Ion transport in ion channels

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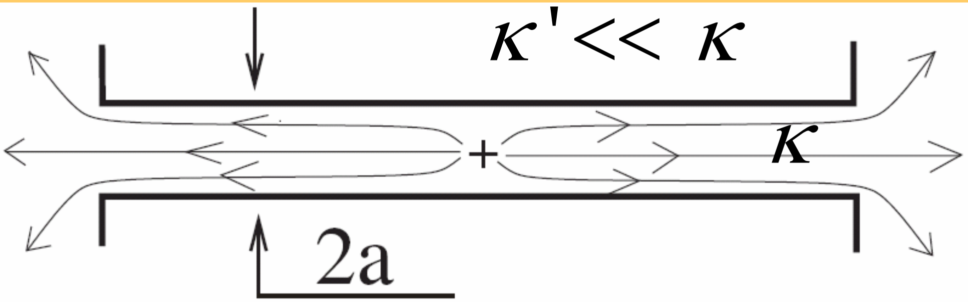
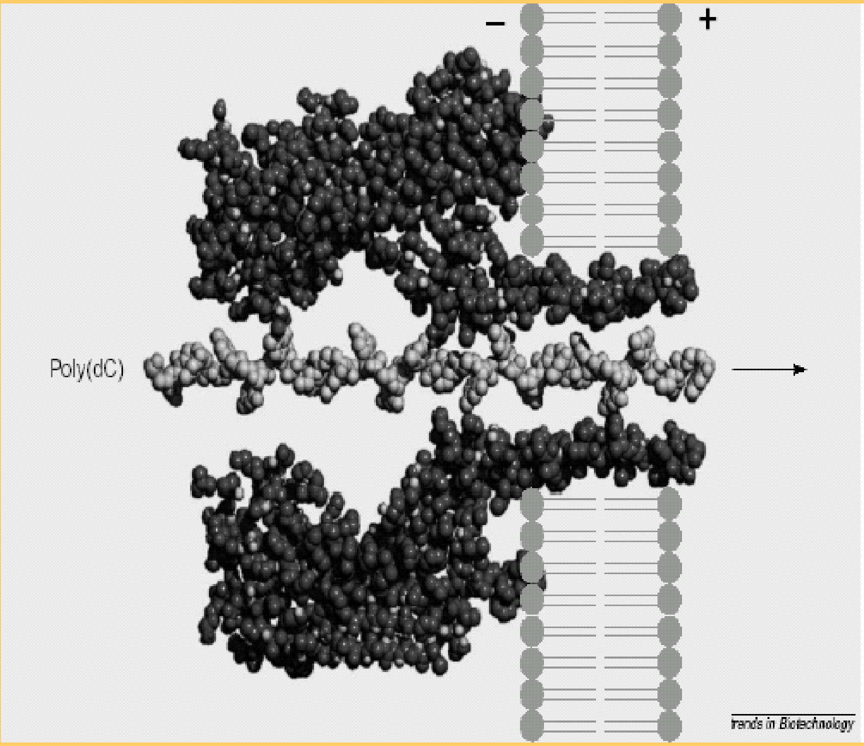
Motivation

- ion channels in biological lipid membranes

  α-Hemolysin:

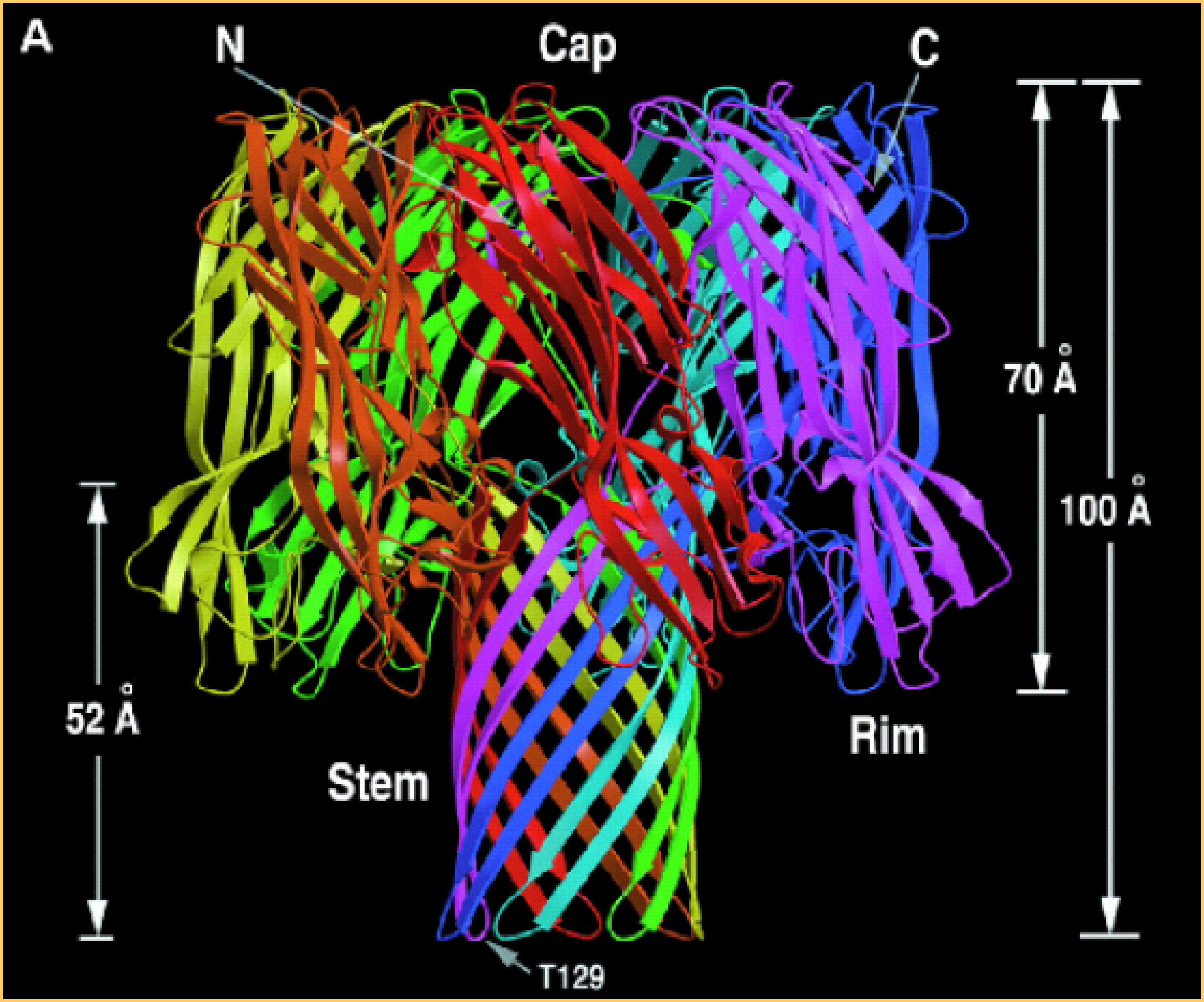




(length L>> radius a)

- water filled nanopores for desalination
- water filled nanopores in silicon oxide films

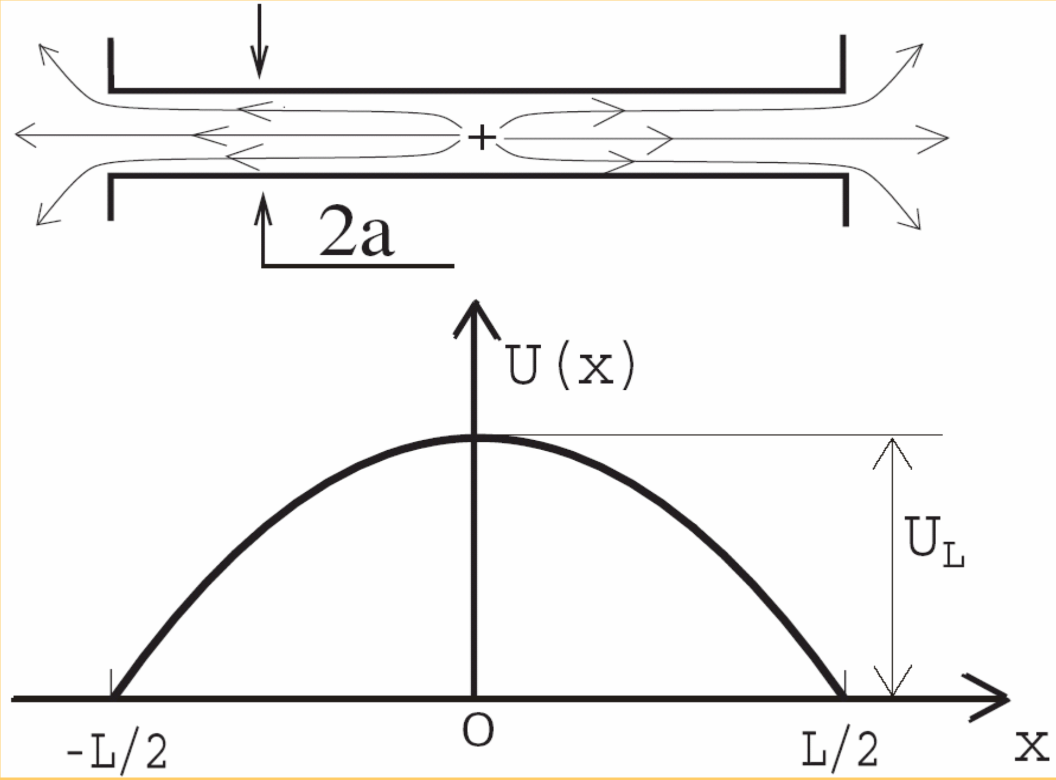
α-Hemolysin:



Self-energy of a single ion

$$U = \frac{\kappa}{8\pi}\int E^2 d^3 r$$

For the central location Gauss theorem: $E_0 = \frac{2e}{\kappa a^2}$

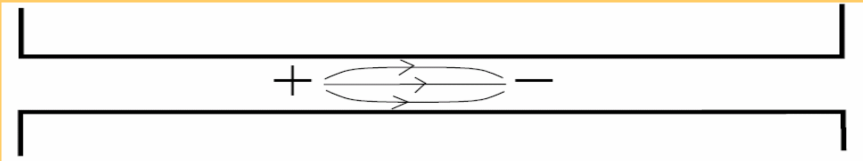


Maximum value of the barrier

$$U_L = \frac{e^2 L}{2\kappa a^2}$$

Pairs exist in ground state

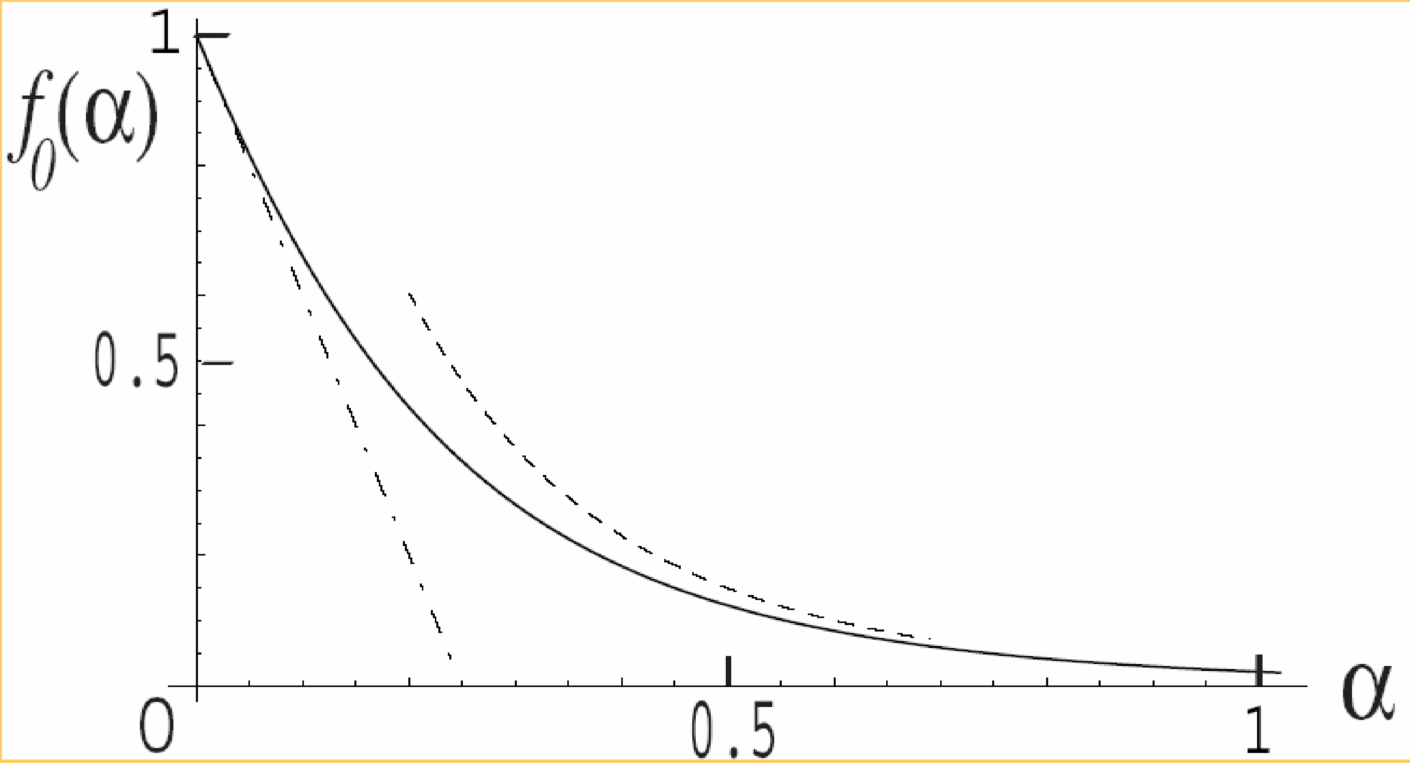
- A pair in the channel:



- Length of a pair: $$x_T = \frac{k_B T}{eE_0} = \frac{a^2}{2l_B} \qquad l_B \equiv \frac{e^2}{\kappa k_B T} = 7\ \mathring{A}$$
- Dimensionless concentration of ions:
$$\alpha = n x_T = c\pi a^2 x_T$$
- Concentration of pairs: $$n_p = 2n^2 x_T \qquad (n_p x_T = 2\alpha^2)$$
- At low concentration $\alpha << 1$ pairs are sparse. At high concentration $\alpha >> 1$ pairs overlap and the concept on pairs is no longer valid.

Main Results:

Transport barrier decreases with ion concentration



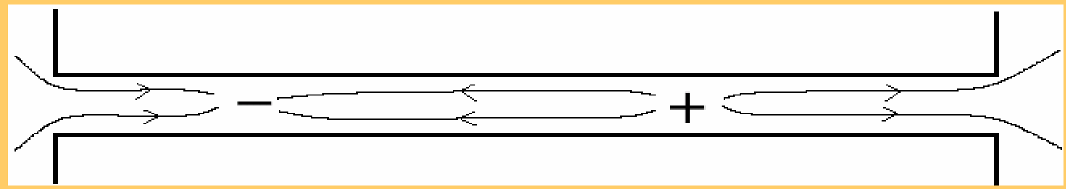
$f_0(\alpha) \equiv U_L(\alpha)/U_L$ is normalized barrier height

α is dimensionless ion concentration

Low concentration: collective ion barrier

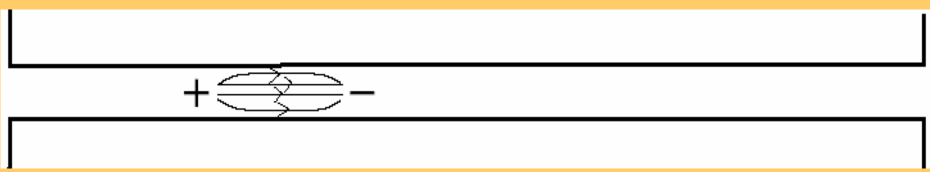
Energy barrier at saddle point is a constant value U_L although there are more than one ions in the channel

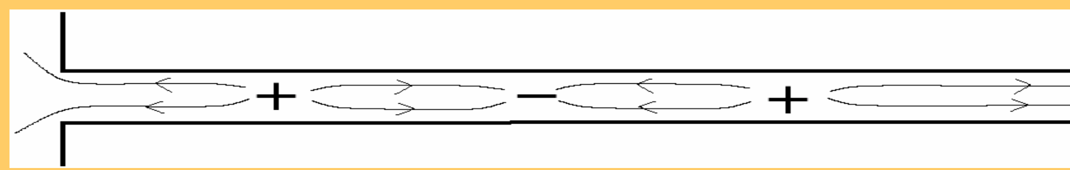
example of two ions:



However, putting an ion to the center of the channel by hand (at saddle state)

→existing pairs are opened in one direction





a pair at ground state

the pair is open at the saddle point

→Pairs are dissolved into single ions sitting alternatively

Low concentration: collective ion barrier

Ions are free to enter

→ Entropy at the energy barrier increases

$$S = 2(N-\Delta N)\ln\frac{eV/l_0^3}{N-\Delta N} + 2\Delta N\ln\frac{e\Delta V/l_0^3}{2\Delta N}$$

the optimum value of S happens at

$\Delta N = \tfrac{1}{2} nL = \tfrac{1}{2} c\pi a^2 L$ and $\Delta S = k_B \Delta N = \tfrac{1}{2} c k_B \pi a^2 L$

→ Barrier in free energy decreases by $\Delta F = -T\Delta S$

→ Result $f_0(\alpha) \cong 1 - 4\alpha$

From low concentration to high concentration: Is there a metal—insulator transition?

Ground state

- At low concentration ion pairs are rare

  distance between pairs >> pair length

- At high concentration: ion pairs overlap

→ concept of pairs is no longer valid

→ *ions are freed, there is no barrier (<u>TRUE ?</u>)*

High concentration: reason of barrier

Electric field in the channel are discrete values (Gauss law)

- At equilibrium electric fields are integers: $E/(2E_0)=n$
- At barrier electric fields are half-integers: $E/(2E_0)=n+\frac{1}{2}$

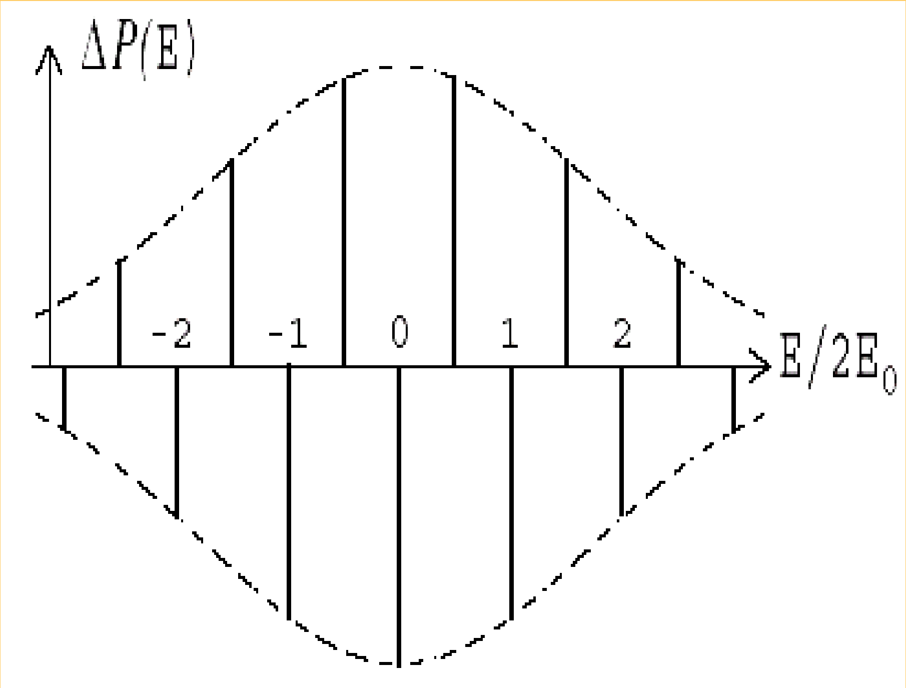
Height of the barrier:

$$U_L(\alpha) \propto \int_{-\infty}^{\infty} E^2 \Delta P(E)\, dE$$

$$\approx -\int_{-\infty}^{\infty} E^2 \cdot \cos[\frac{\pi E}{E_0}] \cdot \exp[-\frac{E^2}{2<E^2>}]dE$$

$$\propto -\int_{-\infty}^{\infty} \cos[\frac{\pi E}{E_0}] \cdot \exp[-\frac{E^2}{2<E^2>}]dE$$

$$\propto \exp[-2\pi^2 <E^2>/E_0{}^2]$$



High concentration: calculation of barrier

$$< E^2 > / E_0{}^2 = 4 n x_D \propto \sqrt{\alpha}$$

$$U_L(\alpha) \propto \exp[-2\pi^2 < E^2 > / E_0{}^2] \propto \exp[-\pi^2 \sqrt{\alpha}]$$

Exact asymptotic:

$$U_L(\alpha) \propto \exp[-8\sqrt{\alpha}]$$

Quantitative method

Partition function

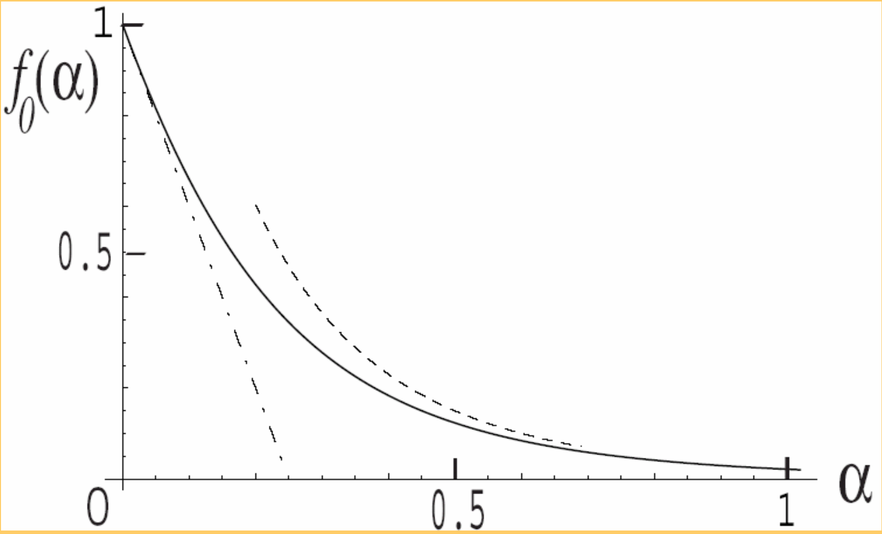
$$Z_L(q,q') = \sum_{N,N'=0}^{\infty} e^{\mu(N+N')/(k_BT)} \frac{1}{N!N'!} \times \prod_{j=1}^{N+N'} \left(\frac{\pi a^2}{l_0^2} \int_{-L/2}^{L/2} \frac{dx_j}{l_0}\right) \cdot e^{-U(q,q')/(k_BT)}$$

$$\rightarrow \int_{-\infty}^{\infty} \frac{d\theta_i d\theta_f}{4\pi^2} e^{iq\theta_i + iq'\theta_f} \int D\theta(x) \exp\{-\frac{k_BT}{2} \int \int_{-L/2}^{L/2} dx dx' \theta(x) \Phi^{-1}(x-x') \theta(x') + 2\pi a^2 c \int_{-L/2}^{L/2} dx \cos\theta(x)\}$$

is mapped to question of 1d quantum mechanics problem with “Schrödinger equation”

$$-\frac{1}{2}\frac{\partial^2 \Psi}{\partial \theta^2} - \alpha \cos\theta \cdot \Psi = -\frac{x_T}{2}\frac{\partial \Psi}{\partial x}$$

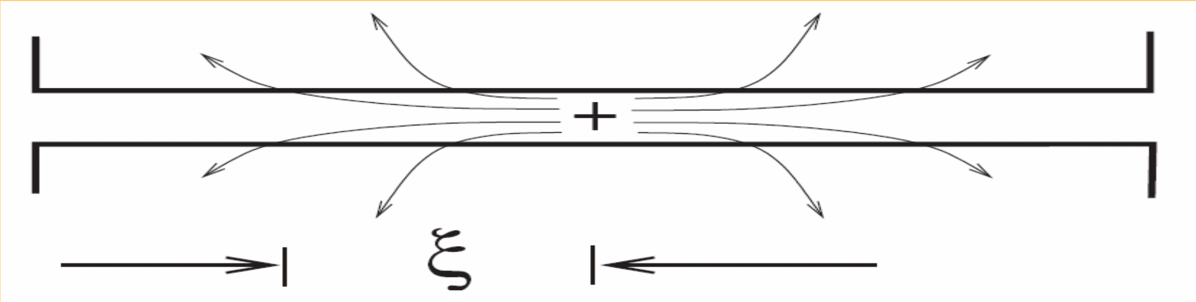
and eventually find the result



Beyond the simplest model

- Ratio of dielectrics κ / κ' is not infinity

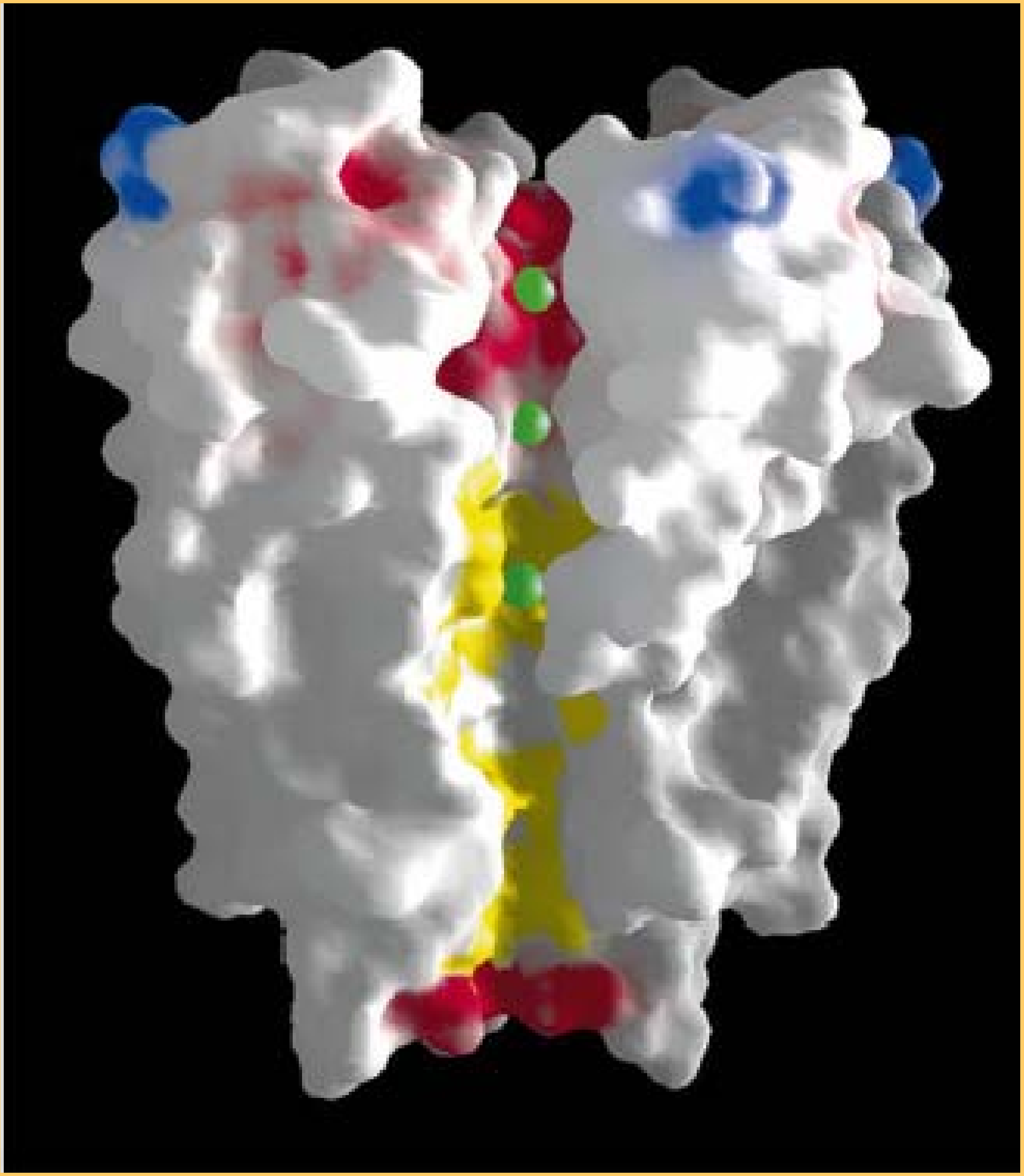
$\rightarrow$Electric field lines begin to leave at $\xi >> a$



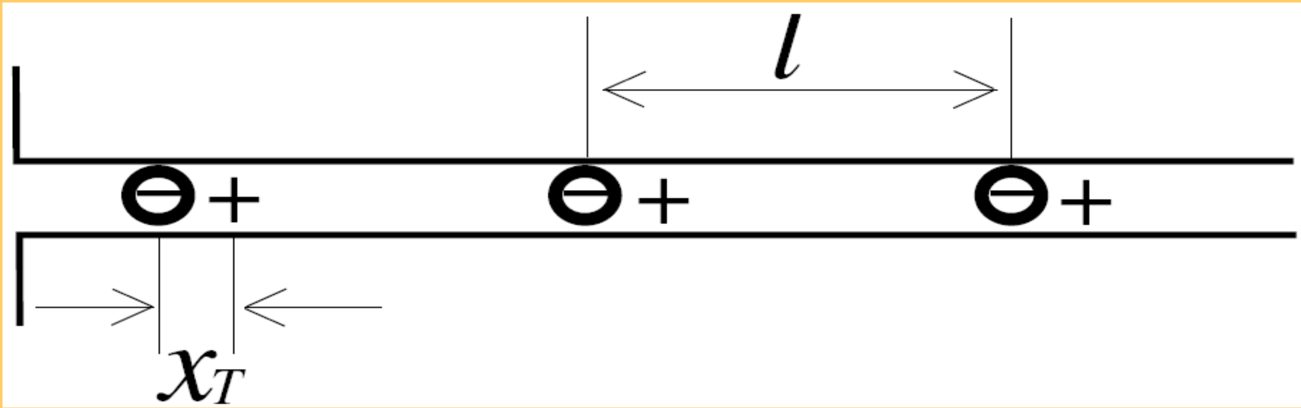
- Channel lengths are finite
- Ions are not planes $\alpha \rightarrow \alpha_{eff}$

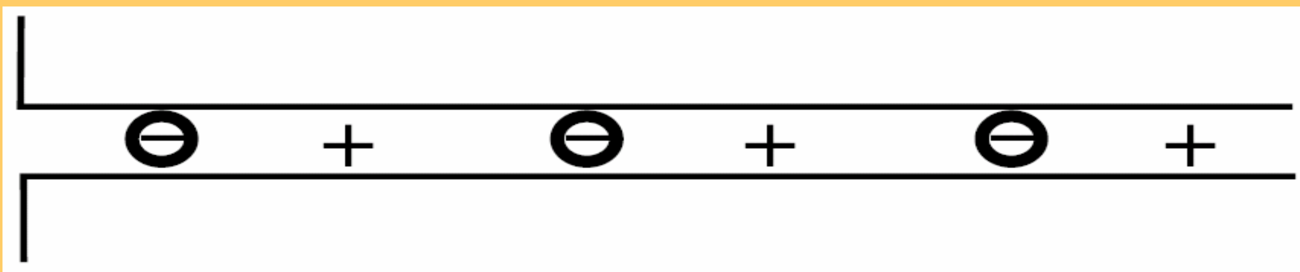
see A. Kamenev, J. Zhang, A. I. Larkin, B. I. Shklovskii *cond-mat/0503027*

Doped channels: K channel



- Doped channel: a simple model





$$\beta = l / x_T << 1$$

$$f_0(\beta) \cong 1 - 4\beta \ln(1/2\beta)$$

Future work: DNA in the channel