Beyond Manning Condensation: Exploring an infinite ergodicity analysis of the behaviour of counterions around cylindrical molecules

Introduction

Polymers, long chains of repeated molecules, can be found in both natural (e.g. DNA) and manufactured (e.g. plastics) materials. When these polymers are in liquid form or immersed in a solvent, some of its ions can become chemically unbound and free-moving. These ions hold an opposing charge to the polymer and are known as counter-ions. This new interaction causes the counterions to become electrostatically bound to the polymer, causing them to condense or 'dress' the surface of the polymer (Manning, 2007), if the polymer's charge density is greater than a critical point.

Method

To investigate the condensing and non-condensed phases, an infinite ergodic analysis, as described by Aghion (Aghion, 2020), combined with statistical mechanics were used to evaluate what happens when the line charge density, λ, reaches the critical threshold, λ_c, which is described by Manning to be specific to cylindrical particles (Manning, 2007), which in this case is a polymer.

Results

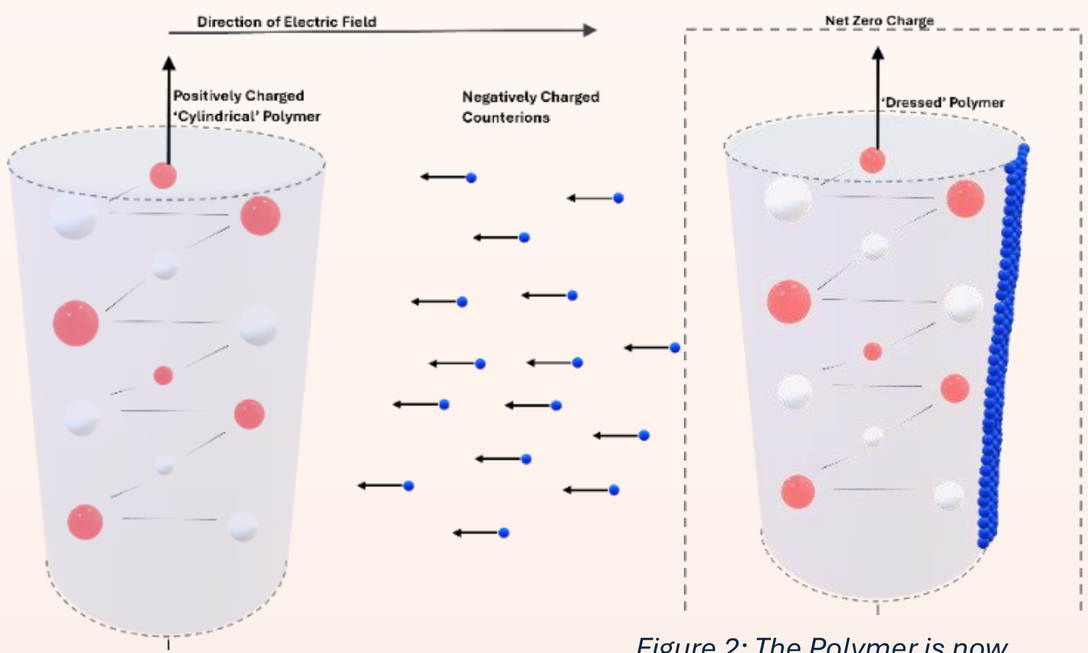

Figure 1: The polymer's charge density is larger than the critical threshold, causing the surrounding counterions to become electrostatically bound to it and so begin to condense.

Figure 2: The Polymer is now 'dressed'.

The general expression for the line critical charge density is:

$$\lambda_c = \frac{4\pi k_B T}{|q|}$$

When the charge density of the polymer is less than the critical threshold, the surrounding counterions will be 'weakly' electrostatically bound and begin to condense onto its surface and 'dress it'. As more counterions condense, the charge potential 'well' created by the polymer will start to become weaken, essentially becoming less attractive to opposing charges. This can cause changes to the polymer's properties, e.g. The rigidity of DNA.

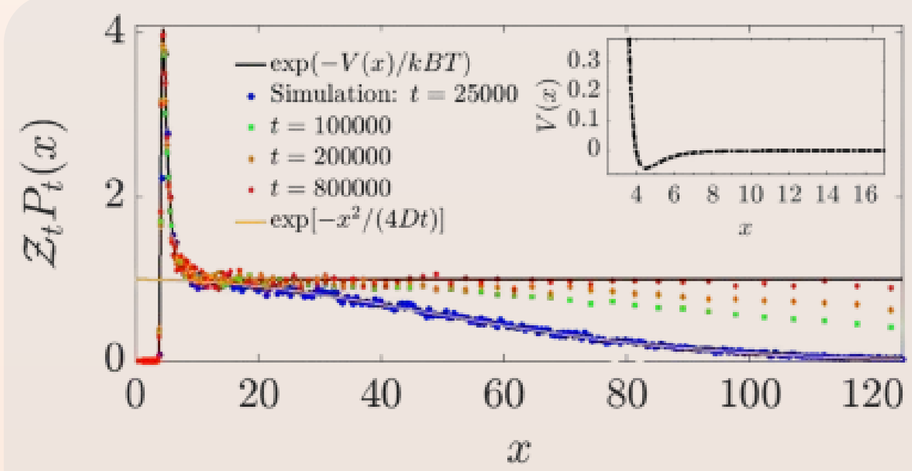

Figure 3: A graph by Aghion illustrating the probability density of a particle with a potential landscape similar to that of a power law decay, over multiple large-value times. [2]

When the polymer's charge density is lower than the critical threshold, the counterions will not condense onto the polymer, leaving them to freely move to infinity. The potential, $V(r) = V_0(r) - k_B T \ln(2\pi r)$, of the counterion once in a non-normalisable Boltzmann state, would produce a power law decay. Looking at Figure 3, it could be said that the trend of the probability density follows an exponential decay, and as the time increases, the curve tends less towards zero.

DNA

As a natural polymer, DNA is a chain of repeated molecules which make up your genetic identity. It is argued that the very strong bending rigidity (perceived stiffness) of DNA is an indirect effect of Manning condensation, where the condensed counterions will oppose each other, meaning they can't move closer to one another to allow the polymer to bend, keeping it rigid.

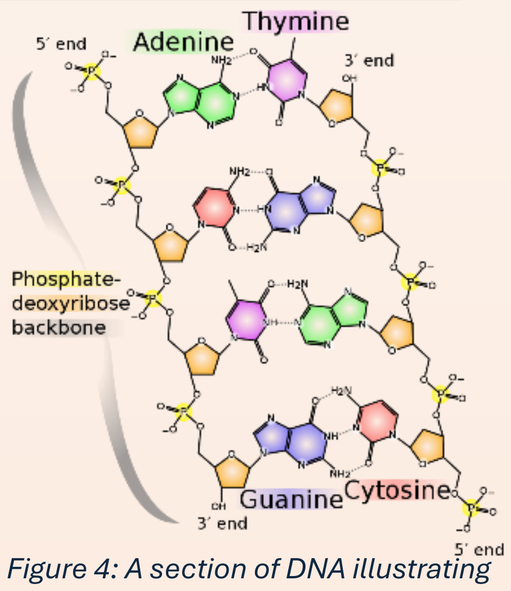

Figure 4: A section of DNA illustrating its polymer nature. (Argasinska, 2024)

Discussion

During the condensation of counterions onto a cylindrical particle like a polymer, it is well documented that the charge density of the polymer must be greater than a critical threshold for the counterions to 'dress' the polymer (Manning, 2007).

After looking at potential landscapes created using an infinite ergodic analysis of non-normalisable Boltzmann states, some of the potentials could be considered comparable, however only after further investigation can this be confirmed.

[1] G. S. Manning, *Counterion Condensation on Charged Spheres, Cylinders and Planes*, J. Phys. Chem. B, **v.111** (29), 8554, 2007

[2] E. Aghion et al., *Infinite Ergodic Theory Meets Boltzmann Statistics*, Chaos, Solitons & Fractals, **v.138**, 109890, 2020

[3] J. Argasinska et al., *Biomacromolecular structures*, EMBL-EBI, 2024, Accessed: 2024, available at: https://www.ebi.ac.uk/training/online/courses/biomacromolecular-structures/dna/

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