Skoltech

Skolkovo Institute of Science and Technology

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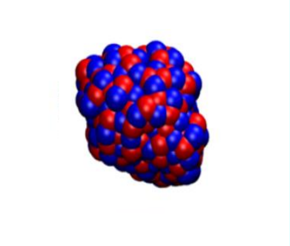
Nikolai Brilliantov



Controlled electrostatic collapse of polyelectrolytes

In collaboration with:

Vladimir Palyulin (Skolkovo Institute of Science and Technology, Moscow, Russia)

Aleksei Gavrilov (Moscow State University, Moscow, Russia)

Yury Budkov (Higher School of Economics, Moscow)

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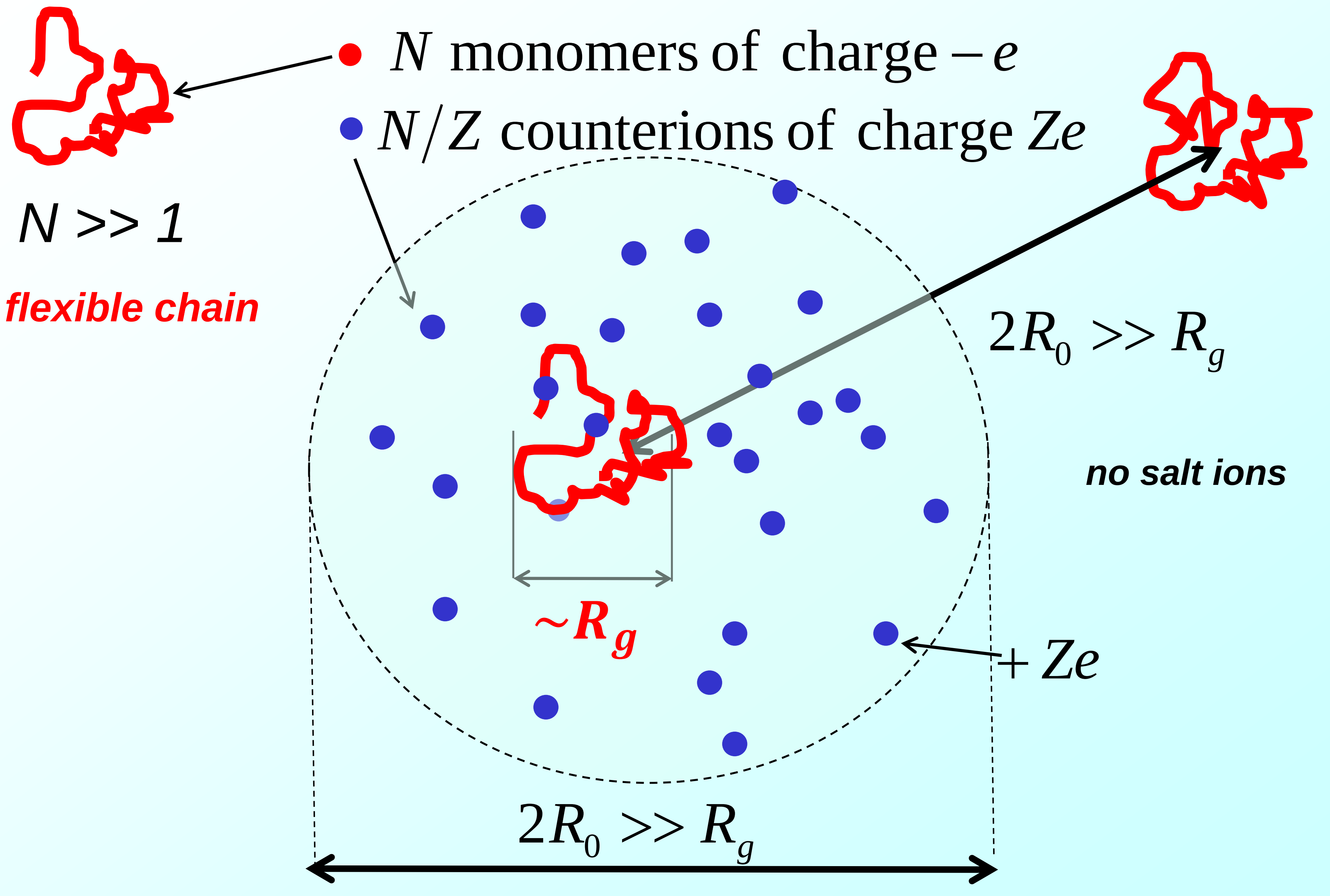
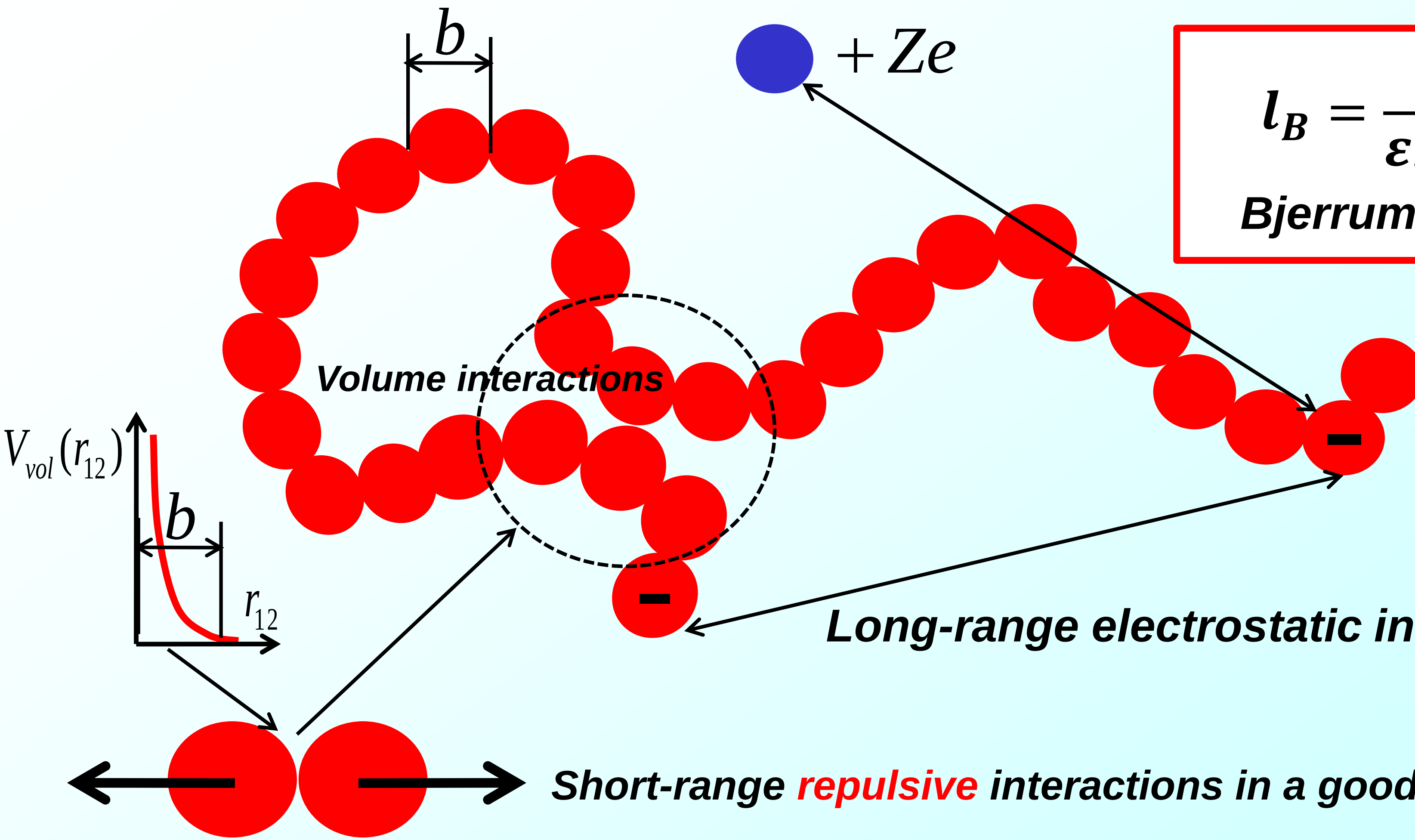
Christian Seidel (Max Planck Institute of Colloidal and Interfaces, Potsdam, Germany)

Anvy Moly Tom, Satyavani Vemparala, and R. Rajesh
(The Institute of Mathematical Sciences, Chennai, India)

Consider a dilute, salt free solution of charged polymer chains in a good solvent



Molecular interactions in a good solvent



$$l_B = \frac{e^2}{\varepsilon k_B T}$$

Bjerrum length

Long-range electrostatic interactions

Short-range repulsive interactions in a good solvent

Long-range electrostatic interactions

$$V_{el}\left(r_{ij}\right) = \frac{q_i q_j}{\varepsilon r_{ij}}$$

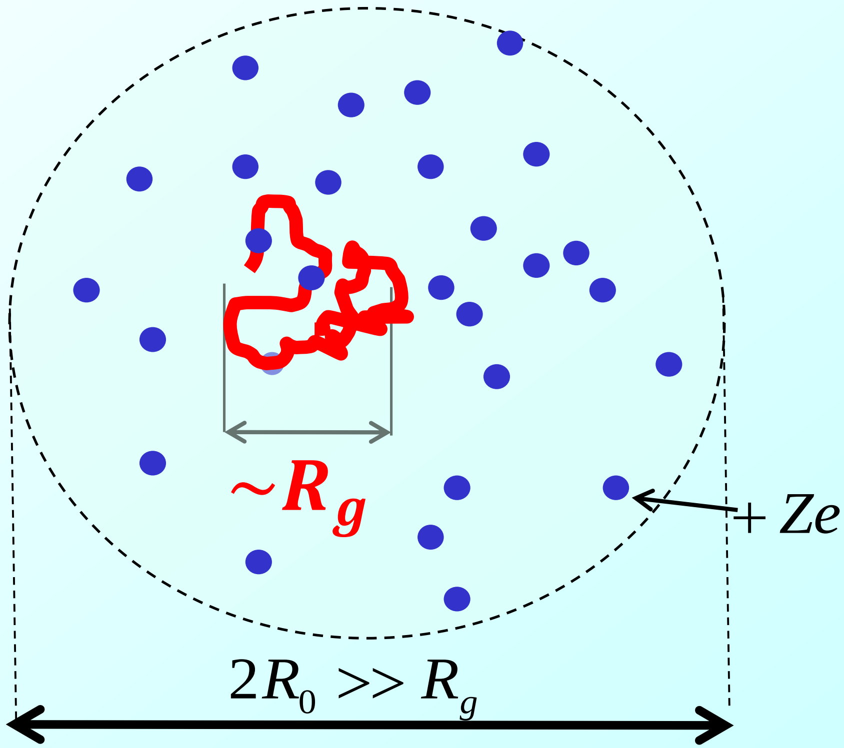
ε *-dielectric permittivity*

The gyration radius R_g may be controlled

1. ***By properties of the solvent, reflected in the l_B***

2. ***By external electric field***

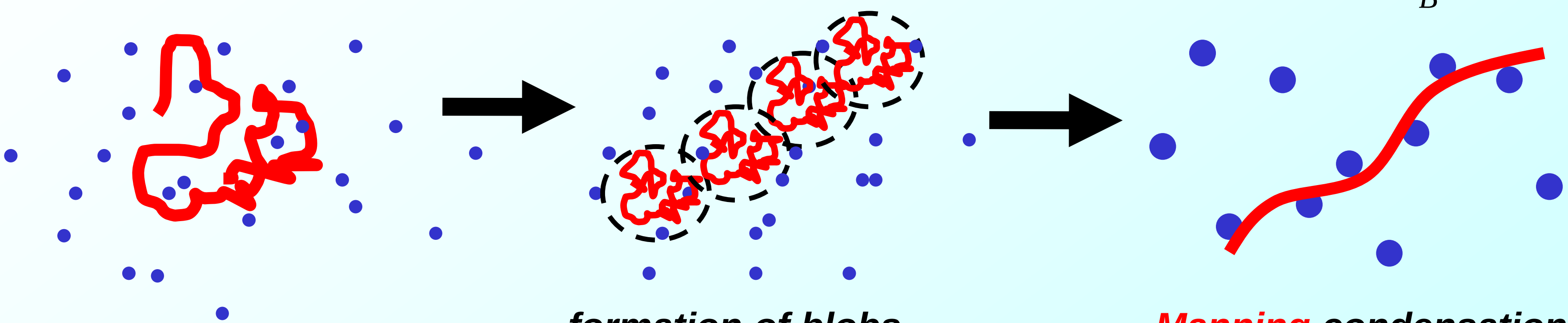
3. ***By concentration of added salt***



Consider variation of a chain conformation with increasing ℓ_B that is, with increasing strength of electrostatic interactions?

$$\ell_B = \frac{l_B}{b}$$

very small ℓ_B | *larger* ℓ_B | *still larger* $\ell_B = 1$

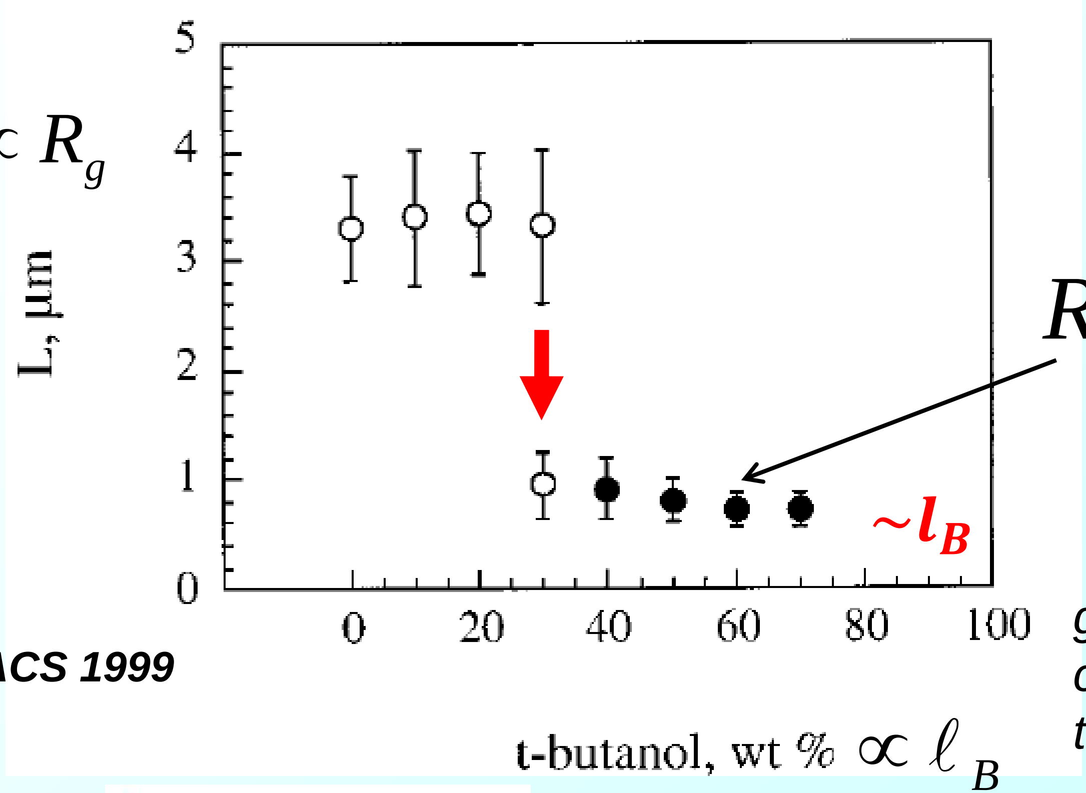


formation of blobs | *Manning condensation*

$R_g \propto N^{3/5}$ | $R_g \propto N$ | $R_g \propto N$

What happens next???

Experiments show collapse:

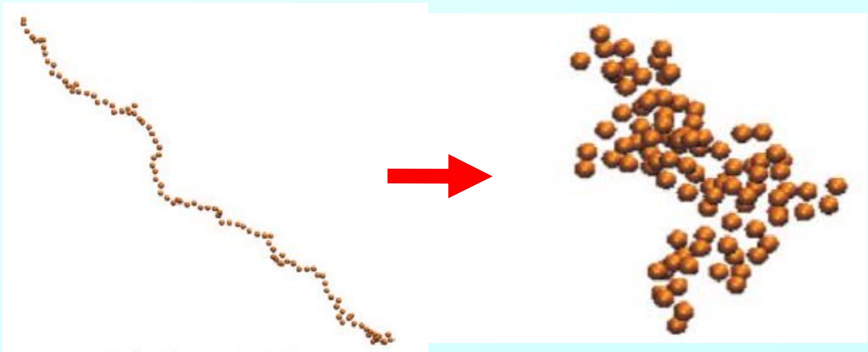


$\propto R_g$

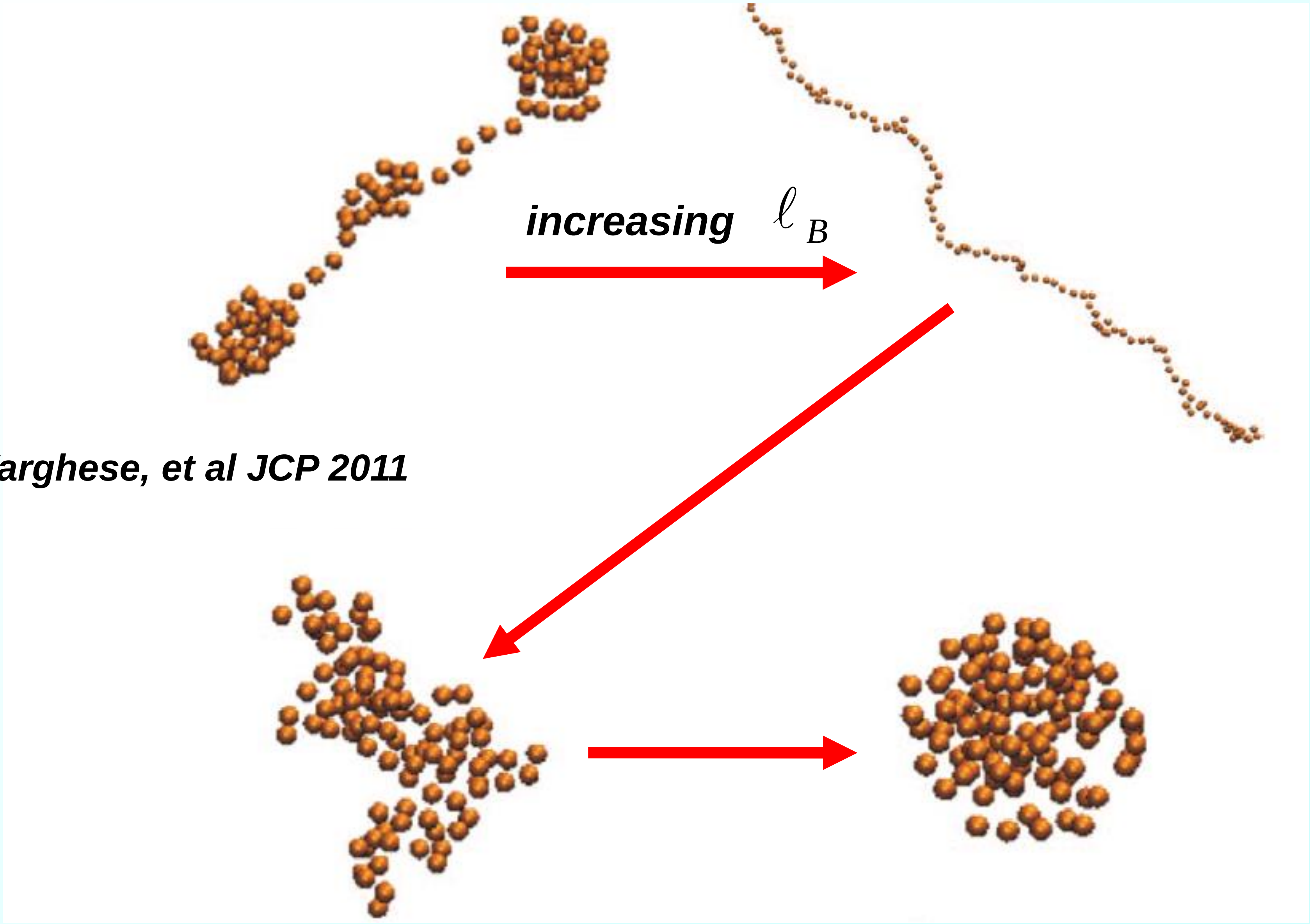
$R_g \propto N^{1/3}$

Melnikov, et al JACS 1999

good solvent for all concentrations of t-butanol



MD shows collapse as well:



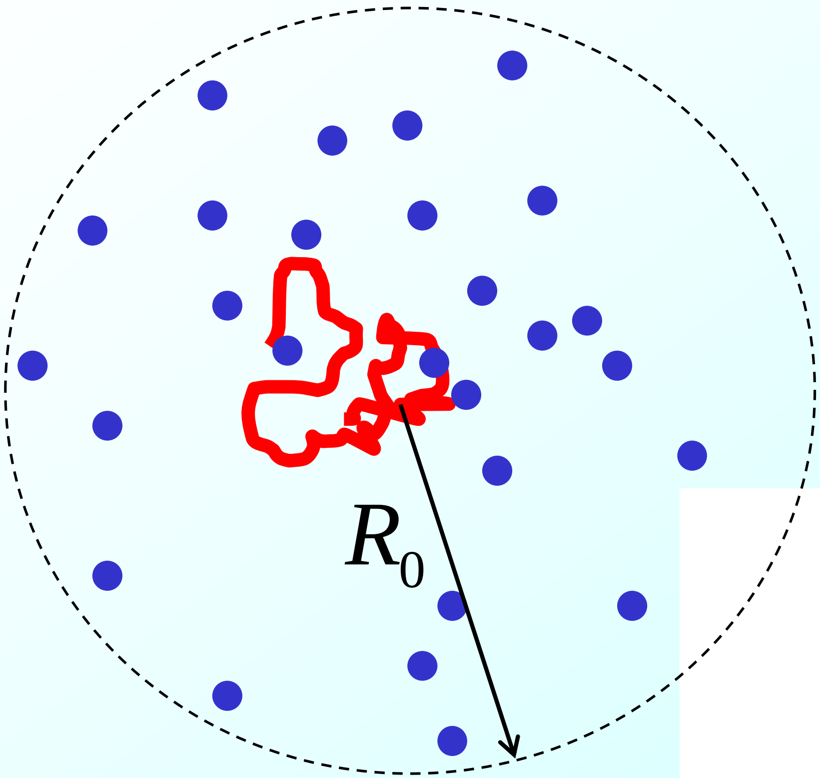
Varghese, et al JCP 2011

The physical picture of the electrostatic collapse :

A key role play counterions:

$$F = U - TS$$ ***- free energy***

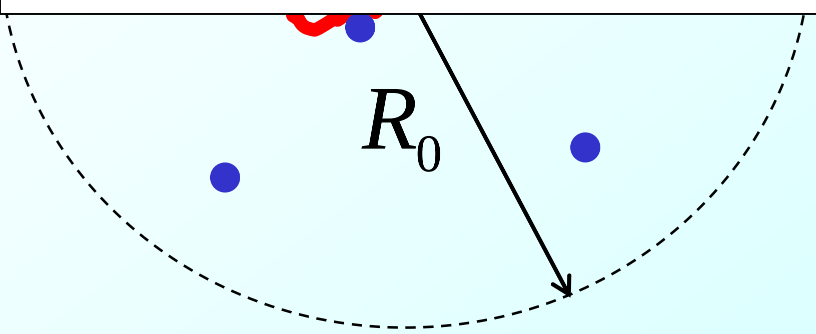
- ***If electrostatic interactions are weak, the entropic term dominates and the counterions are spread over the volume without screening of the monomers***

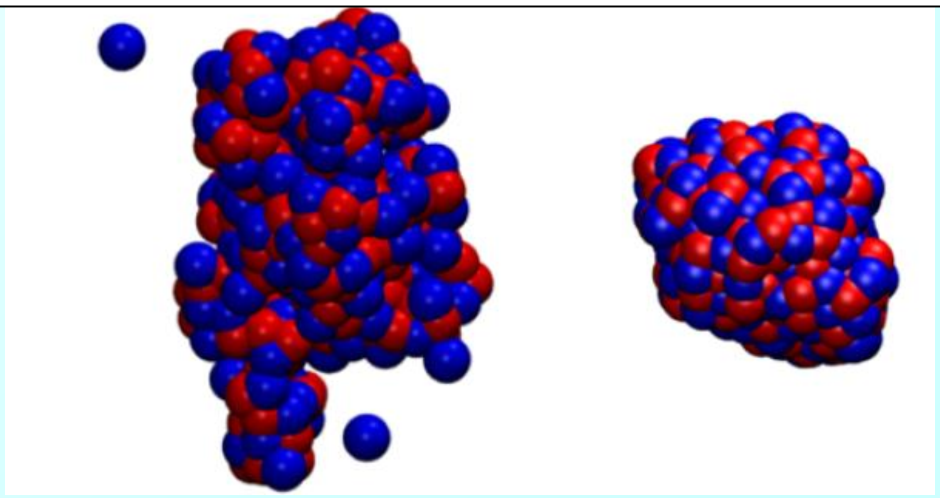


- ***The monomers repulse and the chain has an extended conformation***

Physical picture of the electrostatic collapse :

But why an almost neutral chain is not in a loose coiled conformation?

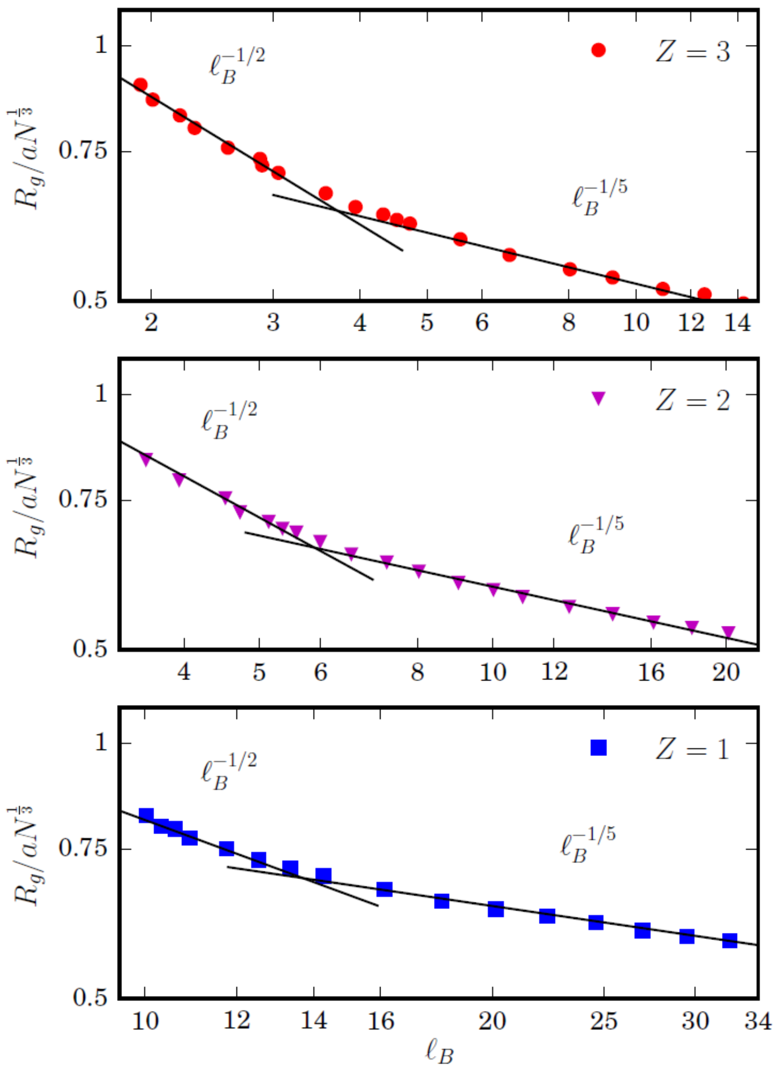


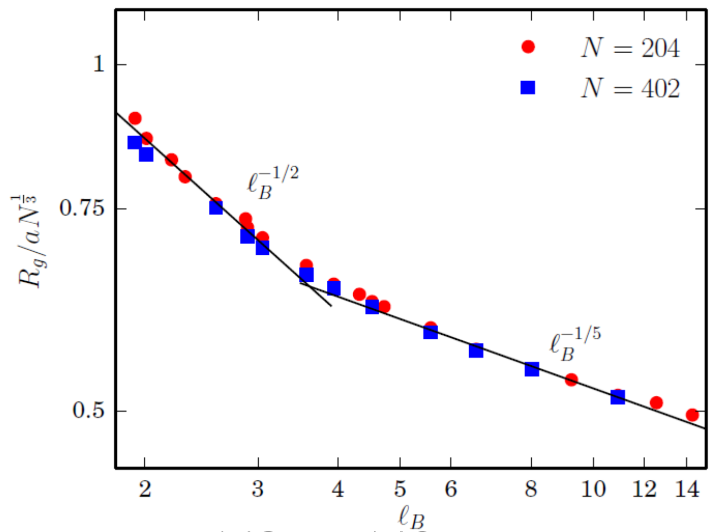


MD study of the *electrostatic collapse: Two collapse regimes*

(Electrostatic and LJ interactions between particles)

A. M. Tom, S.Vemparala, R. Rajesh, & N. Brilliantov, Phys. Rev. Lett. 2016





- $R_g \propto N^{1/3}\ell_B^{-1/2}$ ***--weak collapse***
- $R_g \propto N^{1/3}\ell_B^{-1/5}$ ***--strong collapse***

These effects and dependences may NOT be explained by emerging dipole pairs, where

$$R_g \propto N^{1/3}\ell_B^{-2/3}$$

Counterion fluctuation theory (CFT)

Free energy:

electrostatic interactions

$$F(R_g) = F_{id.ch.}(R_g) + F_{en.}(R_g) + F_{el.}(R_g) + F_{vol.}(R_g)$$

ideal chain — entropy of counterions — all volume interactions

We use the standard expressions for $F_{id.ch.}$, $F_{en.}$, $F_{vol.}$

Electrostatic interactions: $F_{el.mf} + F_{el.fluct}$

mean-field (with average charge) — fluctuations

$$\frac{F}{Nk_BT} = \frac{9}{4N}(\alpha^2+\alpha^{-2}) + \left(\frac{\widetilde{B_2}}{N^{1/2}\alpha}+\frac{\widetilde{B_3}}{\alpha^6}\right) + \frac{3}{Z}(1-\tilde{\rho})\, ln(R_0/b) + \frac{3\sqrt{6}l_B}{5\alpha}(1-\tilde{\rho})(1-3\,R_g/R_0) + \frac{3}{2}\left(\frac{2}{\pi}\right)^{1/3}\frac{\sqrt{6}l_B Z^{2/3}\tilde{\rho}^{4/3}}{N^{1/6}\alpha}$$

fraction of condensed counterions

$$\tilde{\rho} = \frac{N_{c.in}}{N_c}$$

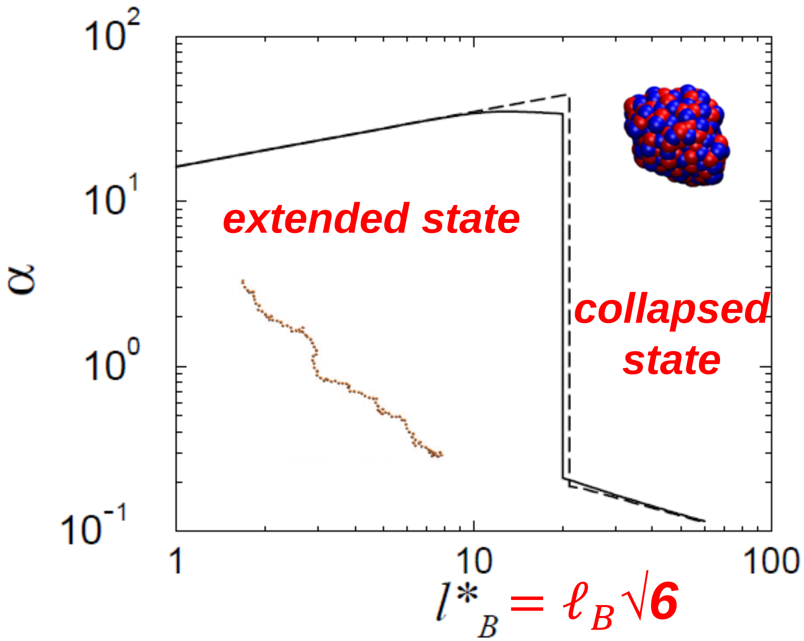
expansion factor

$$\alpha = \frac{R_g}{R_{g.id}} = \frac{6^{1/2}R_g}{N^{1/2}b}$$

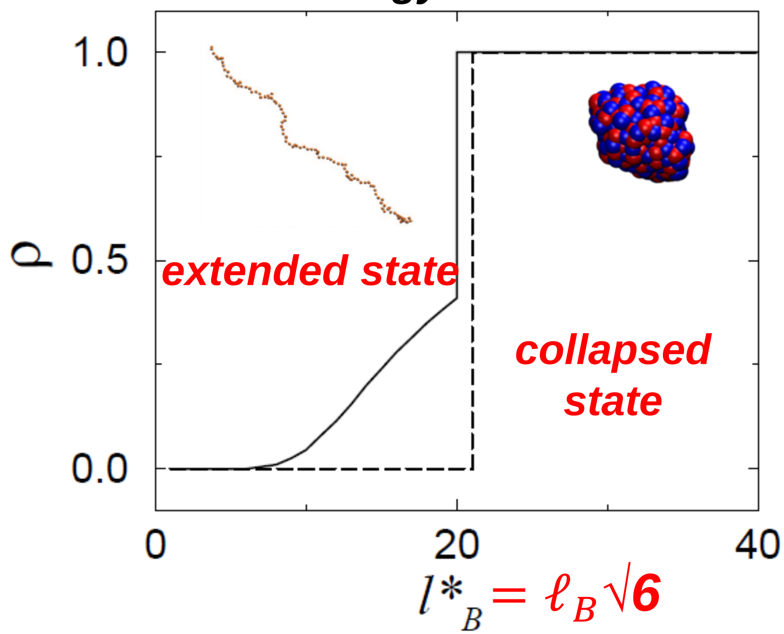
Minimizing $F = F_{id.ch.} + F_{en.} + F_{el.} + F_{vol.}$

with respect to the gyration radius and counterion density, we obtain:

expansion factor



reduced counterion density inside the gyration volume



Brilliantov, Kuznetsov, Klein, Phys. Rev. Lett. 1998

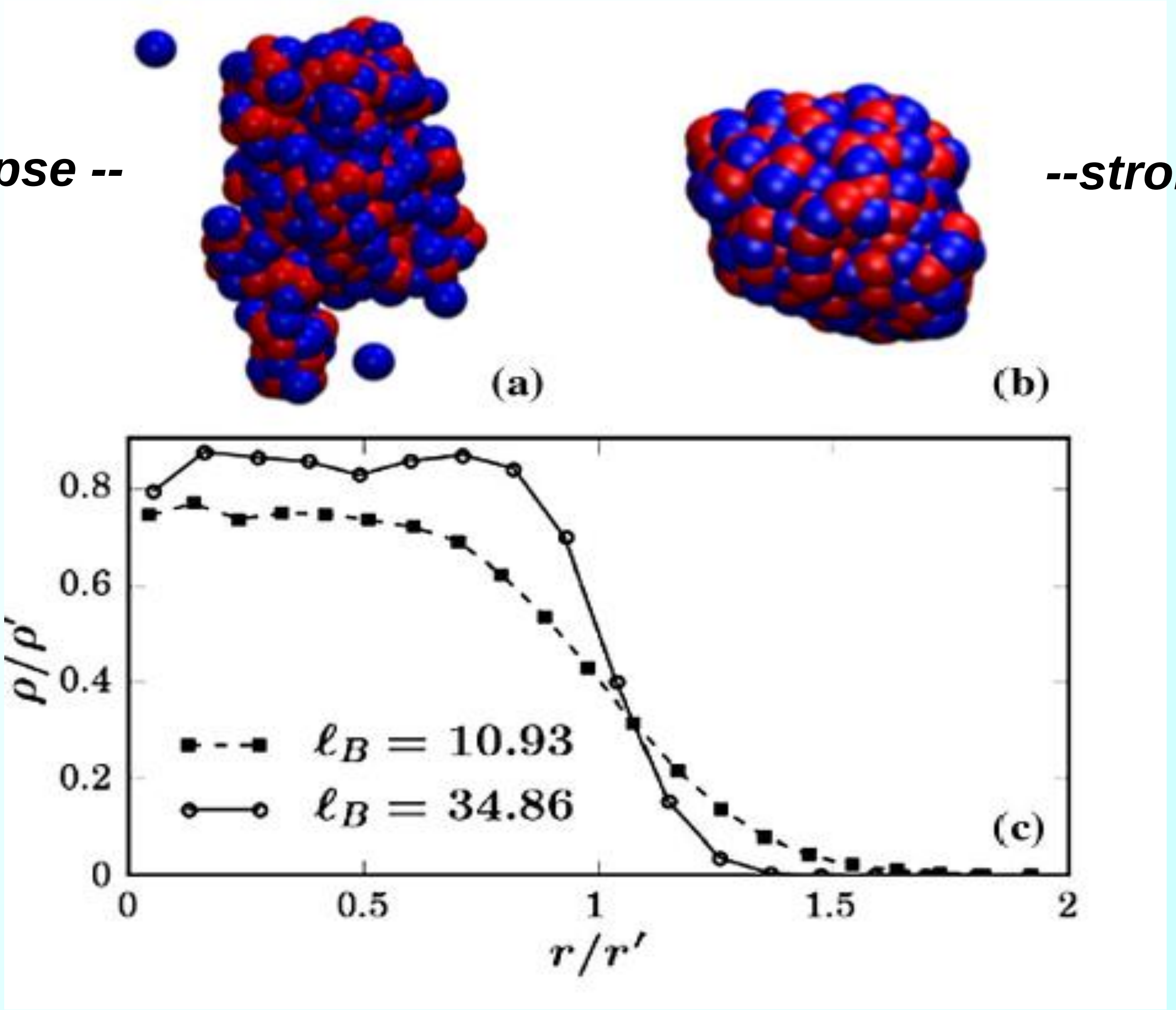
The condition of a free motion of counterions within a globule, i.e. the validity of the CFT:

$$\frac{E_{OCP}}{E_{dip}} = \frac{9c}{2}\frac{d_0}{a_c} = 1.77\frac{\Gamma d_0}{l_B} = 5.02\frac{d_0 Z^{5/3}}{b\alpha N^{1/6}} > 1$$

Collapse is accompanied by the condensation of the counterions inside the globule:

A. M. Tom, S.Vemparala, R. Rajesh, & N. Brilliantov Phys. Rev. Lett. 2016; Soft Matter 2017

weak collapse --



--strong collapse

Counterion fluctuation theory

$$\alpha = \frac{R_g}{R_{g.id}} = \frac{6^{1/2} R_g}{N^{1/2} b}$$

Analytic estimates for different cases:

- **Entropic term dominates:** $\ell_B N^{\frac{1}{2}} \ll \alpha R_0 / b \longrightarrow \alpha \gg 1$

$$R_g \sim \ell_B{}^{1/3} N$$ -- stretched chain

- **Counterion fluctuation term dominates:** $\ell_B N^{\frac{1}{2}} \gg \alpha R_0 / b \longrightarrow \alpha \ll 1$

$$\alpha^3 > \tilde{B}_3 N^{-1/2} / \tilde{B}_2$$

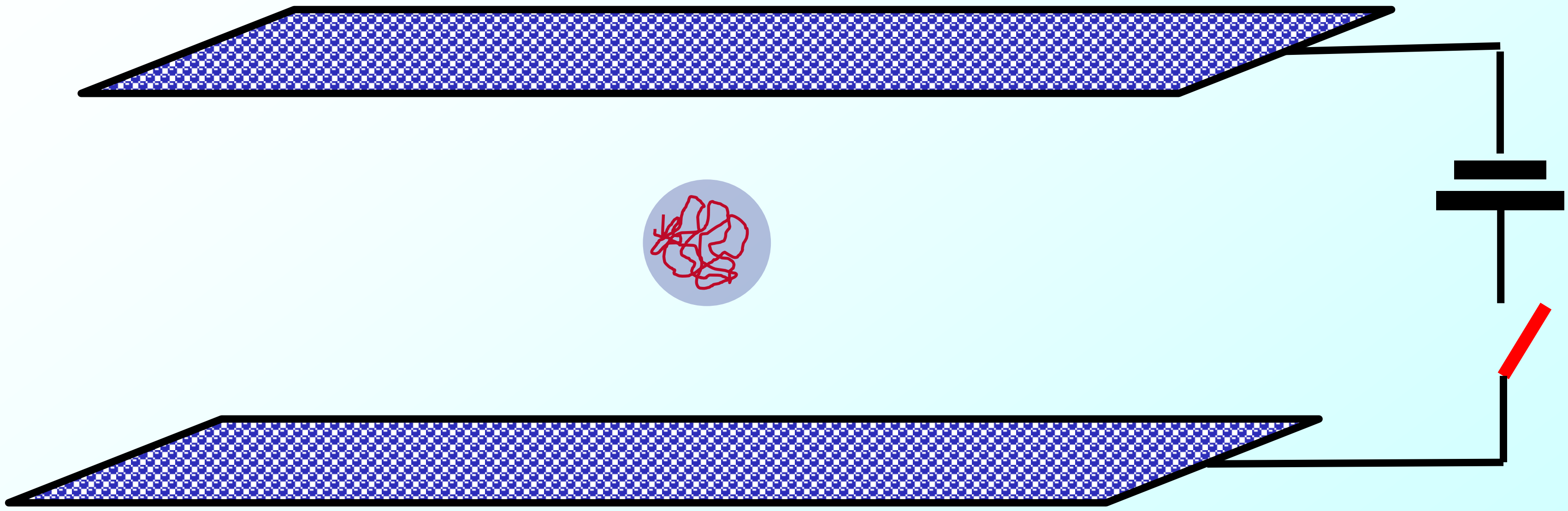
$$R_g \sim \ell_B{}^{-1/3} N^{1/3}$$ -- weak collapse

$$\alpha^3 < \tilde{B}_3 N^{-1/2} / \tilde{B}_2$$

$$R_g \sim \ell_B{}^{-1/5} N^{1/3}$$ -- strong collapse

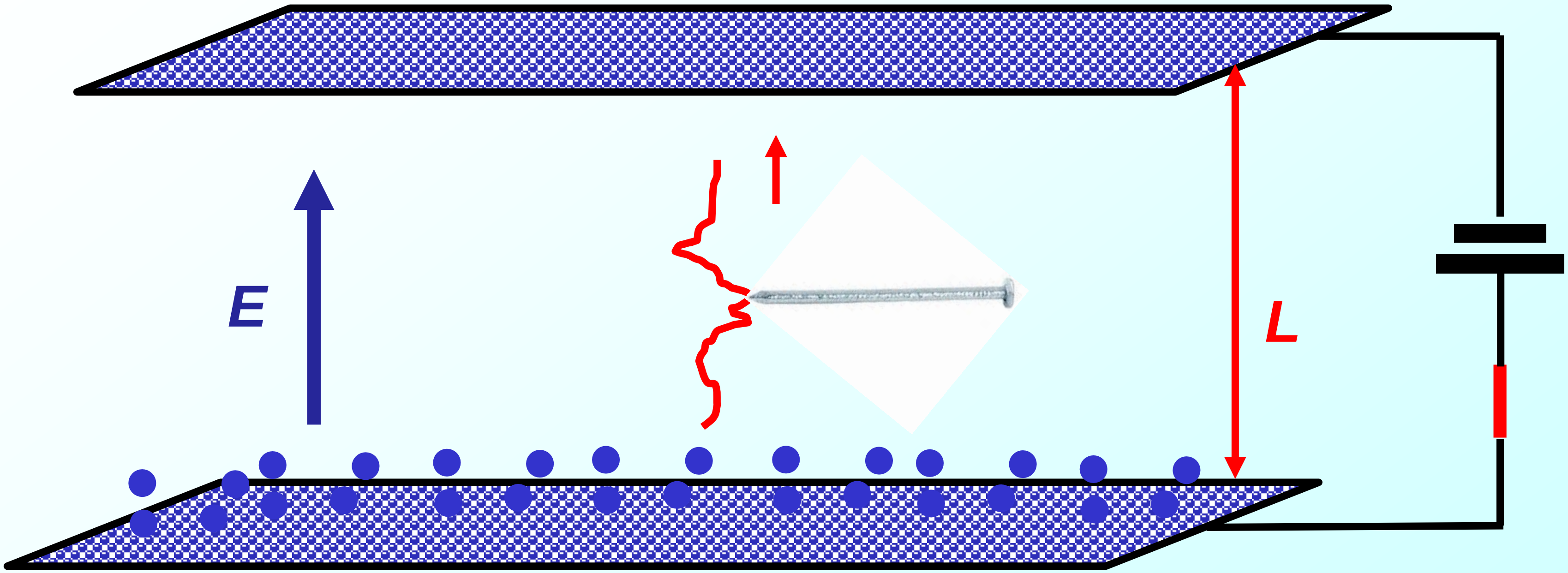
Field-regulated collapse

Polyelectrolytes in Electric fields



- Suppose that a PE chain in a good solvent has a globular conformation due to electrostatic collapse
- What happens if we switch on electrostatic field?

counterions will decondense and move towards low potential area, leaving the chain unscreened; the chain will expand



electrostatic interactions of chain and monomers

$$F(R_g) = F_{id.ch.}(R_g) + F_{en.}(R_g) + F_{el.}(R_g) + F_{vol.}(R_g)$$

ideal chain ***entropy of counterions*** ***all volume interactions***

$$+F_E(R_g)$$

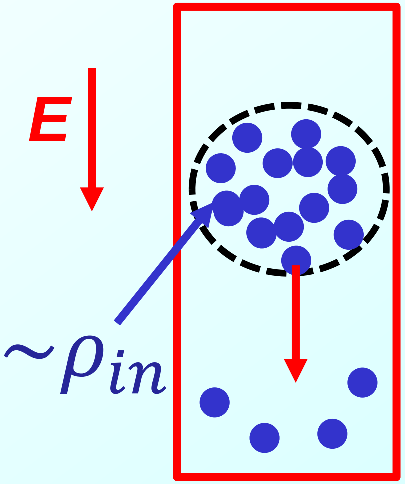
electrostatic interactions of the chain and counterions with the field E

For the case $eEL/\,k_BT \gg 1$

Two main negative terms compete:

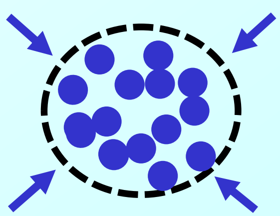
$$\frac{F_{ch.E}}{Nk_BT} \sim -\left(1-\tilde{\rho}\right)\frac{eEL}{k_BT}$$

-- tries to decrease $\tilde{\rho} \sim \rho_{in}$



and

counterion fluctuation term: $\sim -\ell_B \tilde{\rho}^{\frac{4}{3}}/\alpha N^{1/6}$ ***-- tries to increase*** $\tilde{\rho} \sim \rho_{in}$

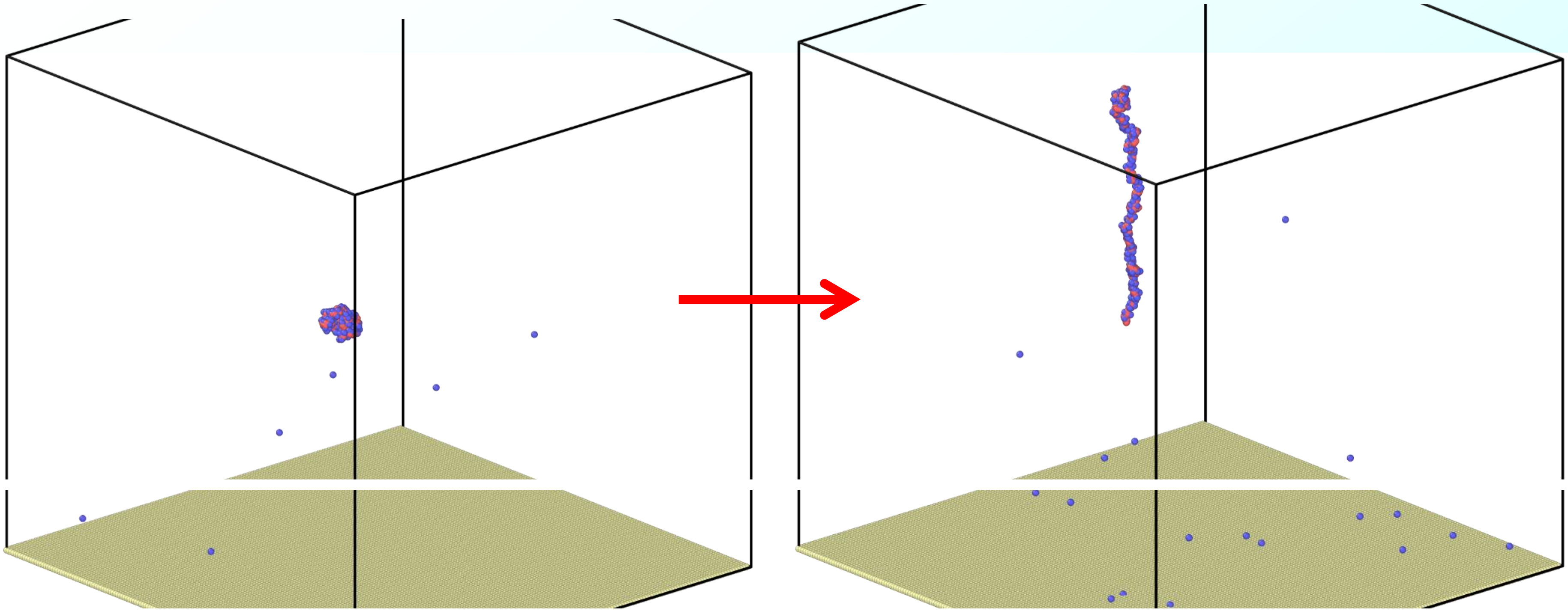


External field term wins if: $\frac{\ell_B}{\alpha N^{\frac{1}{6}}} \ll eEL/k_B\mathbf{T} \rightarrow \boldsymbol{\alpha} \gg \mathbf{1}$

$R_g \sim {\ell_B}^{1/3} N$ ***-- stretched chain***

$E_c \sim \frac{l_B^{7/6}}{L}$ ***-critical field***

Similar setup for unfixed chain: R. Netz, PRL 2003

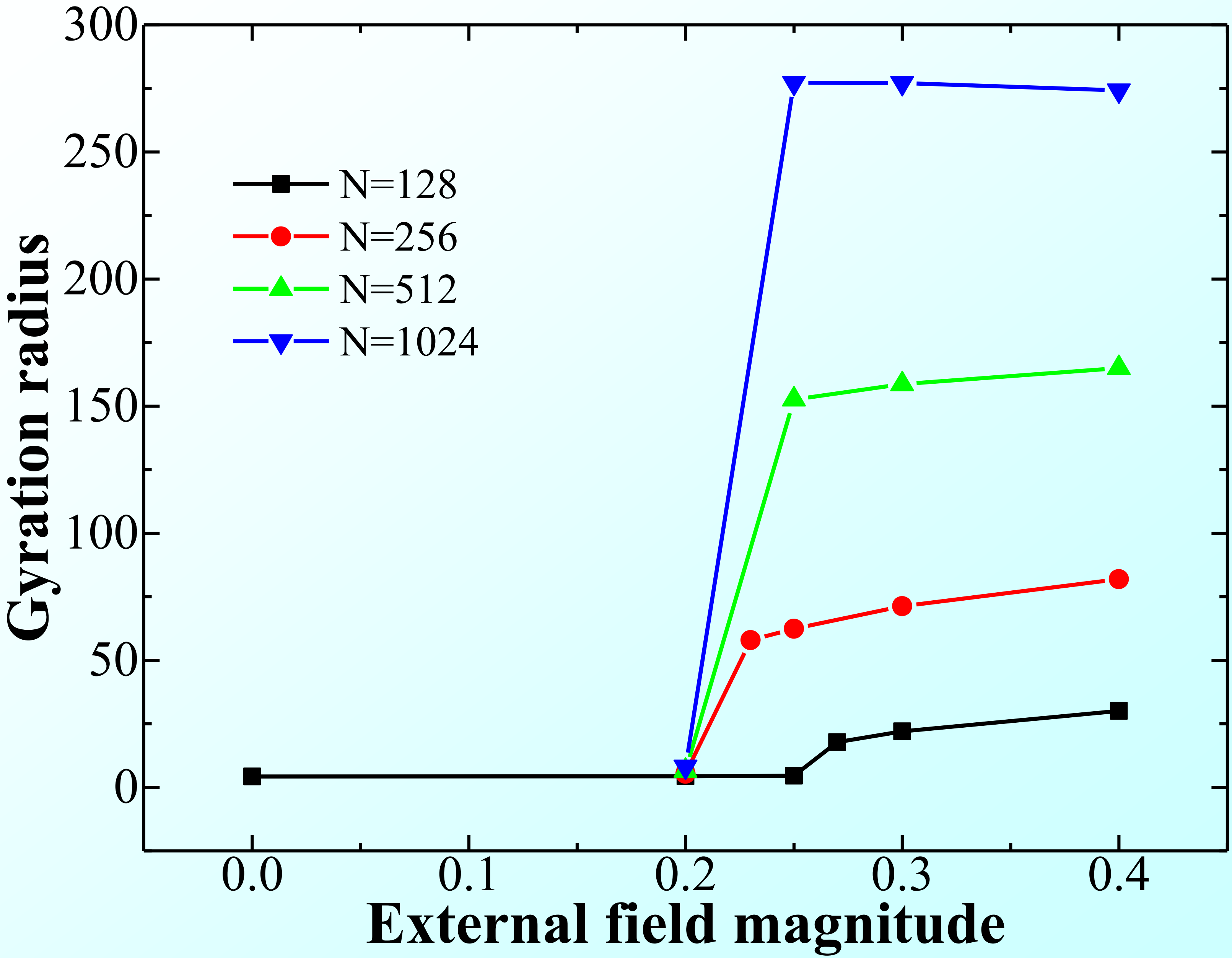


External field term wins if: $\frac{\ell_B}{\alpha N^{\frac{1}{6}}} \ll eEL/k_B T \longrightarrow \alpha \gg 1$

$R_g \sim \ell_B{}^{1/3} N$ ***-- stretched chain***

$E_c \sim \frac{l_B^{7/6}}{L}$ ***-critical field does not depend on N***

Simulations: Critical Field is almost size-independent

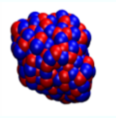


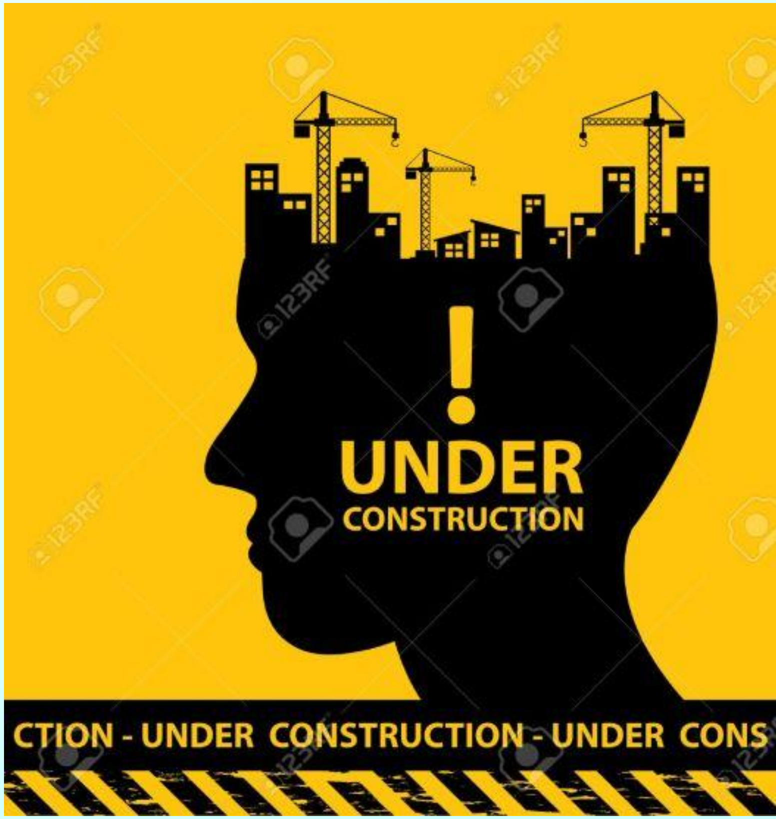
Collapse regulated by added salt

With the addition of salt ions the electrostatic component of the free energy will be less important than the entropic and volume component.

Hence the common swelling $R_g \sim N^{0.6}$ is expected.

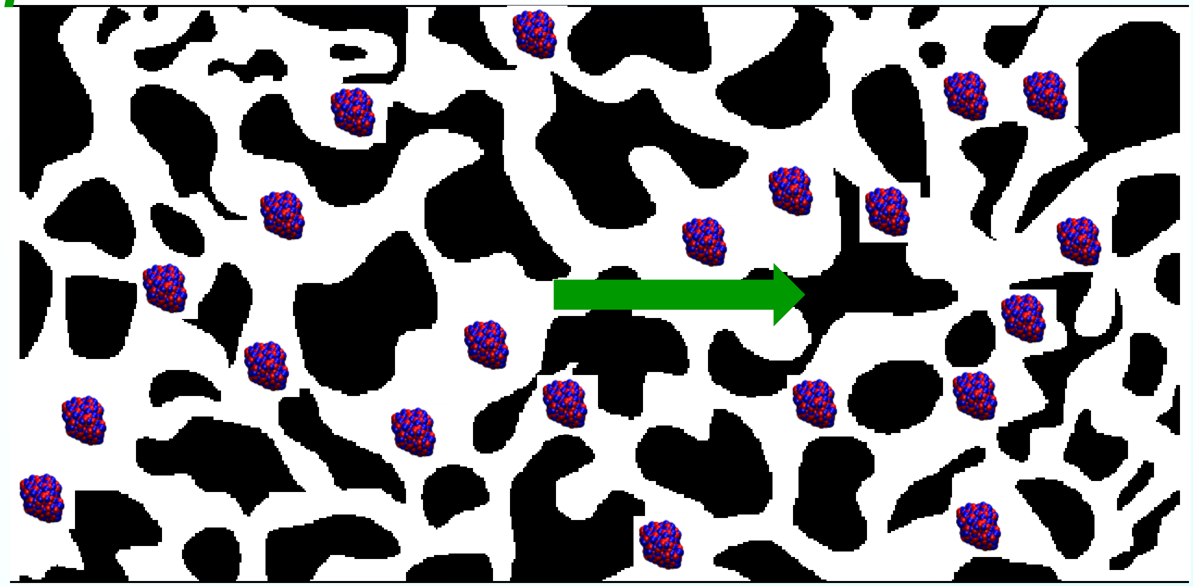
The theory is

 **+ *salt*** ⟹ 



Possible practical problems

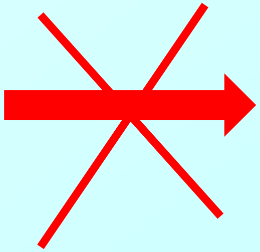
porous media



“Easy Flux” of solvent with polymer

added salt

Flux is stuck



Conclusion:

Take-home message

Electrostatic collapse is driven by correlated fluctuations of charge density and not by dipole-dipole interactions

Two regimes of electrostatic collapse of a polyelectrolyte chain are observed: a weak electrostatic collapse and strong electrostatic collapse

External electric field can suppress the electrostatic collapse; in static case the critical field does not depend on the chain length.

Added salt can also suppress the electrostatic collapse.

Controlling the electrostatic collapse by the characteristics of the solvent a flux through porous media may be regulated