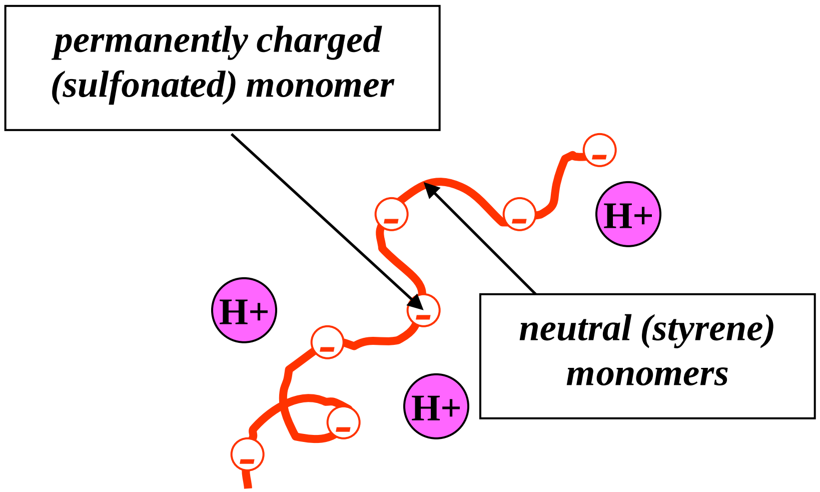
Lecture 1: Neutral brushes. Scaling model of a neutral planar polymer brush (mushroom and brush regimes). Effect of solvent. Strong stretching approximation: chain trajectory and parabolic potential. Internal structure of a planar brush. Response of polymer brush to compression. Curved polymer brushes. Scaling model of star-like and comb-like molecular brushes (stars and combs in solution).

Lecture 2: Charged brushes. Strong and weak polyelectrolytes. Scaling model of strong PE planar brush. Main regimes of PE brush (counterion and salt dominated). Local electroneutrality approximation. Parabolic potential and internal structure of planar PE brush. Interactions between planar PE brushes. Curved PE brushes (scaling model).

Corona of neurofilament (NF) as a cylindrical PE brush.

Strongly and weakly dissociating polyelectrolytes

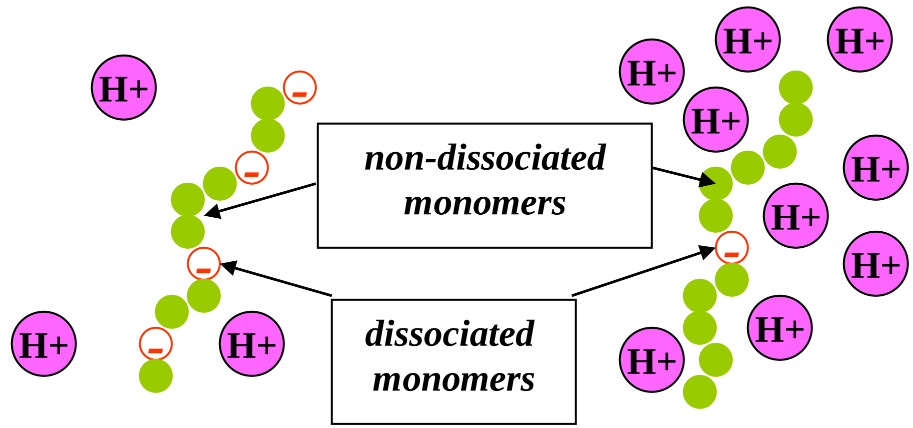
Strong polyelectrolyte:



Poly(styrene/styrenesulfonate)

fraction of charged monomers is independent of salinity, pH,…, pre-determined by chemical composition (sequence)

Weak polyelectrolyte (polyacid):



high pH ***low pH***

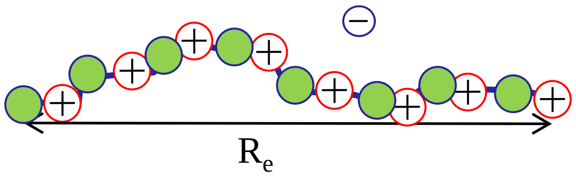
Poly(acrylic acid)

fraction of charged monomers (=degree of ionization) depends on local concentration of H^+ ions ($pH=-\log[H^+]$) via ionization/recombination equilibrium

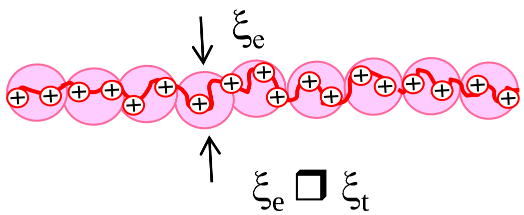
Individual polyion and charged surface

Theta solvent for flexible backbone

Net charge per chain $Q = fN$



Electrostatic blob = tension blob



Polyion size R_e is governed by balance of Gaussian chain elasticity

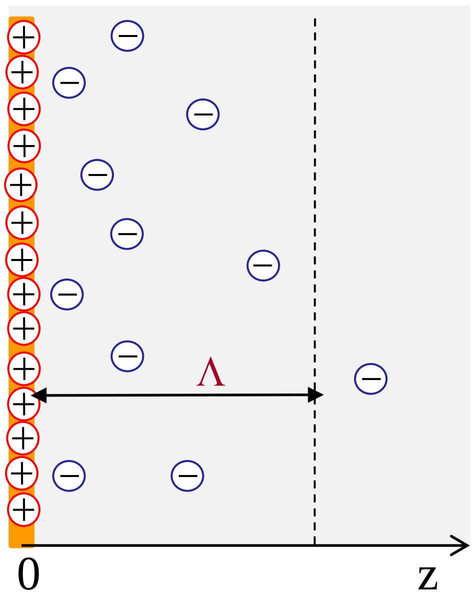
$F_{elastic} /k_BT$ ❐ R_e^2/a^2N

and intra-molecular Coulomb repulsion

$F_{Coulomb} /k_BT$ ❐ l_BQ^2/R_e Bjerrum length $l_B = e^2 /\varepsilon k_BT$

Balancing $F_{Coulomb}$ ❐ $F_{elastic}$ gives

R_e ❐ $a^{2/3}l_B^{1/3}Nf^{2/3}$ ❐ ξ_eN_b ← number of blobs



Dimensionless electrostatic potential $\psi(z) = e\Psi(z)/k_BT$

$$\frac{d^2\psi}{dz^2} = -4\pi l_B[c_+(z) - c_-(z)]$$

$$c_+(z) = c_+(0)\exp(-\psi(z))$$

$$c_-(z) = c_-(0)\exp(\psi(z))$$

Boundary conditions:

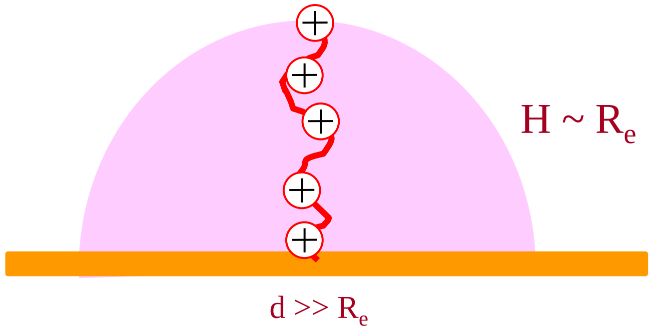
$$\left(\frac{d\psi}{dz}\right)_{z=0} = -\frac{2}{\Lambda} \qquad \left(\frac{d\psi}{dz}\right)_{z=\infty} = 0$$

Gouy-Chapman length $\Lambda = s/(2\pi Ql$

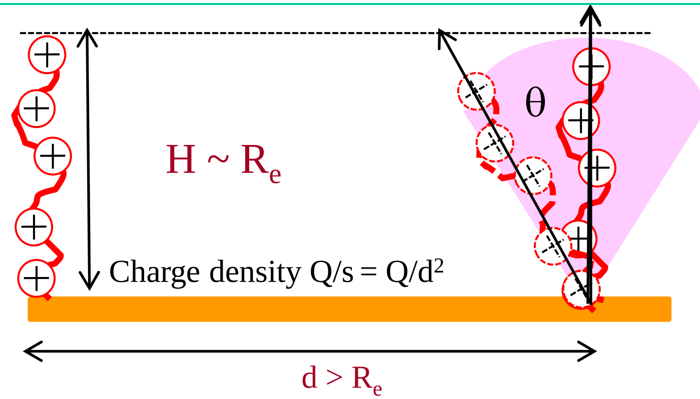
Salt-free solution, $c_+(z) = 0$

$c_-(z) = 1/[2\pi l_B(z+\Lambda)^2]$ $\psi(z) = -2\ln[(z+\Lambda)]$

Tethering PE chains to substrate



single polyion regime

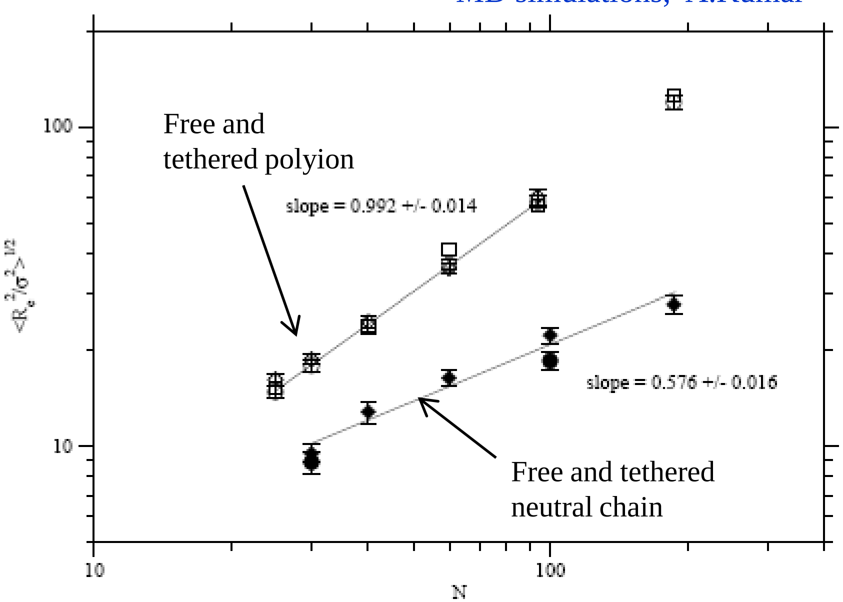


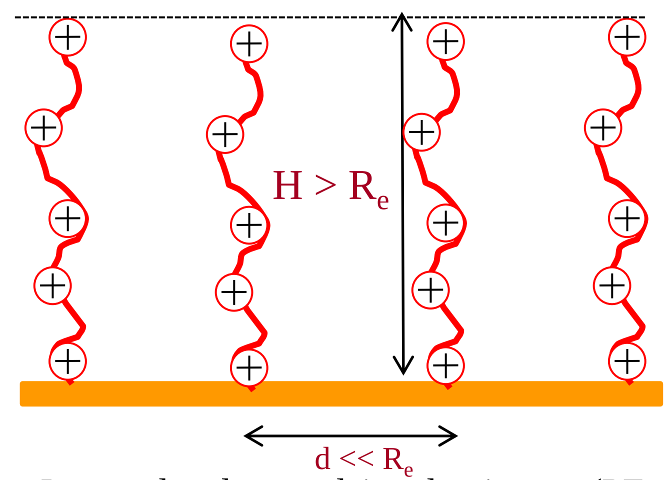
Increase in energy $\Delta W/k_BT \,\square\, l_B Q^2 R_e(1-\cos\theta)/s \quad \square\, l_B Q^2 R_e \theta^2/s$

$\Delta W/k_BT = 1$ gives orientation angle $\theta \quad \square\, N_b^{-1/2}(s/R_e^2)^{1/2}$

Intramolecular repulsion dominates (oriented polyion regime)

MD simulations, A.Kumar

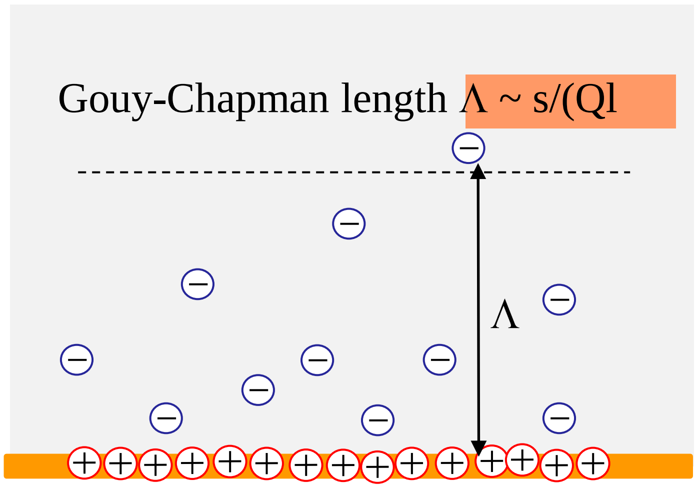




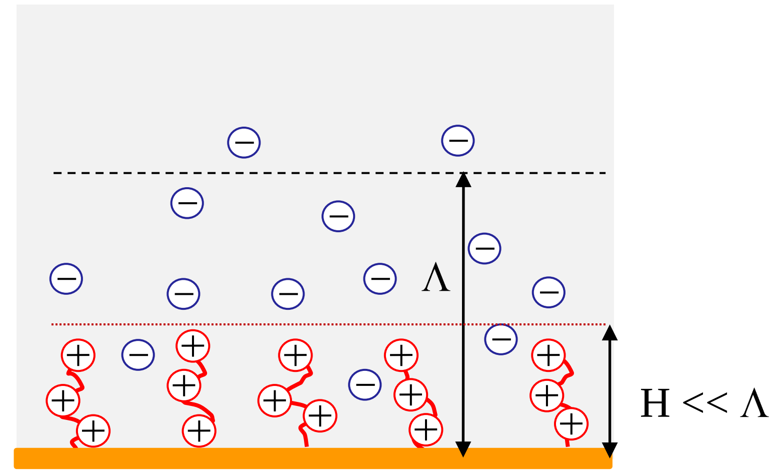
Intermolecular repulsion dominates (PE brush regimes)

Intermolecular repulsion regime

Planar charged surface



Pincus, 1991



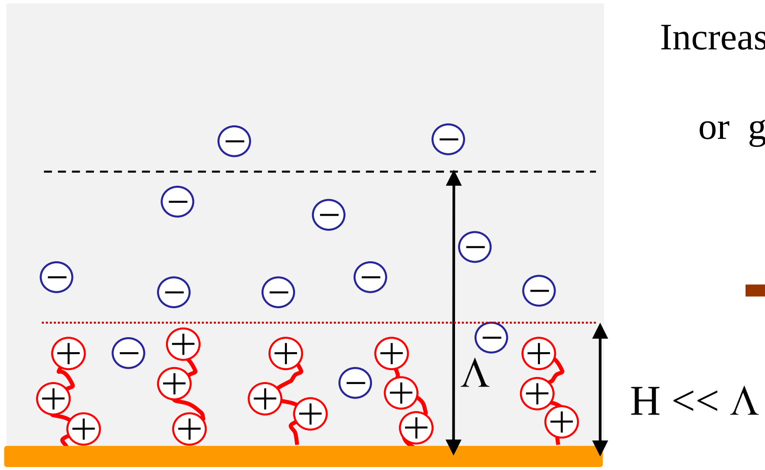
Majority of mobile counterions leave the brush, and chains are stretched due to intermolecular Coulomb repulsions

Stretching force $F_{electrostatic} \sim k_B T l_B Q^2/s$

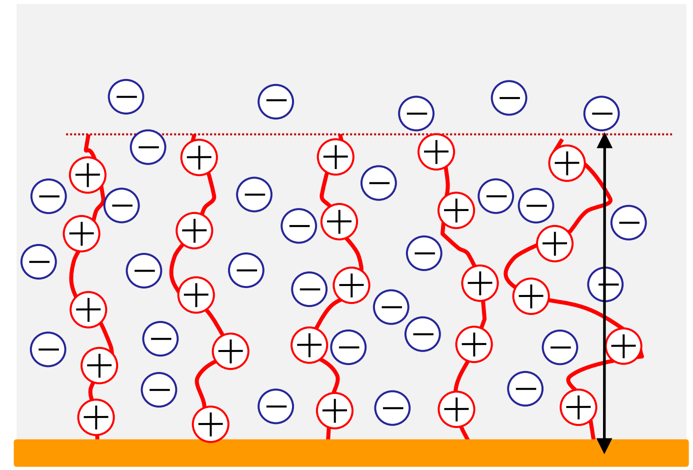
Elastic force $F_{elastic} \sim k_B T\, H/a^2 N$ *(Gaussian elasticity)*

Balance of forces gives $H \sim a^2 l \quad N^3 f^2/s$. Narrow regime

Osmotic brush regime (low salt)



Increase in chain charge
$Q = f N$
or grafting density
$\rho = d^{-2}$



Majority of mobile counterions leave the brush

Strong attraction to polyions entraps counterions inside osmotic PE brush. Bare polyion charge is almost totally compensated.

Counterion osmotic stretching against Gaussian elastic force

Balance of forces gives $H \sim H_0 \sim a f^{1/2} N$. Main regime of salt-free PE brush

Diagram of states of PE brush (low salt)

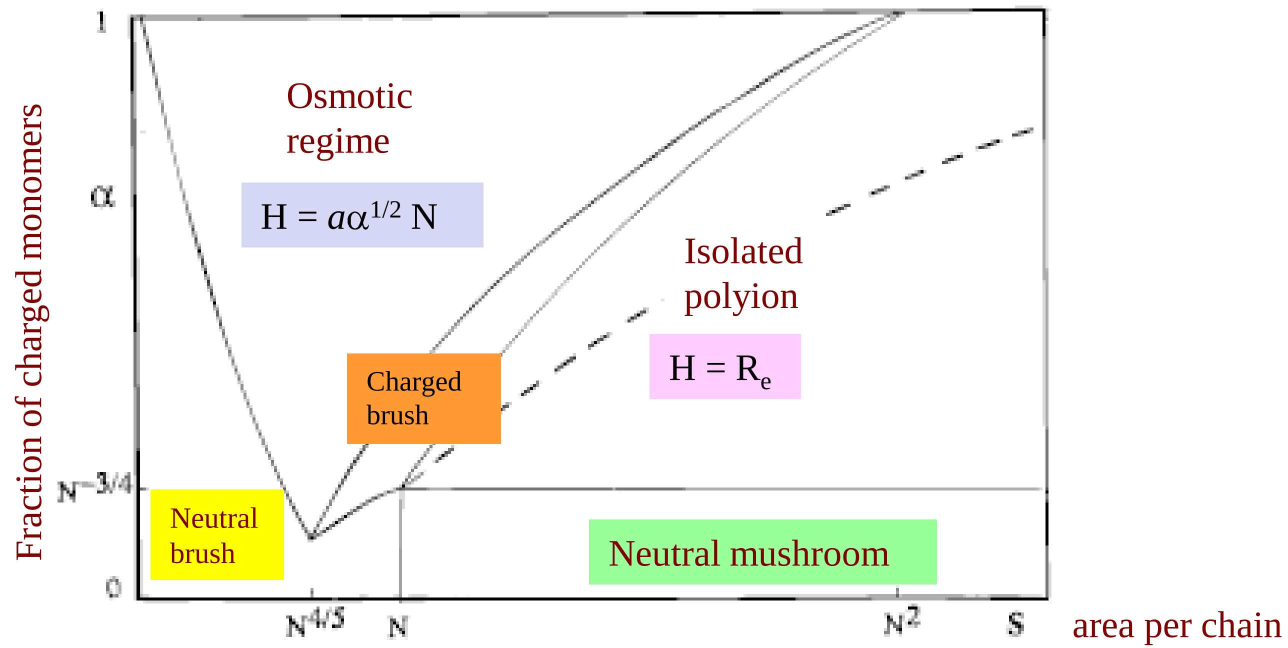
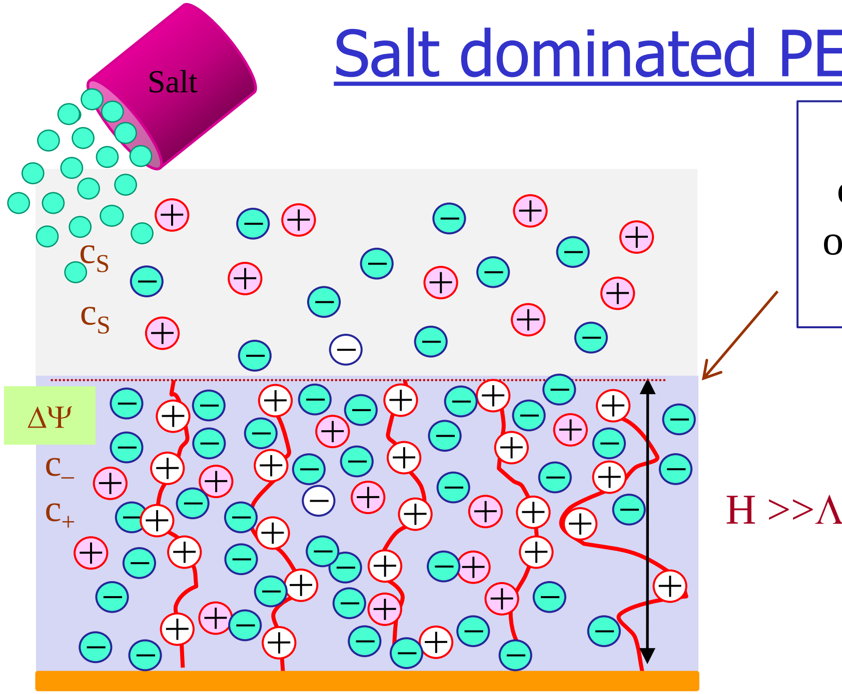
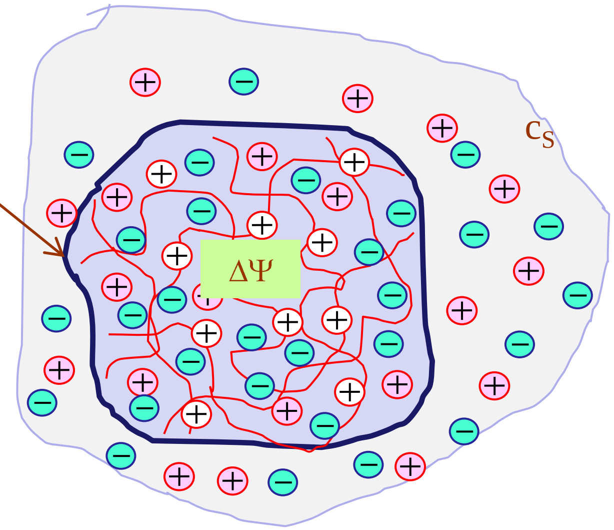


Figure 2. Diagram of states of a planar polyelectrolyte brush in α, s coordinates.

Salt dominated PE brush regime (high salt)



Volume with concentration of immobilized charge fc



Electroneutrality: $fc + c_+ = c_-$

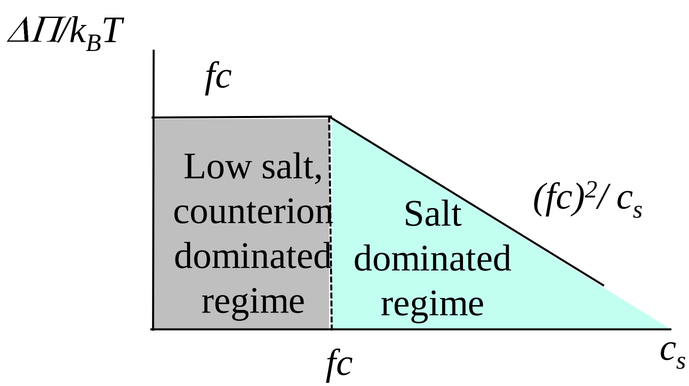
Donnan equilibrium: $c_+ c_- = c_s^2$

$c_+ = c_s \exp(-e\Delta\Psi/k_BT)$

$c_- = c_s \exp(e\Delta\Psi/k_BT)$

Differential ion pressure: $\Delta\Pi/k_BT = c_+ + c_- - 2c_s$

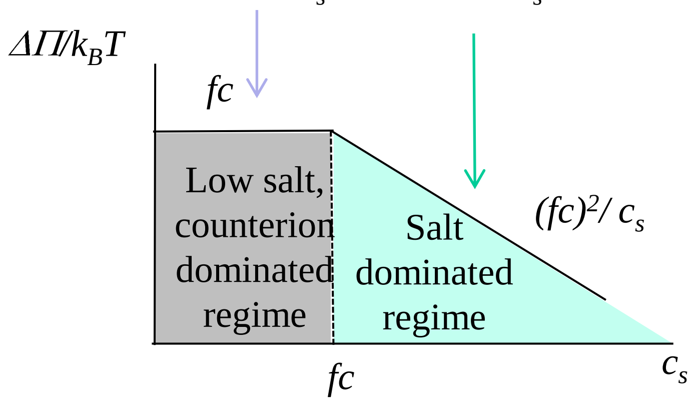
$$\simeq \begin{cases} fc & \text{when } fc >> c_s \\ (fc)^2/c_s & \text{when } fc << c_s \end{cases}$$



Effect of added salt : standard PE brush model

Elastic force $F_{elastic} \sim k_B T H / a^2 N$ (Gaussian elasticity at all concentrations of salt c_s)

Two regimes for $\Delta\Pi$: $fc \gg c_s$ and $fc \ll c_s$

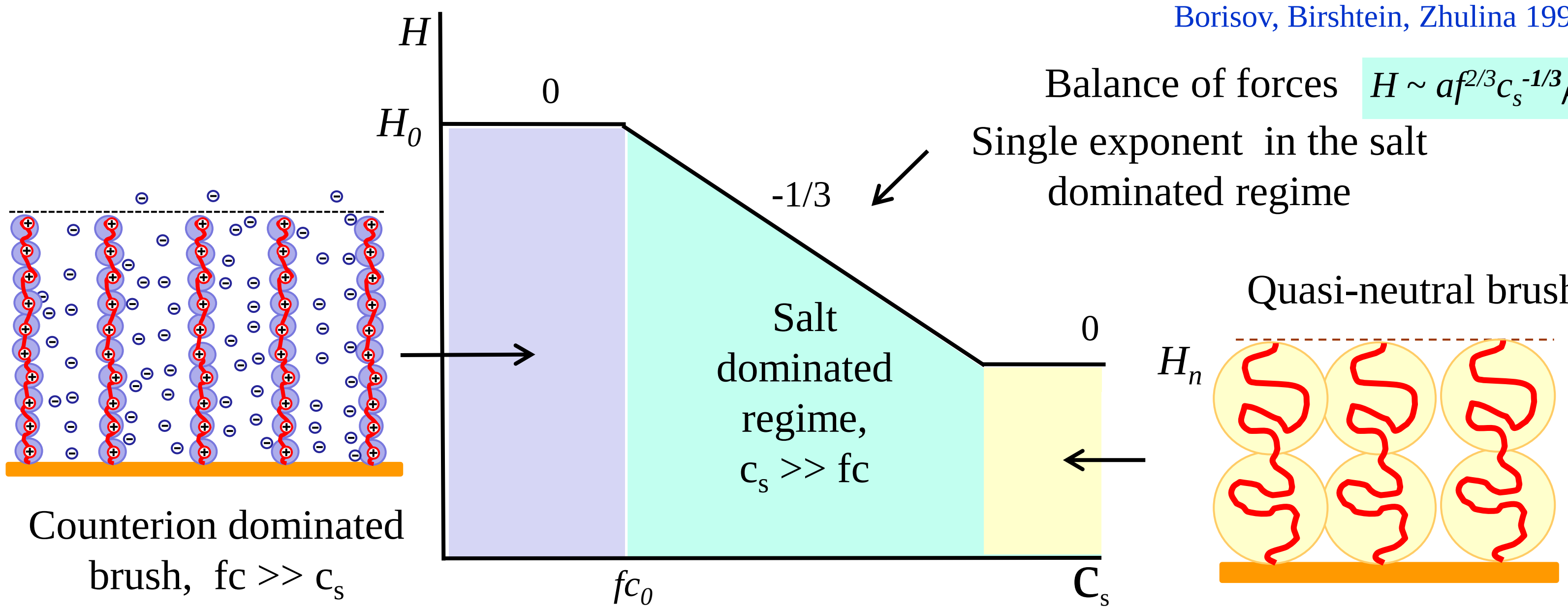


Pincus 1991

Borisov, Birshtein, Zhulina 1991

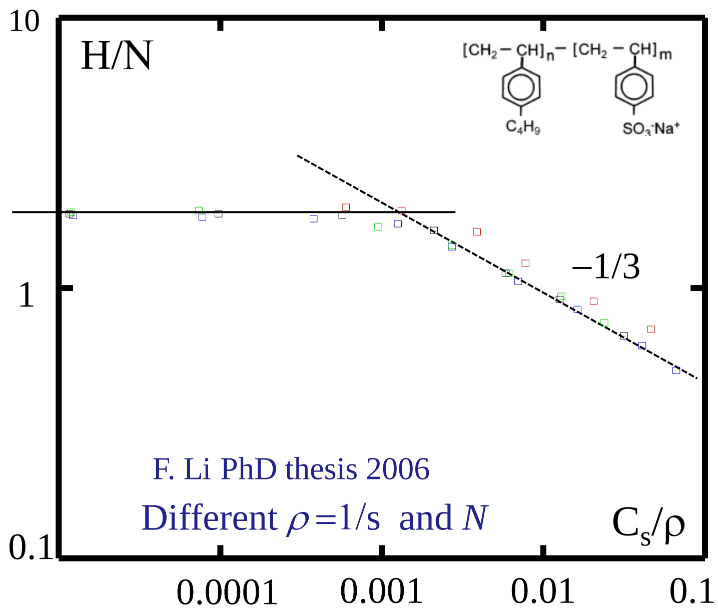
Balance of forces $H \sim a f^{2/3} c_s^{-1/3} \rho^{1/3} N$

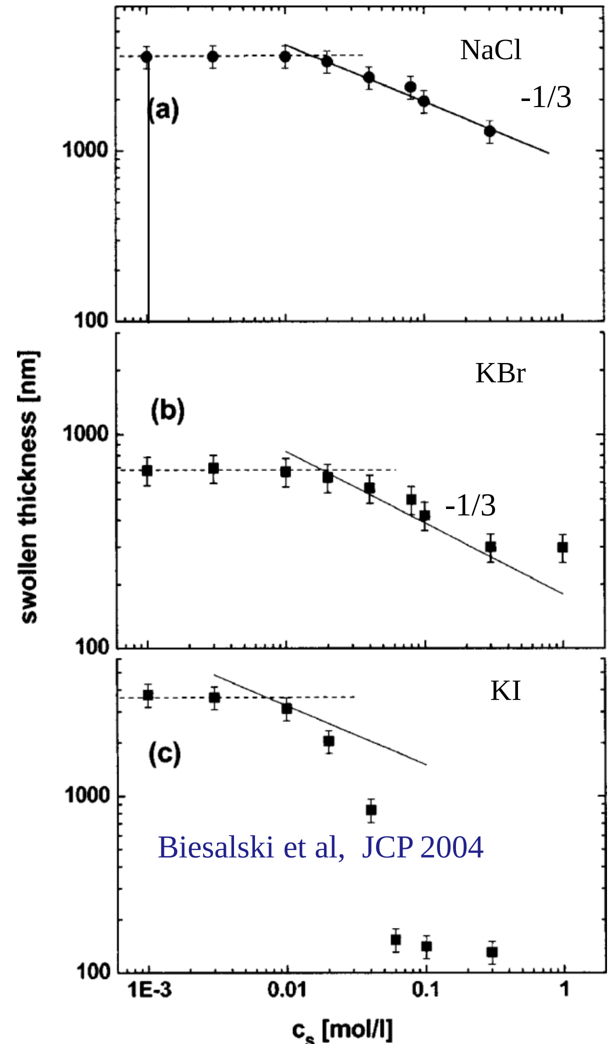
Single exponent in the salt dominated regime

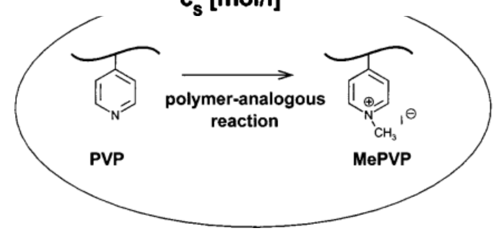


Counterion dominated brush, $fc \gg c_s$

Experimental test of osmotic and salt dominated regimes

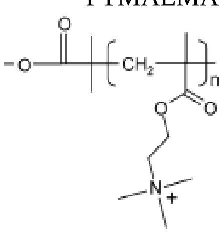


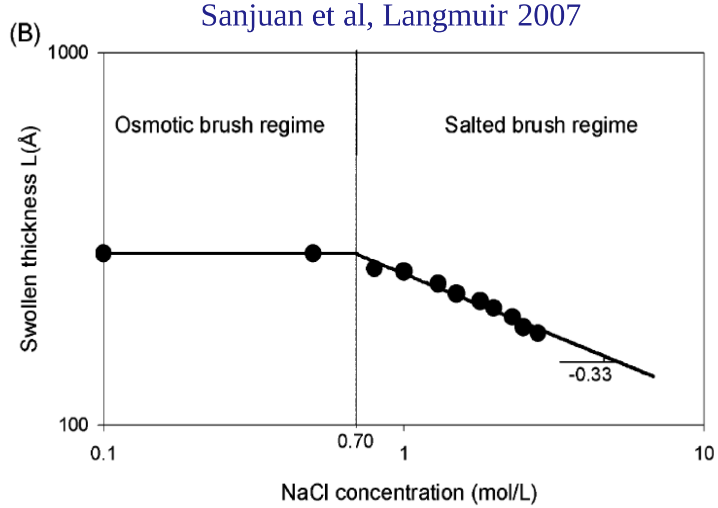




Sanjuan et al, Langmuir 2007

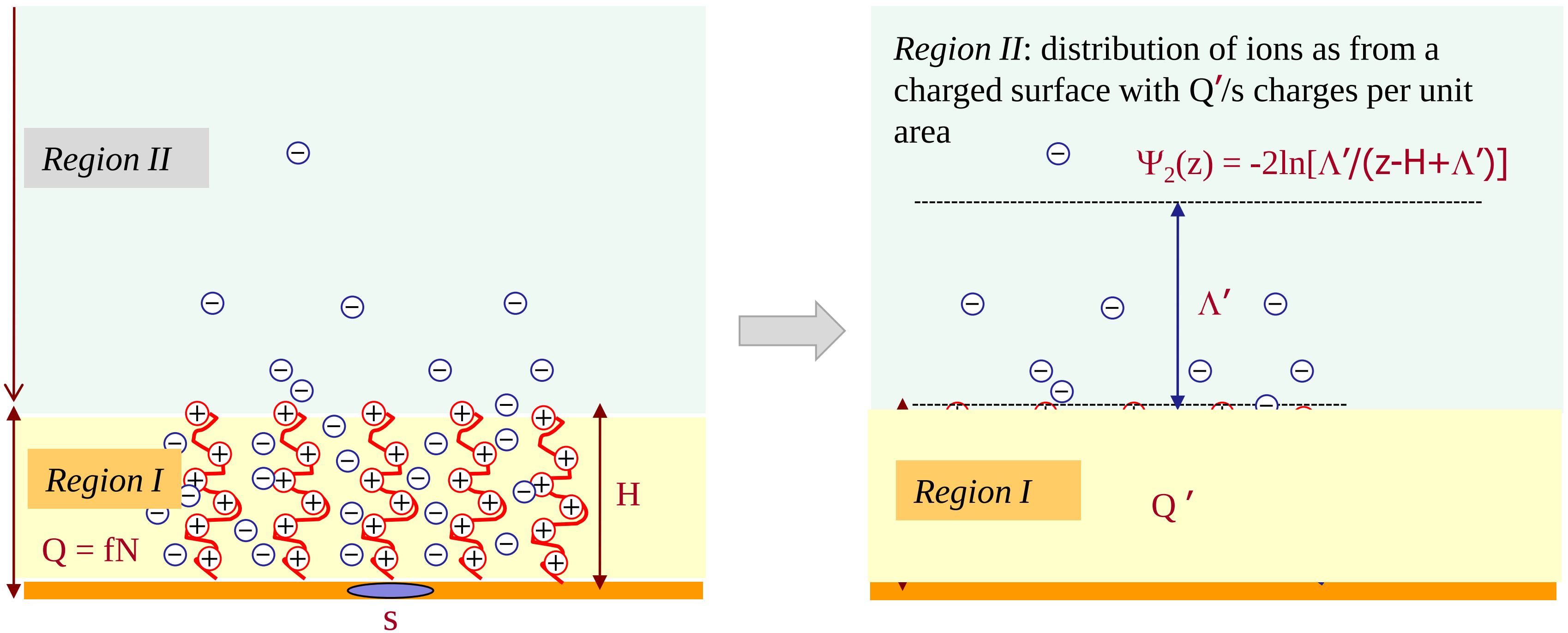
PTMAEMA





Self-Consistent Field (SCF) model of salt-free PE brush

Zhulina, Borisov 1997



Gouy-Chapman length $\Lambda = s/(2\pi Q l_B)$ associated with net charge Q/s per unit area

Gouy-Chapman length $\Lambda' = s/(2\pi Q' l_B)$ associated with uncompensated brush charge Q'/s per unit area

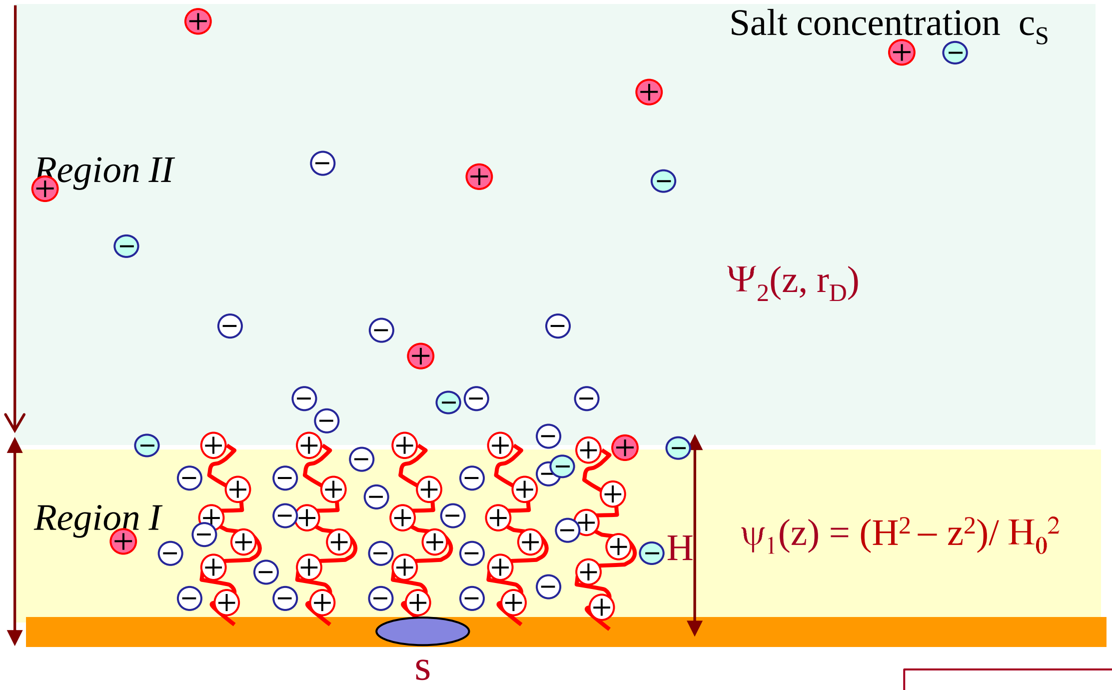
Region I: for chains with Gaussian elasticity and no excluded volume interactions, molecular field acting at a monomer located at distance z from the surface, $\delta f_{interaction}[\phi]/\delta\phi = f\,\psi(z) = \mathrm{Const} - 3\pi^2 x^2/8a^2N^2$

⇩

Electrostatic potential in the brush $\psi_1(z) = (H^2 - z^2)/H_0^2$
where $H_0 = (8/3\pi^2)^{1/2} a f^{1/2} N$ is characteristic electrostatic length.

SCF model of salt-added PE brush

Zhulina, Wolterink, Borisov 2000



Important length scales:

electrostatic length $H_0 = (8/3\pi^2)^{1/2}\, a f^{1/2} N$

Debye radius $r_D = (8\pi l_B c_s)^{-1/2}$

Gouy-Chapman length $\Lambda = s/(2\pi Q l_B)$

Reduced parameters:

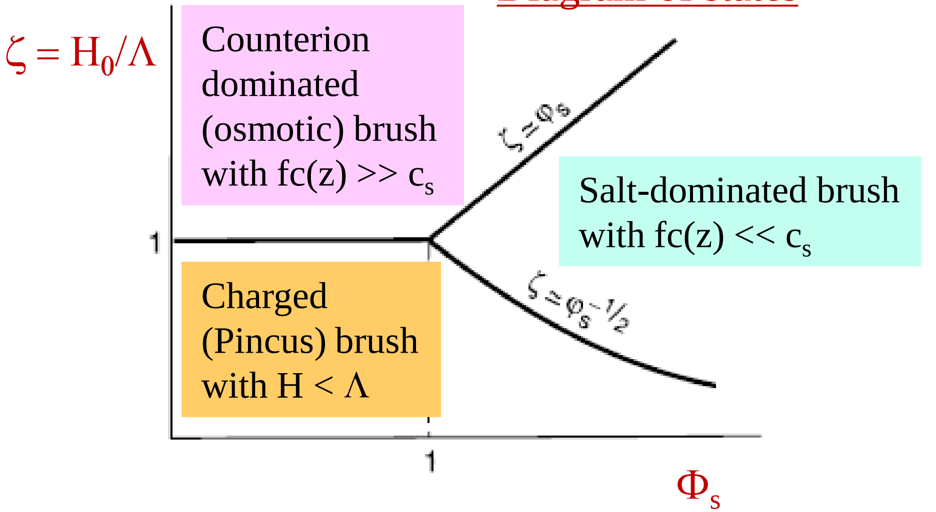
$\zeta = H_0/\Lambda$ (measure of PE brush charge compensation)

$h = H/ H_0$

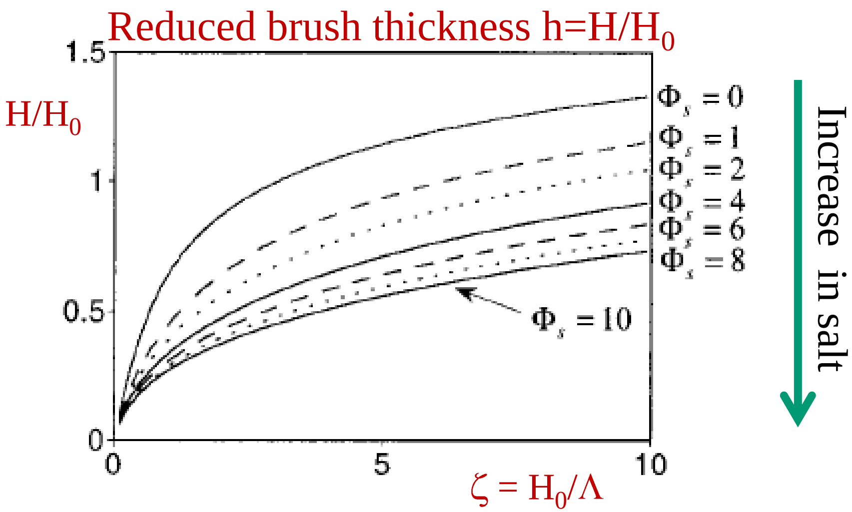
$\Phi_s = 2\pi l_B H_0^2 c_s = (H_0/2r_D)^2$

Output of SCF model:
confirmed scaling dependences for PE brush thickness H
+ crossover regions
+ internal brush structure (density distributions).

Diagram of states



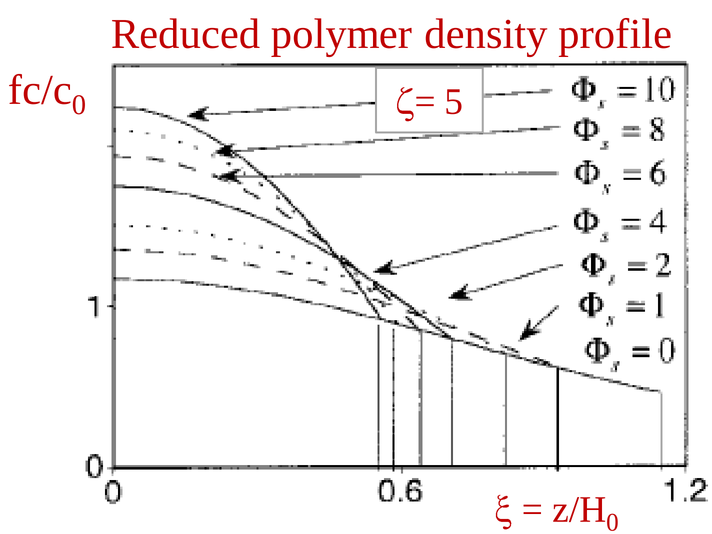
Internal structure of PE brush

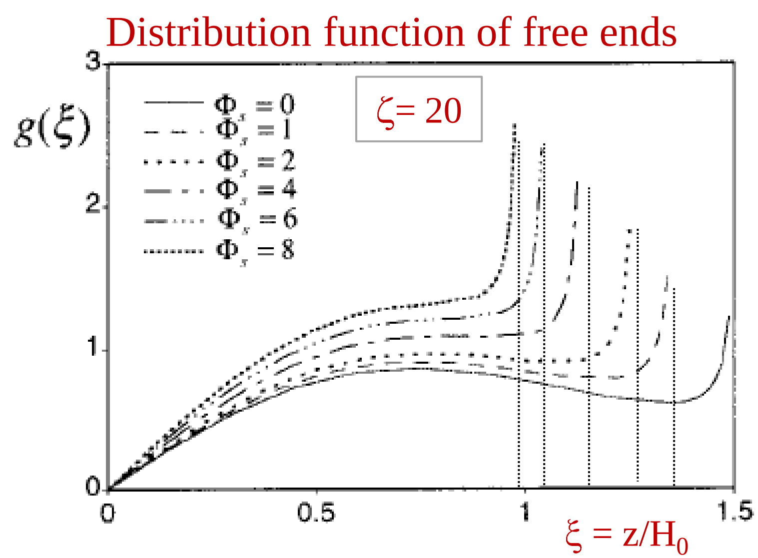


Reduced distance $\xi = z/H_0$

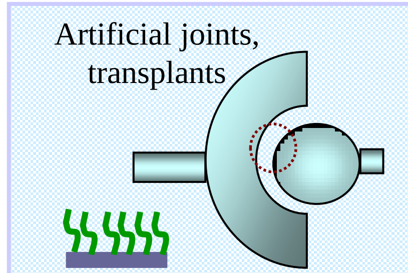
Average net charge concentration

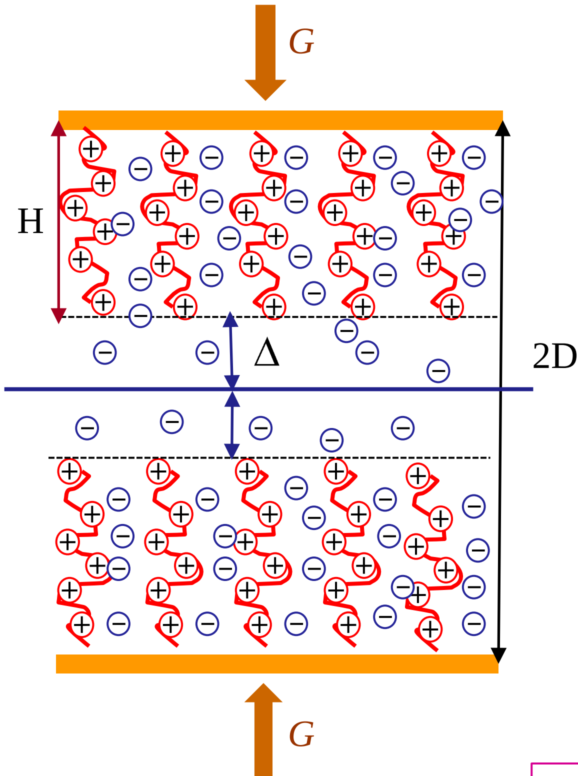
$c_0 = fN/sH_0$





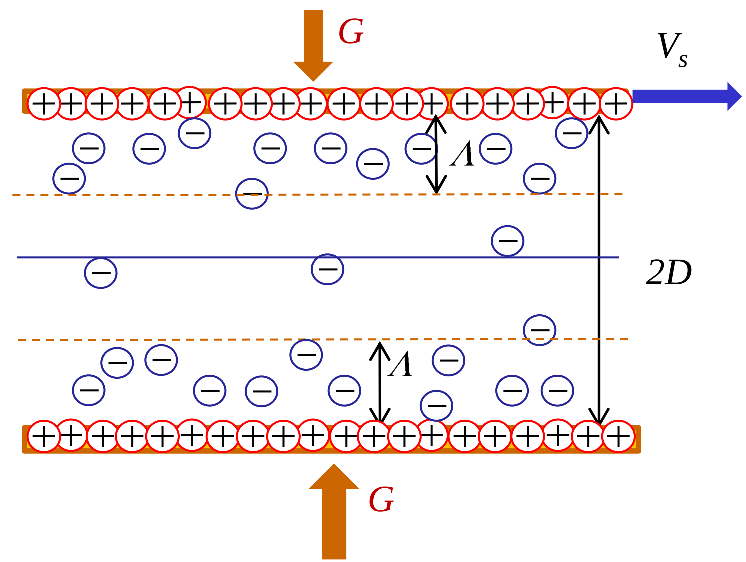
Interactions between PE brushes





Normal force G per unit area (pressure)

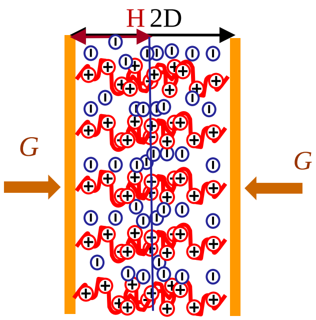
For comparison: two surfaces with the same surface charge density Q/s



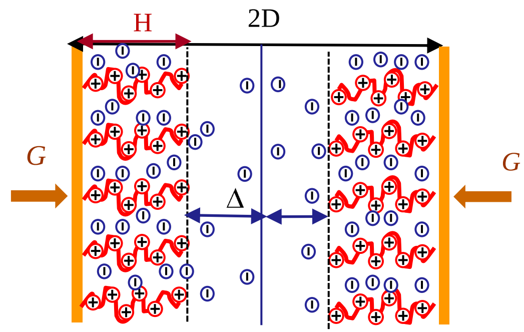
Goal: to highlight the role of tethered polymer on resistance to compression of two opposing PE bearing surfaces

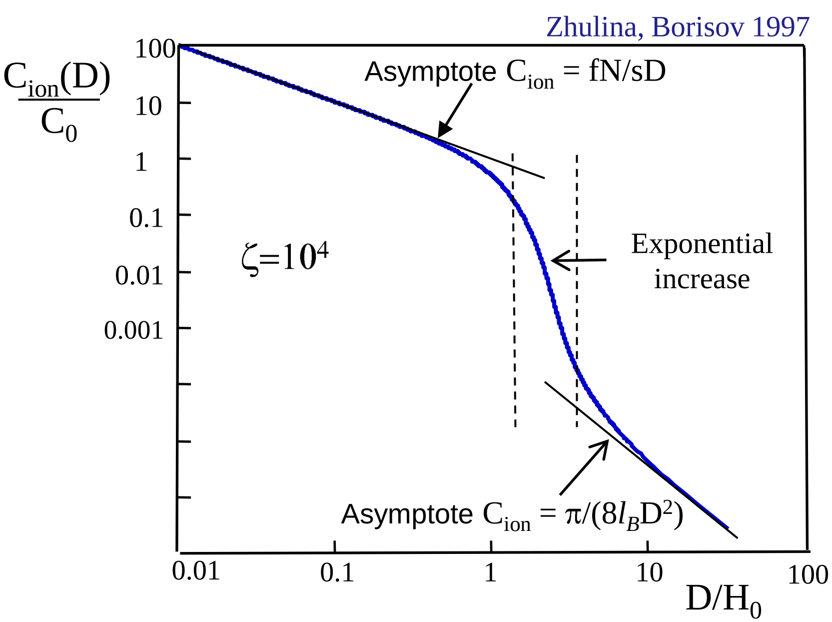
Compression of apposing PE brushes *versus* planar surfaces

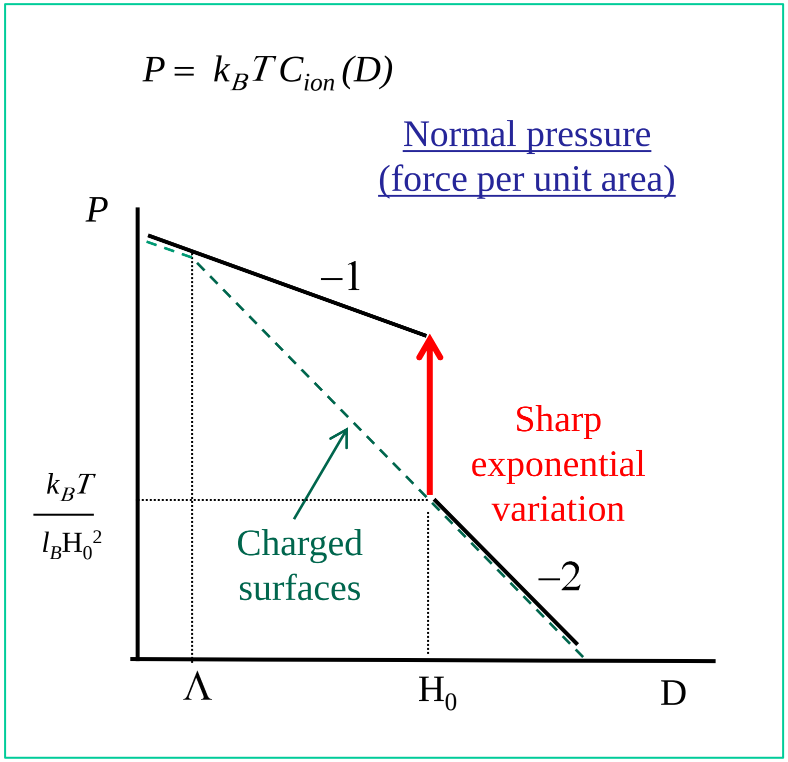
Strong compression



Weak compression







Two main regimes of PE brush compression:

$D >> H_0$ $P \sim D^{-2}$ (compression of ion tail)

$D << H_0$ $P \sim D^{-1}$ (confinement of ions in the body of PE brush)

with sharp crossover between them

Curved PE brushes (scaling model)

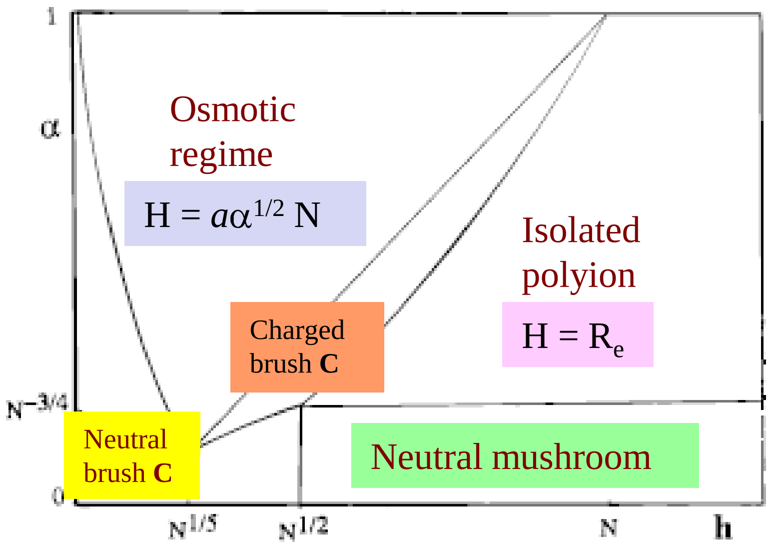
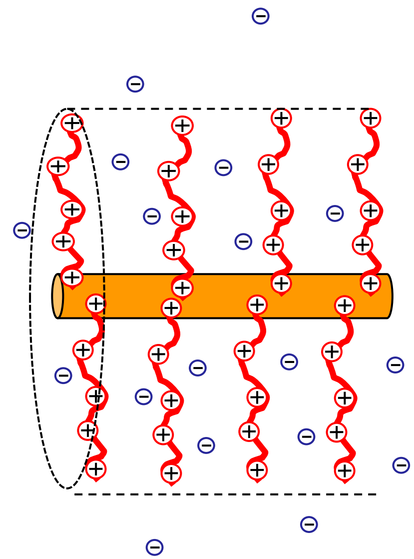


Figure 3. Diagram of states of a cylindrical (bottle) brush in α, h coordinates.



Linear grafting density 1/h chains

Osmotic, isolated polyion and neutral mushroom regimes are similar for all geometries

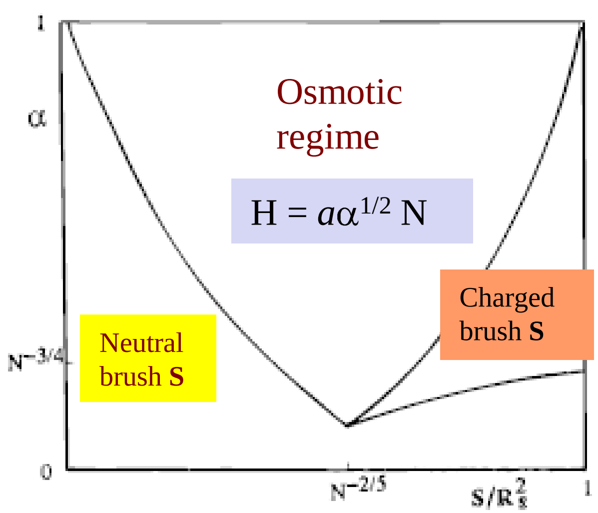
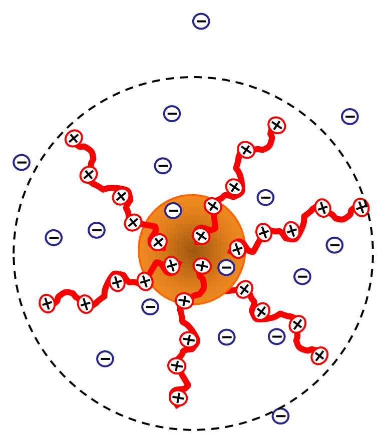


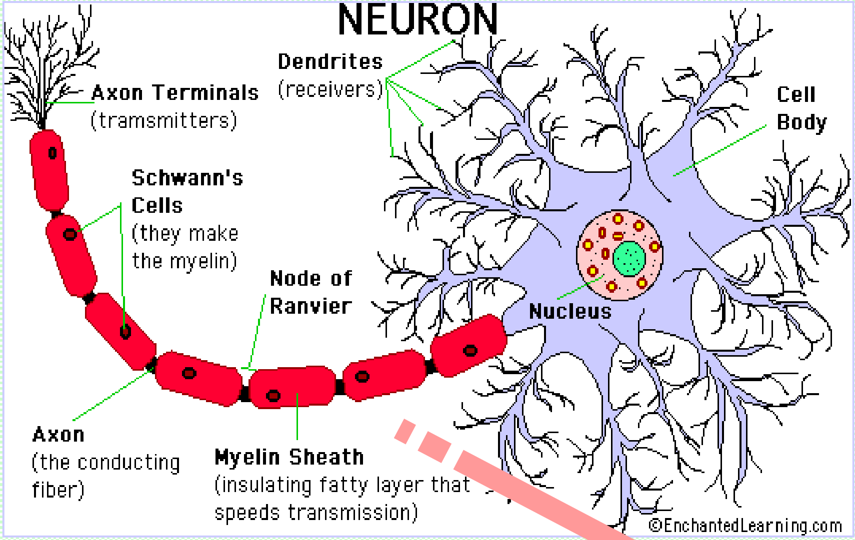
Figure 5. Diagram of states of a spherical brush in $\alpha, s/R_s^2$ coordinates.



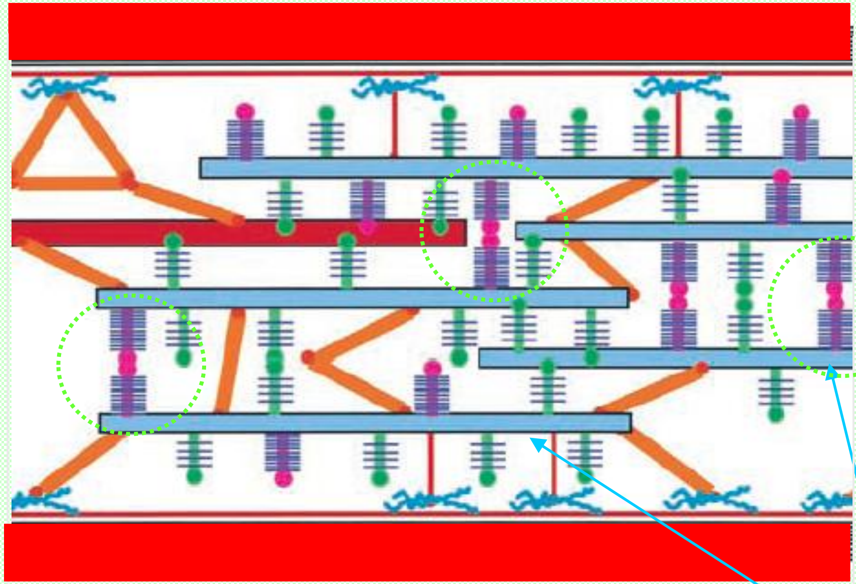
Angular grafting density p >>1 chains

Scaling dependences in charged brush and neutral brush regimes depend on brush geometry

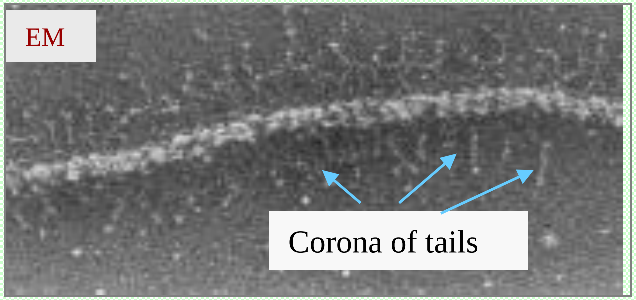
Cytoskeleton in axon of neuron



Schematic of axonal cross-section Rao et al *JCB* 2002

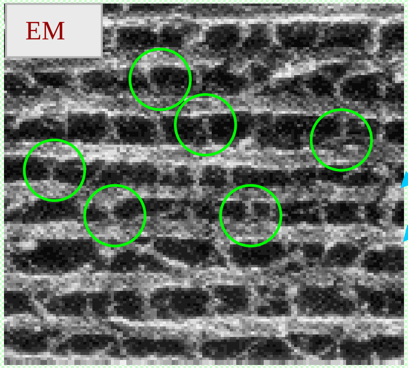


Individual neurofilament NF



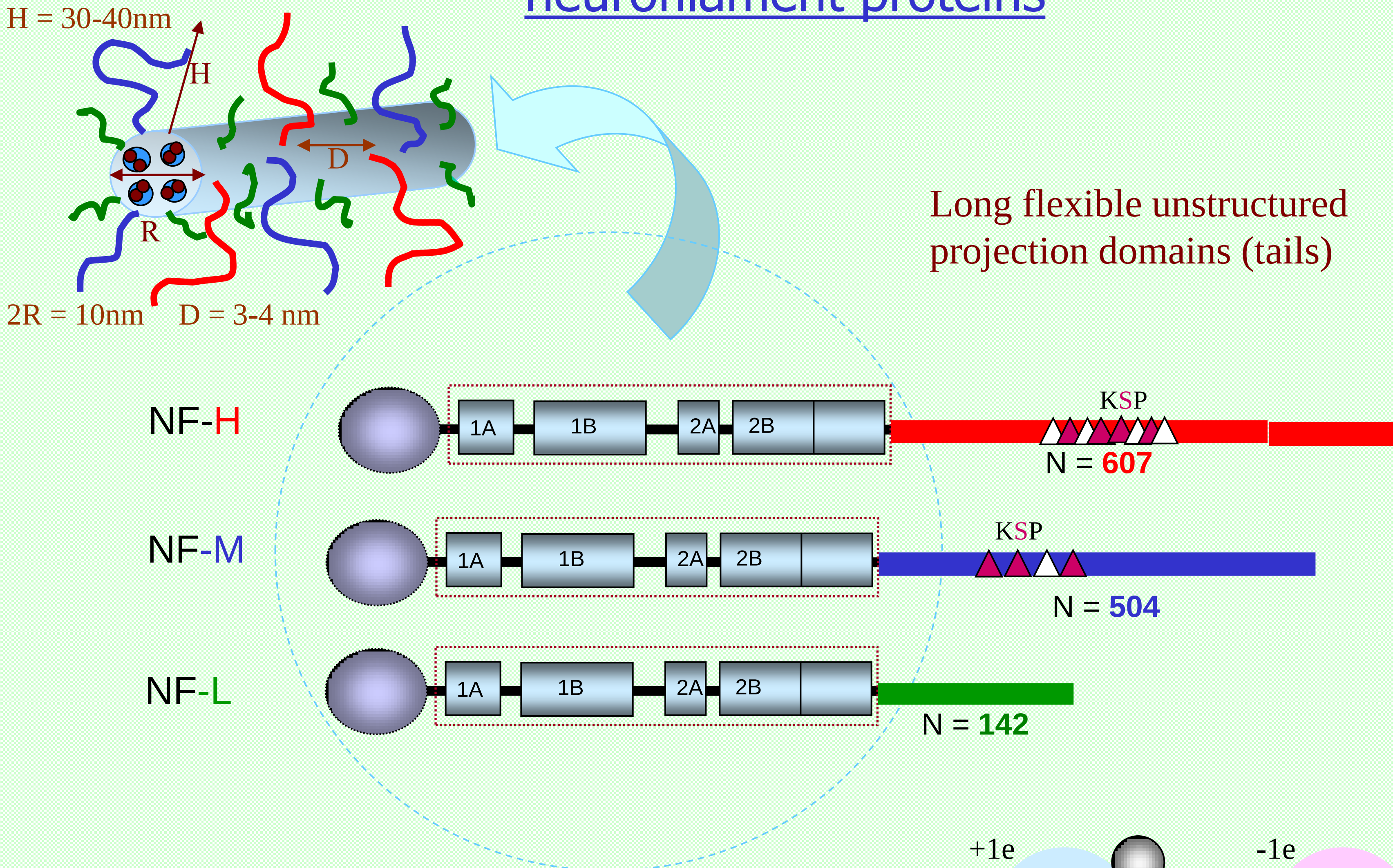
Fuchs & Cleveland *Science* 1998

Hirokawa *JCB* 2000

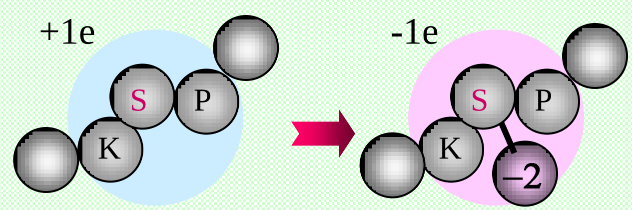


Neurofilament network in axon

Corona of neurofilament is formed by tails of triplet neurofilament proteins



H- and M-tails contain serine S in KSP (△) repeats that can be phosphorylated (charged)



Features of NF brush

- Cylindrical charged brush (with thickness D >> core radius R)
- Combines weak and strong polyelectrolyte properties
- Complex architecture:

  Three types of projections, H- M- and L- tails, with different lengths and degrees of ionization, NF composition varies;

  Phosphorylation changes charge distribution on the longest H-tail: transforms gradient polyampholyte into block polyelectrolyte;

  Shortest L-tails are necessary for filament assembly (they must be present in NF brush)
- Long tails can cross-bridge

SF-SCF modeling NF brush of H, M and L tails with amino acid resolution

Coarse-grained tails with no elements of secondary structure, all monomers have same size a = 0.6 *nm*

Conservation of actual charge distributions on the tails (+ phosphorylation of serines in KSP motifs)

Tethering tails with varied ratio (L:M:H = 7:3:2 in wild-type NF) to impermeable charged cylinder that mimics NF backbone

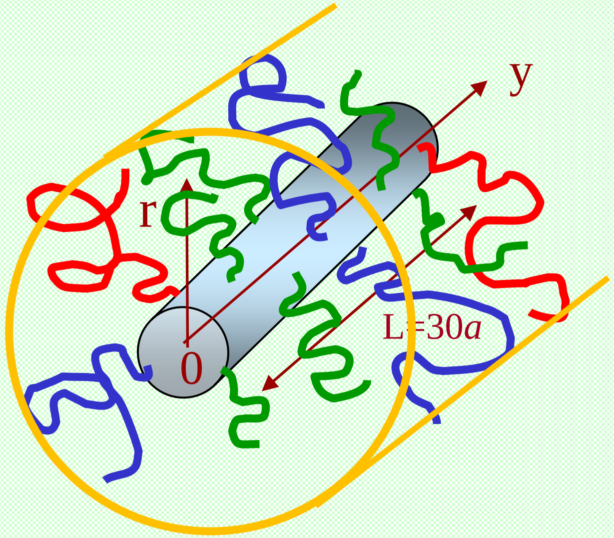
SF-SCF numerical method:

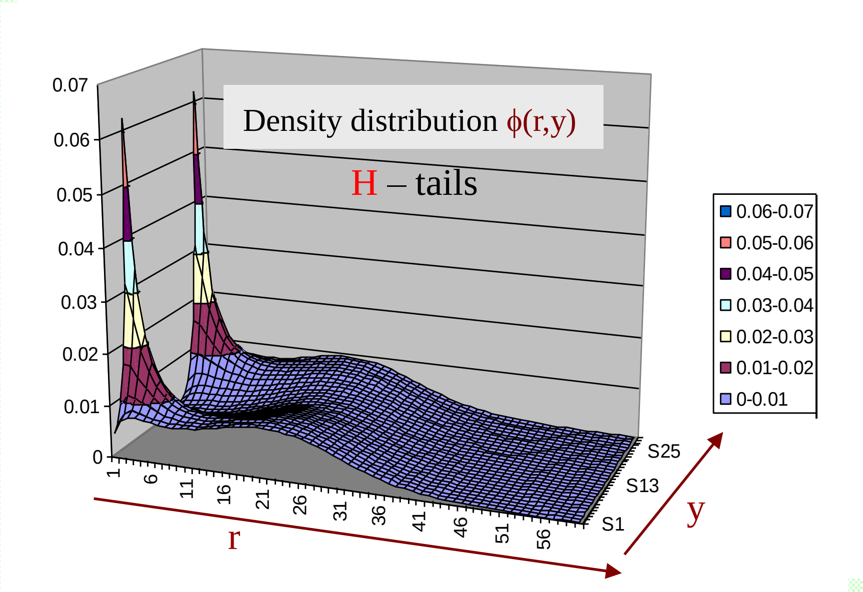
Electrostatic interactions are treated on the Poisson-Boltzmann level

Nonelectrostatic interactions are treated within the Bragg-Williams approximation

Gaussian statistics for tethered chains

1-G, 2-G versions

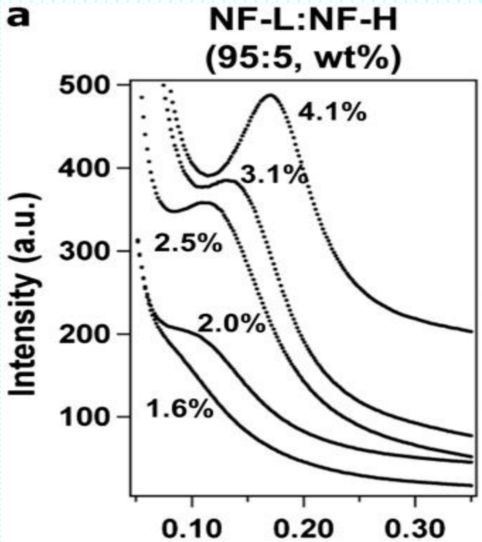


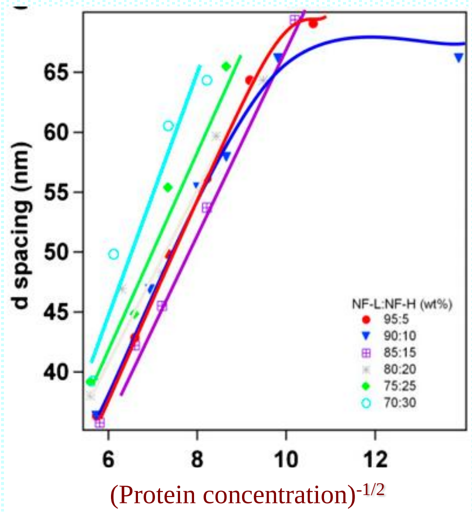


NF-NF interactons: nematic order in neurofilament hydrogel

J.Jones & C.Safinya *BJ* 2008

Nematic-to-isotropic transiton in solution of reconstituted LH- filament (SAXS)

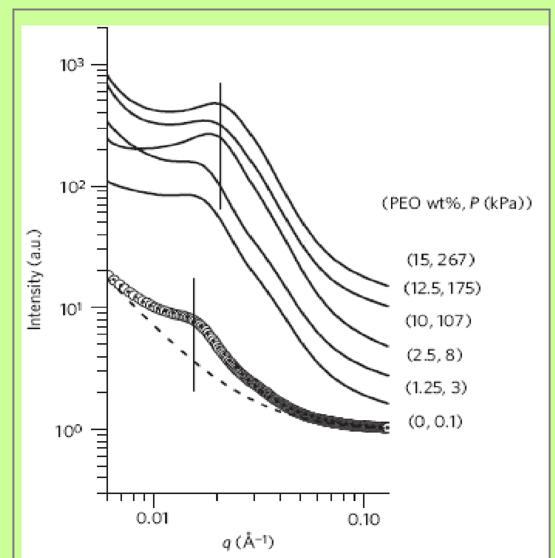




NF-NF distance $d \sim \varphi^{-1/2}$

Reconstituted NFs of various compositions (ratios H:M:L) subjected to external pressure P due to added PEG (plotted along Y-axis)

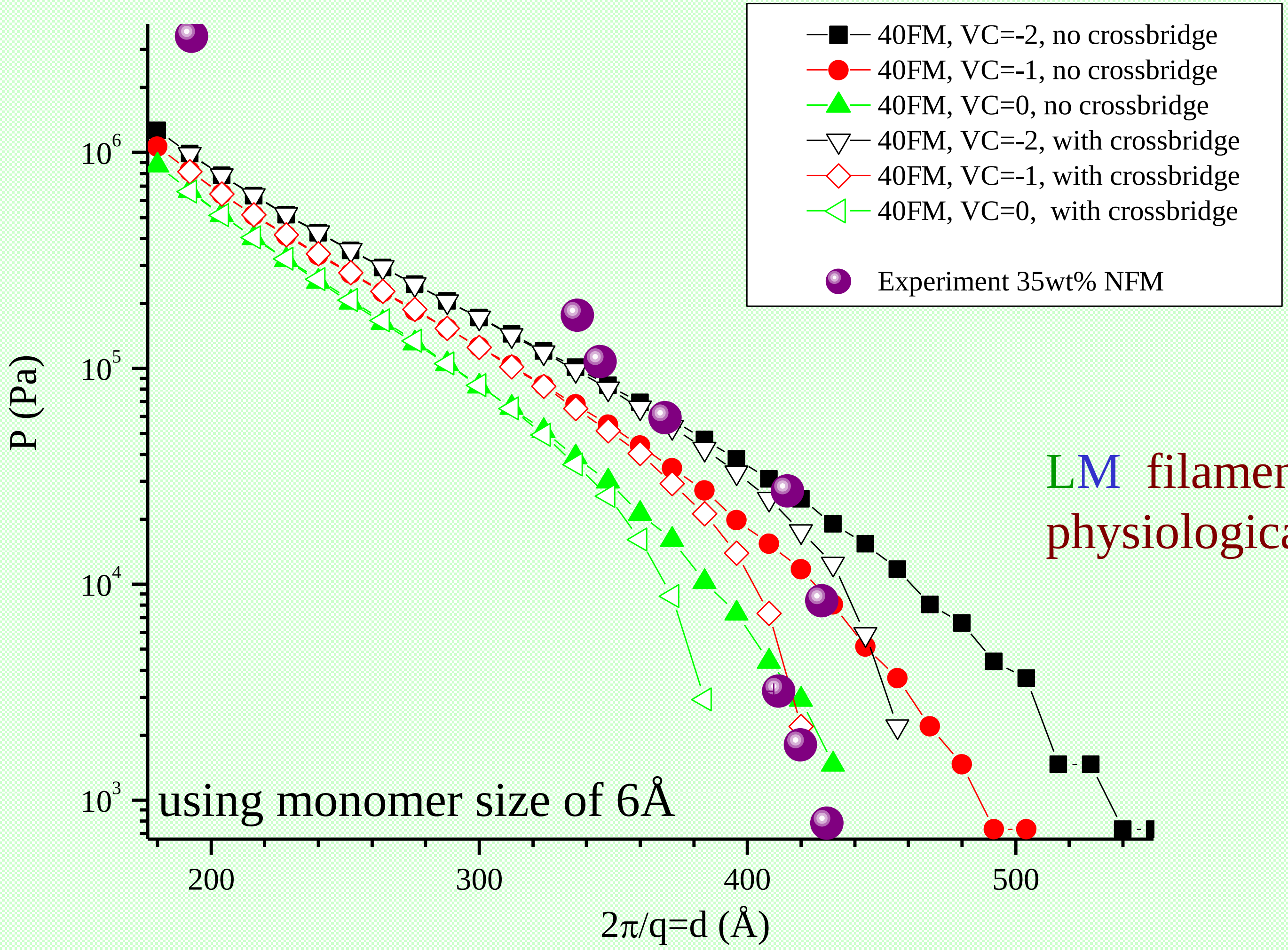
R.Beck et al. *Nature Materials* 2010



Comparison between SF-SCF and experimental pressure-distance profiles

Theory vs. Experiment: 150mM

$P_{theor} = -d(F^{int})/dV$



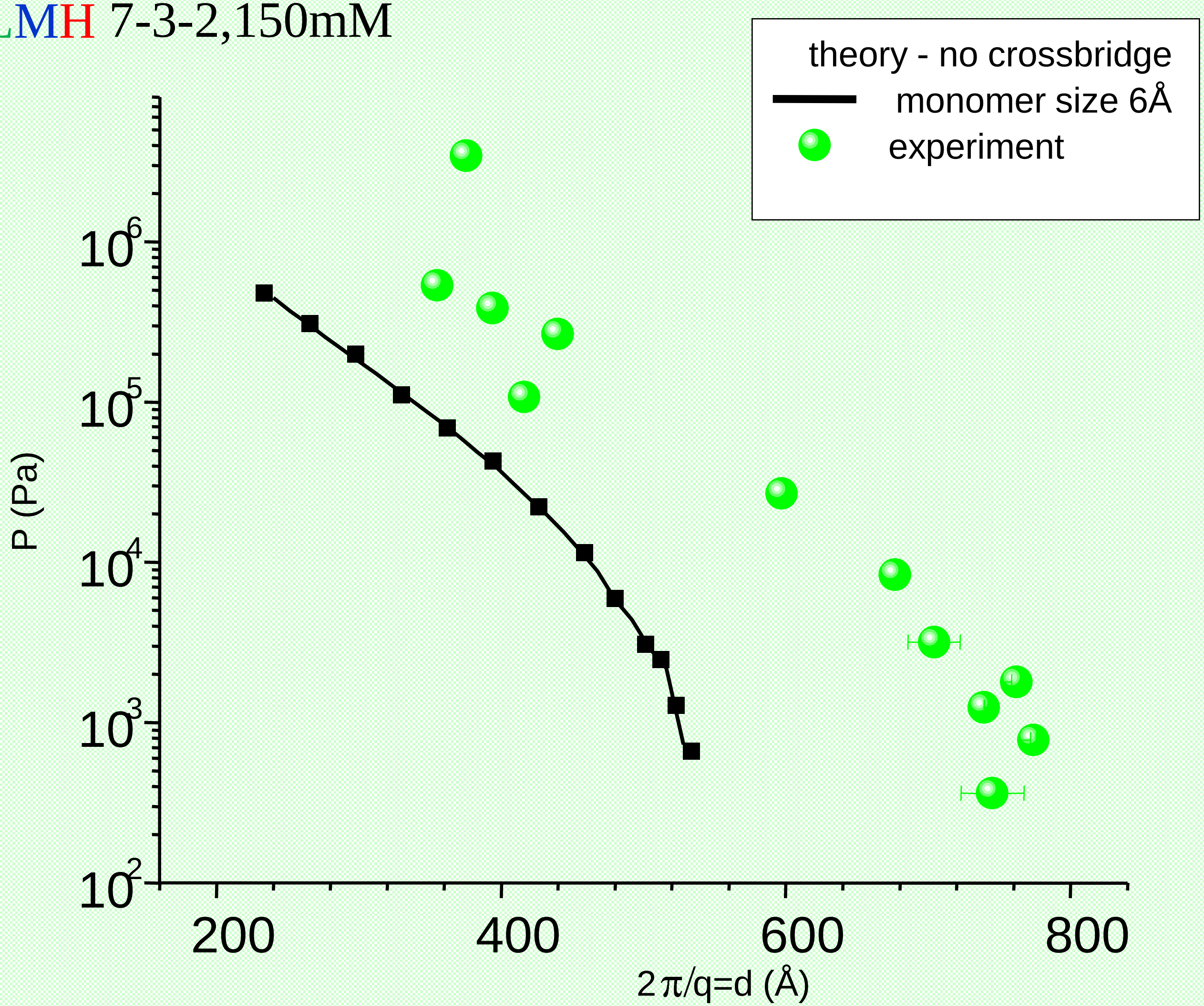
LM filament under physiological conditions

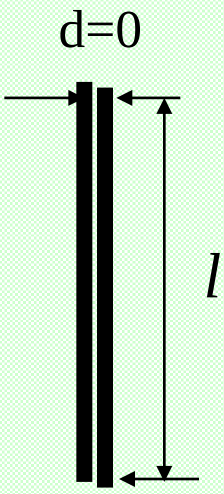
R.Beck et al. *Nature Materials* 2010

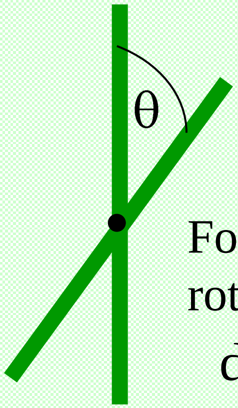
Comparison between SF-SCF and experimental pressure-distance profiles

Wild-type neurofilament

LMH 7-3-2,150mM







For freely rotating rods, $d_{av} \sim l$

R.Beck et al. *Nature Materials* 2010