Polymer brushes

Ekaterina Zhulina

Institute of Macromolecular Compounds,
Russian Academy of Sciences,
St. Petersburg, Russia

“Polymers in Soft and Biological Matter”
July 30 – August 1, 2012, Boulder CO, USA
Overview of the course “Polymer brushes”


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**

**Grafting density** $1/s = d^2$

**Degree of chain polymerization** $N \gg 1$

**Brush thickness** $H$

**Free ends**

**Examples of brush applications**

- Stabilization of colloids
- Artificial joints, transplants
- Drug delivery by biodegradable micelles
- Diagnostics of mutations
- DNA microarrays
Brush-like structures in biological systems

**Extracellular biopolymers**

Cell of *Pseudomonas putida* KT2442

- Thick planar brush of anionic polysaccharides

**Casein micelle in milk**

- Calcium phosphate
- κ (β)-casein (GMP)

- Loose short planar brush of anionic GMP

**Aggrecan (articulate cartilage)**

- Core protein
- GS-GAG side chains
- Cylindrical / spherical charged brush of GS-GAG side arms

**Microtubule (MT+ MAP)**

**Neurofilament (NF)**

- Parkinson, ALS and Alzheimer’s diseases are linked to disorganization of cytoskeleton in neurons

**Neuron**

**Erythrocyte**
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

$$R_0 = aN^v = aN^{3/5}$$

Overlap concentration

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

Semidilute solution (melt of concentrational blobs)

$$\phi_N \gg \phi_N^*$$

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

Average end-to-end distance

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

Interaction free energy

$$F_{int} \sim k_BT N_B$$

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.

- **2R₀**
  - H ~ R₀
  - θ-solvent (τ = 0), weakly adsorbing surface

- **R₀**
  - H ~ R
  - Athermal sovent (τ = 1), nonadsorbing surface

- **R**
  - H ~ R
  - Poor solvent (τ < 0), partial surface wetting
Increasing chain grafting density: transition from mushroom to brush regime

Flexible chains under good and $\theta$-solvent conditions

Poor solvent conditions ($\tau < 0$)

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

- $d << R_0$
- $H > aN^{1/2}$
- laterally uniform collapsed brush

- $d >> R_{\text{globule}}$
- separate globules

- $d >> R_{\text{micelle}}$
- aggregates (pinned, octopus) micelles
Brush in athermal solvent, $\tau = (T - \theta)/T = 1$

Grafting area per chain $s = d^2$

Volume fraction of monomers $\phi_N = Na^{3/sH}$

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

Interaction free energy $F_{\text{interaction}}/k_B T \propto N_B \propto N\phi_N$

Elastic free energy $F_{\text{elastic}}/k_B T \propto H^2/R^2(\phi_N) \propto H^2/(\xi^2 N_B)$

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

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

Brush free energy in athermal solvent $F/k_B T \propto N_B \propto aNs^{-5/6}$

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

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

S. Alexander, 1977
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

To the left of blue line:

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

$\sigma = d^{-2}$

$\sigma^* = N^{-6/5}$

$\phi_N = \phi$

$\phi^* = P^{-4/5}$

Volume fraction of mobile polymer $\phi$
Mushroom in contact with solution of mobile P chains

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

Melt of chains of blobs:

- $N_{BN} = N\phi^{5/4}$
- $N_{BP} = P\phi^{5/4}$

Flory theorem

- $R^2 = b^2N$ (melt)

$N$-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

Dilute solution of P chains

\[ \sqrt{N} < P < N \]

Semidilute solution of P chains

Grafting density \( \sigma = D^{-2} \)

Volume fraction of mobile polymer \( \phi \)
Compression of brush by solution of mobile P chains

Dilute solution of P chains

Semidilute solution of 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

$H = N \sigma / \phi$

Below green line P chains penetrate the brush

Grafting density $\sigma = D^2$

Volume fraction of mobile polymer $\phi$

$\phi^* \quad \phi^{**}$

Dilute solution of P chains

Semidilute solution of P chains

$P^{-6/5}$

$N^{-6/5}$

$\phi^* \quad \phi^{**}$

$1$
Interpenetration of mobile P-chains in brush of N-chains

When size of tension blob $\xi_t = \text{size of } P\text{-chain in solution}$, 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 \( \xi_t \)

**Grafting density** \( \sigma = d^2 \)

**Volume fraction of mobile polymer** \( \phi \)

- **Dilute solution of P chains**
- **Semidilute solution of P chains**

- **N \(^{\frac{1}{2}}\) < P < N**
- **N\(^{-6/5}\)**
- **N\(^{-6/5}\)**

- **Brush compressed by solution of P chains**
- **Mushrooms**

**Weakly stretched brushes**
Inferior solvent strength: Brush in a theta solvent, \( \tau = 0, \ w = a^6 \)

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

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

Interaction free energy (per chain) \( \frac{F_{\text{interaction}}}{k_B T} \square N_B \square N\phi_N \)

Elastic free energy \( \frac{F_{\text{elastic}}}{k_B T} \square H^2/R^2 \square H^2/(a^2N) \)

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

Brush thickness in theta solvent \( H_0 \square N_B \xi \square aNs^{-1/2} \)

Brush free energy in theta solvent \( F/k_B T \square N_B \square aNs^{-1} \)
Diagram of states of planar brush in contact with pure solvent above $\theta$-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 \( \theta \)-point.**
**Lateral decomposition of brush into pinned micelles.**

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

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**Stretching of a single globule**

Halperin & Zhulina, 1991; Williams 1995
Dimensions of pinned micelles

**Dimensions of pinned micelles**

Williams 1993, Klushin 1995

**Definitions:**
- $R$ – radius of the micellar core; $R \propto (Np/\tau)^{1/3}$
- $D$ – radius of the micellar corona; $D \propto (ps)^{1/2}$
- $p$ – aggregation number
- $S$ – grafting area per chain

**Free energy (per chain)**

$F = F_{\text{leg}} + F_{\text{surface}}$

Free energy of leg (string of thermal blobs)

$F_{\text{leg}}/k_B T \propto D/\xi \propto (ps)^{1/2} \tau/a$

Surface free energy

$F_{\text{surface}}/k_B T \propto [R^2/\xi^2]/p \propto N^{2/3} \tau^{4/3}/p^{1/3}$

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

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

**Wide regime of pinned (octopus) micelles**

$a^2 N^{1/2} \tau^{-1}$ \quad $s_{\text{low}} < s < s_{\text{high}}$ $a^2 N^{4/3} \tau^{2/3}$

**Single globules**

$s > s_{\text{high}}$

**Laterally homogeneous stretched brush**

$s_{\text{low}} < s$
Brush diagram of states below Θ-point

\[ \tau = \frac{(T - \theta)}{T} < 0 \]

- \( -\tau N^{1/2} \)
- Collapsed brush
- \( s = R_{\text{globule}}^2 \)
- Pinned micelles
- Collapsed globule
- Brush in \( \theta \)-solvent
- Mushroom in \( \theta \)-solvent

Increase in area per chain: \( s/\alpha^2 N \)

Inferior solvent strength
Novel model of polymer dry brush.

Semenov 1985

Concept of polymer trajectory: \( x(n) \)

In terms of trajectory \( x(n) \):

Elastic free energy of chain with end position \( y \)

Elastic free energy per chain

Minimization of \( F_{\text{elastic}} \) with additional constraint (\( \oint dn = N \) for any \( y \)) gives:

\[
\frac{d}{dn} = E(y, x) = \left( \frac{\pi}{2N} \right) (y^2 - x^2)^{1/2}
\]

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 \( \sim 10\% \) lower than in box-like model with fixed free ends.
Generalization to brush swollen with solvent.

Free energy per chain:

\[ F = F_{\text{elastic}} + F_{\text{interactions}} \]

\[ F_{\text{elastic}} = \int F_{\text{elastic}}(y)g(y)dy \]

\[ F_{\text{interaction}} = \int f_{\text{interaction}}(x)dx \]

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:

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

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

virial expansion at \( \phi \ll 1 \)

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

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: $\xi_t = R^2/h = \xi^2N_B/h = N^{3/4}s^{1/4}/h^{3/4}$

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

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

Blob size $\xi$ increases with distance $r$

$H \sim N^\beta \quad \beta < 1$

Molecular brushes: stars, combs, …

Scaling models of self-assembly (micelles)

Stabilization of colloids

Bending bilayers
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 $F/k_BT = \int dr/\xi(r) \propto p^{1/2} \ln(H/R)$

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

Normalization of polymer density profile gives brush thickness $H \propto ap^{1/5}N^{3/5}$

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

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

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

Number of chains $p \propto R^2/s \propto R^2/d^2$

$$\text{Scaling model of spherical polymer brush}$$

Daoud & Cotton 1982
Scaling model of cylindrical polymer brush

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 $$\phi(r) \propto [\xi(r)/a]^{-4/3}$$

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

Normalization of polymer density profile gives brush thickness $$H/a \propto a(a p_2)^{1/4} N^{3/4}$$

Free energy per chain $$F/k_B T \propto (a p_2)^{5/8} N^{3/8}$$
Comb-like polymer (molecular brush)

Local structure of molecular brush
Free energy per graft \( F = F_m + F_n \)
Free energy of cylindrical bush of side chains \( F_n/k_BT \propto (a/h)^{5/8} n^{3/8} \)
Pincus elasticity for stretched swollen segment of backbone \( F_m/k_BT \propto h^{5/2}/(a^{5/2}m^{3/2}) \)
Balancing \( F_n \) and \( F_m \) gives \( h \)
Cylindrical brush thickness \( H \propto an^{3/5}(n/m)^{3/25} \)
For densely grafted molecular brushes \( h \propto am \) and transition to cylindrical brush with \( p_2 = 1/(am) \)

Large scale features of molecular brush

Diagram of states of comb-like macromolecule

End-to-end distance \( R \sim H(L_p/H)^{1/5}N_H^{3/5} \)
Persistence length \( L_p/H \rightarrow ? \)
Number of superblobs \( n \)
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.