# ICFP M2 – SOFT MATTER PHYSICS
# Tutorial 7. Manning condensation on DNA

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DNA is a polymer containing charges : a so-called polyelectrolyte. In addition to potentially altering the monomer-monomer interactions and thus the chain conformation, these charges interact with counterions from the solvant. This interaction can even lead to a massive condensation of the counterions around the chain – the latter becoming "dressed" by counterions and thus bearing a reduced effective charge. Here, we would like to understand this phenomenon using Manning's seminal argument, and estimate further the free-counterion fraction related to the osmotic pressure. For the latter purpose, we recall the general Debye-Hückel framework for electrolyte solutions.

## I Condensation criterion

We describe the chain as an infinite and straight line, along the axis of which identical charges $e$ are equally spaced with spatial period $b$. The chain is in a solvant of permittivity $\epsilon$.

**1** Comment on the validity of the straight-cylinder assumption.

**2** Give the electric field $E$ and the potential $\Phi$ at distance $d$ from the axis.

**3** We consider a monovalent counterion of charge $-e$ placed at distance $d$ from the axis. Calculate the interaction energy and show that the average counterionic concentration scales as $c \sim d^{-2\xi}$, where $\ell_\mathrm{B} = \xi\, b$ is a characteristic length – to be described.

**4** Evaluate the number of counterions, per charge on the chain, between the axis and an arbitrary distance $d_\mathrm{max}$.

**5** Show that condensation of counterions along the chain is expected for $\xi > 1$.

**6** Assuming that, when $\xi > 1$, the condensation brings back $\xi$ to 1 by reducing the effective chain charges, estimate the fraction of neutralized chain charges as a function of the initial $\xi$. How is this result modified for a counterion of charge $ze$ ?

**7** Estimate the condensation-induced neutralization of charges on DNA ($b \approx$ 0.17 nm) at 37°C.

## II Debye-Hückel theory

We consider an assembly of different ions of types $i$, with charges $z_i\, e$, and global average concentrations $c_i^\circ$, thermalized in a solvant at temperature $T$.

**1** Express the electroneutrality constraint.

**2** In the following, we consider a given – fixed – test ion of type $j$ creating an electrostatic potential $\phi(r)$ at a distance $r$. What is the energy of another ion, of type $i$, placed in this potential ?

**3** How is the local average concentration $c_i(r)$, of ionic species $i$ at distance $r$ from the test ion, modified with respect to $c_i^\circ$ due to the interaction with the test ion ?

**4** What is the local charge density $\rho(r)$ at distance $r$ from the test ion ?

**5** In a static description, how are $\phi$ and $\rho$ related in a solvant of permittivity $\epsilon$ ? Obtain the so-called Poisson-Boltzmann equation satisfied by the electric potential $\phi$.

**6** Assuming a dilute solution, linearize the previous equation. What length scale $\lambda_{\mathrm{D}}$ does naturally appear ?

**7** Solve for $\phi(r)$ and interpret the meaning of $\lambda_{\mathrm{D}}$. One can invoke a vanishingly small ionic size $a$ in order to discuss prefactors.

# III Free counterions and osmotic pressure

We come back to the polyelectrolyte modelled in the first section, and we consider a situation where $\xi < 1$. We call $n$ the net number of charges on one chain, $N$ the number of chains, $V$ the volume, and we further assume $\lambda_{\mathrm{D}}$ to be much larger than the monomeric size $a$. Our aim is now to study the free counterions in solution in presence of the chains, by invoking the Debye-Hückel framework.

**1** Express the total potential $\psi(d)$ created by one chain at a given point located at distance $d$ from the axis. Show that it depends only on the variable $s = d/\lambda_{\mathrm{D}}$.

**2** Provide a low-$s$ asymptotic expression for $\psi$, and separate it into two contributions – a chain one $\psi_1$ and a counterionic one $\psi_2$.

**3** Calculate the work $W = n \int_0^e \psi_2 \, \mathrm{d}e'$, needed to establish the counterionic atmosphere of the chain, by effectively loading the chain charge (integration variable : $ne'$) from 0 to $ne$.

**4** What is the associated energy per unit volume ? How does it depend on the total polyelectrolytic charge concentration $c_{\mathrm{tot}}$ ?

**5** Recall the bare osmotic pressure $\Pi_0$ corresponding to a dilute homogeneous solution of monovalent counterions of concentration $c_{\mathrm{tot}}$. Explain the latter choice of concentration.

**6** Express the real osmotic pressure $\Pi = \Pi_0 + \Delta\Pi$, in presence of the chain.

**7** Determine the osmotic coefficient $\Pi/\Pi_0$ and interpret it as the fraction of free counterions. Discuss the case $\xi > 1$.