# Polymer brushes

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# Overview of the course "Polymer brushes"

**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).

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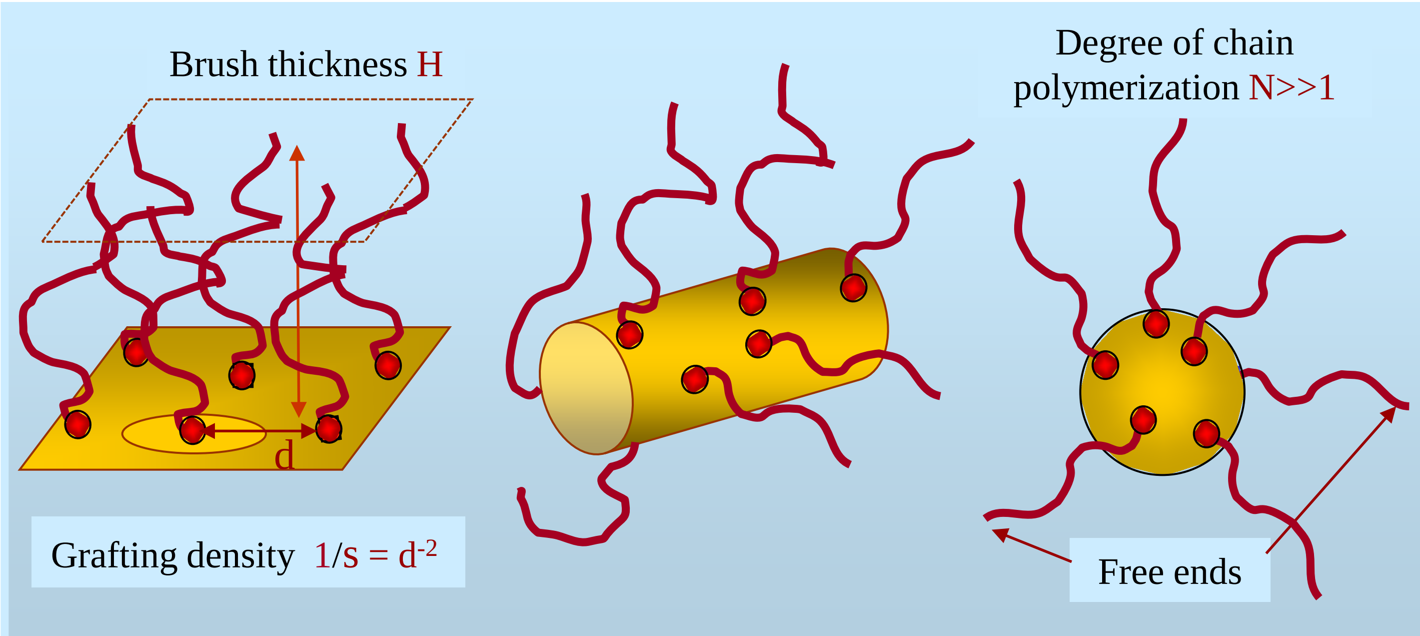
**Lecture 2: Charged brushes.** Strong and weak polyelectrolytes. Scaling model of strong PE planar brush. Main regimes of PE brush (counterion and salt dominated). Local electroneutrality approximation. Parabolic potential and internal structure of planar PE brush. Interactions between planar PE brushes.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

↓ ↓

**Lecture 3: Polymer micelles.**
Micellization of neutral diblock copolymers in dilute solution in selective solvent. CMC. Strong segregation limit and narrow interface approximation. Star-like and crew-cut spherical micelles. Cylindrical and lamellar aggregates. Morphological transitions sphere-cylinder-lamella. Micelles with charged coronae.
Diblock copolymer aggregates in semi-dilute solutions and melts. Strong and weak segregation limit.
Multi-compartment micelles (MCMs).

# What is a polymer brush ?

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

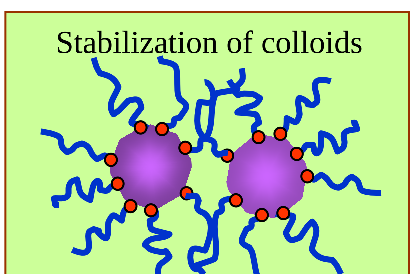


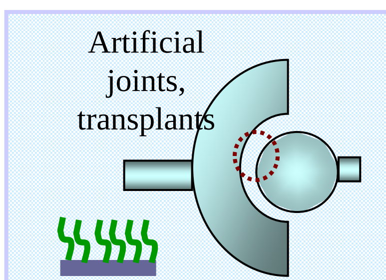

Attachment: chemical bond, specific ligand, physical adsorption, self-assembly, etc.

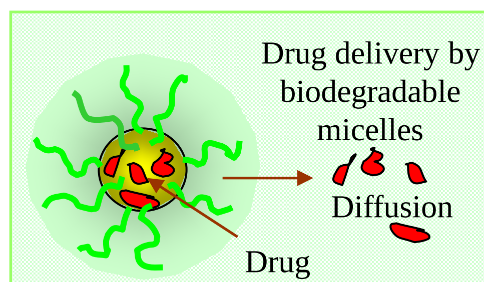
Substrate: bio surface, solid-liquid, air-liquid, liquid-liquid interfaces, self-assembled surfaces, etc.

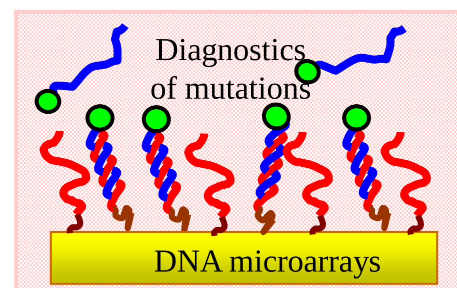
Depending on geometry of substrate brushes are planar, cylindrical or spherical

## Examples of brush applications

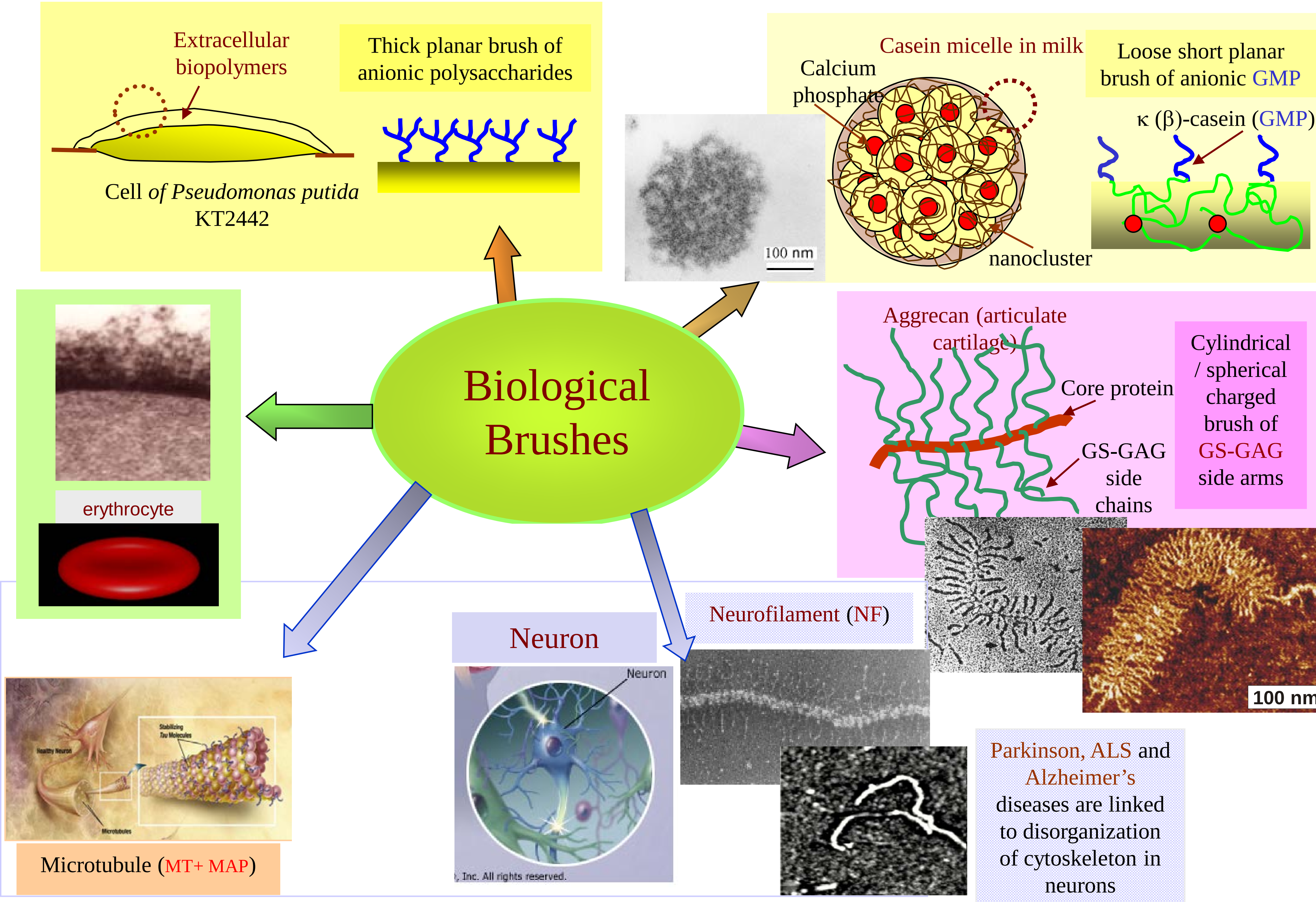


# Brush-like structures in biological systems

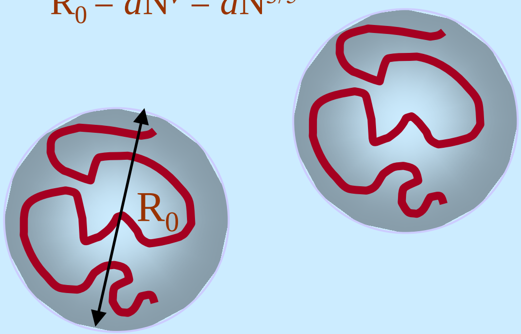


# Scaling theory of semidilute polymer solutions

Flexible chains (ratio of Kuhn segment length A and monomer size $a$, p=A/a =1. Athermal solvent: second virial coefficient of monomer-monomer interactions $v = \tau a^3 = a^3$ (or, $\tau = 1$).

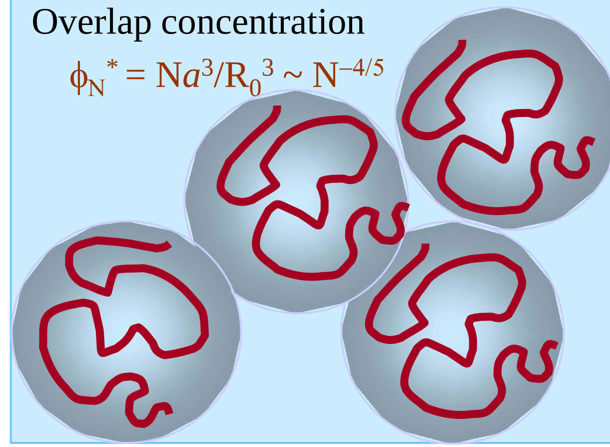
Average end-to-end distance

$R_0 = aN^{\nu} = aN^{3/5}$



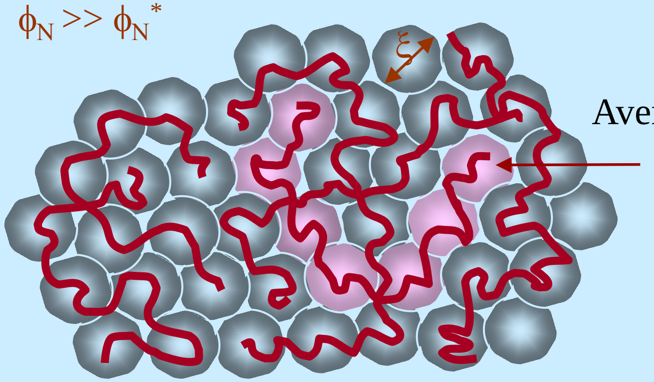

Overlap concentration

$\phi_N^* = Na^3/R_0^3 \sim N^{-4/5}$



Semidilute solution (melt of concentrational blobs)

$\phi_N >> \phi_N^*$




Blob size $\xi/a \sim v^{1/4}\phi_N^{-3/4}$

Average end-to-end distance

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

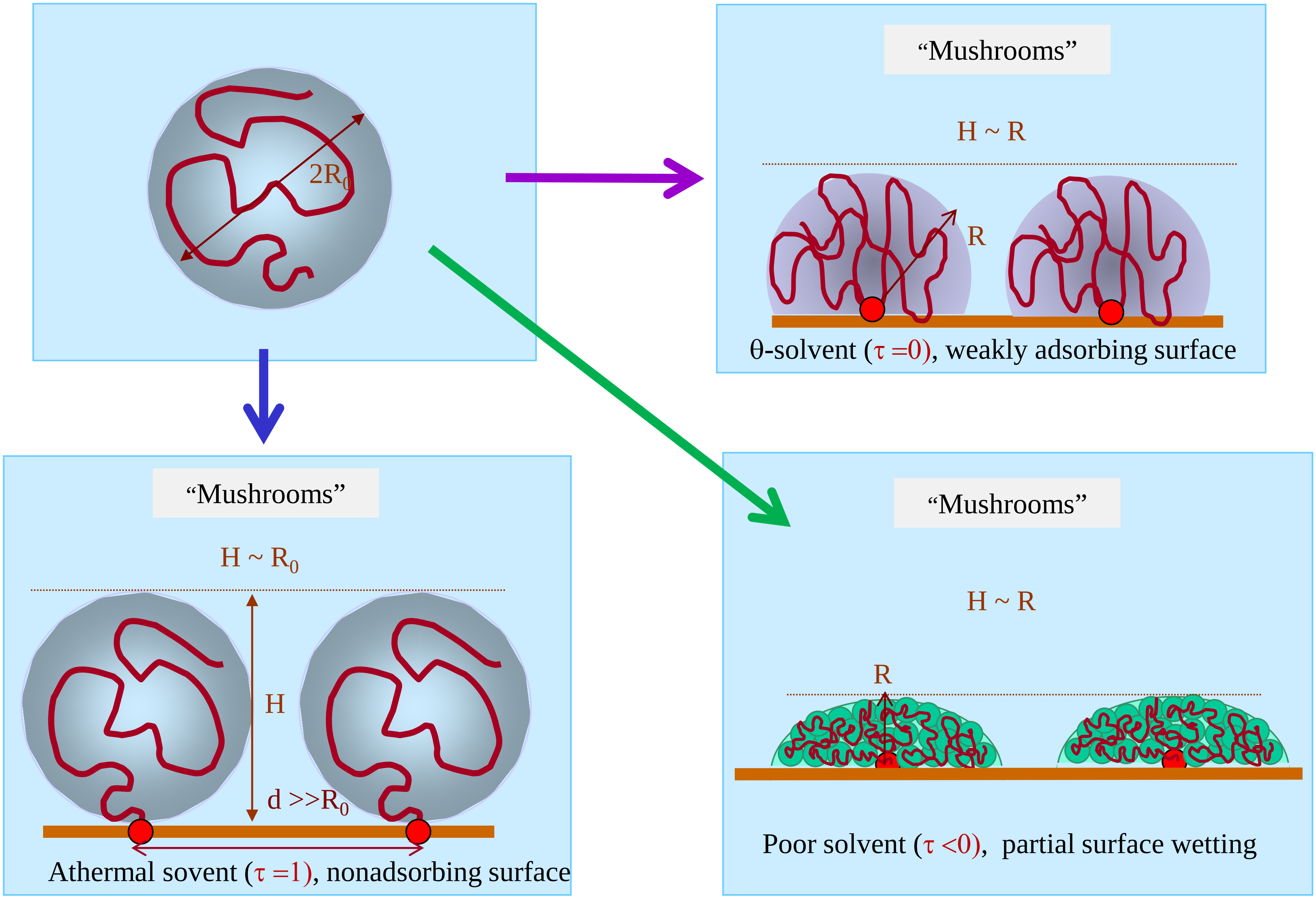
Interaction free energy

$F_{int} \sim k_B T N_B$

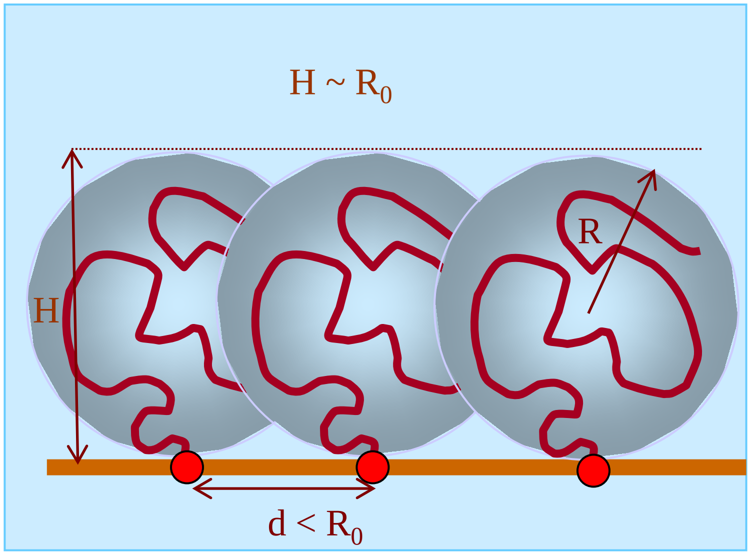
Inferior solvent strength ($\tau < 1$) leads to decrease in size of concentrational blob and its eventual de-swelling.
Chain statistics becomes Gaussian when $v < \phi_N$

In a theta-solvent, $\tau = 0$, size of concentrational blob $\xi/a \sim \phi_N^{-1}$

# Loose chain grafting to a substrate. Mushroom regime: tethered chains do not "feel" each other.

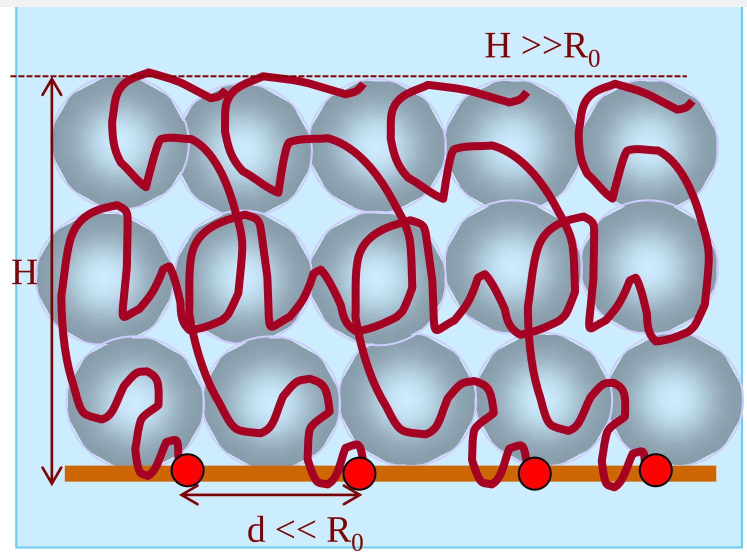


# Increasing chain grafting density: transition from mushroom to brush regime

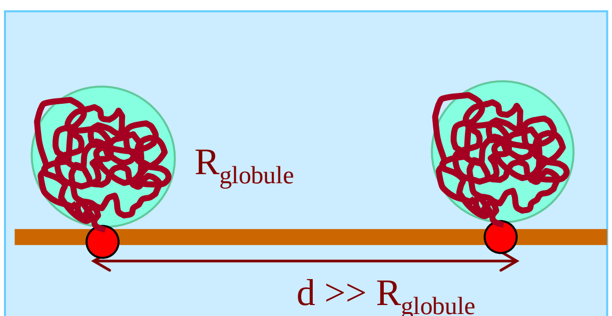



Flexible chains under good and θ-solvent conditions

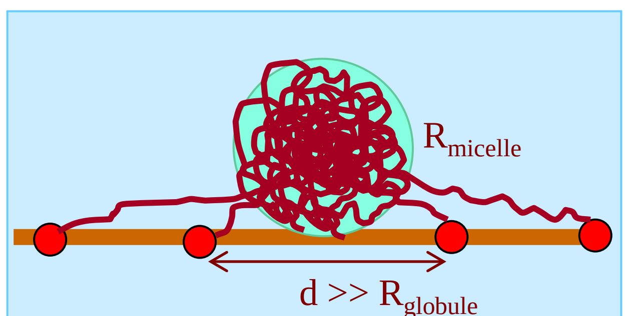
Brush with laterally uniform density – semi-dilute solution with unknown concentration $\phi_N$ because chains can stretch



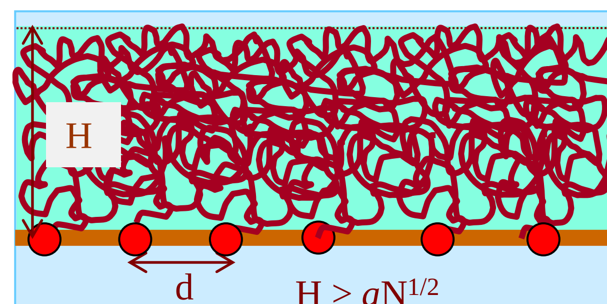

Poor solvent conditions ($\tau < 0$)




separate globules




aggregates (pinned, octopus) micelles

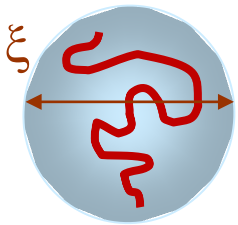



laterally uniform collapsed brush

# Brush in athermal solvent, $\tau = (T - \theta)/T = 1$

S. Alexander, 1977

Grafting area per chain $s = d^2$  Volume fraction of monomers $\phi_N = Na^3/sH$



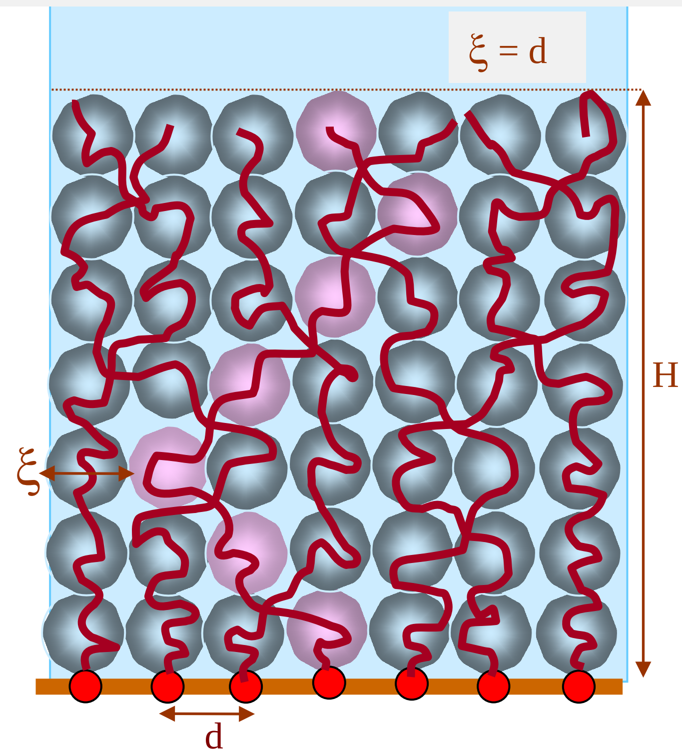

$\xi$ ❒ $a\phi_N^{-3/4}$ ❒ $ag^{3/5}$

number of monomers per blob

Number of blobs $N_B = N/g$ ❒ $N\phi_N^{5/4}$

End-to-end distance $R^2$ ❒ $\xi^2 N_B$ ❒ $a^2 N\phi_N^{-1/4}$

Brush in contact with athermal solvent




Free energy (per chain) $F = F_{interaction} + F_{elastic}$

Interaction free energy (per chain) $F_{interaction}/k_BT$ ❒ $N_B$ ❒ $N\phi_N^{5/4}$

Elastic free energy $F_{elastic}/k_BT$ ❒ $H^2/R^2(\phi_N)$ ❒ $H^2/(\xi^2 N_B)$

Minimization with respect to $\phi_N$ gives equilibrium value of $\phi_N = s^{-2/3}$ and size of concentrational blob $\xi$ ❒ $s^{1/2} = d$

Brush thickness in athermal solvent $H$ ❒ $N_B\,\xi$ ❒ $aNs^{-1/3}$

Brush free energy in athermal solvent $F/k_BT$ ❒ $N_B$ ❒ $aNs^{-5/6}$

# Brush in athermal solvent. MD simulation

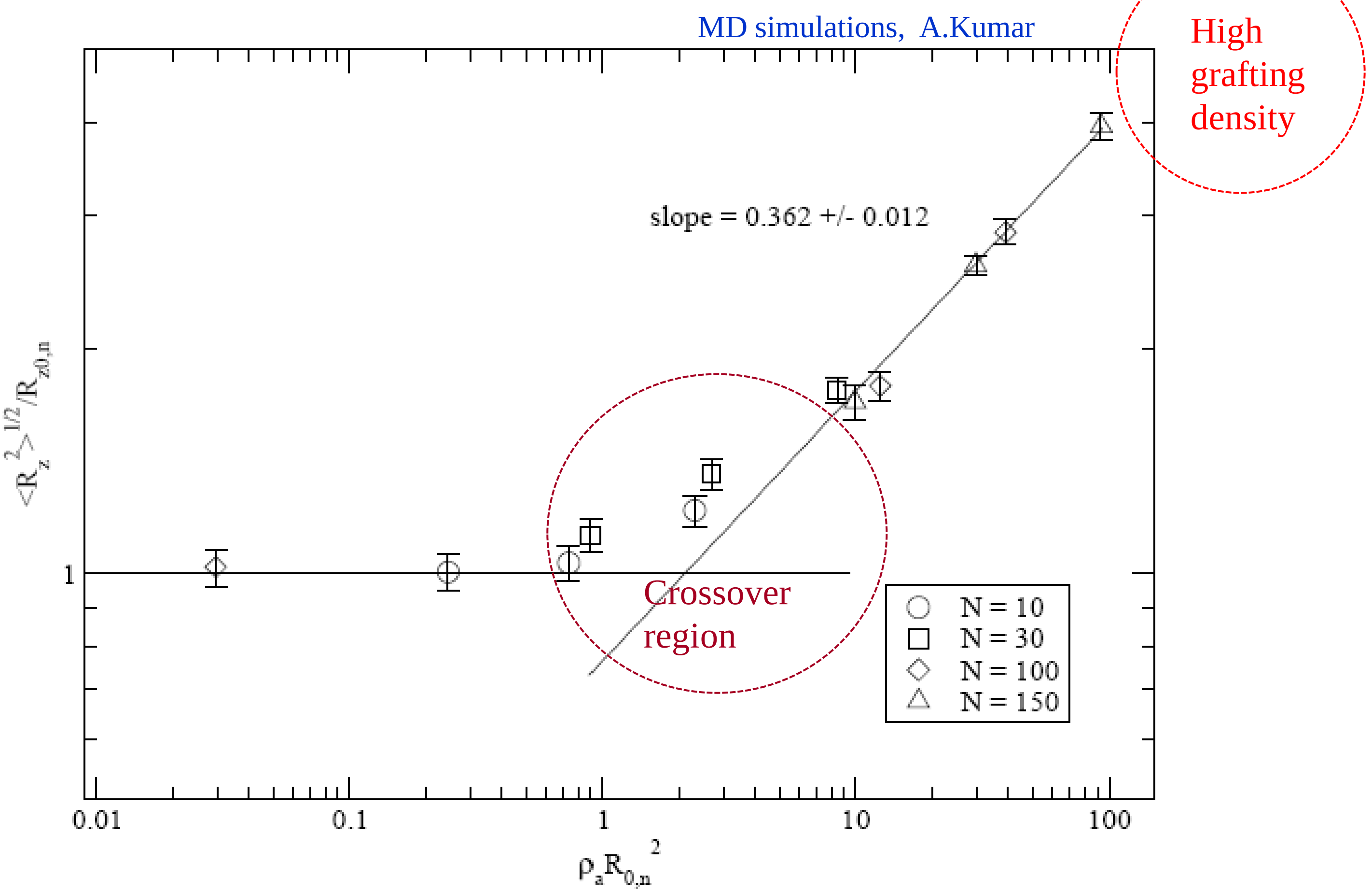
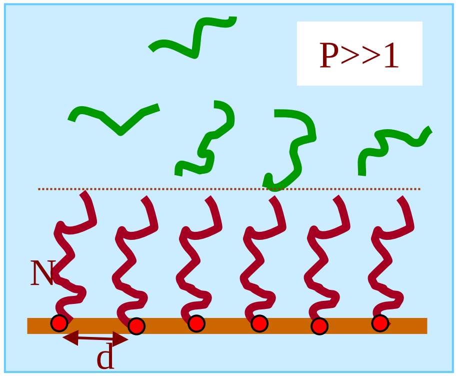



Figure 3: Root-mean-square end-to-end distance in the $z-$ direction $< R_z^2 >^{1/2}$ for a neutral brush normalized by corresponding end-to-end distance in $z-$ direction of a mushroom chain $R_{z0,n}$ plotted as a function of anchoring density $\rho_a$ normalized by corresponding overlap coverage of a mushroom chain $R_{0,n}^{-2}$. The line with slope $0.362 \pm 0.012$ is the best fit for the rightmost six set of points.

# Alexander–de Gennes (AG) model

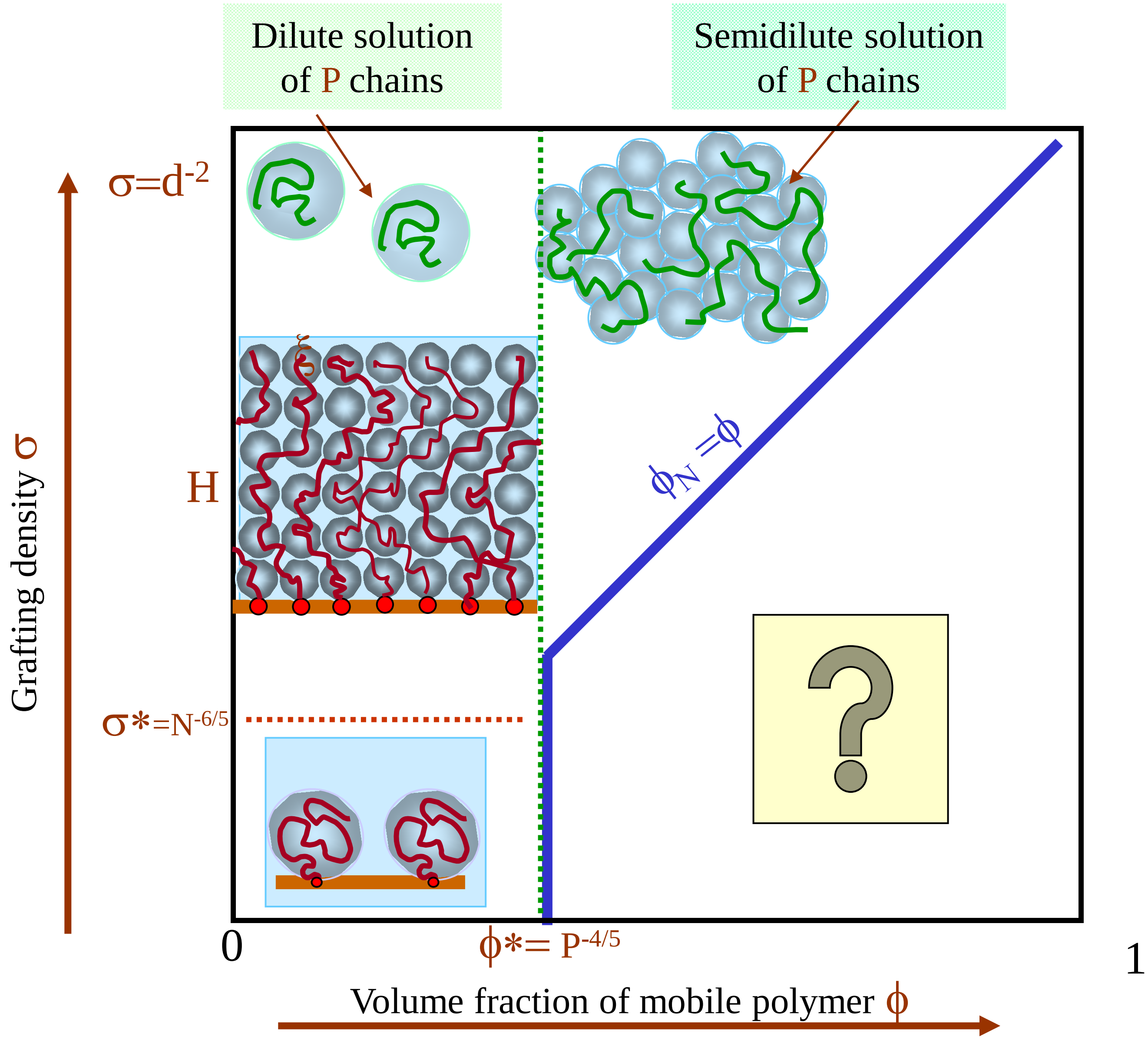
De Gennes, 1980



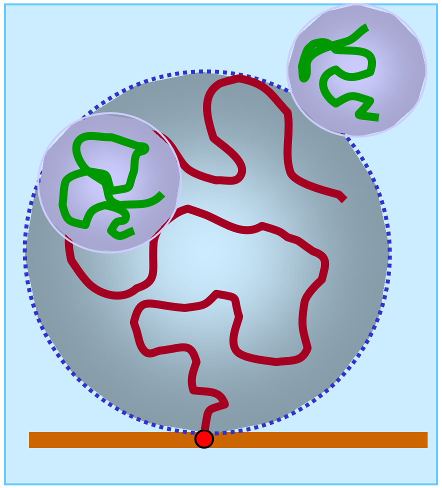

$N^{1/2} < P < N$

To the left of blue line:

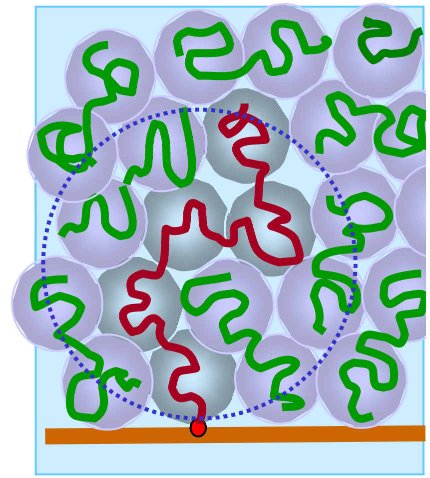
Brush dominated regimes, “mushroom” and Alexander brush. Here, $\xi_P > \xi_N$, P and N chains are demixed



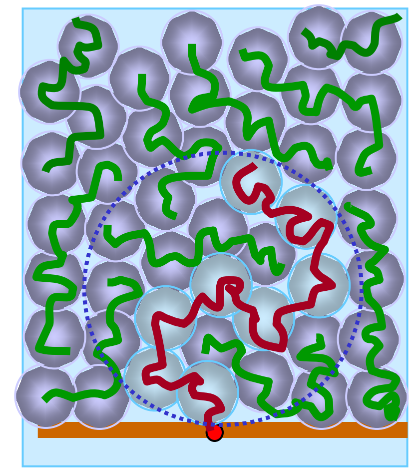
# Mushroom in contact with solution of mobile P chains



$\phi \ll \phi^*$

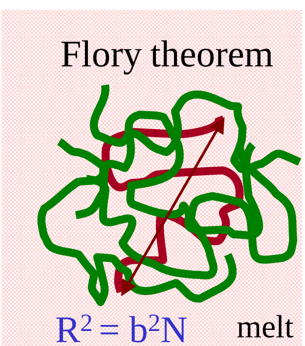


$\phi^* < \phi \ll \phi^{**}$



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

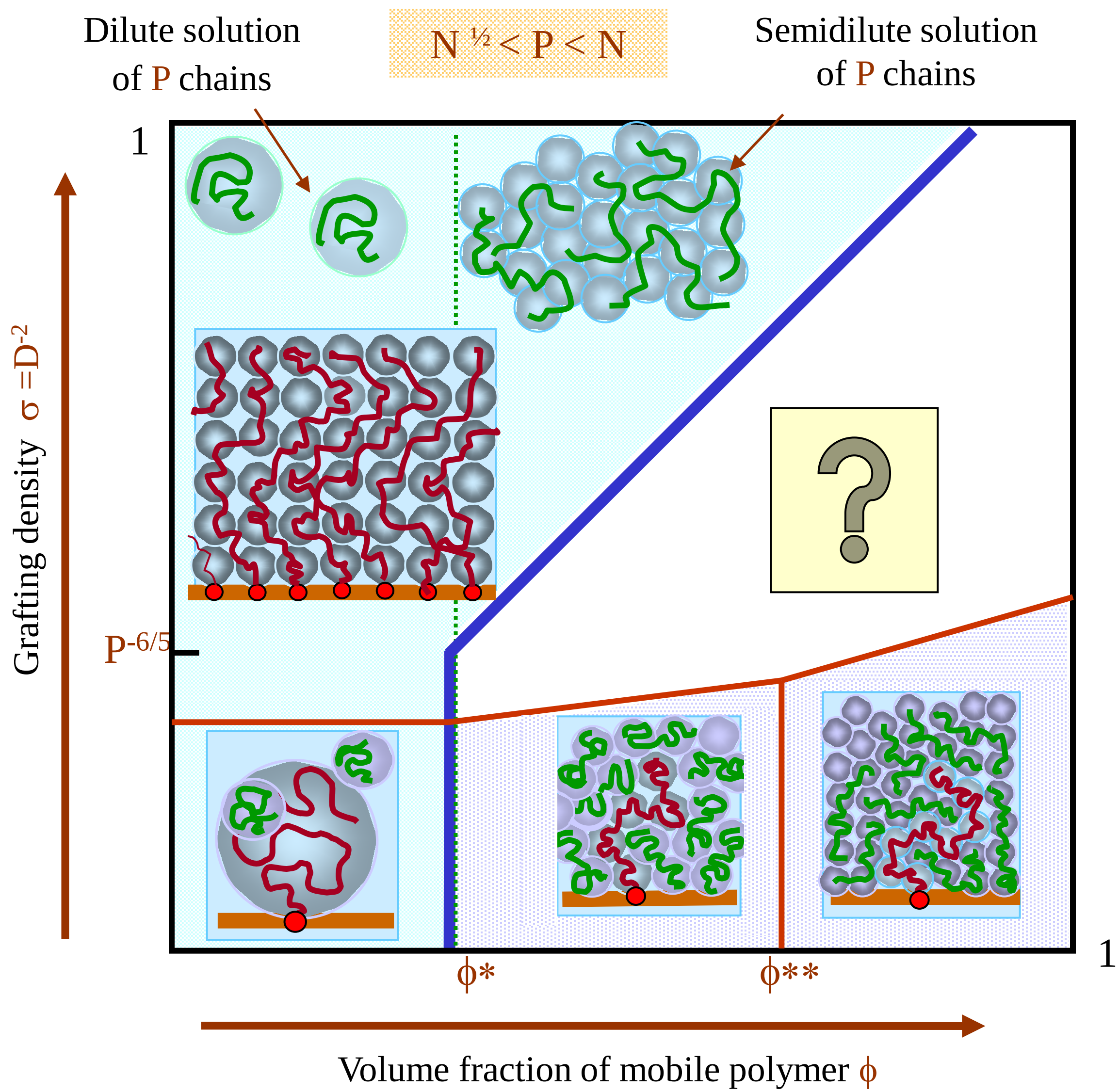
Melt of chains of blobs: $N_{BN} = N\phi^{5/4}$ $N_{BP} = P\phi^{5/4}$



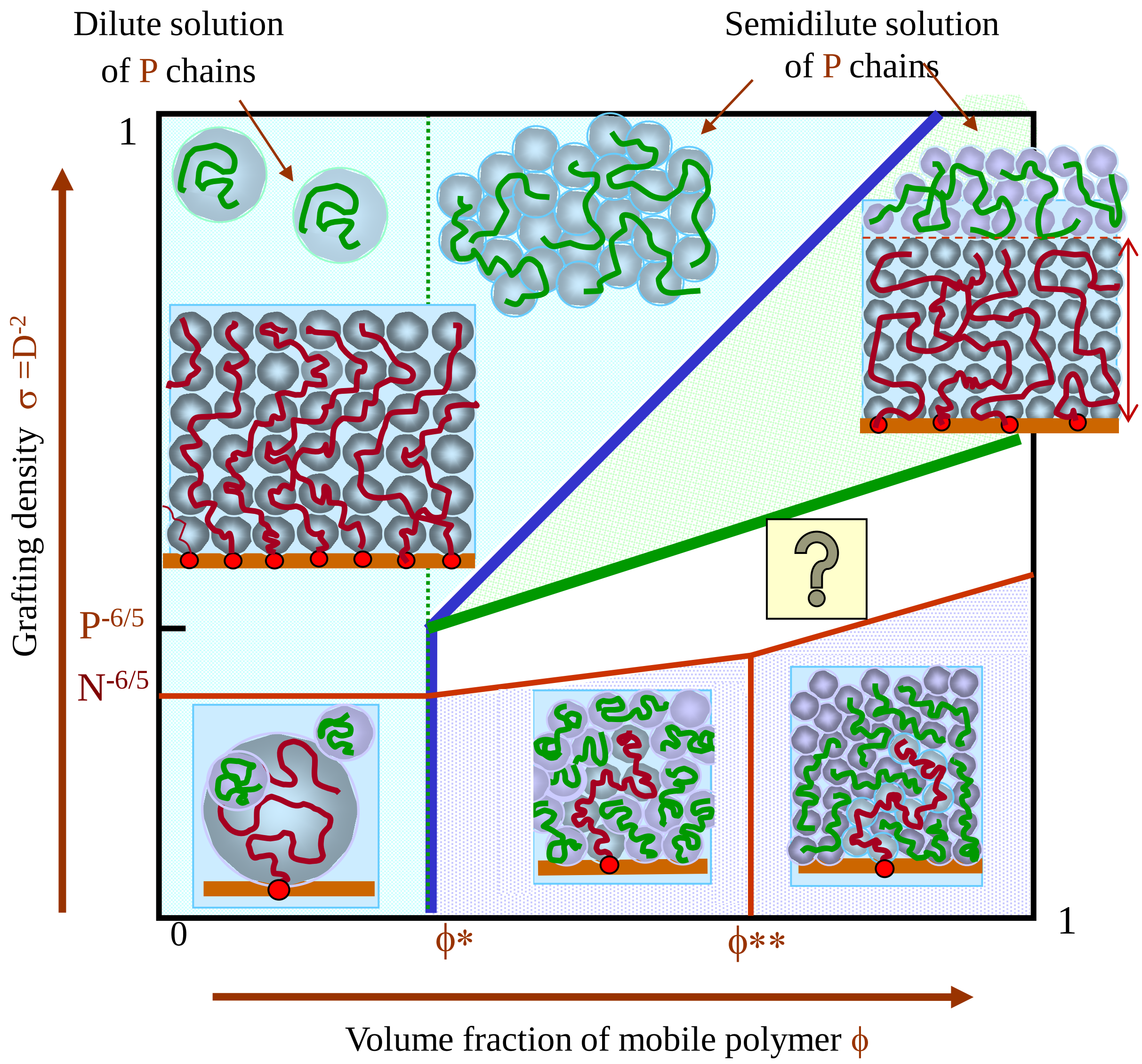

N- chain is swollen when $N_{BP} < N_{BN}^{1/2}$

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

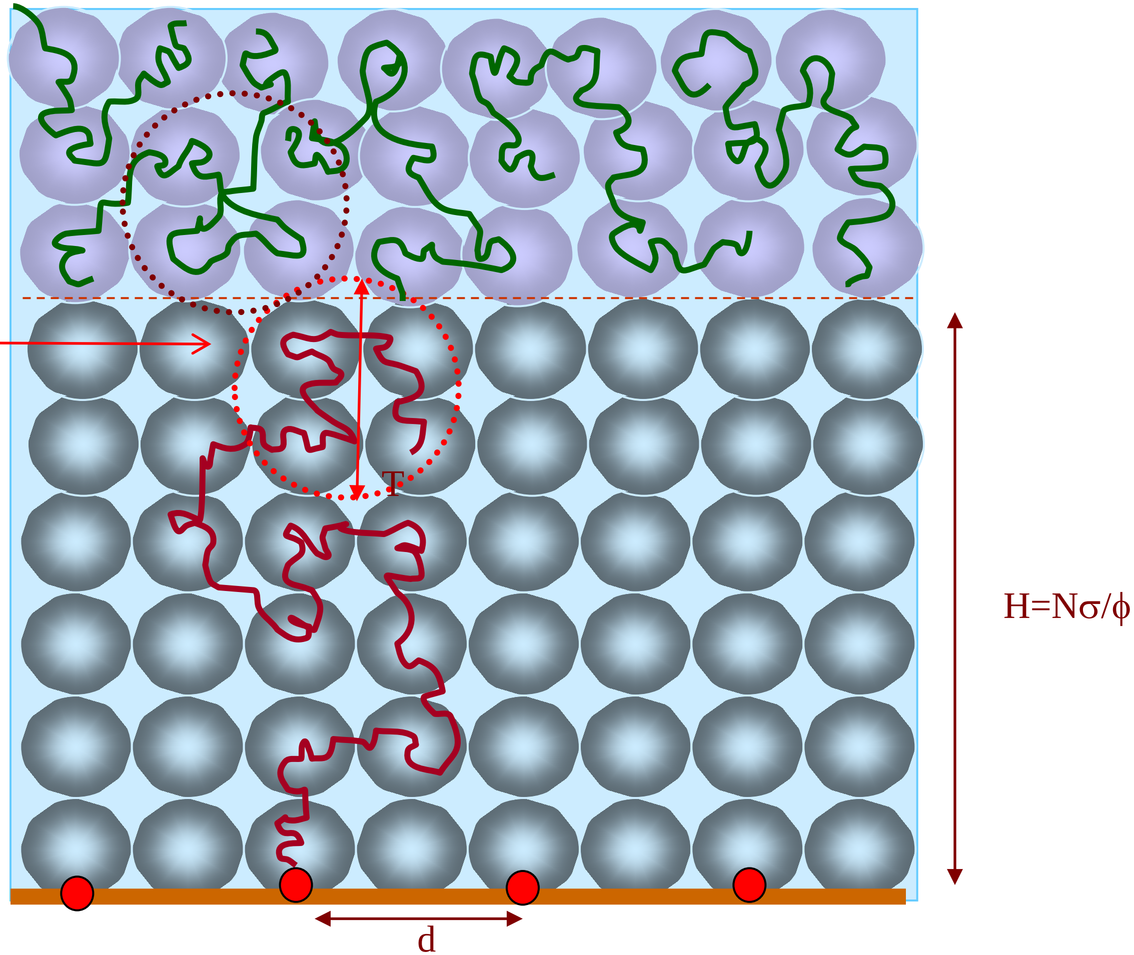
Below green line P chains penetrate the brush

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

Tension blob

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

(unstretched portion of N-chain) determines penetration length



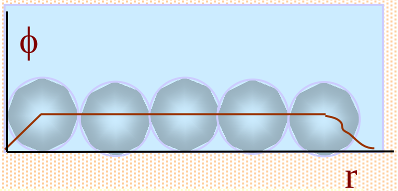

When size of tension blob $\xi_t$ = size of P-chain in solution, mobile chains penetrate throughout the brush of N-chains. Brush remains (weakly) stretched.

# Diagram of states and summary of A-G model

Chain free end is within last blob

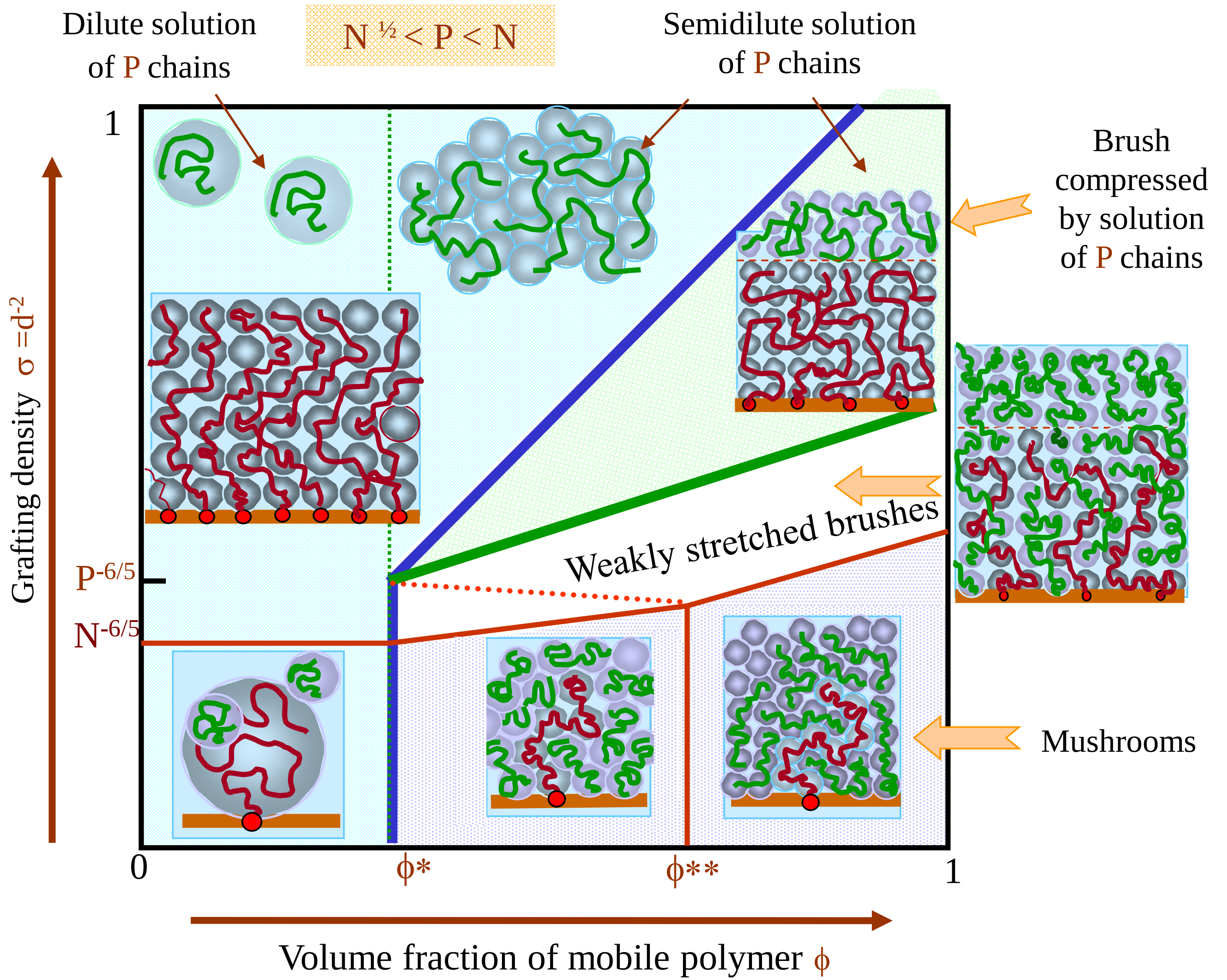
Blobs have same size

Polymer density profile is flat except for first and last blobs



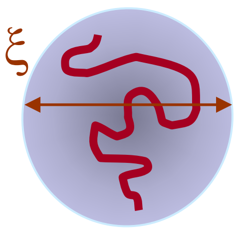

Tethered chains are stretched normally to the surface, $H \sim N$

Concept of brushes interpenetration : tension blob $\xi_t$



# Inferior solvent strength: Brush in a theta solvent, $\tau = 0$, $w = a^6$

T.M. Birshtein & E.B. Zhulina, 1983




ξ ❐ $a\phi_N^{-1} = ag^{1/2}$

number of monomers per blob

Number of blobs $N_B = N/g$ ❐ $N\phi_N^{2}$

End-to-end distance $R^2 = a^2N$

Free energy (per chain) $F = F_{interaction} + F_{elastic}$

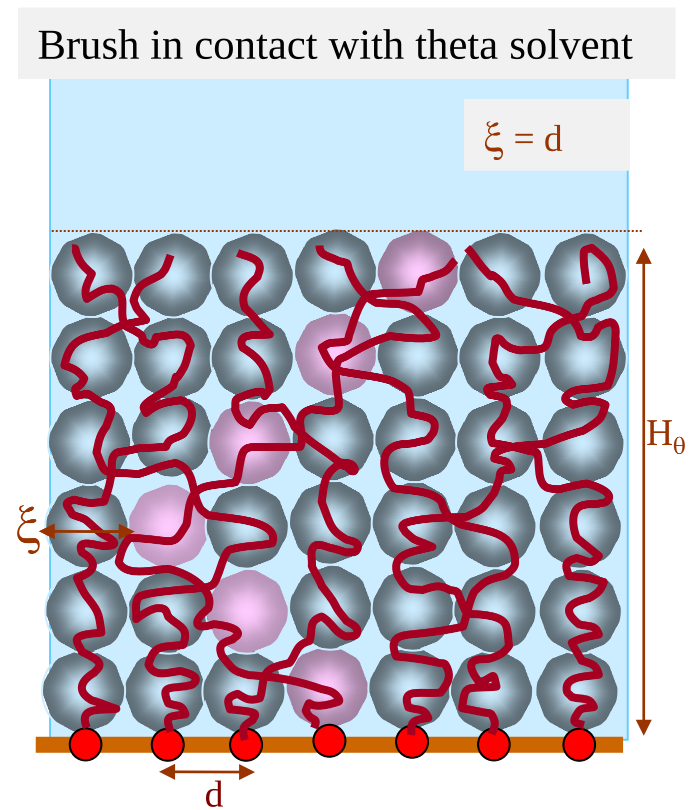
Interaction free energy (per chain) $F_{interaction}/k_BT$ ❐ $N_B$ ❐ $N\phi_N^{2}$

Elastic free energy $F_{elastic}/k_BT$ ❐ $H^2/R^2$ ❐ $H^2/(a^2N)$

Minimization with respect to $\phi_N$ gives equilibrium value of $\phi_N = s^{-1/2}$ and size of concentrational blob ξ ❐ $s^{1/2} = d$

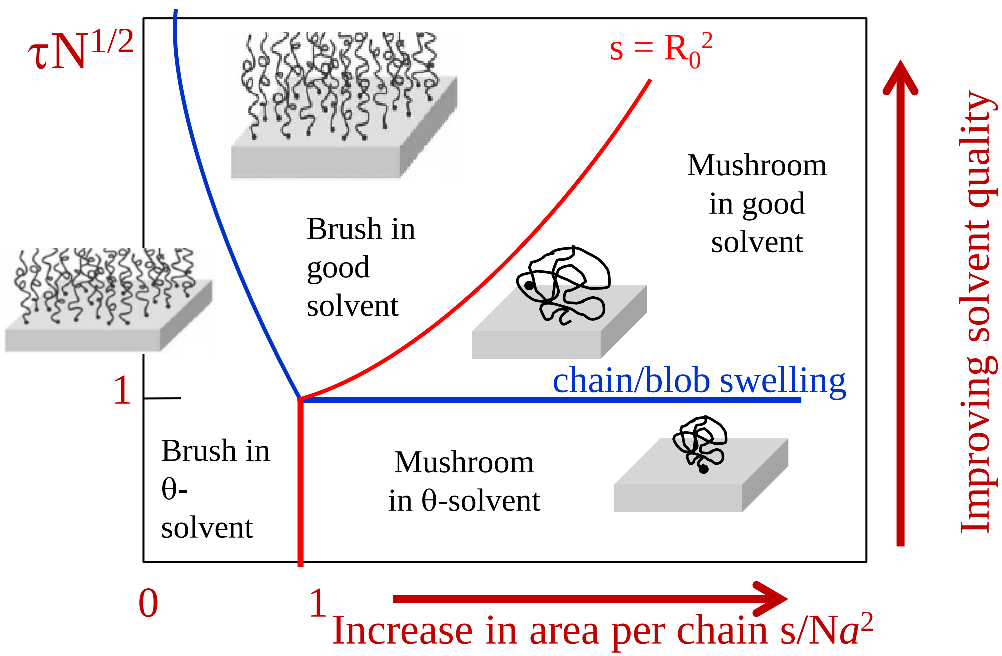
Brush thickness in theta solvent $H_\theta$ ❐ $N_B\,\xi$ ❐ $aNs^{-1/2}$

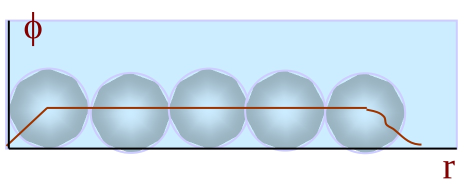
Brush free energy in theta solvent $F/k_BT$ ❐ $N_B$ ❐ $aNs^{-1}$



# Diagram of states of planar brush in contact with pure solvent above θ-point

$\tau = (T - \theta)/T > 0$



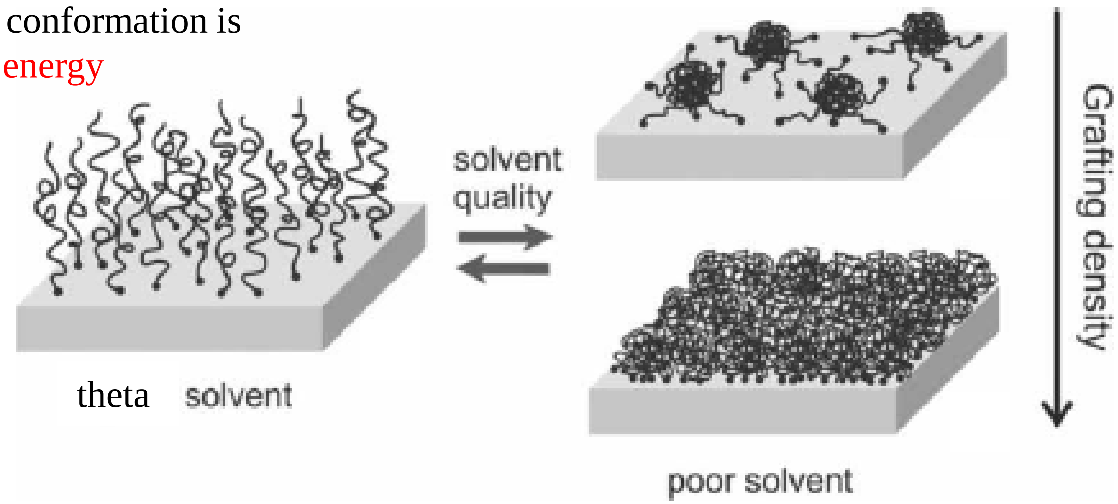

Free chain end is within last blob, polymer density profile is flat everywhere except for first and last blobs

Physical transparency of brush model based on blob concepts

Tethered chains are noticeably stretched normally to the surface, $H \sim N$.

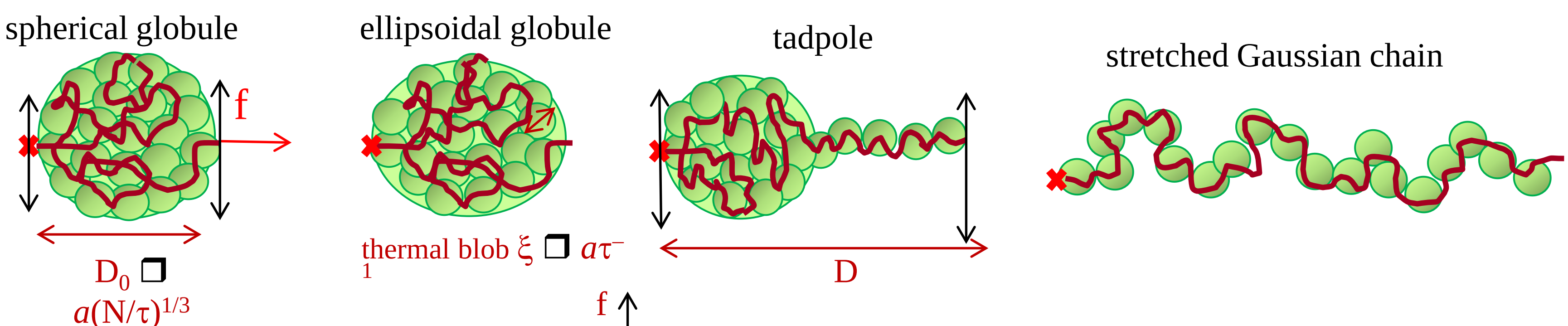
# Inferior solvent strength below θ-point.
# Lateral decomposition of brush into pinned micelles.

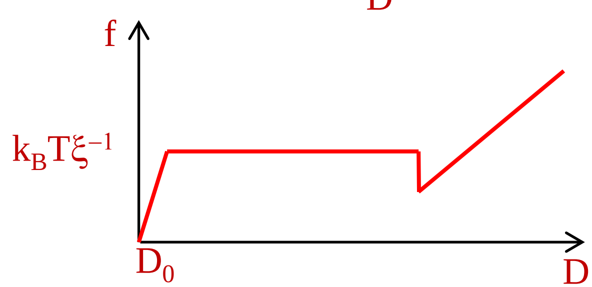
In collapsed brush, chain conformation is governed by surface free energy




## Stretching of a single globule

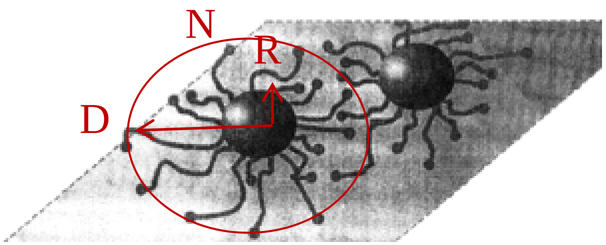
Halperin & Zhulina, 1991; Williams 1995



# Dimensions of pinned micelles

Williams 1993, Klushin 1995

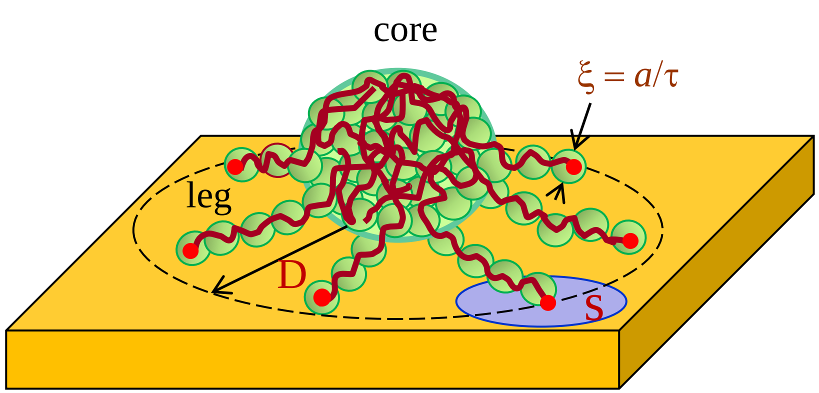



R – radius of the micellar core ; R❐$(Np/\tau)^{1/3}$

D – radius of the micellar corona; D ❐ $(ps)^{1/2}$

p – aggregation number

s – grafting area per chain




Free energy (per chain) $F = F_{leg} + F_{surface}$

Free energy of leg (string of thermal blobs)
$F_{leg}/k_BT$ ❐ $D/\xi$ ❐ $(ps)^{1/2}\,\tau/a$

Surface free energy $F_{surface}/k_BT$ ❐ $[R^2/\xi^2]/p$
❐ $N^{2/3}\,\tau^{4/3}/p^{1/3}$

Minimization with respect to p gives equilibrium aggregation number p ❐ $N^{4/5}\,\tau^{2/5}/s^{3/5}$

Boundaries for this regime are given by p =1 (or $s_{high}$ ❐ $a^2N^{4/3}\tau^{2/3} >> R^2_{globule}$) and D ❐ R (or $s_{low}$ ❐ $a^2N^{1/2}\tau^{-1}$ and D ❐ R ❐ $aN^{1/2}$ )

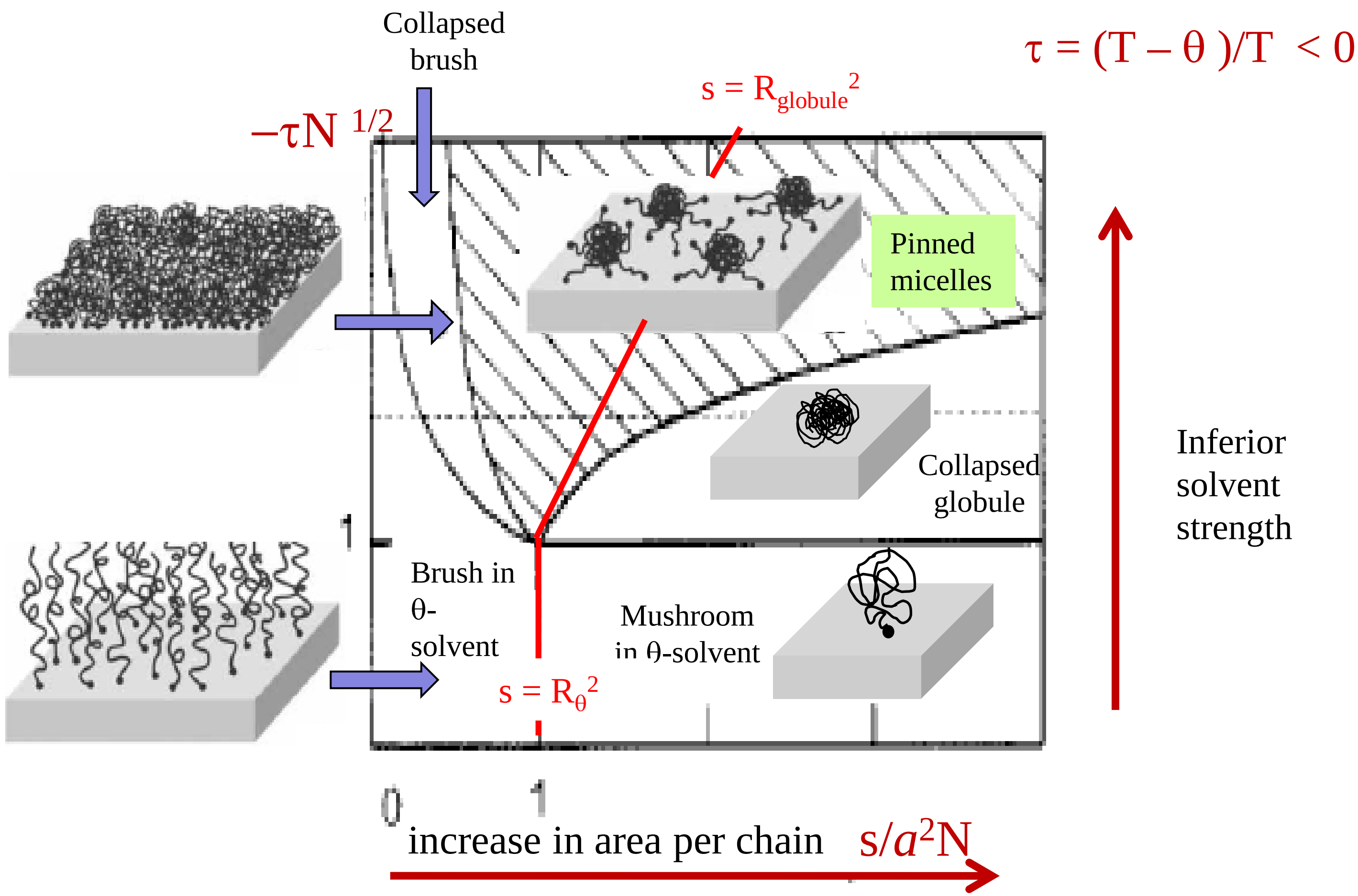
Wide regime of pinned (octopus) micelles $a^2N^{1/2}\tau^{-1}$ ❐ $s_{low} < s < s_{high}$ ❐ $a^2N^{4/3}\tau^{2/3}$

Single globules $s > s_{high}$

Laterally homogeneous stretched brush $s_{low} < s$

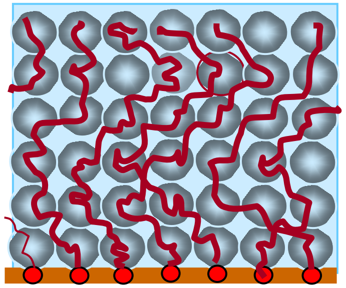
❐

# Brush diagram of states below Θ-point



# Novel model of polymer dry brush.

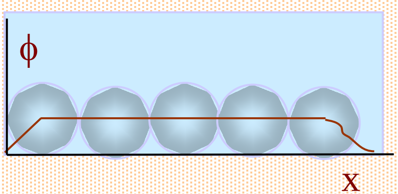
Alexander – de Gennes (AG) model, 1977-1980



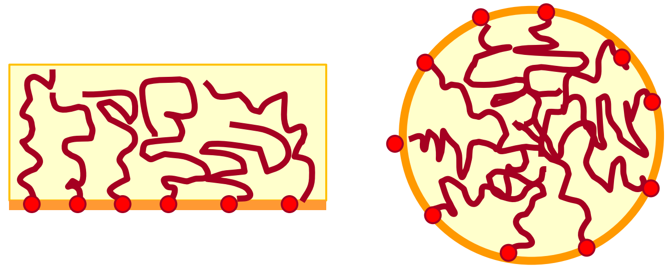
Free chain end are within last blobs

Chains are stretched equally

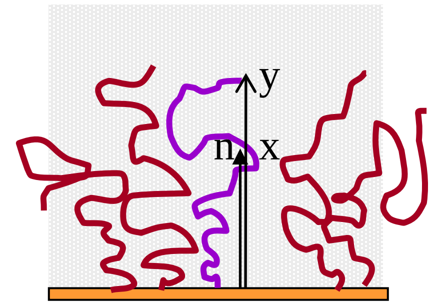
Polymer density profile is flat except for first and last blobs




Semenov 1985



Concept of polymer trajectory: $x(n)$




In terms of trajectory $x(n)$:

Elastic free energy of chain with end position $y$

$$F_{elastic}(y)/k_BT = (3/2a^2)\int_0^y dx^2/dn$$

Elastic free energy per chain

$$F_{elastic} = \int F_{elastic}(y)g(y)dy$$

distribution function of free ends

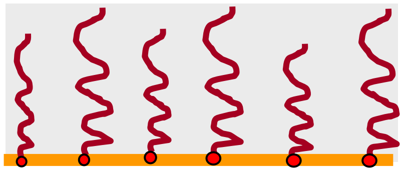
Minimization of $F_{elastic}$ with additonal constraint ($\int dn = N$ for any $y$) gives: chain extensibility $dx/dn = E(y,x) = (\pi/2N)(y^2 - x^2)^{1/2}$

Dry brushes (no solvent): chains are exposed to self-consistent parabolic molecular field and are stretched unequally and nonuniformly. Free ends are distributed throughout the brush. Free energy is by ~10% lower than in box-like model with fixed free ends.

# Generalization to brush swollen with solvent.

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

Free energy per chain: $F = F_{elastic} + F_{interactions}$



$F_{elastic} = \int F_{elastic}(y)g(y)dy$

$F_{interaction} = s\int f_{interaction}(x)dx$

Result of minimization free energy $F$:

Extensibility $E(y,x) = dx/dn = (\pi/2N)(y^2 - x^2)^{1/2}$

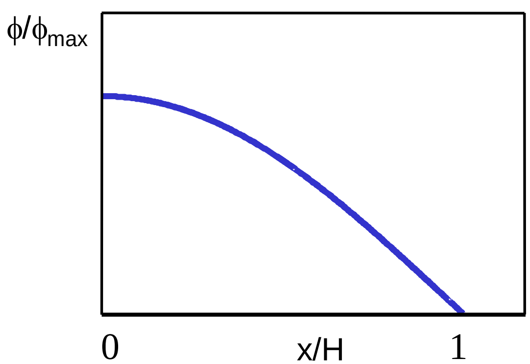
Basic equation for polymer density profile:

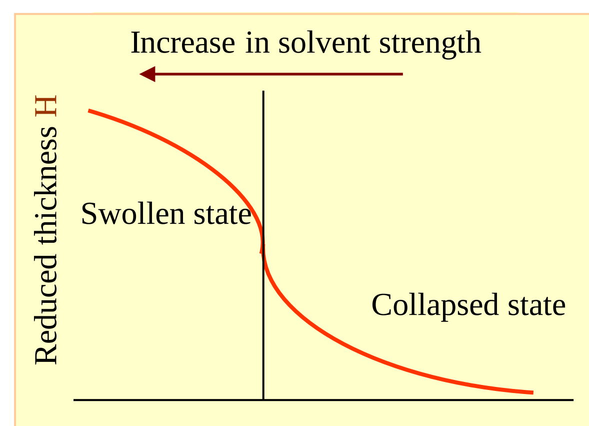
$$\boxed{\delta f_{interaction}[\phi]/\delta\phi = Const - 3\pi^2 x^2/8a^2N^2}$$

$f_{interaction}[\phi] = (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)$

virial expansion at $\phi \ll 1$

$f_{interaction}[\phi] = (1/2-\chi)\phi^2 + 1/6\phi^3 + .. = v\,\phi^2 + w\phi^3 + \ldots$

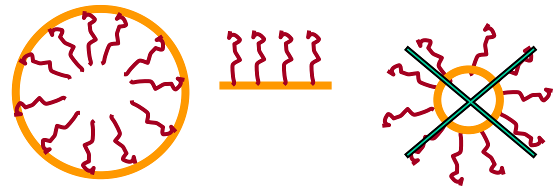



In swollen brushes with Gaussian chain elasticity, molecular potential is the same as in a dry brush (parabolic). The polymer density profile is not flat. Shape of profile and distribution of free ends depend on solvent quality. Inferior solvent strength leads to gradual brush collapse.

# Novel features with respect to A-G model.

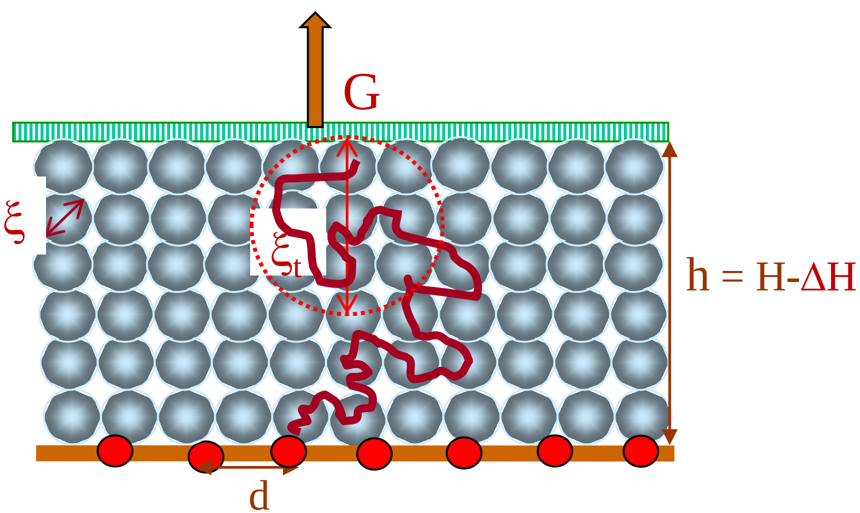
- Internal brush structure: polymer density profile $\phi(x)$ and distribution of free ends $g(y)$ in planar and curved (convex) polymer brushes.



- Weaker response to compression at small deformations $\Delta q = \Delta H/H \ll 1$.
  In A-G model restoring force $G \sim \Delta q$.
  In SCF model $G \sim (\Delta q)^2$ in good solvent and $G \sim (\Delta q)^{3/2}$ in theta-solvent.

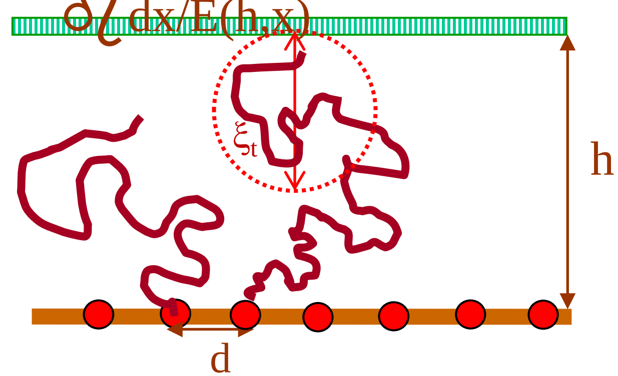
- Different interpenetration length: size of last tension blob $\xi_t$

In A-G model: $\xi_t = R^2/h = \xi^2 N_B/h = N^{3/4} s^{1/4}/h^{3/4}$

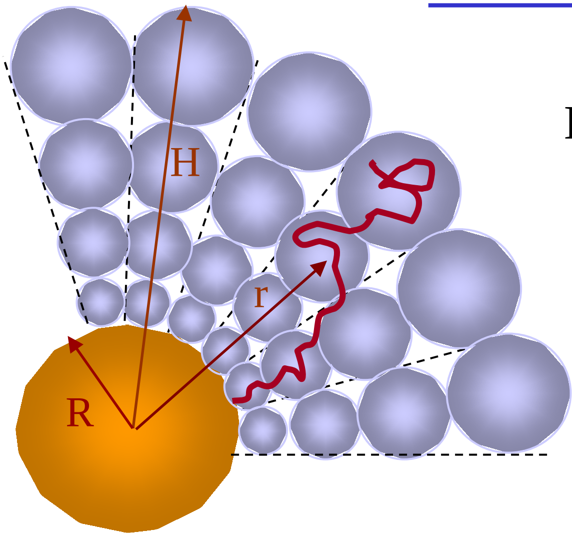



In SCF model: $\xi_t = (R^2/h)^{1/3} = a^{4/3} N^{2/3}/h^{1/3}$

$$(\xi_t/a)^2 = \int_{h-\xi_t}^{h} dn = \int dx/E(h,x)$$



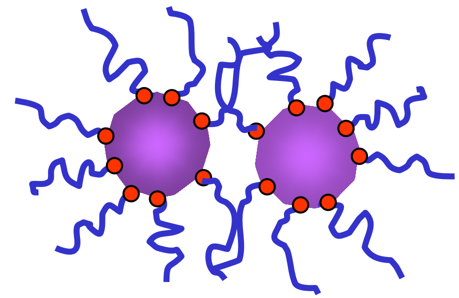
# Curved polymer brushes



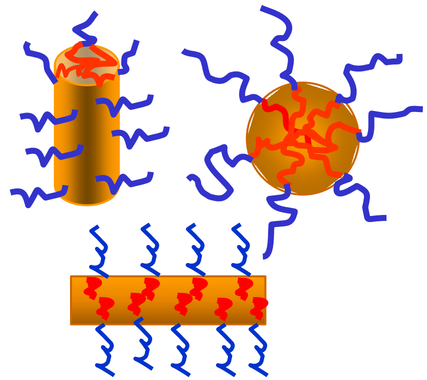

Blob size ξ increases with distance r

$H \sim N^{\beta}$ $\beta < 1$

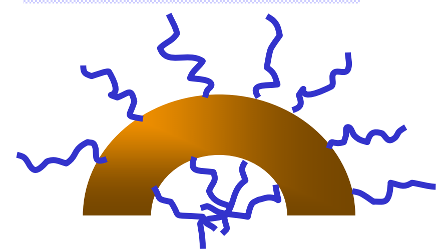
Stabilization of colloids

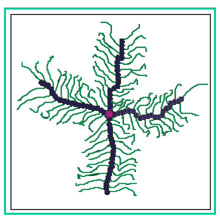


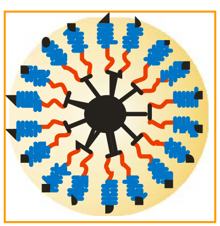
Scaling models of self-assembly (micelles)

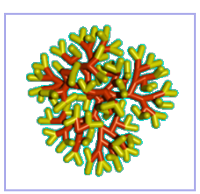


Bending bilayers

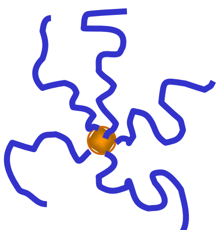


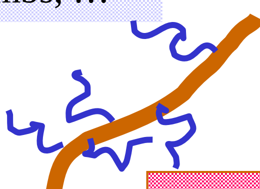


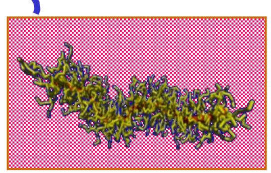




Molecular brushes: stars, combs, …

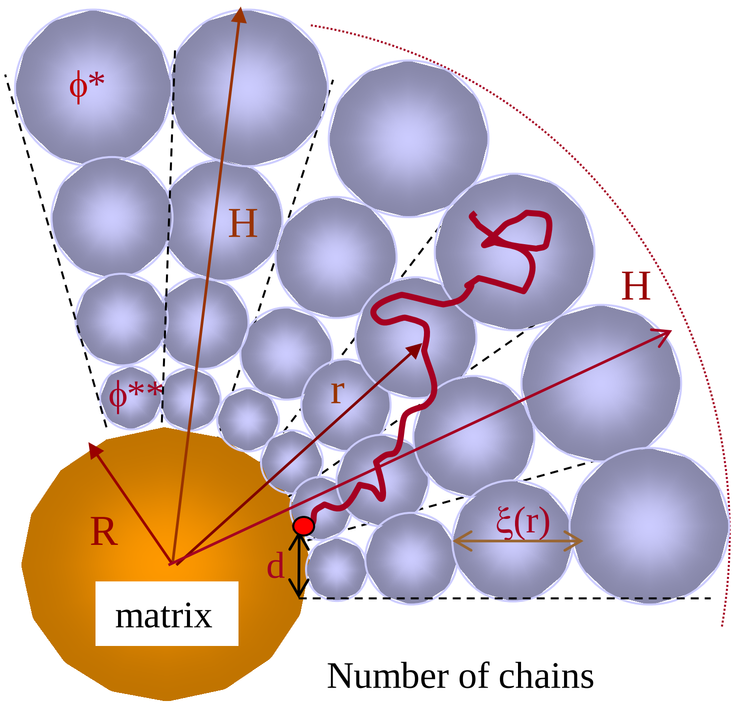






# Scaling model of spherical polymer brush

Daoud & Cotton 1982




Number of chains
$p$ ❐ $R^2/s$ ❐ $R^2/d^2$

Blob size $\xi$ increases with distance r
(dense packing of concentrational blobs):

$$\xi(r) = d(r/R) = r/p^{1/2}$$

Free energy per chain $F/k_BT$ ❐ $\int dr/\xi(r)$ ❐ $p^{1/2}\ln(H/R)$

Polymer density profile $\phi(r)$ ❐ $[\xi(r)/a]^{-4/3}$ ❐ $p^{2/3}(a/r)^{4/3}$

Normalization of polymer density profile $\int r^2 dr\,\phi(r) = pN$
gives brush thickness $H$ ❐ $ap^{1/5}N^{3/5}$

In contrast to a planar brush, polymer density in a spherical brush changes

from $\phi^* = \phi(r = H)$ ❐ $p^{2/5}N^{-4/5}$

to $\phi^{**} = \phi(r = R)$ ❐ $(s/a^2)^{-2/3}$

# Scaling model of cylindrical polymer brush

Birshtein & Zhulina 1987

Dense packing of concentrational blobs

$2\pi r L = (2\pi R L/s)\xi(r)^2$

⇩

$\xi(r) = d(r/R)^{1/2}$

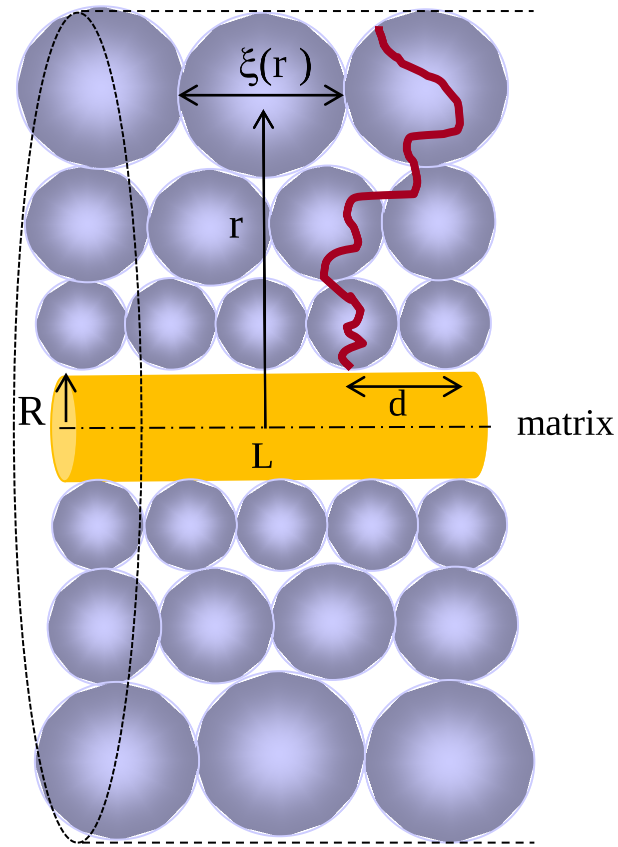
Polymer density profile $\phi(r)$ ❒ $[\xi(r)/a]^{-4/3}$ ❒ $p_2^{2/3}(a/r)^{2/3}$

where $p_2 = R/d^2$ is number of chains per unit length of cylindrical matrix

Normalization of polymer density profile $\int r dr \phi(r) = p_2 N$

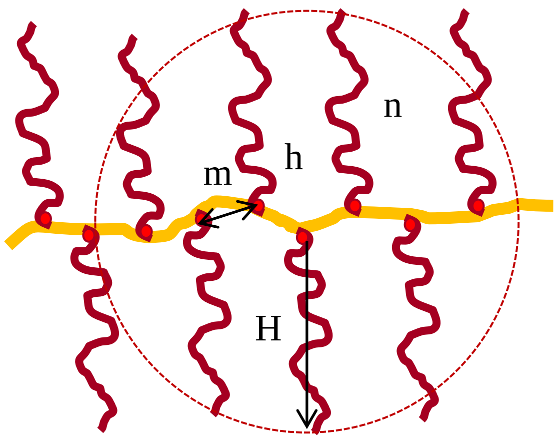
gives brush thickness $H/a$ ❒ $a(ap_2)^{1/4}N^{3/4}$

Free energy per chain $F/k_BT$ ❒ $(ap_2)^{5/8}\, N^{3/8}$



# Comb-like polymer (molecular brush)

Birshtein et al 1987




"Superblob" of size H

## *Local structure of molecular brush*

Free energy per graft $F = F_m + F_n$

Free energy of cylindrical bush of side chains $F_n / k_B T$ ❒ $(a/h)^{5/8}\, n^{3/8}$

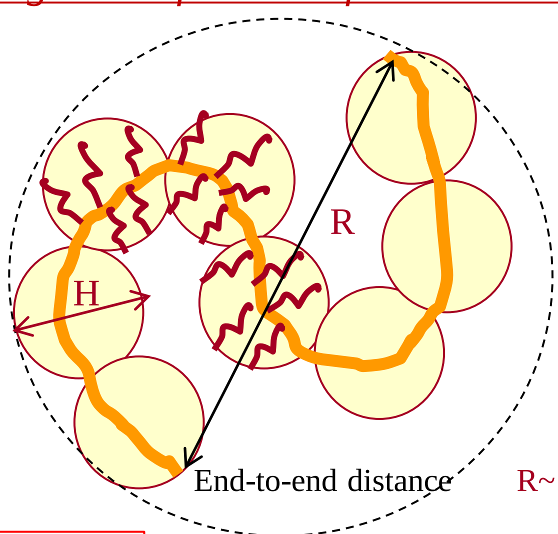
Pincus elasticity for stretched swollen segment of backbone $F_m / k_B T$ ❒ $h^{5/2} / (a^{5/2} m^{3/2})$

Balancing $F_n$ ❒ $F_m$ gives $h$ ❒ $an^{3/5}(n/m)^{3/25}$

Cylindrical brush thickness $H$ ❒ $an^{3/5}(n/m)^{3/25}$

For densely grafted molecular brushes $h$ ❒ $am$ and transition to cylindrical brush with $p_2 = 1/(am)$

## *Large scale features of molecular brush*



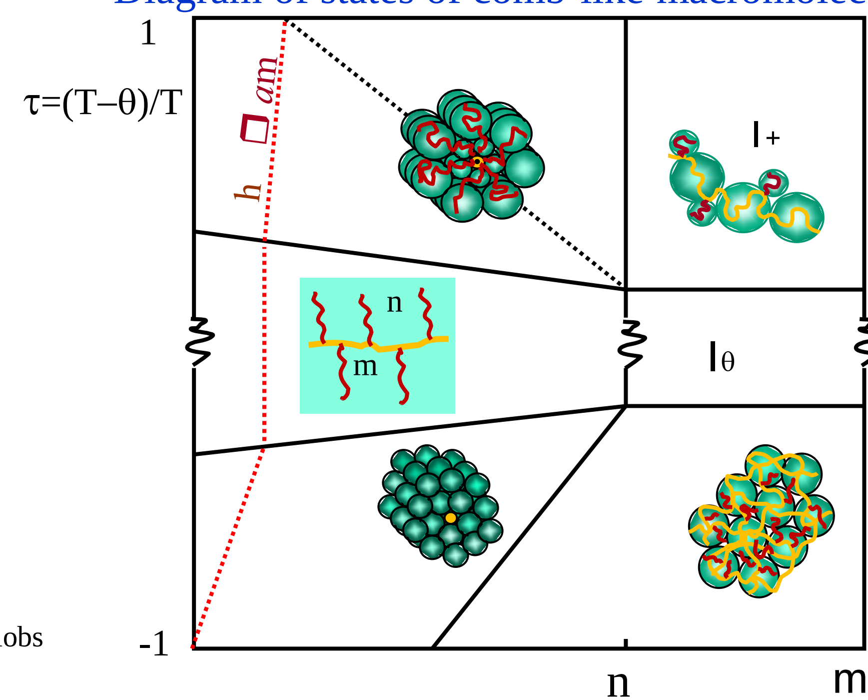

Persistence length

$R \sim H(L_p/H)^{1/5} N_H^{3/5}$

Number of superblobs

$L_p/H$ –?

## Diagram of states of comb-like macromolecule

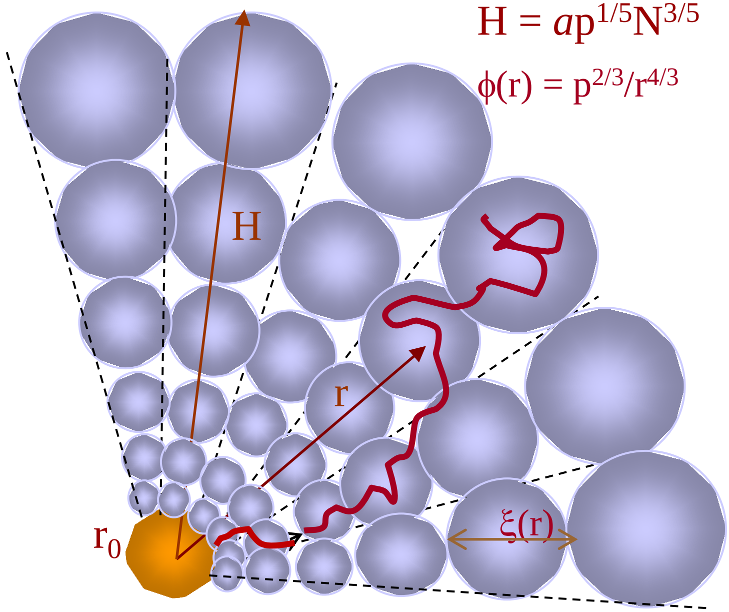


# Semi-dilute solution of star-like polymers

Daoud & Cotton 1982

$H = ap^{1/5}N^{3/5}$

$\phi(r) = p^{2/3}/r^{4/3}$




$r_0 = ap^{1/2}$

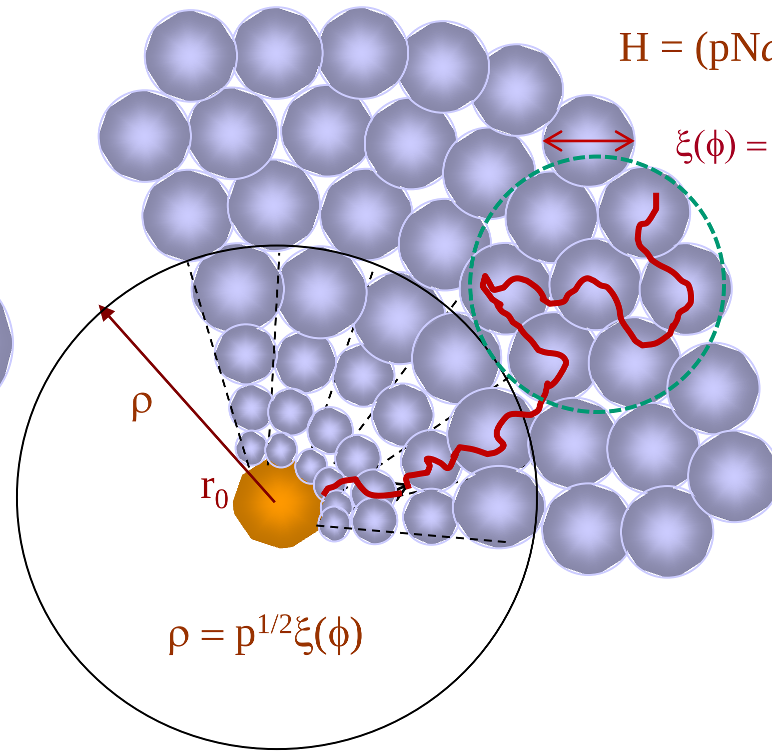
Overlap concentration $\phi^* = p^{2/5}/N^{4/5}$
is on the order of magnitude of
concentration in the last blob

Birshtein & Zhulina 1984

Quasi-globular regime
with star segregation

$H = (pNa^3/\phi)^{1/3}$

$\xi(\phi) = a\phi^{-3/4}$




Non-uniformly
stretched chain
segment

At $\phi > \phi^{**} = p^{8/5}/N^{4/5}$
peripheral segment becomes unstretched, and in semi-dilute solution of branches stars penetrate each other.