

# Lecture 13: Ion Channels and Nanopores

13.1

## "Classical" Fractionalization

### 13.0 Two senses of quantum

Quantum dynamics: interference, coherence, etc.

Quantum discreteness: charge unit for electrons + ions  $s_z$

The second is deeply related to the first, since  $e_{\text{electron}} = \hbar e_{\text{field}}$   
↑  
in classical  
Lagrangian

But quantum discreteness is much more robust; in particular, it withstands temperature quite well, and its effects remain visible at room temperature <sup>(+ above)</sup> in many ways.

In this lecture we'll use classical dynamics (mainly) but play with quantum discreteness. We'll find remarkable realizations of confinement and fractionalization.

## 13.1 The Problem of Ion Channels + Transport

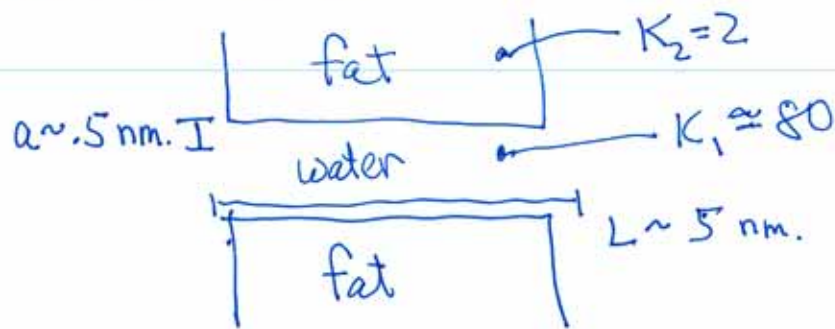
refs. : Minnesota group cond-mat 0503027, 0505490, 0510327 ...

R. Mackinnon: Nobel lecture (biological ion channels, for real)

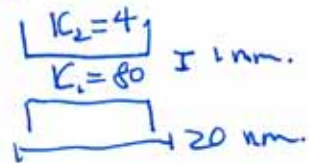
nobelprize.org/nobelprizes/chemistry/laureates/mackinnon-lecture.pdf  
[chemistry 2003]

13.1.1 Transport of ions into + out of cells is an extremely important aspect of biology.  $\phi$ /ATP pump; nerve signals; pH regulation, ...  
↳ controls how fast we think!

It occurs in a highly regulated way, through pores in the cell ~~cell~~ membrane. A cartoon version:

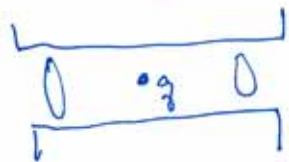


13.1.2 Artificial versions can be constructed too. They are used for desalination + other purposes. 1d nanowires are closely related, too. Si film



13.1.3 Because of the big ratio  $K_1/K_2 \approx 40$ , electric field lines want to stay within the pore. This leads to "1d" Coulomb behavior,  $\Phi \sim |x|$ . This tends to forbid isolated charges (confinement).

13.4 More precisely



$$E_0 = \frac{2q}{8\pi\epsilon_0 K_1 a^2}$$

$$(K_1 E_0 2\pi a^2 = 4\pi q)$$

$$\text{Energy } U_L = \frac{K_1 E_0^2 V}{8\pi} = K_1 \left( \frac{2q}{K_1 a^2} \right)^2 \frac{L\pi a^2}{8\pi} = \frac{q^2 L}{2K_1 a^2} \propto L$$

$\left( \frac{1}{4} \frac{q^2 E_0 L}{\epsilon_0} \right)$



13.5 Numerically, for the bionanopore

$q = e$     $L = 5 \text{ nm} = 5 \times 10^{-7} \text{ cm}$     $\kappa_1 = 80$     $a = .5 \text{ nm}$

$$U = \frac{e^2 L}{2\kappa_1 a^2} = \frac{\alpha \hbar c}{2\kappa_1 a^2} = \frac{\alpha \hbar c \cdot 5 \times 10^{-7} \text{ cm}}{2 \times 80 \times (5 \times 10^{-8} \text{ cm})^2}$$

$$\approx \frac{1}{137} \frac{1}{8} 10^7 \left( \frac{\hbar c}{\text{cm}} \right) \cdot \frac{10^{-27} \text{ erg-sec}}{1.6 \times 10^{-12} \frac{\text{erg}}{\text{eV}}} \cdot 3 \times 10^{10} \frac{\text{cm}}{\text{sec}}$$

$$= \frac{3}{137 \times 8 \times 1.6} 10^{7-27+10+12} \text{ eV} = 1.7 \times 10^{-3} \text{ eV}$$

$$= 1.7 \times 10^{-1} \text{ eV} = 1.7 \times 10^3 \text{ K}$$

This creates a significant barrier for transport.  $e^{U/kT} \sim e^{1.7 \times 10^3 / 3 \times 10^2} \sim e^6$

- But not an overwhelming one. This is, I think, no coincidence - biology wants flexible control.

Note that the resistance  $R \sim e^{0/T}$  is highly non-Ohmic ( $\propto e^L$ ).

13.1.6 Of course the presence of other ions ~~is~~ affects this.

The first thing to notice is that ions in the channel are effectively confined. They cannot separate by much more than

$$x_T \approx \frac{T}{qE_0} = \frac{a^2}{2l_B}$$

where  $l_B \equiv \frac{q^2}{\epsilon_0 k_B T}$ .

For  $q=e, \epsilon_0=80, T=300K$

$$l_B = .6 \text{ nm. (check!)}$$

The 'mesons' are (marginally) 1d objects.

13.17 ~~Let~~ Let  $c$  be the density of ions in the bath.

What is the concentration of "mesons" (compact pairs) in the channel?

First ignore channel constraint on single ions, but consider its geometry

$$1d \text{ concentration of positive ions} = \pi a^2 c \equiv n$$

$$\text{Concentration of } \begin{array}{l} \nearrow \text{pairs} \\ \text{"} \\ \text{compact } n_p \end{array} = n^2 \cdot 2x_T = 2\alpha n, \text{ with } \alpha \equiv \frac{\pi c a^4}{2l_B}$$

But, compact pairs in fact don't care about the constraint, so this is a good estimate of  $n_p$ .

The average overlap  $\Rightarrow n_p x_T = 2\alpha^2$ . So  $\alpha$  is the characteristic dimensionless number.

13.1.8 Results:

For small  $\alpha$ , correction

$$U_L(\alpha) = (1 - 4) U_L(0)$$

For large  $\alpha^*$

$$U_L(\alpha) = 2^7 \pi^2 \alpha^{3/4} \exp\{-8.5\} U_L(0)$$

With voltage applied

$$R(V) \sim \exp\left\{ \frac{U_L(\alpha) - qV/2}{T} \right\}$$

← N.i. 1/2

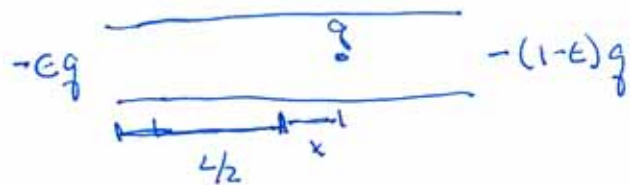
Formal theory not time (very pretty).

\*short" channel (no leakage)



### 13.1.9 Qualitative Story -

To minimize energy, the bath produces appropriate screening charges. These are not quantized.



Minimize field energy

$$\propto (-2\epsilon)^2 \left(\frac{L}{2} + x\right) + (2 - 2\epsilon)^2 \left(\frac{L}{2} - x\right)$$

$$0 = \epsilon \left(\frac{L}{2} + x\right) - (1 - \epsilon) \left(\frac{L}{2} - x\right)$$

$$\epsilon = \frac{1}{L} \left(\frac{L}{2} - x\right) = \frac{1}{2} - \frac{x}{L}$$

$$\text{Field energy} \propto \left(\frac{1}{2} - \frac{x}{L}\right)^2 \left(\frac{L}{2} + x\right) + \left(\frac{1}{2} + \frac{x}{L}\right)^2 \left(\frac{L}{2} - x\right) \propto \left(1 - \frac{2x}{L}\right)^2$$

parabolic shape, maximized at  $x=0$ ,  $\epsilon = \frac{1}{2}$

$$U_L(x) = U_L(0) \left(1 - \frac{2x}{L}\right)^2$$



Separating a pair always costs this <sup>barrier</sup> ~~factor~~ -  
regardless of concentration - because to move charge the  
image charges have to pass through  $\frac{1}{2}$ , and at that  
point the field just hops between  $\pm E_0/2$ !

13.9

13.1.9 The effect of concentration is more subtle. It  
arises not from energy, but from entropy.

At the critical concentration, pairs within the  
poor need not be compact, since the field is as bad  
as it can be. We have an "ordered free plasma".

The liberation of pairs contributes a large entropy  
if the concentration is large, only a small entropy if it is  
small, ~~otherwise~~

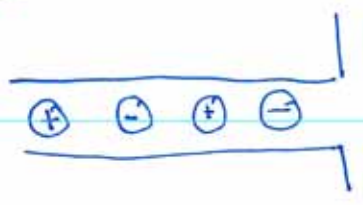
The importance of the voltage  $\eta$  to lower the barrier  
at the critical distribution where image charges are  $\frac{1}{2}$ . This  $\frac{V}{2T}$ !

## 13.2 Embedded Charges

13.2.1 The observed resistances are less than our considerations so far would suggest. Nature's trick is to embed charges in the pore (=doping!).

The most straightforward case is ~~to~~ to embed a periodic array of  $\oplus$  charges (say). - ion come in to screen them. The net effect is that we've increased the ion density, enhancing the entropy effect!

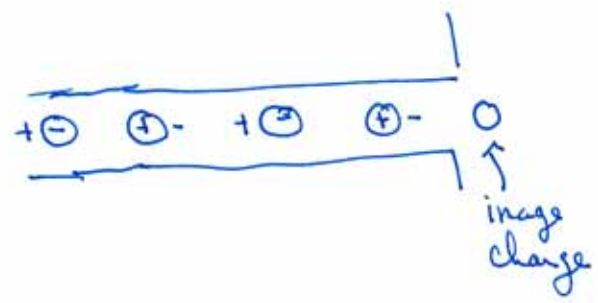
13.2.2 A very interesting, qualitatively new effect occurs for an alternating array.



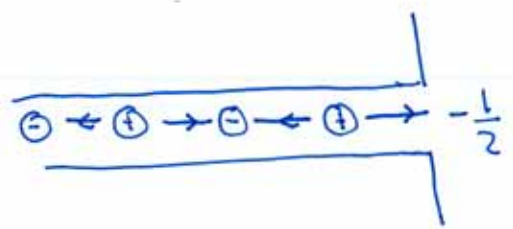
Now there are two candidate "ground states"

states"

i) ion binding



ii) empty pore



→ = 1/2 unit of flux

- i) has low energy and low entropy (ions localized)
- ii) has high energy and high entropy (ions free to roam)

The entropy difference depends on concentration.

$$\ln N! - \ln(N-n)! \sim + n \ln N$$

$$\left[ N \ln N - (N-n) \ln(N-n) \right] \sim n \ln N$$

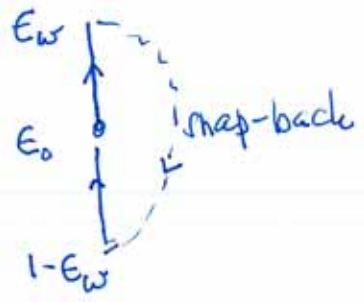
↳  $\ln N - \frac{n}{N}$



As a function of <sup>increasing</sup> concentration, there is a 1<sup>st</sup> order transition, at which the pore suddenly empties out (!)

13.2.3 To transport charge, we must go through a full cycle of image charges

history:



The 'worst' image charge  $E_w$  - i.e. the one for which the free energy is not unfavorable, - determines the barrier. [mini-max].

For the 0 ground state, the  $\frac{1}{2}$  state is worst! Thus near the transition the ~~resistance~~ barrier (and the resistance) get small.

For the  $\frac{1}{2}$  "empty" ground state the 0 "empty" ~~ground~~ state is the minimax:

