about the elastic properties of the cortex. [Digital image kindly supplied by D. Discher; see Discher, 2000.]

6.7 Inner ear

A. J. Hudspeth and coauthors found a surprising phenomenon while studying signal transduction by the inner ear. Figure 6.13a shows a bundle of stiff fibers (“stereocilia”) projecting from a sensory cell. The fibers sway when the surrounding inner-ear fluid moves. Other micrographs (not shown) revealed thin, flexible filaments (“tip links”) joining each fiber in the bundle to its neighbor (wiggly line in the sketch, panel (b)).

The experimenters measured the force-displacement relation for the bundle by using a tiny glass fiber to poke it. A feedback circuit maintained a fixed displacement for the bundle’s tip, and reported back the force needed to maintain this displacement. The surprise is that the experiments gave the complex curve shown in panel (c). A simple spring has a stiffness $k = \frac{df}{dx}$ that is constant (independent of x). The diagram shows that the bundle of stereocilia behaves as a simple spring at large deflections, but in the middle it has a region of *negative* stiffness!



at one end of the tip door was effectively a

it can wander at will, applied force the curve we will never observe

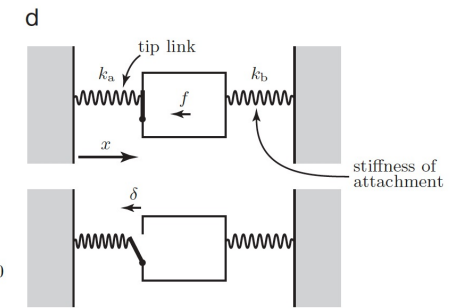
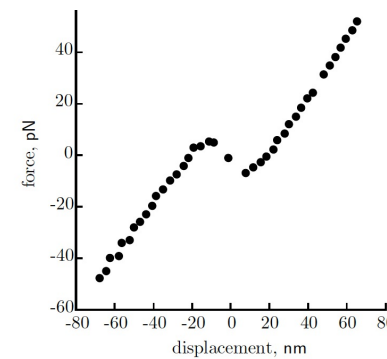
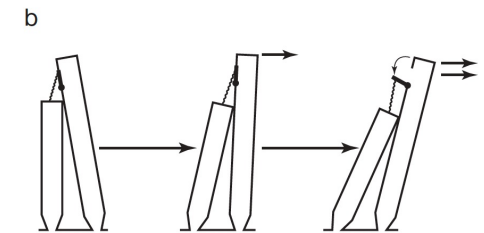
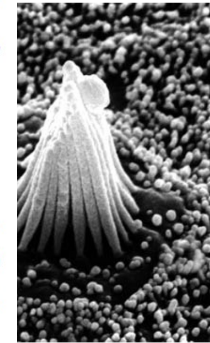
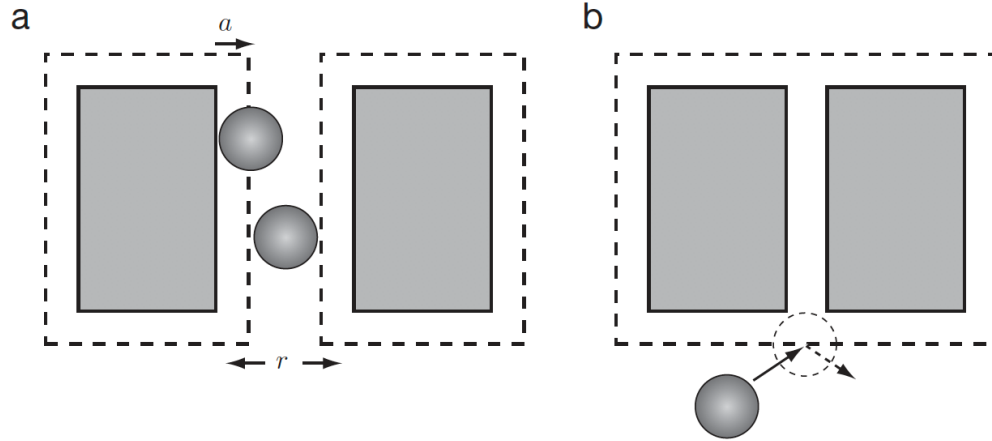


Figure 6.13: (Scanning electron micrograph; diagram; experimental data; diagram) (a) Bundle of stereocilia projecting from an auditory hair cell. [Digital image kindly supplied by A. J. Hudspeth.] (b) Pushing the bundle to the right causes a relative motion between two neighboring stereocilia in the bundle, stretching the tip link, a thin filament joining them. At large enough displacement the tension in the tip link can open a “trap door.” (c) Force that must be applied to a hair bundle to get various displacements. Positive values of f correspond to forces directed to the left in (b); positive values of x correspond to displacements to the right. [Data from Martin et al., 2000.] (d) Mechanical model for stereocilia. The left spring represents the tip link. The spring on the right represents the stiffness of the attachment point where the stereocilium joins the main body of the hair cell. The model envisions N of these units in parallel.

Depletion pressure: assembling effect



Ion distribution at a charged surface

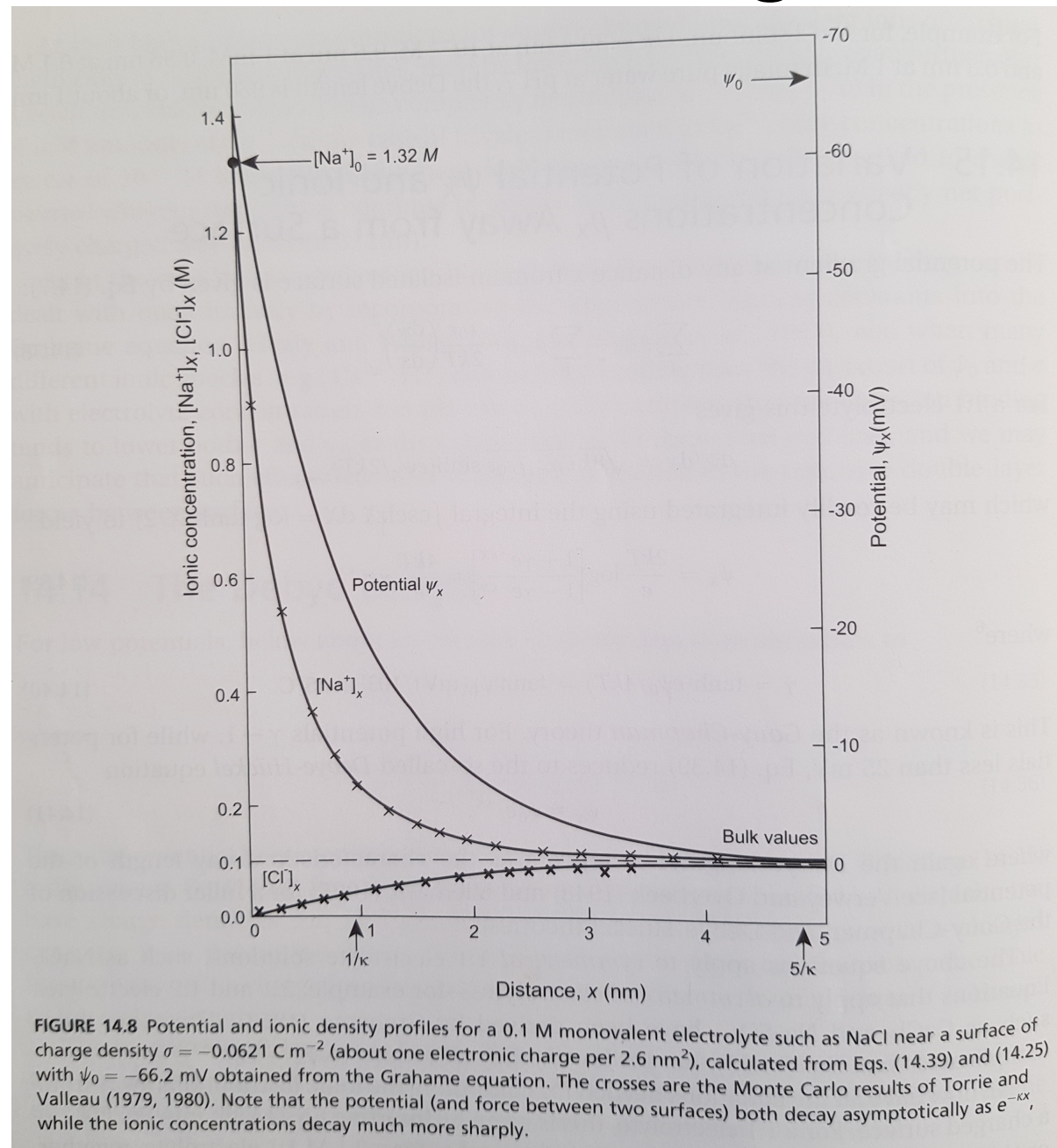
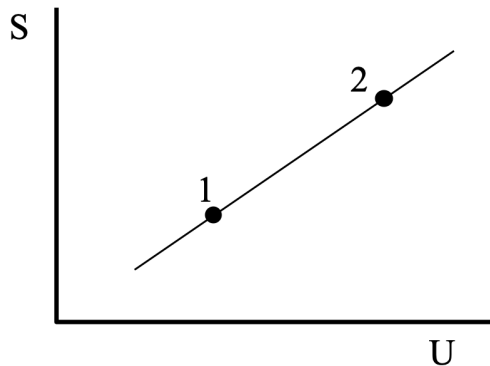


FIGURE 14.8 Potential and ionic density profiles for a 0.1 M monovalent electrolyte such as NaCl near a surface of charge density $\sigma = -0.0621 \text{ C m}^{-2}$ (about one electronic charge per 2.6 nm^2), calculated from Eqs. (14.39) and (14.25) with $\psi_0 = -66.2 \text{ mV}$ obtained from the Grahame equation. The crosses are the Monte Carlo results of Torrie and Valleau (1979, 1980). Note that the potential (and force between two surfaces) both decay asymptotically as $e^{-\kappa x}$, while the ionic concentrations decay much more sharply.

Quiz

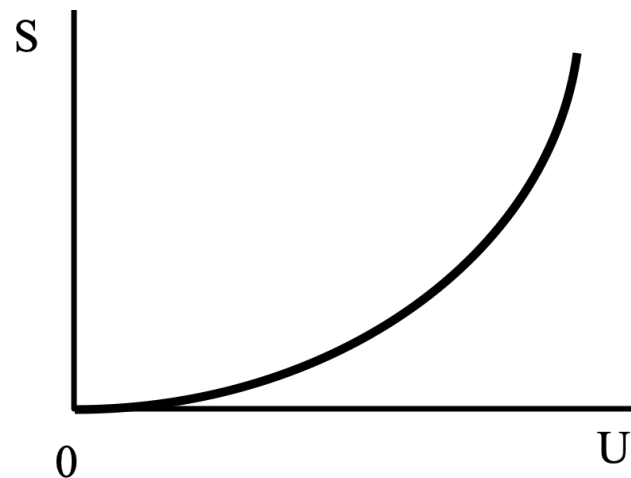
Temperature

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) $T_1 < T_2$

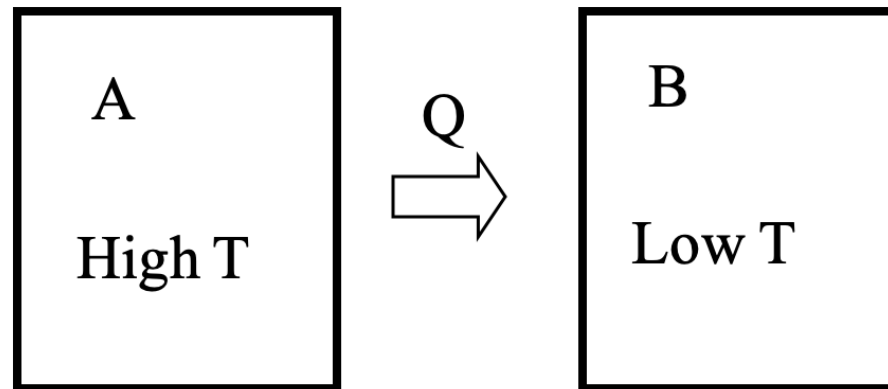
According to the following graph of entropy vs. energy, the temperature of the system, in the limit $U \rightarrow 0$, is approaching...



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

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 $S_{\text{tot}} = S_A + S_B$ as a result of the heat transfer?

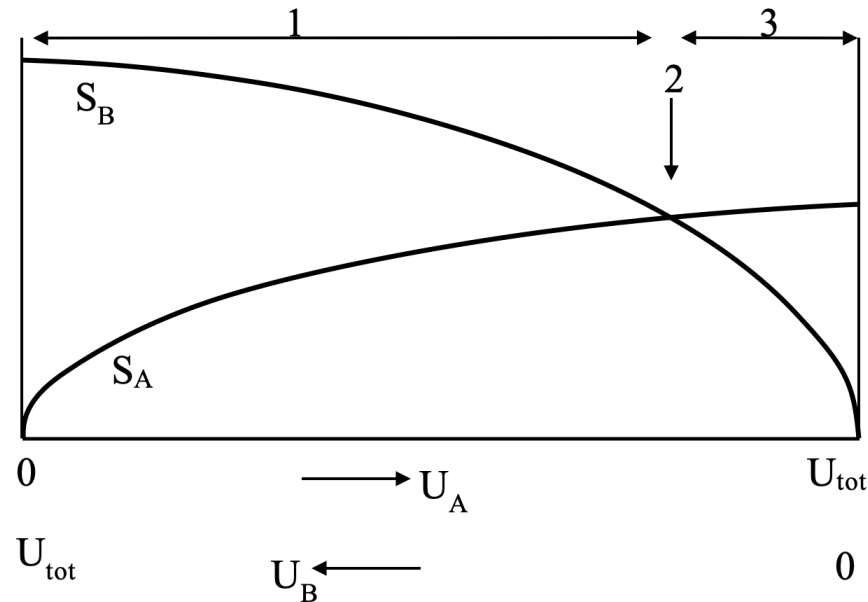
- A) S_{tot} increased B) S_{tot} decreased C) S_{tot} remained constant

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, $|\Delta S_A| = |\Delta S_B|$

Entropy and internal energy

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



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 1, which system is hotter?

- A) System A is hotter.
- B) System B is hotter.
- C) Impossible to tell.

Reactions

For this reaction at STP (standard temperature and pressure)



Assume the H_2O is liquid. Is $P\Delta V$

(A) positive, (B) negative, or (C) zero?

Is the magnitude of the internal energy change $|\Delta U|$

(A) greater than 286 kJ/mol,

(B) less than 286 kJ/mol, or

(C) equal to 286 kJ/mol ?

Consider the reaction $\text{H} + \text{H} \rightarrow \text{H}_2$ taking place in at STP, an isothermal (273K), constant pressure(1 atm), environment.

$T\Delta S$ for this system is A) positive, B) negative or, C) zero.

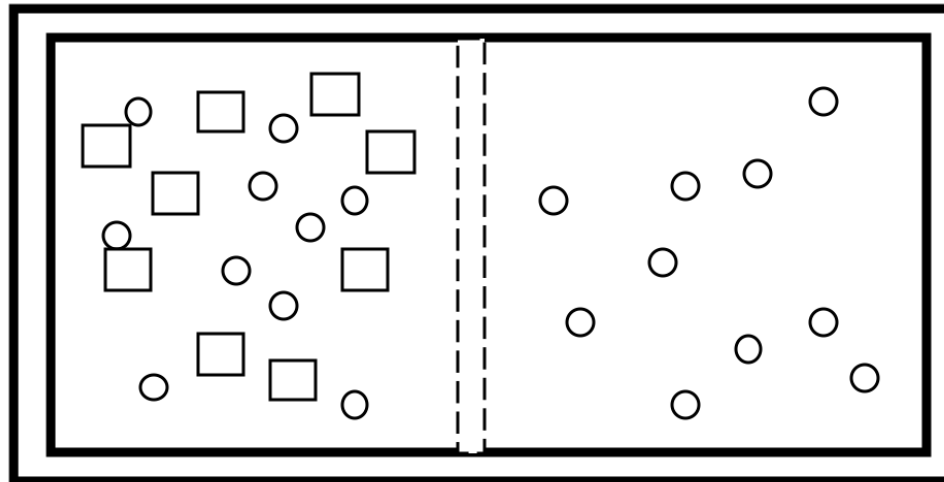
$P\Delta V$ for this system is A) positive, B) negative or, C) zero.

ΔU for this system is A) positive, B) negative or, C) zero.

ΔG for this system is A) positive, B) negative or, C) zero.

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.

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 $I_Q = (\text{energy change } \Delta U)/(\text{time } \Delta t)$ 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?

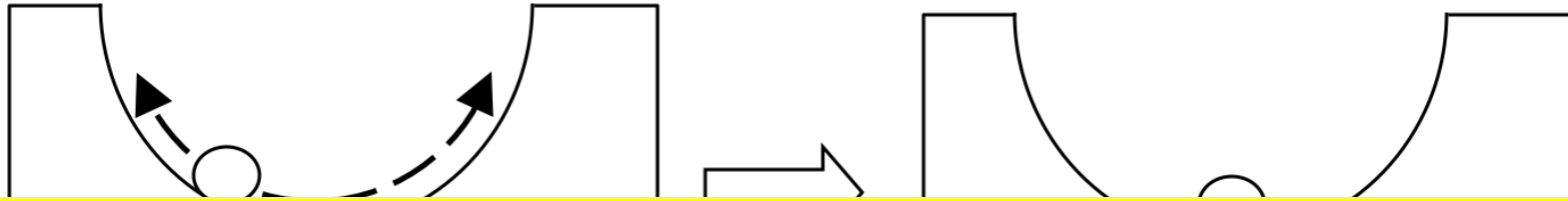
A) increases by 2 (takes longer to cool) B) decreases by 2 (cools faster) C) decreases by 4 D) increases by 4 E) some other answer



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

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 [$\Delta S = Q/T$, 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.

Is internal energy U and entropy S intensive or extensive?

- A) both are intensive
- B) both are extensive
- C) one is intensive, the other extensive

If the number of particles N in a system is doubled at constant pressure p and constant temperature T , then

the volume V of the system

- A) doubles
- B) remains constant
- C) increases, but does not double

the chemical potential μ of the system

- A) doubles
- B) remains constant
- C) increases, but does not double

What happens to the Gibbs Free Energy?

- A) doubles
- B) remains constant
- C) increases, but does not double

A macroscopic sample is in equilibrium at temperature T and pressure p . The temperature T and the pressure p both increase. The Gibbs free energy of the sample

- A) increased
- B) decreased
- C) impossible to say, without more info