Insertion Into Brushes

A bird's-eye view

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Colloids/Proteins/Cells
- Adsorption isotherm
- Concentration profiles
- T effects

Protein Binding DNA Chips?
- Adsorption Isotherms

Martha Bulik 1999...

AFM-sharp tips
- Force laws

Copolymer Exchange
- Rate Constants

INSERTION INTO BRUSHES: WHERE? WHAT?
So...

Need: $F$ of particle

3 ingredients:

(1) Two limits: “Large” vs. “Small”
   “Small” = Insertion $\Rightarrow$ weak perturbation

(2) $F_{\text{ins}} = \text{work against unperturbed brush } \Pi(z)$
   “universal penalty”

(3) Attraction & Adsorption modes
   case specific

Then:

Some open questions

What did we actually do?±some details
Compressive vs. Insertive modes

Compression mode

$H_0 << R << \infty$

Insertion mode: short ranged Perturbation of $\phi(z)$

$H_0 >> R >> a$
Insertion Mode-Concentration Profile I

$R_p = 4$
$H = 30$

Small particle: circumvented by chain trajectories

$\Phi(z) \approx \Phi(z)$ of unperturbed layer

$\Pi(z) \approx \Pi(z)$ of unperturbed layer as determined by $\Phi(z)$

The insertion penalty
The Osmotic Insertion Penalty

Work against $\Pi(z) = \Pi(\phi(z))$ of the unperturbed brush

AFM tip etc

$F_{\text{ins}} \approx \int_{D}^{H_0} \Pi(z) A(z) dz$

$\approx$ sphere/globular protein

$F_{\text{ins}} \approx \Pi(z) V_p$

$H_0$

$A(z)$

$D$

$z$
Insertion of a Sphere: Osmotic Penalty

\[ \overline{R}_p = R_p + \frac{a}{2} \]

\[ F_{\text{ins}} \left( \frac{\xi}{\overline{R}_p} \right)^3 \]

Surface effects

\[ z_{\text{max}} \approx 35 \]
\[ z \approx 24 \]
\[ z \approx 4 \]

\[ F_{\text{ins}} \approx \Pi V_p \approx kT \left( \frac{R_P}{\xi} \right)^3 \]

The Osmotic Penalty - Comments

**Bulk vs. Brush**

**Brush**

- $\Pi(z)$ anisotropic
- $F_{\text{ins}}(z) \approx \Pi(z) V$ \( R \ll H, z \ll H \)
- Elastic & Interaction free energies

**Bulk**

- $\Pi$ isotropic
- $F_{\text{ins}} = \Pi V$ \text{ any } R, z
- Interaction free energy

$F_{\text{ins}}$ : effect of density

Decreasing $\Sigma$ at constant $T$ \( \Rightarrow \)

Brush collapse via $T$ tuning at constant $\Sigma$ \( \Rightarrow \)

Increase $\Pi(z)$ & $F_{\text{ins}}$

Decrease $\Pi(z)$ & $F_{\text{ins}}$

$\Sigma$ area per chain

$F_{\text{ins}}$ \( \Rightarrow \)

“Osmotic Archimedes Principle”

“Osmotic buoyancy”
Three Adsorption Modes

- **Primary Adsorption** - at the surface (Surface-Particle attraction)
- **Secondary Adsorption** - at the brush’s outer edge (vdW attraction)
- **Ternary Adsorption** - within the brush (Polymer-Particle attraction)
Weak Non-Specific Ternary Adsorption

- No specific adsorption site
- Uniform surface
- $-\varepsilon kT$ per monomer in contact
- $\varepsilon \ll 1$ below adsorption threshold
  - No bulk complexation
  - Weak perturbation

\[ F_{\text{att}} \approx -\varepsilon kT c(z) A_p a \]

Proposed for proteins but more suitable for colloids
Strong Specific Ternary Adsorption: 2 Cases

$F_{\text{attraction}} \gg kT$
Specific Adsorption Site
Binds definite number of monomers

Strong Adsorption
$\Rightarrow$ Weak Perturbation

Antibodies - 2 types of binding sites:

Backbone adsorption

Terminal adsorption
The Insertion Mode

Open (?) Questions:

- What is small?
- The cross-over between small and big?
- Surface & edge effects?
- Shape effects?

In any case

physically transparent & simple approximation complementing
the “compression + Derjaguin’s” approximation for “large” particles
Colloids/Proteins (primary, ternary X3)
- Adsorption isotherms-SCF
- Concentration profiles-SCF
- $F_{\text{ins}}$ - simulation: MC+Umbrella sampling
- Collapse effects-SCF
- (I) UCST - “classical”
- (II) LCST - “non classical” PNIPAM

AFM-sharp tips
- Force laws

Copolymer Exchange
- Rate Constants
- Concentration Effects (slow down)
AFM force laws: Colloidal vs. Sharp tips
Figure 1. Force–displacement curves for a brush with grafting density (a) $\rho_a = 0.1\sigma^{-2}$ and (b) $0.07\sigma^{-2}$ for chain length $N = 100$, compressed by an identical brush (○), an infinite, bare surface (△), and an AFM tip. The radii ($r_{cyl}/\sigma$, $r_{pb}/\sigma$) of the tip are (7, 10) (×), (10, 14) (●), (14, 20) (■), and (16, 100) (▲). The distance $D$ between the surfaces is scaled by the chain length $N$ and the number of surfaces bearing end-grafted polymer, $n_a$.

**Simulation: Sharp Tip vs. “Planar Piston”**

M. Murat & GS Grest, Macromolecules **1996**, **29**, 8282

**Sharp tips:** (i) No compression (ii) weaker force law (iii) no theory
AFM: Insertion vs. Compression Force Law

SCF concentration profile
marginal solvent

Murat & Grest parameters
\( \Pi_0 \approx 0.12kT/a^3 \)

\( F_{ins} \approx \int_{D}^{H_0} \Pi(z) A(z) dz \)

planar piston = cylindrical tip + Derjaguin’s approximation

AFM sharp tips vs. Colloidal tips & SFA

SFA & Cylindrical AFM tip in the compression regime (compression + Derjaguin’s approx’)

SFA Experiments can be fitted by BOTH the Alexander model AND the SCF parabolic profile

Cylindrical tip in the insertion regime: Osmotic Penalty

\[ f_{\text{ins}} = A_{\text{cyl}} \Pi = \text{const}' \]

 Alexander model

\[ f_{\text{ins}} = A_{\text{cyl}} \Pi_0 \left( 1 - \frac{D^2}{H_0^2} \right)^2 \]

 SCF parabolic profile

Qualitatively different predictions

AFM sharp tip force laws can distinguish between the 2 models
Repression of Primary Protein Adsorption

Two competing terms:

(1) Surface contact: $U_{ads}$

(2) Osmotic Penalty at the surface

$\Pi \approx \frac{kT}{\xi^3}$ \quad & \quad $\xi \approx \Sigma^{1/2}$

Adsorption isotherm:

$\Gamma \approx K(\Sigma, N, V_{protein})c_{protein}$

$K(\Sigma, N, V_{protein}, A_{protein}) = \exp\left(-\frac{\Delta F}{kT}\right)$

$\ln \Gamma \approx \ln c_{protein} + \frac{U_{ads}}{kT} - \frac{V_{protein}}{\Sigma^{3/2}}$

Why PEG works?

Dense brushes repress protein adsorption
Fibrinogen: Primary Adsorption?

\[ \ln \Gamma \approx \text{const} - \frac{V_{\text{protein}}}{\sum^{3/2}} \]

Why PEG works?

fit: \[ V_{\text{protein}} \approx 2 \times 10^5 \, \text{Å}^3 \]

literature: anhydrous fibrinogen

fit: \[ V_{\text{protein}} \approx 4.8 \times 10^5 \, \text{Å}^3 \]

Biochemistry 2000, 39, 3441-3451.