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On the origin of the slow mode and low *q* upturn in salt-free polyelectrolyte solutions

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Introduction

THEORY

The osmotic pressure of salt-free polyelectrolyte solutions is controlled by the contribution of free counterions[1-3] ($\approx k_B\,T$/free counterion):

$$\frac{\Pi}{k_B T} \approx fc + \frac{1}{\xi^3} \approx fc \qquad (1)$$

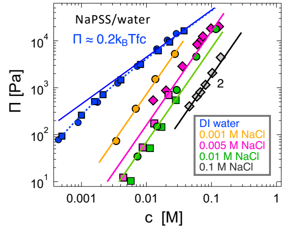
c is the monomer concentration and f the fraction of monomers with a free counterion.

Polyelectrolyte solutions are therefore expected to be highly incompressible and scatter weakly at low q:

$$S(0) = k_B T c \frac{dc}{d\Pi} \approx f^{-1} \qquad (2)$$

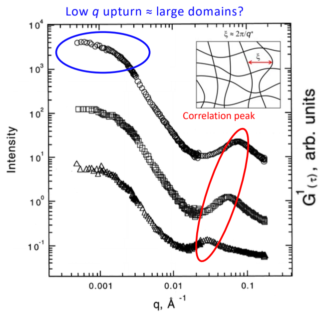
EXPERIMENTS

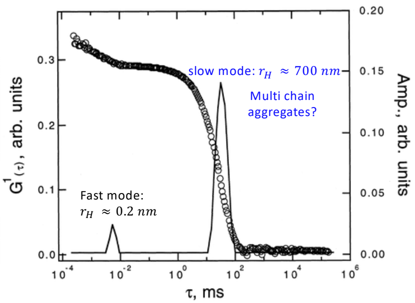
Osmotic pressure data confirm Eq. 1:[1]



Scattering experiments show two unexpected features of salt-free polyelectrolyte solutions:

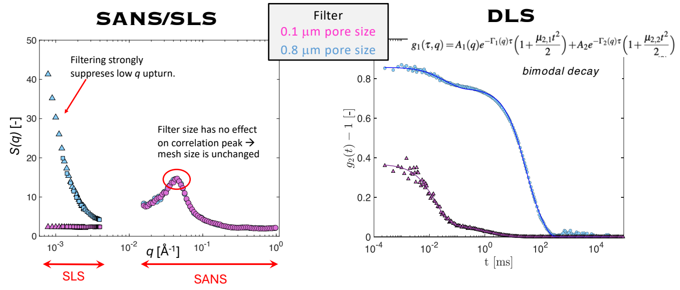
1) A huge upturn at low *q*
2) A *'slow mode'* in dynamic light scattering





- SANS data[4] show a huge upturn at low q, which is incompatible with Eq. 2
- Dynamic light scattering suggests the presence of large domains (≈100s nm)
- The presence of large domains is incompatible with the incompressible nature of polyelectrolyte solutions

New results: Light and neutron scattering



- Filtration through sufficiently small pore sizes suppresses the low *q* upturn and DLS slow mode
- Correlation peak is insensitive to filtration → polymer mesh size is not changed
- The solutions are stable for at least 1 month after filtering (slow mode and upturn do not re-appear)
- No mass loss detected from density measurements → No polymer removed during filtration

Scattering intensity without low-*q* upturn contribution

Combining SLS and DLS, we can calculate the scattering intensity of a polyelectrolyte solution without the contribution of the slow mode:

1 From the measure light scattering intensity (ΔR), we calculate the structure factor ($S(q)$):

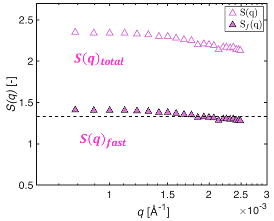
$$\Delta R(q) = \underbrace{K}_{\text{Optical contrast}} \rho_{pol}^2 N_A S(q)$$

2 The relative amplitude of the fast decay in DLS is used to isolate the structure factor without the slow mode:

$$S(q)_{fast} = \frac{A_1(q)}{A_1(q) + A_2(q)} S(q)$$

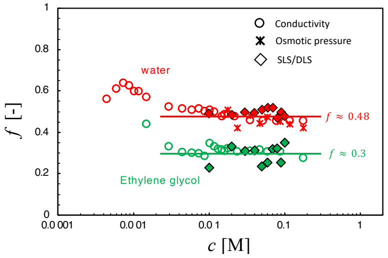
3 Extrapolating to q → 0 gives $S(0)$, which can be related the fraction of free counterions f

$$S(0) = 1/f$$

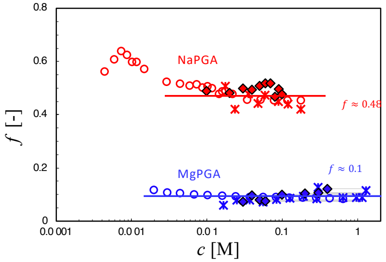


Fraction of free counterions evaluated with different methods

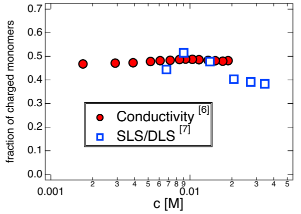
Sodium Polyglutamate



Na⁺ vs. Mg²⁺ counterions



Sodium carboxymethyl cellulose



Electrical conductivity, osmotic pressure (freezing point depression), and SLS/DLS yield consistent values for the fraction of free counterions, demonstrating that the scattering intensity of polyelectrolytes, after removal of the slow mode by filtration or DLS splitting, matches the values expected by de Gennes' scaling theory.

References

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Acknowledgements

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Find out more:
https://polyelectrolyte.science

Conclusions

Salt-free polyelectrolyte solutions are highly incompressible, so long-ranged concentration fluctuations should be suppressed. The slow mode in DLS and the low-*q* upturn in SANS have therefore puzzled researchers for decades. We show that filtration removes both features and develop a method to calculate the scattering intensity without the upturn contribution. The corrected intensity agrees quantitatively with theory.