Polymer Brushes

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« Simple Views on Polymers at Surfaces and Interfaces:
Simposium Honoring P.- G. de Gennes »

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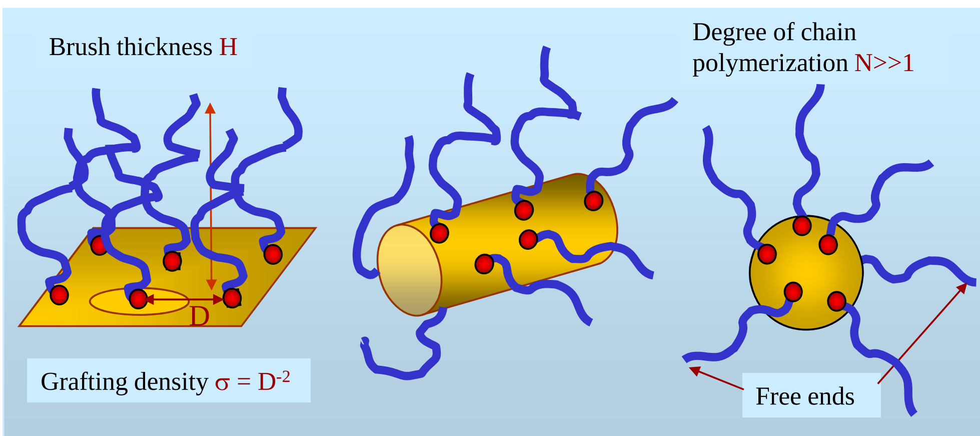
Outline

- What is a polymer brush ?
- Alexander – de Gennes polymer brush model
- Impact of Alexander- de Gennes model and its extensions
- Polymer brush in biology

What is a polymer brush ?

Brush: array of polymer molecules (synthetic, biopolymer,..) end-attached to substrate

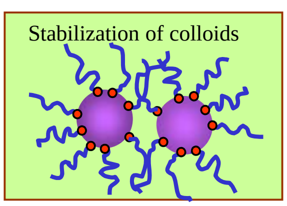


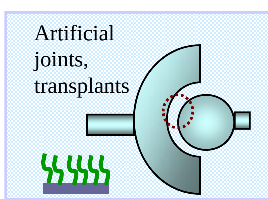
Attachment: ● chemical bond, specific ligand, physical adsorption, self-assembly, etc.

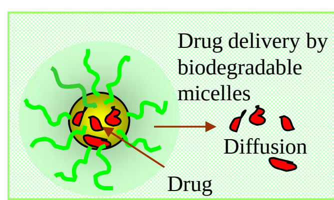
Substrate: bio surface, solid-liquid, air-liquid, liquid-liquid interfaces, self-assembled surfaces, etc.

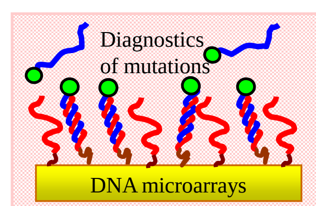
Depending on geometry of substrate brushes are planar, cylindrical or spherical

Examples of brush applications



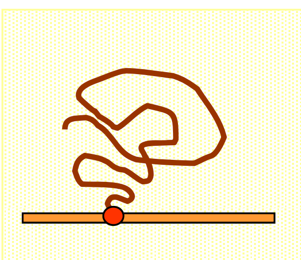




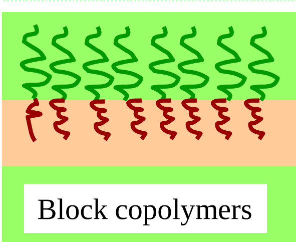


Prior to Alexander - de Gennes brush model

Before A-G brush model: single tethered polymer was treated mostly as the Gaussian (fantom) chain



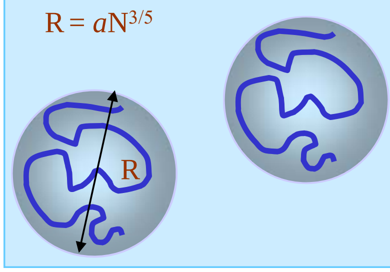
Brush-like structures in microsegregated block copolymers



Scaling theory of semidilute polymer solution

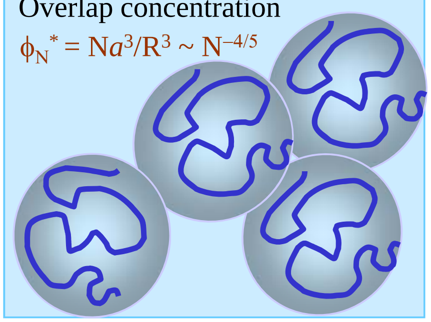
Average end-to-end distance

$R = aN^{3/5}$



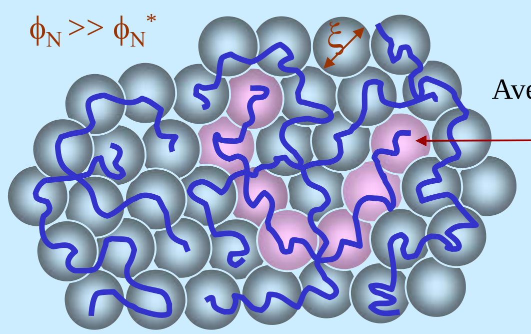
Overlap concentration

$\phi_N^* = Na^3/R^3 \sim N^{-4/5}$



Semidilute solution (melt of blobs)

$\phi_N >> \phi_N^*$



Blob size $\xi/a \sim \phi_N^{-3/4}$

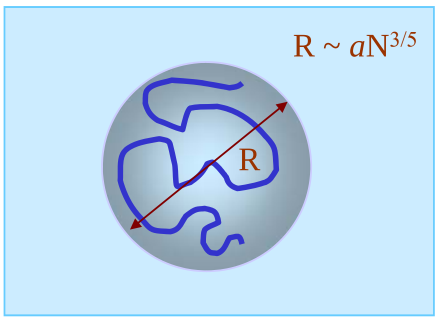
Average end-to-end distance

$R^2 \sim \xi^2 N_B$

Interaction free energy

$F_{int} \sim k_B T N_B$

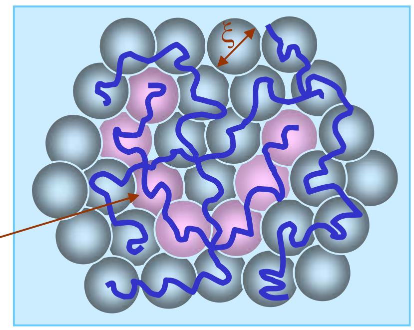
Chain end-tethering to a substrate

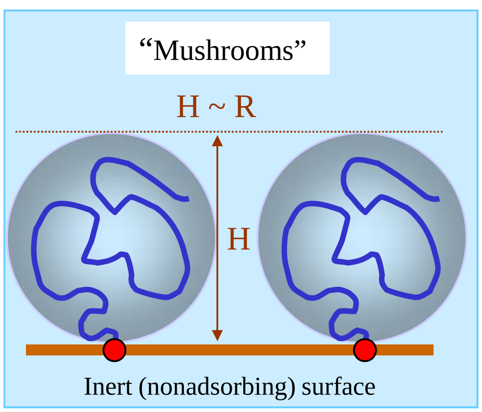


$F_{int}/k_BT \sim N_B$

$F_{elastic}/k_BT \sim 1$

(Gaussian chain of blobs)



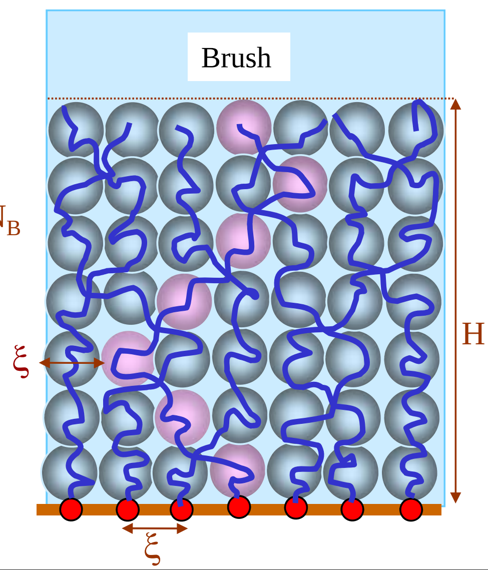


$F_{int}/k_BT \sim N_B$

$F_{elastic}/k_BT \sim N_B$

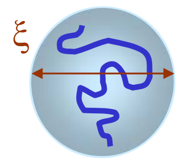
$H \sim \xi N_B$

(Stretched string of blobs or directed random walk)



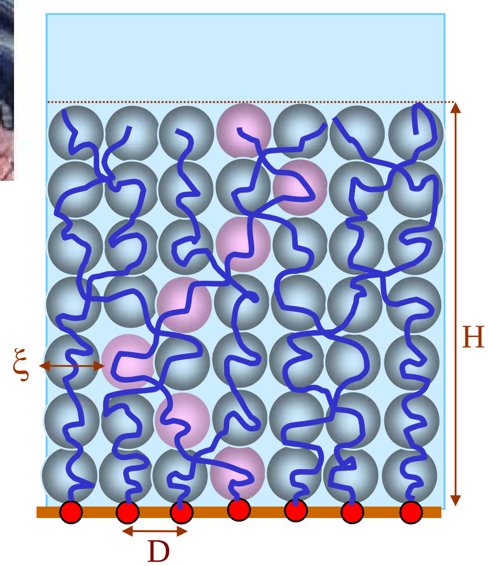
Brush in solvent (S. Alexander 1977)

Free brush $\xi = D$



$D = \xi = ag^{3/5}$

↑ number of monomers per blob

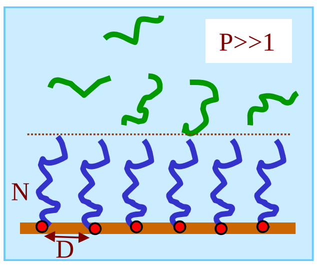


Number of blobs $N_B = N/g$

Free energy (per chain) $F = k_BTN_B$

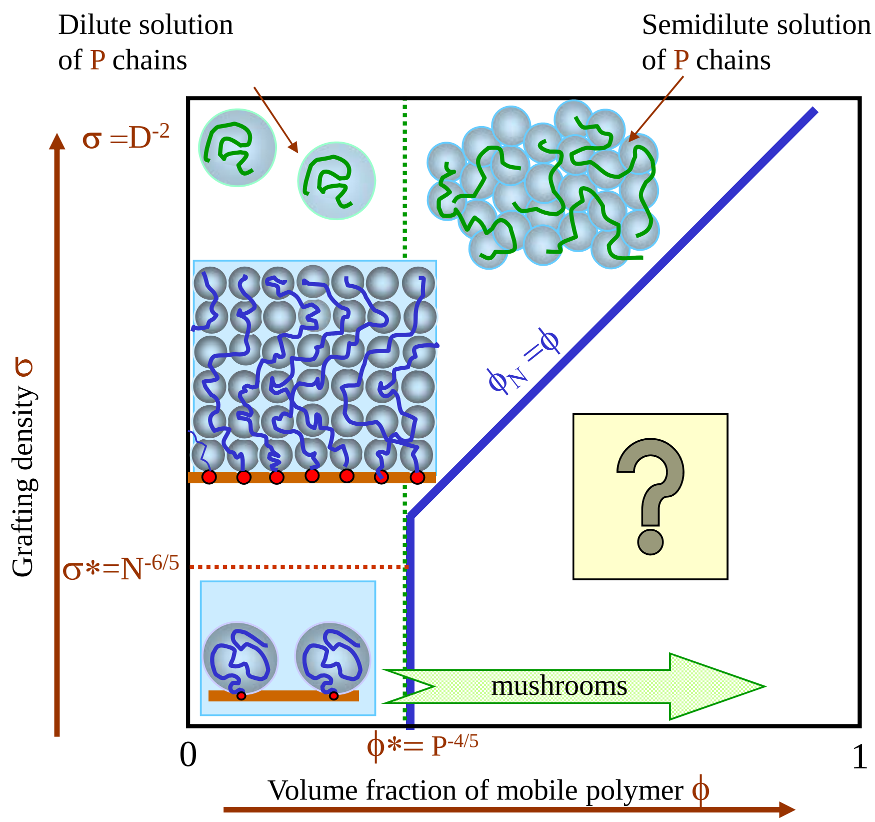
Brush thickness $H = N_B\,\xi \sim N$

Brush in contact with polymer solution (P.- G. de Gennes 1980)

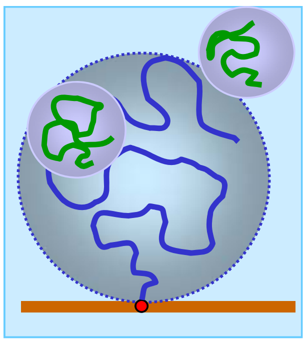


To the left of blue line:

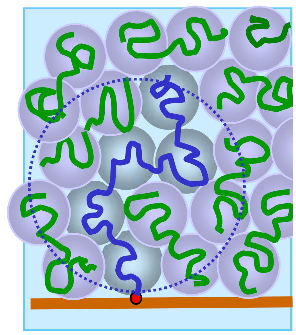
brush dominated regimes, “mushroom” and Alexander brush. Here, $\xi_P > \xi_N$, P and N chains are demixed



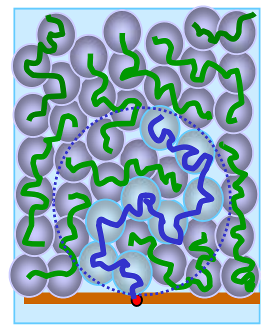
Mushroom in contact with solution of mobile P chains



$\phi << \phi^*$

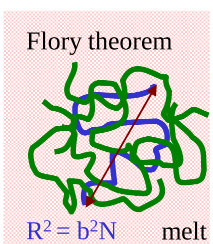


$\phi^* < \phi << \phi^{**}$



$\phi^{**} < \phi << 1$

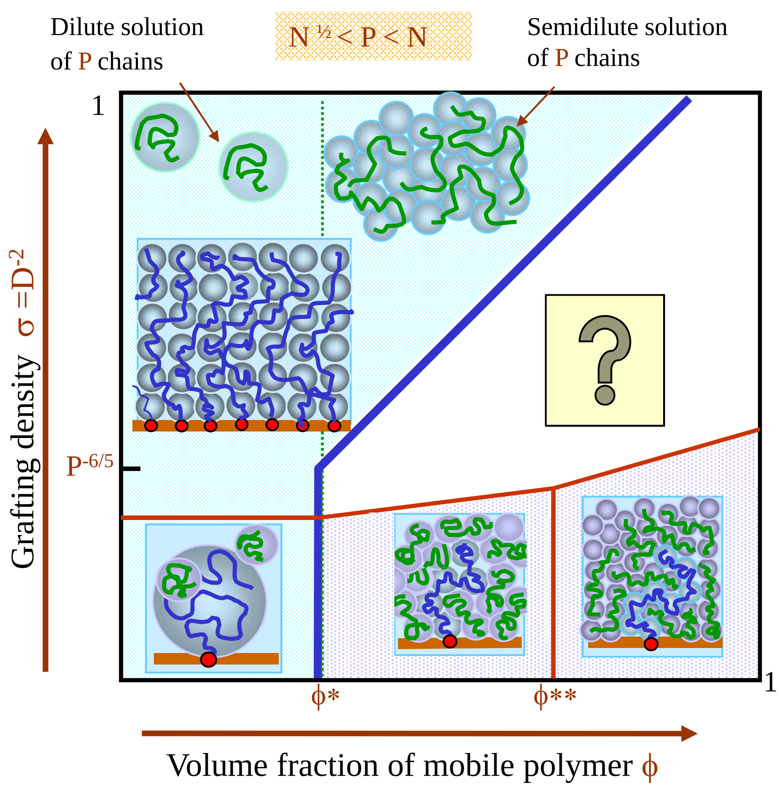
Melt of chains of blobs: $N_{BN} = N\phi^{5/4}$ $N_{BP} = P\phi^{5/4}$



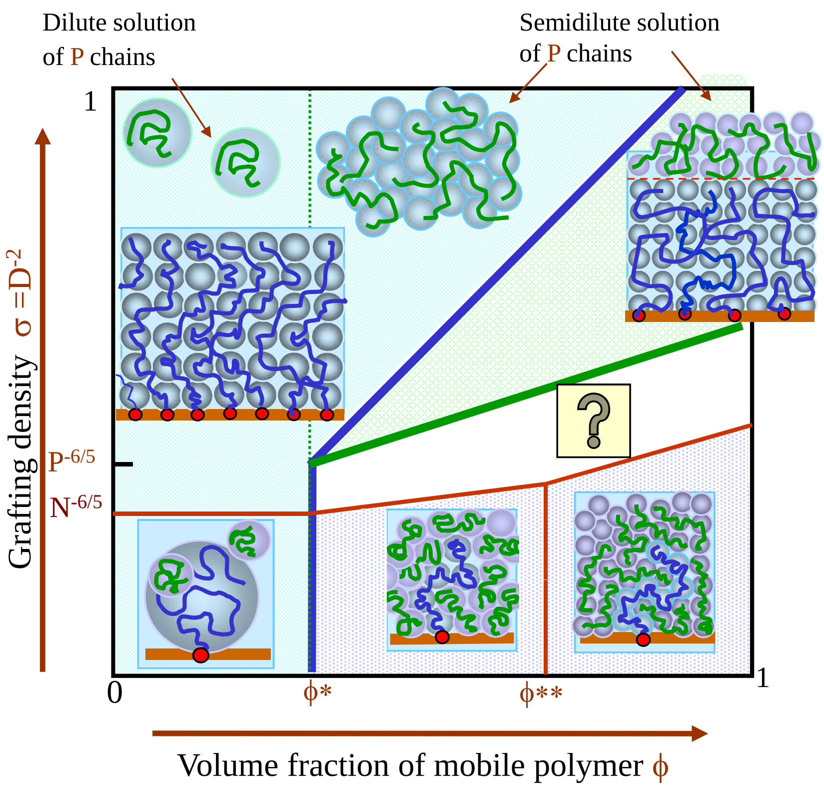
N- chain is swollen when $N_{BP} < N_{BN}^{1/2}$

N- chain is Gaussian chain of blobs when $N_{BP} > N_{BN}^{1/2}$

Solution dominated regimes of the brush



Compression of brush by solution of mobile P chains



Between blue and green lines $\xi_P = \xi_N$, but P and N chains are demixed because grafted chains are stretched. Brush is compressed by solution of P chains

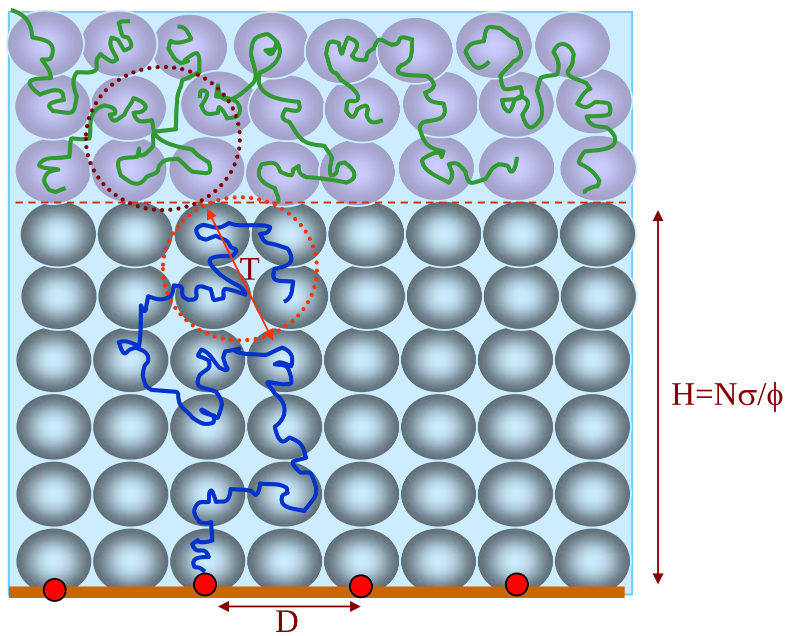
Below green line P chains penetrate the brush

Interpenetration of mobile P- chains in brush of N-chains

Tension blob

$T \sim N_B \xi^2/H$

(unstretched portion of N-chain) determines penetration length



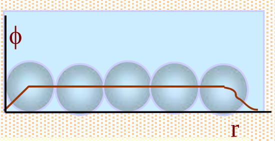
When tension blob T becomes equal to the size of P-chain in solution, mobile chains penetrate throughout the brush of N-chains. Brush remains (weakly) stretched.

Diagram of states and summary of A-G model

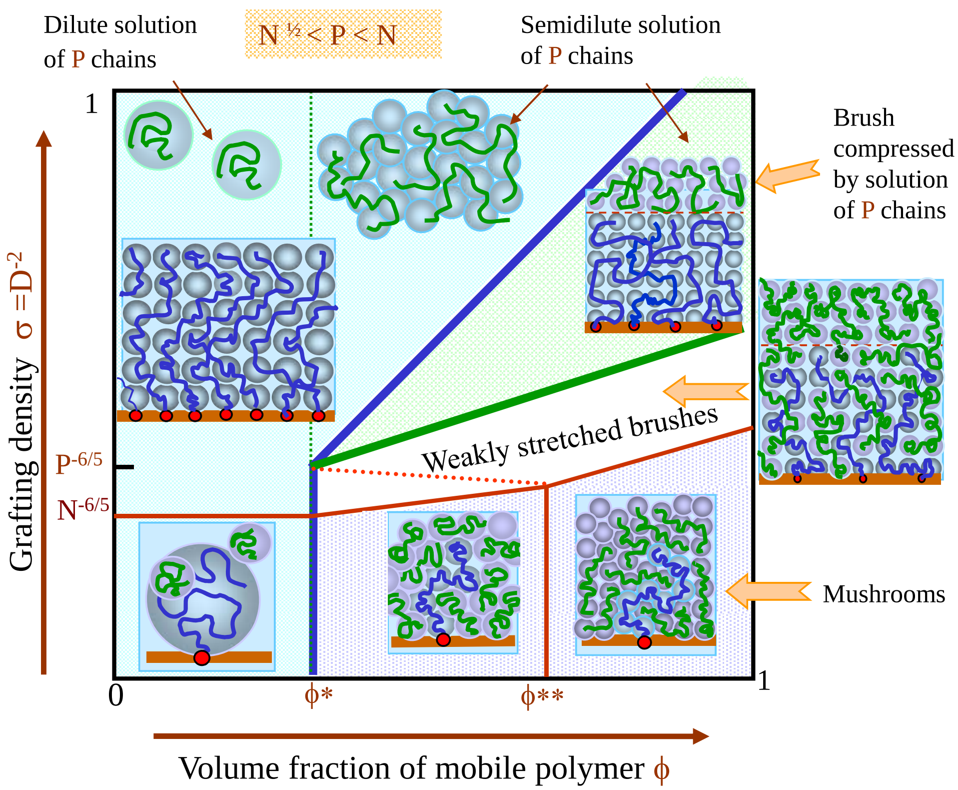
Chain free end is within last blob

Blobs have same size

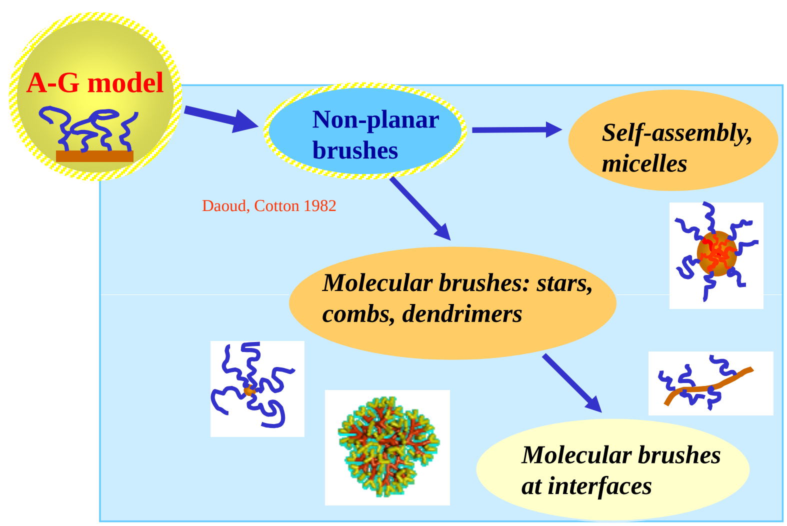
Polymer density profile is flat except for first and last blobs

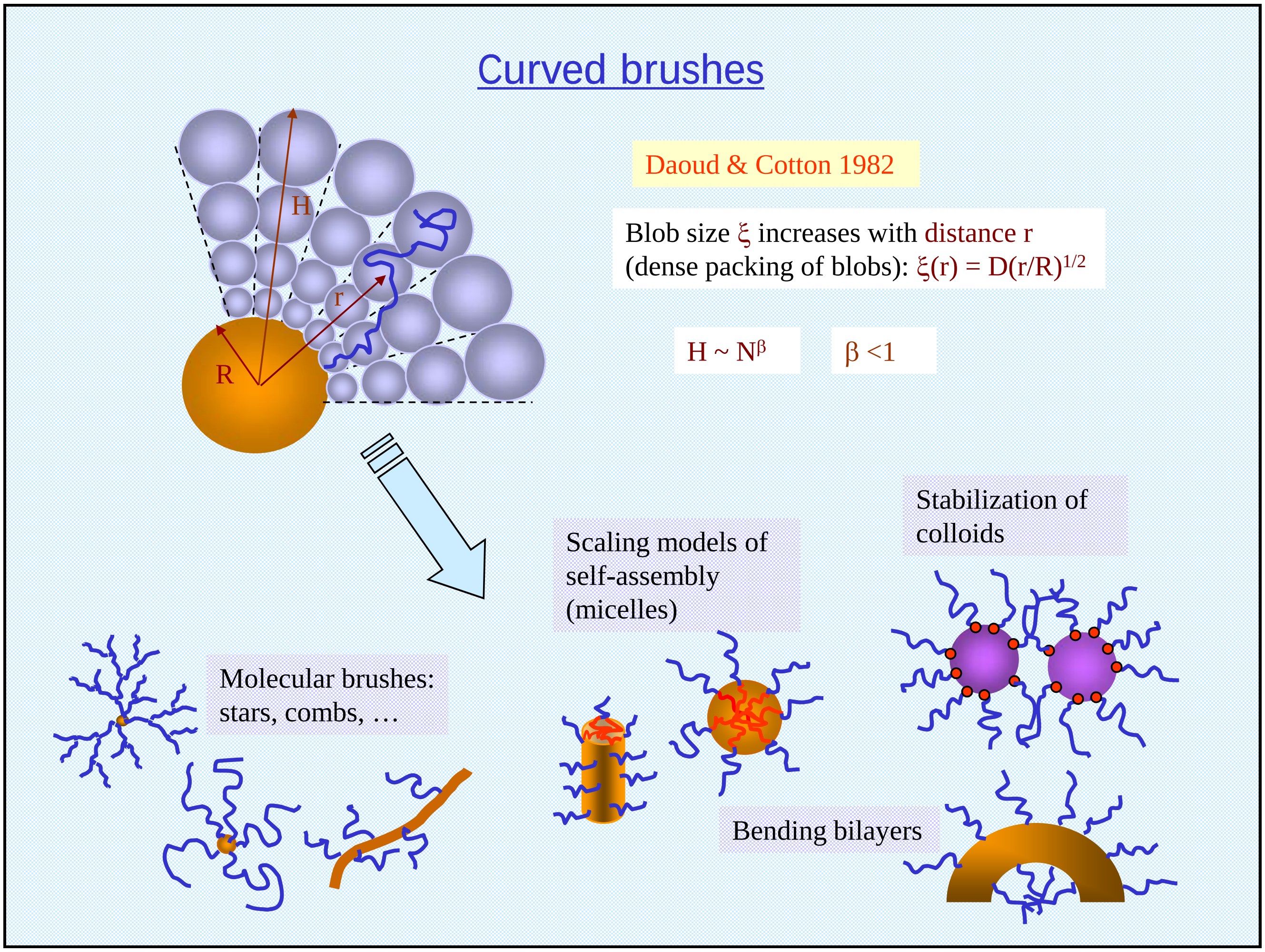


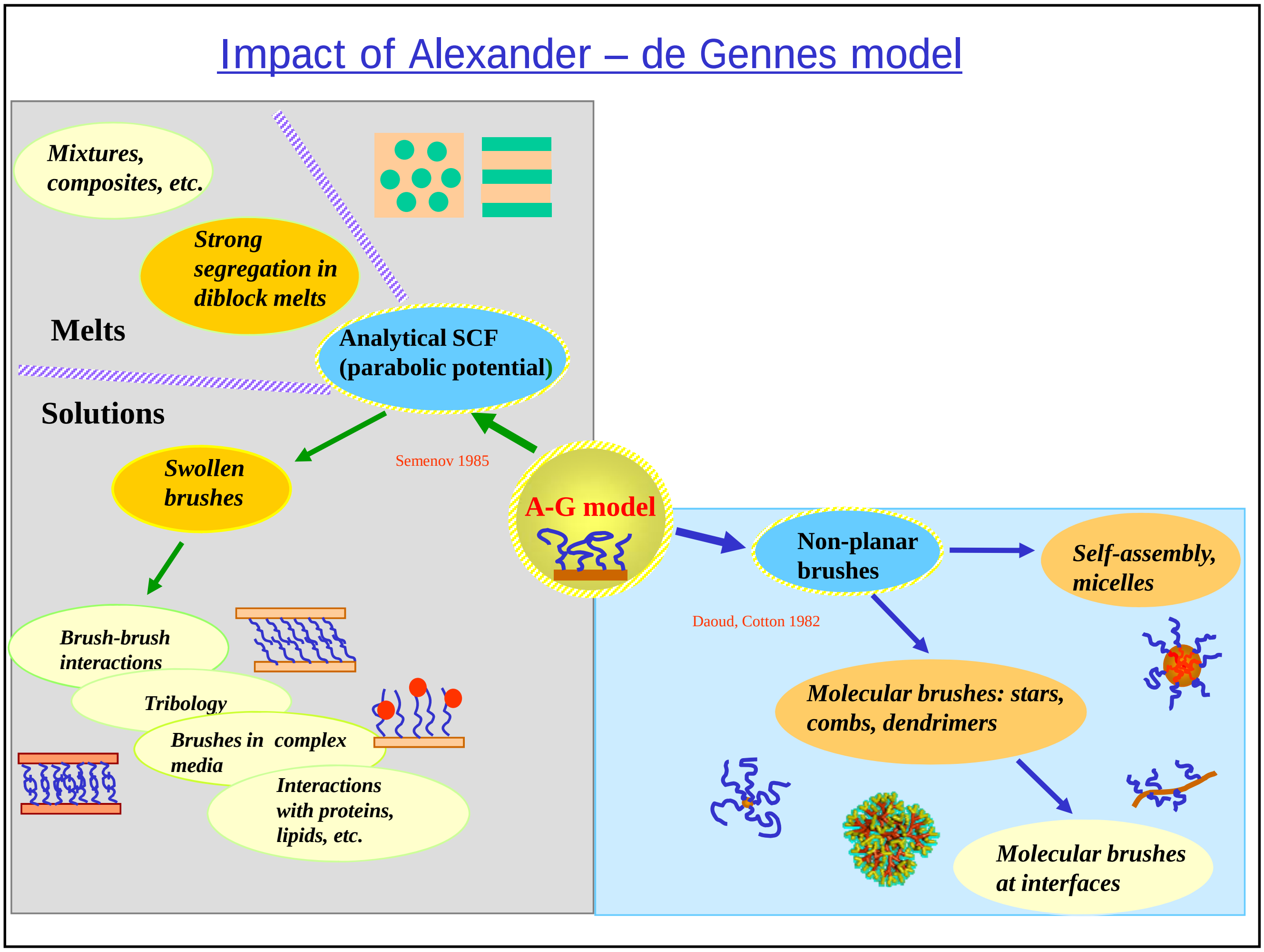
Tethered chains are stretched normally to the surface, H ~ N



Impact of Alexander – de Gennes model

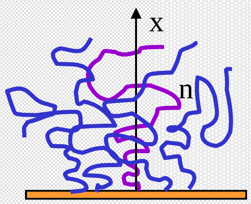



Curved brushes
H
r
R
Daoud & Cotton 1982
Blob size ξ increases with distance r
(dense packing of blobs): $\xi(r) = D(r/R)^{1/2}$
$H \sim N^{\beta}$
$\beta < 1$
Stabilization of colloids
Scaling models of self-assembly (micelles)
Molecular brushes: stars, combs, …
Bending bilayers


Impact of Alexander – de Gennes model
Mixtures, composites, etc.
Strong segregation in diblock melts
Melts
Analytical SCF (parabolic potential)
Solutions
Swollen brushes
Semenov 1985
A-G model
Brush-brush interactions
Tribology
Brushes in complex media
Interactions with proteins, lipids, etc.
Non-planar brushes
Self-assembly, micelles
Daoud, Cotton 1982
Molecular brushes: stars, combs, dendrimers
Molecular brushes at interfaces

Analytical SCF model (parabolic potential)

Polymer trajectory: x(n)



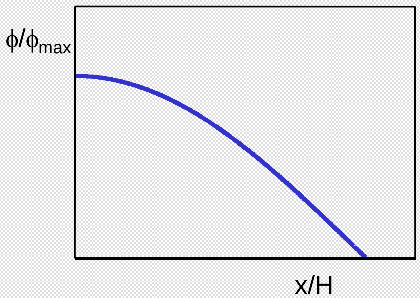
Semenov 1985

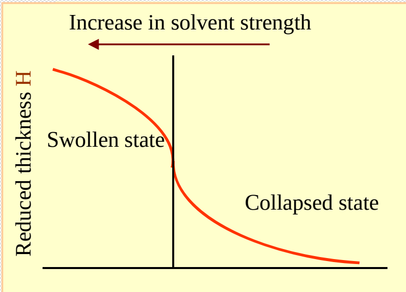
Dry brushes (no solvent): chains are stretched unequally and nonuniformly. Free ends are distributed throughout the brush

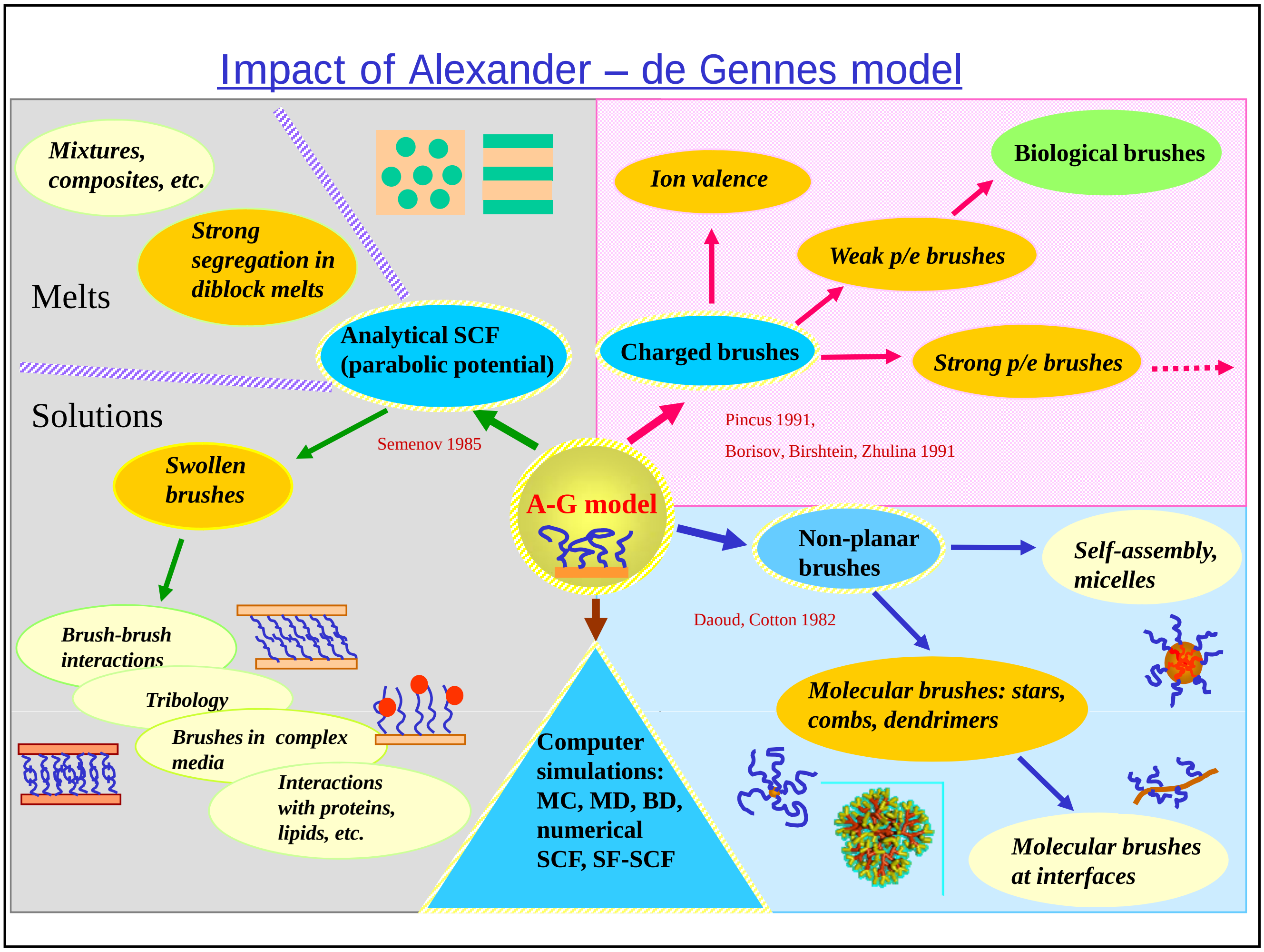
Polymer density profile is not flat. Shape depends on solvent quality. However, all scaling dependences for average brush characteristics hold. Collapse is gradual.

Swollen brushes

Milner, Witten, Cates 1988
Zhulina, Pryamitsyn, Borisov 1989






Impact of Alexander – de Gennes model
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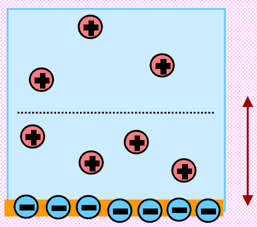
Interactions with proteins, lipids, etc.
A-G model
Computer simulations: MC, MD, BD, numerical SCF, SF-SCF
Ion valence
Biological brushes
Weak p/e brushes
Charged brushes
Strong p/e brushes
Pincus 1991,
Borisov, Birshtein, Zhulina 1991
Non-planar brushes
Self-assembly, micelles
Daoud, Cotton 1982
Molecular brushes: stars, combs, dendrimers
Molecular brushes at interfaces

Polyelectrolyte brushes (scaling model)

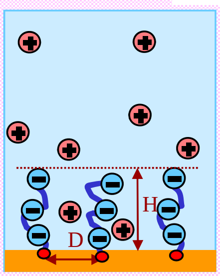
Pincus 1991



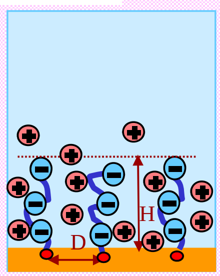
Gouy-Chapman length $\Lambda \sim 1/\sigma$

Surface charge σ

$\sigma = Q/D^2 = \alpha N/D^2$



$\Lambda > H$, charged (Pincus) brush



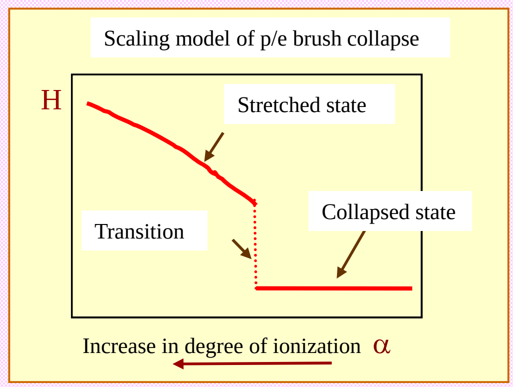
$\Lambda < H$, osmotic brush

Addition of salt provides another length scale

r_D- Debye radius (salted brush)

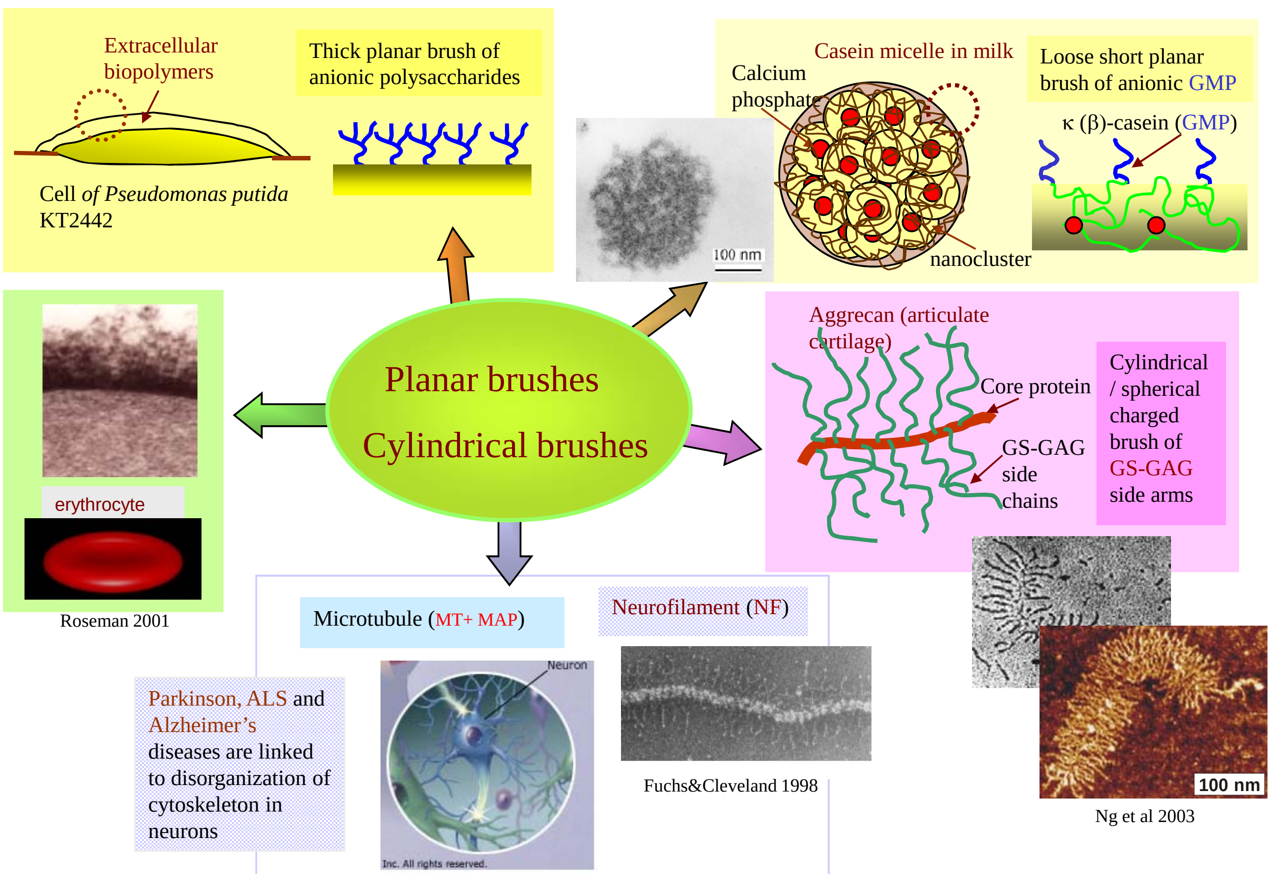
Borisov, Birshtein, Zhulina 1991

In contrast to neutral brush, collapse induced by binary monomer-monomer attraction is jump-like



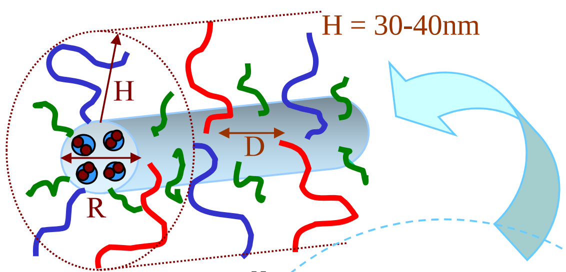
Polyelectrolyte brush is more diverse than a neutral brush (electrostatic + nonelectrostatic interactions), stimuli-responsive (ionic strength, pH, ion valence)

Brush-like structures in biological systems

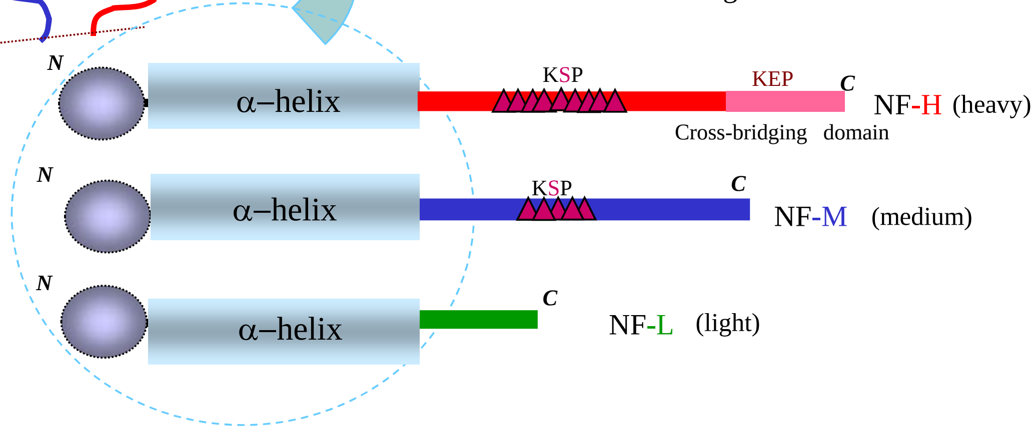


Triplet neurofilament proteins (constituents of NF)

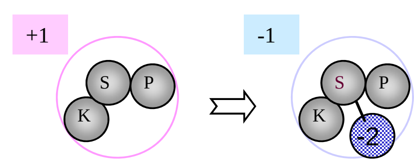
Mukhopadhyay, Kumar and Hoh, *BioEssays* 2004



Long flexible unstructured projection domains (tails) constitute a cylindrical polymer brush around rigid NF backbone



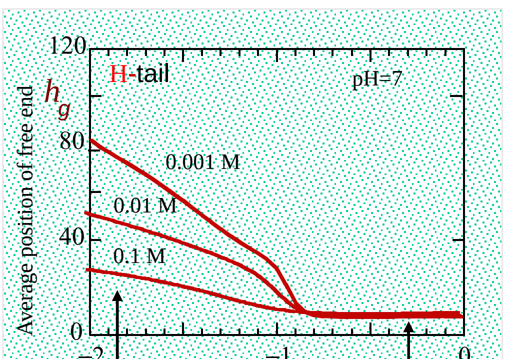
H- and M-tails contain serine S in KSP (▲) repeats that can be phosphorylated (charged)



SF-SCF brush model: collapse-to-stretching transition in H-tails

Zhulina & Leermakers *BJ* 2007

Phosphorylation (charging H-tails)

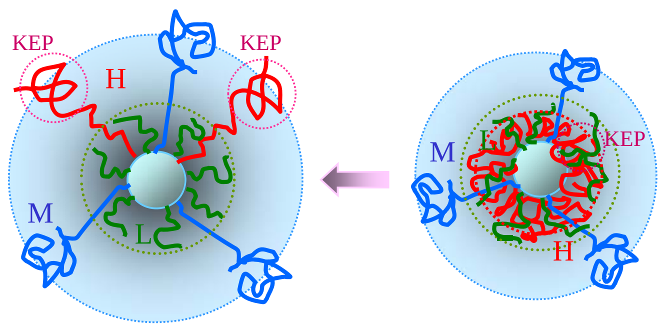


Stretched state (KEP domain is outside)

H - tails are collapsed until ~ 50 % KSP repeats are phosphorylated

Phosphorylated NF

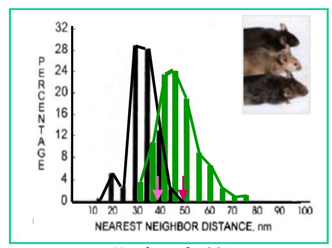
Dephosphorylated NF



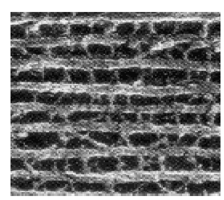
SF-SCF brush model predicts: phosphorylation induced translocation of H-tails leads to

(a) increase in brush thickness (NF-NF distances in axon)

(b) stabilization of NF network through cross-bridging between KEP domains



Hsieh et al 1994

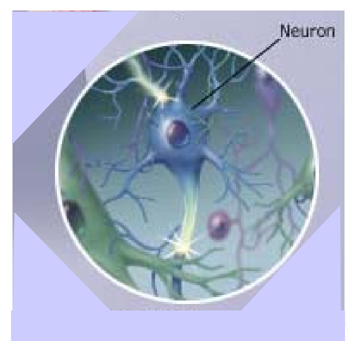


Hirokawa 1982

Conclusions

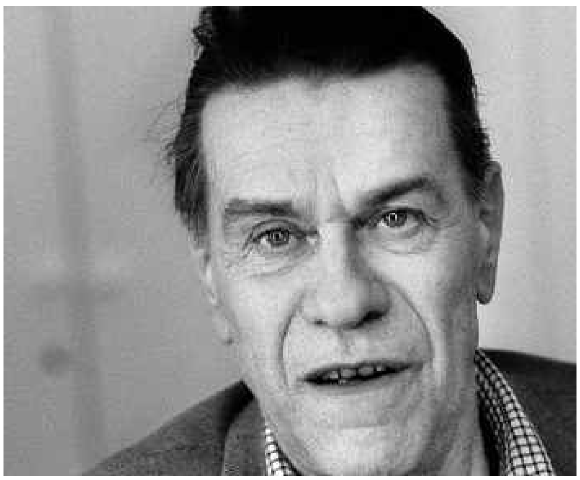
From brush scaling model to cytoskeleton in neurites

- Charged brushes
- Non-planar brushes
- Numerical SF-SCF



Elasticityof NF network,
effect of NF composition, …

Remembering Pierre - Gilles de Gennes



The **1991 PHYSICS NOBEL PRIZE** goes to Pierre-Gilles de Gennes of the College de France in Paris "for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers."