Week 4

Entropy and entropic forces

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:

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

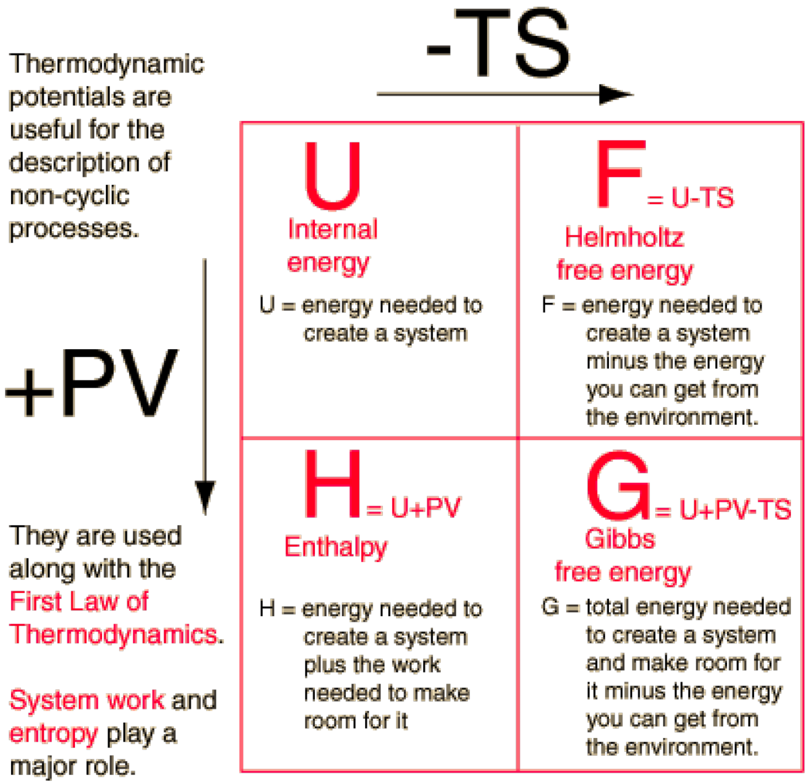
Reaction rates

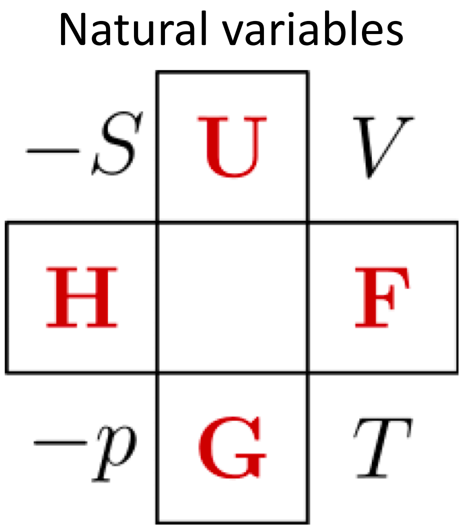
+ why F is a natural variable for (NVT)

- Tilstandsvariable: S, N, V, U, P
- 1. lov: $\Delta U = Q + W$
- 2. lov: $\Delta S \geq 0$ for isolert system
- 3. lov: $S \rightarrow$konstant når $T \rightarrow 0$
- Likevekter
  - Termisk: $\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2} \Leftrightarrow$ $T_1 = T_2$
  - Mekanisk: $\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2} \Leftrightarrow$ $P_1 = P_2$
  - Kjemisk: $\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2} \Leftrightarrow$ $\mu_1 = \mu_2$
- Definert
  - Temperatur: $\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}$
  - Trykk: $P \equiv T \left(\frac{\partial S}{\partial V}\right)_{N,U}$
  - Kjemisk potensial: $\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$
  - Varmekapasitet: $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,V}$

Termodynamiske potensialer

- Indre energi: $U = U(S, V, N)$
- Entalpi: $H \equiv U + PV = H(S, P, N)$
- Helmholtz: $F \equiv U - TS = F(T, V, N)$
- Gibbs: $G \equiv U - TS + PV = G(T, P, N)$





- U(S,V), H(S,P), F(V,T), G(P,T)

Tolkning og bruk av potensialene, "fri energi"

Potensialene er energien som skal til for å lage systemet fra ingenting med de naturlige variablene hold konstant.

- V konstant: U – energien for å lage et system
- P konstant: H – energien for å lage et system pluss arbeidet for å lage plass til det
  - Normale forhold i en lab
  - Entalpien for reaksjon, formasjon, smelting, fordamping, blanding
  - Målt og tabulert for de fleste stoffer!
- T konstant: F – energien for å lage et system minus varmen som strømmer inn fra omgivelsene
- P, T konstant: G – energien for å lage et system pluss arbeidet for å lage plass til det minus varmen som strømmer inn fra omgivelsene
  - Målt og tabulert for mange stoffer og prosesser
  - Spontan prosess når Gibbs energi for reaktantene større enn for produktene
- Eller omvendt: den energien som er "fri" til å brukes når et system "forsvinner"

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

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

Solving, we find

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

Protein folding

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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,*]

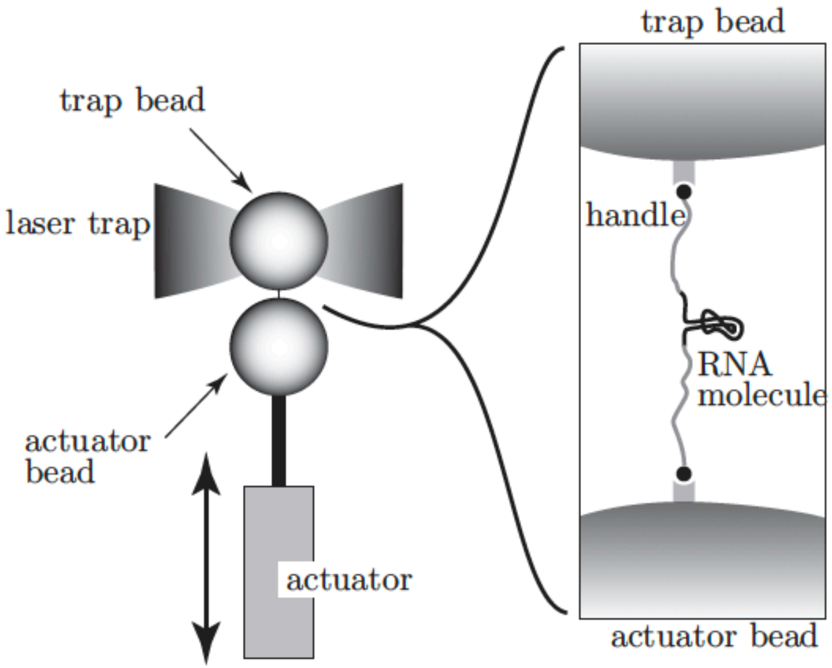
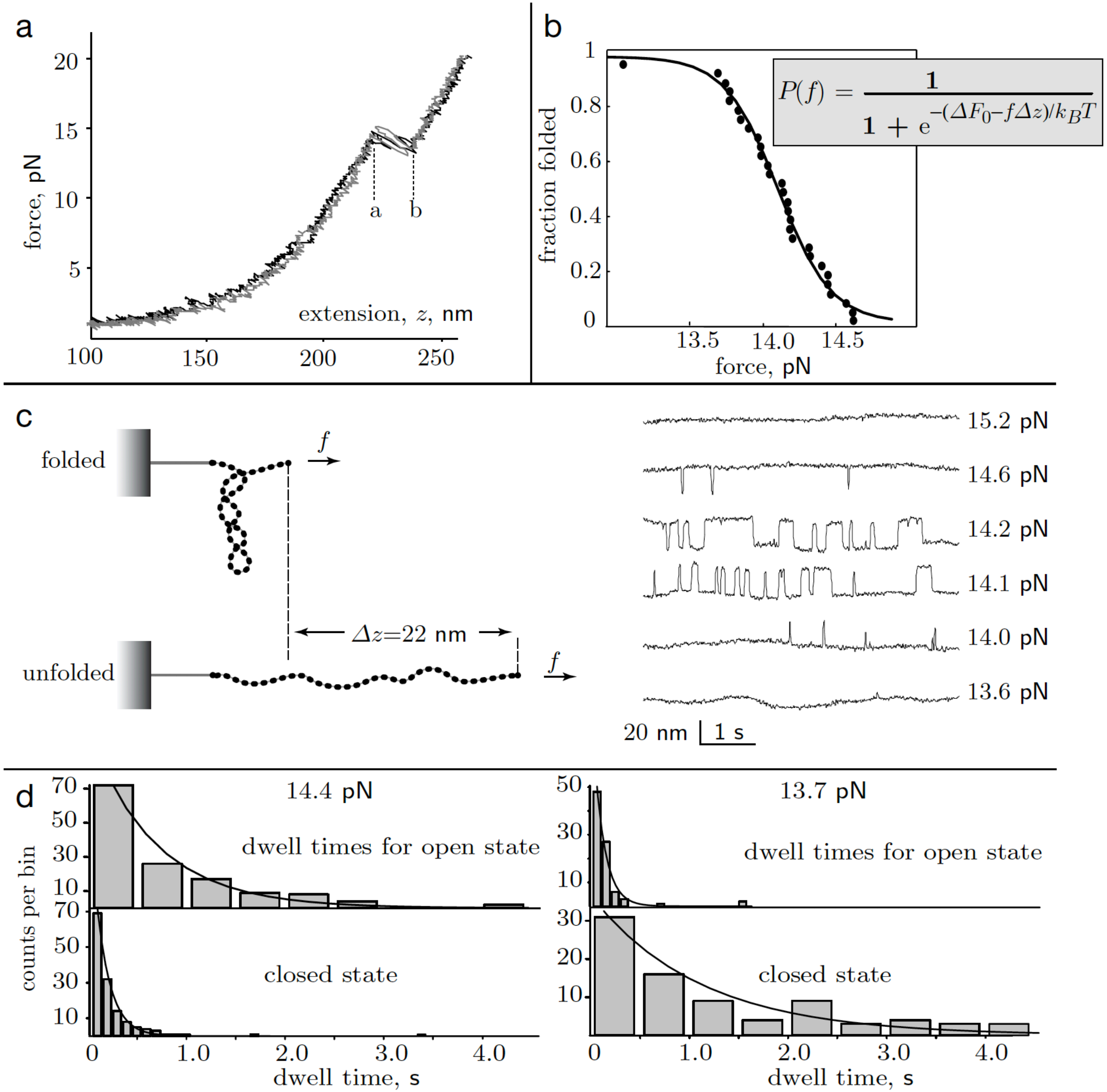
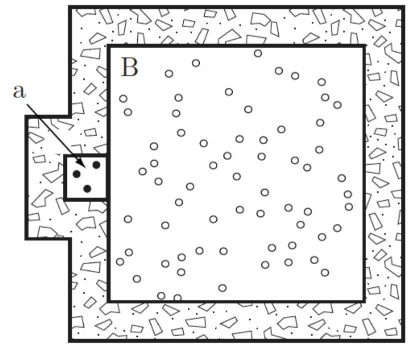


Figure 6.9: (Schematic.) Optical tweezer apparatus. A piezo-electric actuator controls the position of the bottom bead. The top bead is captured in an optical trap formed by two opposing lasers, and the force exterted on the polymer connecting the two beads is measured from the change in momentum of 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 ($\approx 3000\,\mathrm{nm}$), the RNA is tiny ($\approx 20\,\mathrm{nm}$). [Figure kindly supplied by J. Liphardt.]





small system in thermal equilibrium with large
⇒ (NVT) => F

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 $\sqrt{\langle(\Delta x)^2\rangle} = 35\,\mathrm{nm}$, and from this he computed the spring constant k. What value did he find?

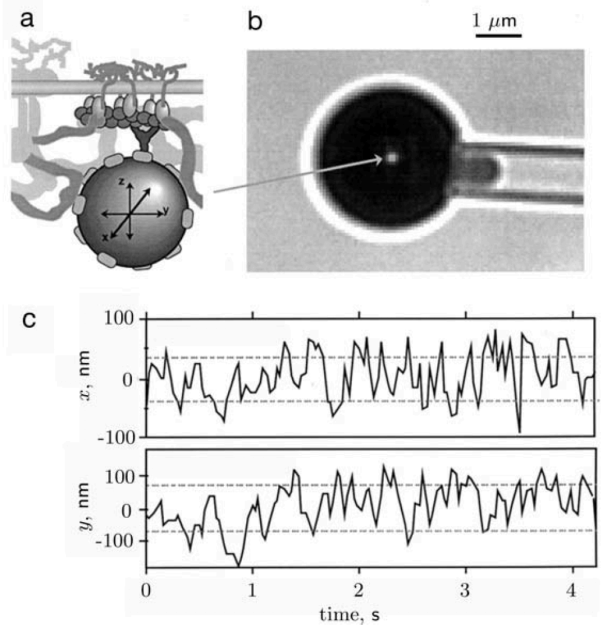


Figure 6.12: (Schematic; optical micrograph; experimental data.) (a) Attachment of a single fluorescent nanoparticle to actin in the red blood cell cortex. (b) The red cell, with attached particle, is immobilized by partially sucking it into a micropipette (right) of diameter 1 μm. (c) Tracking of the 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)).

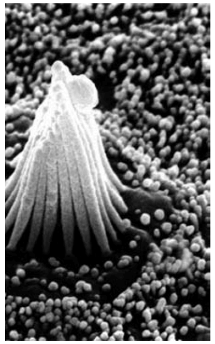
The experimenters measured the force-displacement relation for the bundle by using a tiny glass fiber to poke it. A feedback circuit maintained a fixed displacement for the bundle's tip, and reported back the force needed to maintain this displacement. The surprise is that the experiments gave the complex 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!

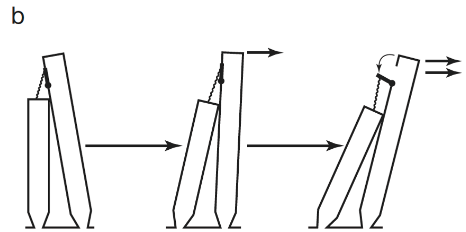
To explain their observations, the experimenters hypothesized a trap-door at one end of the tip link (top right of the wiggly line in panel (b)), and proposed that the trap-door was effectively a two-state system.

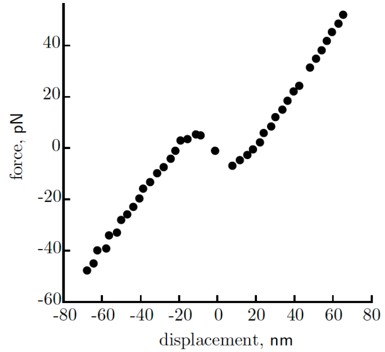
a. Explain qualitatively how this hypothesis helps us to understand the data.

b. In particular explain why the bump in the curve is rounded, not sharp.

c. In its actual operation the hair bundle is not clamped; its displacement can wander at will, subject to applied forces from motion of the surrounding fluid. At zero applied force the curve shows *three* possible displacements, at about −20, 0, and +20 nm. But really we will never observe one of these three values. Which one? Why?







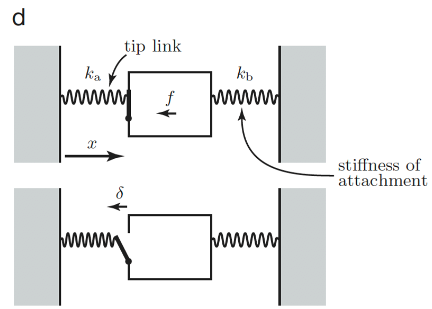
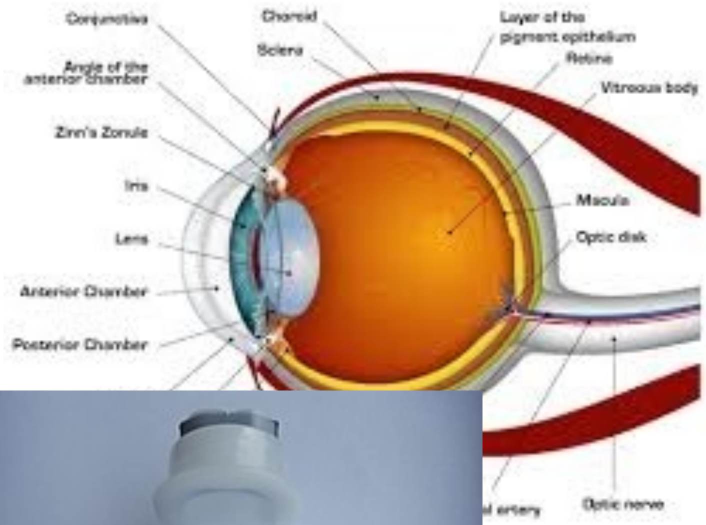
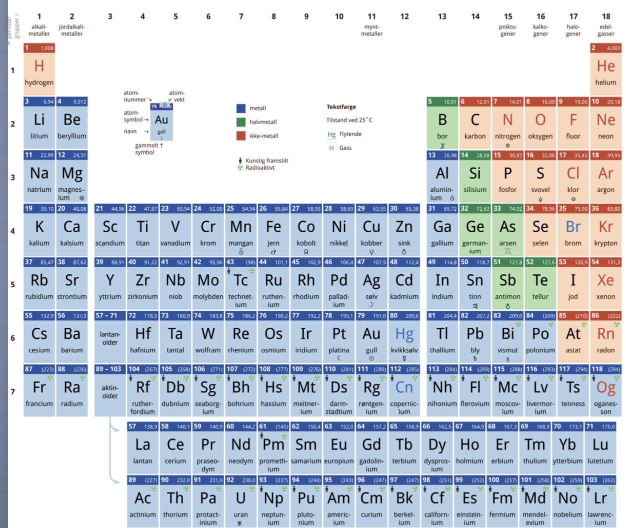
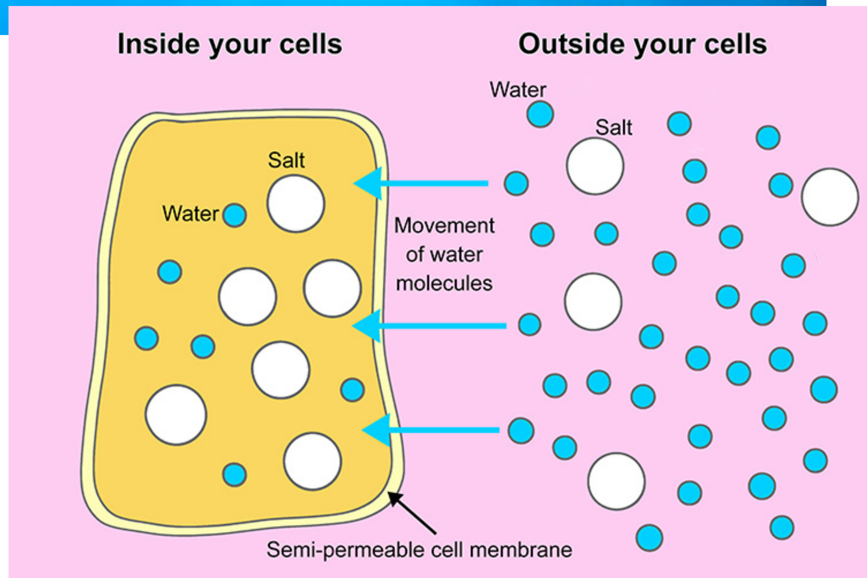


Figure 6.13: (Scanning electron micrograph; diagram; experimental data; diagram) (a) Bundle of stereocilia projecting from an auditory hair cell. [Digital image kindly supplied by A. J. Hudspeth.] (b) Pushing the bundle to the right causes a relative motion between two neighboring stereocilia in the 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.

Why do your eyes hurt in fresh water?







Depletion pressure