Insertion Into Brushes

A bird's-eye view

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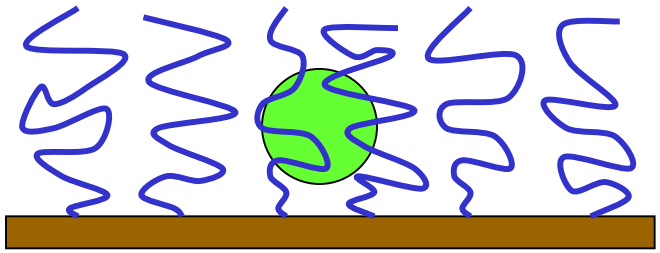
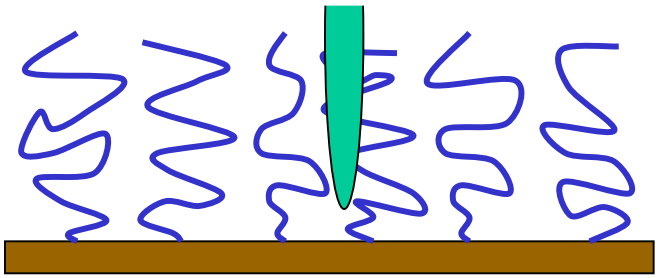
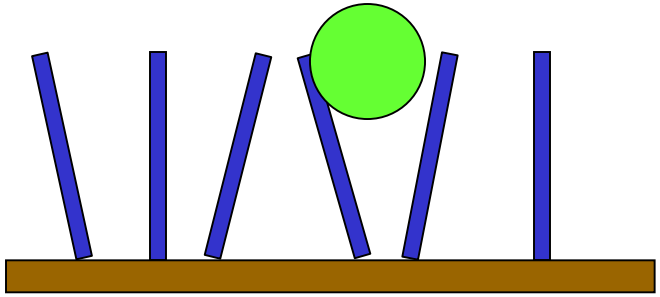
INSERTION INTO BRUSHES: WHERE? WHAT?



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

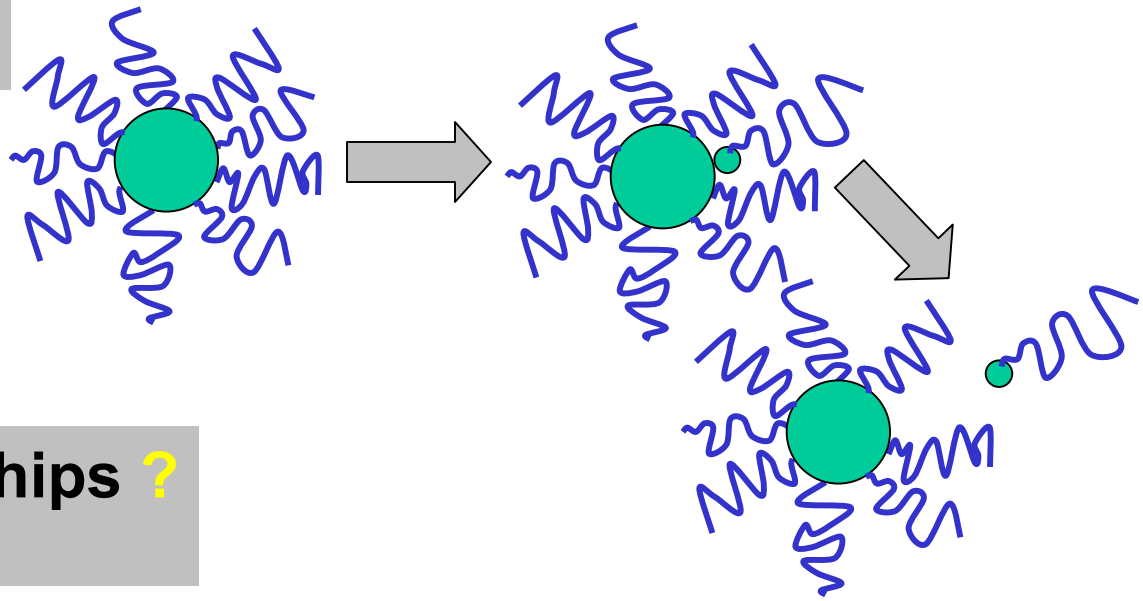


AFM-sharp tips
- Force laws



Protein Binding DNA Chips ?
- Adsorption Isotherms

Martha Bulik 1999…



Copolymer Exchange
- Rate Constants

So…

Need: F of particle

3 ingredients:

(1) Two limits: “Large” vs. “Small”

“Small” = Insertion ⇒ weak perturbation

(2) F_{ins} = work against unperturbed brush Π(z)
“universal penalty”

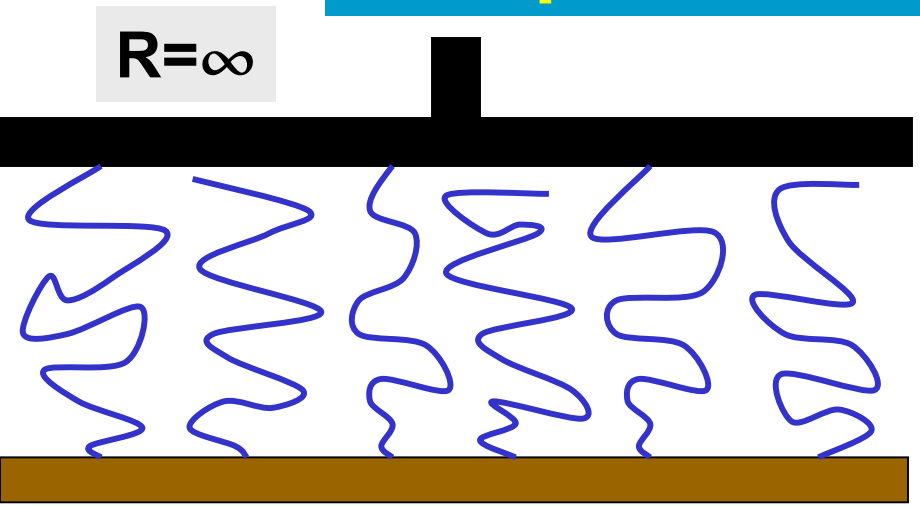
(3) Attraction & Adsorption modes
case specific

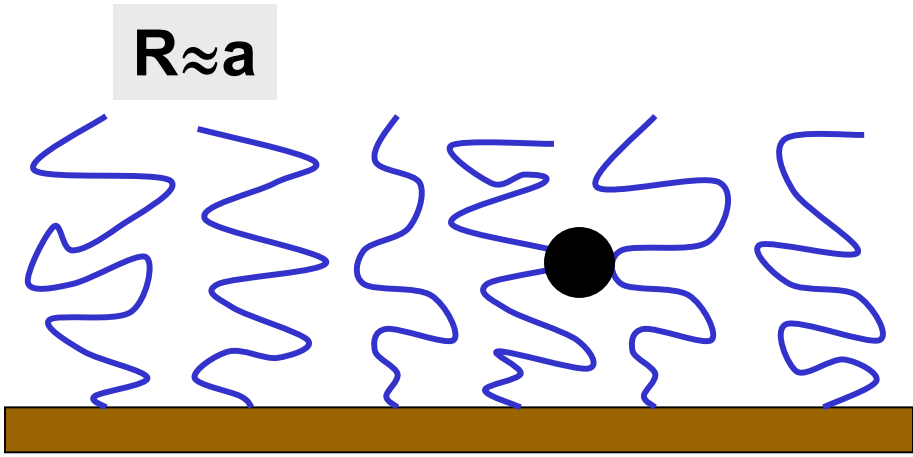
Then:

Some open questions

What did we actually do?±some details

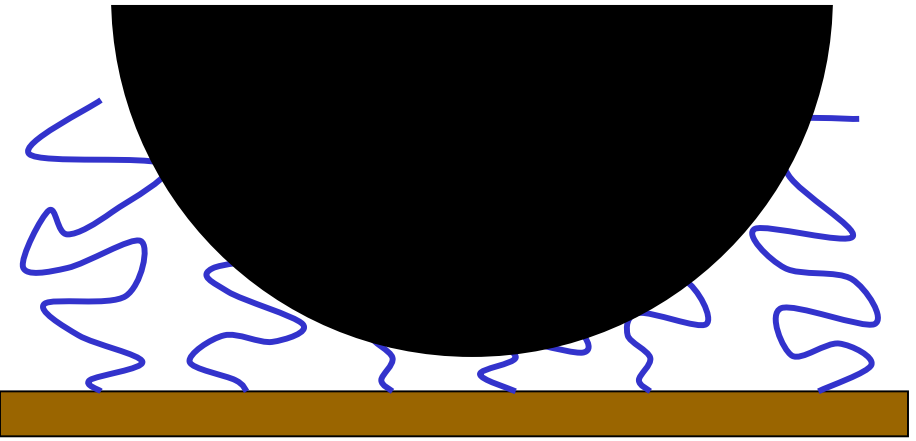
Compressive vs. Insertive modes





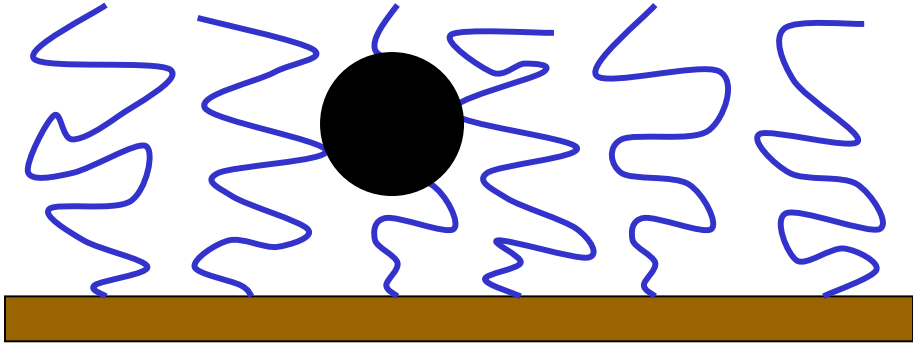
Compression mode

$H_0 << R < \infty$

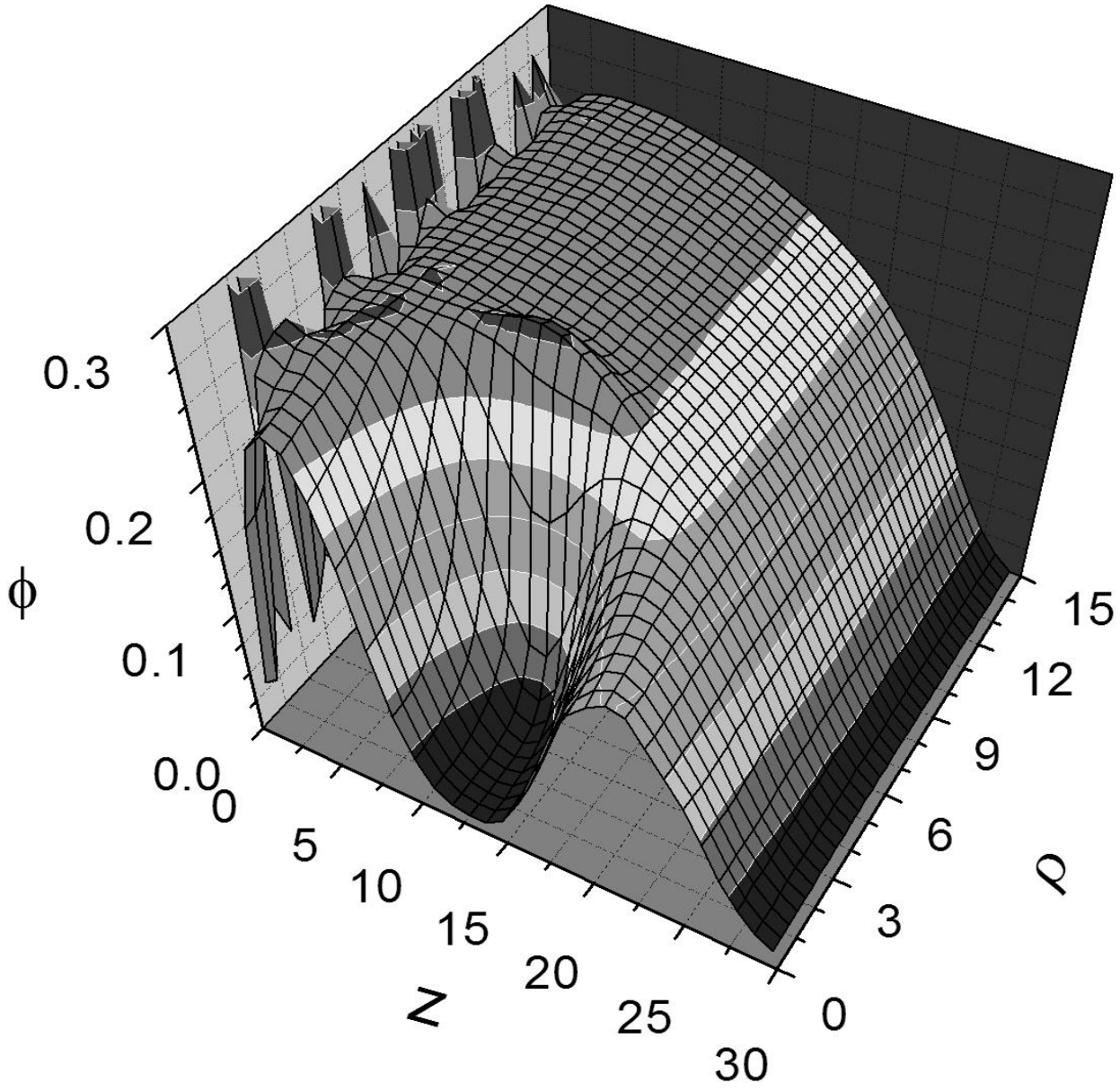


Insertion mode: short ranged Perturbation of $\phi(z)$

$H_0 >> R >> a$



Insertion Mode-Concentration Profile I



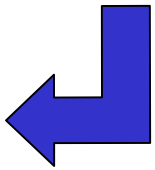
R_p=4
H=30

V. Ermilov, A. Lazutin & AH: Macromolecules (2010)

Insertion limit

Small particle: circumvented by chain trajectories

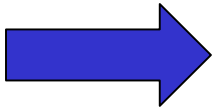
Φ(z) ≈ Φ(z) of unperturbed layer



Φ(z) via Simulations, SCF etc

&

Π(z) ≈ Π(z) of unperturbed layer as determined by Φ(z)



The insertion penalty

The Osmotic Insertion Penalty

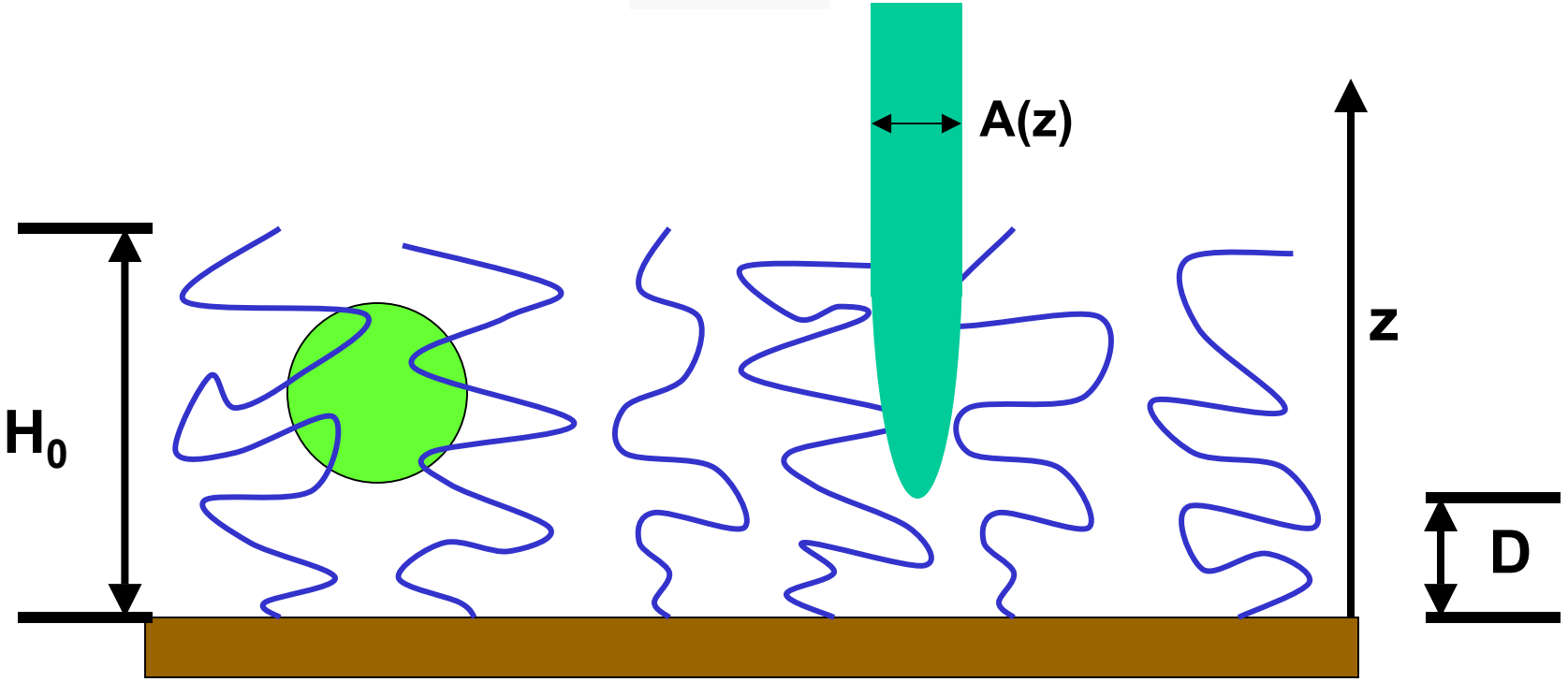
Work against $\Pi(z) = \Pi(\phi(z))$ of the unperturbed brush

- AFM tip etc — general

$$F_{ins} \approx \int_D^{H_0} \Pi(z) A(z) dz$$

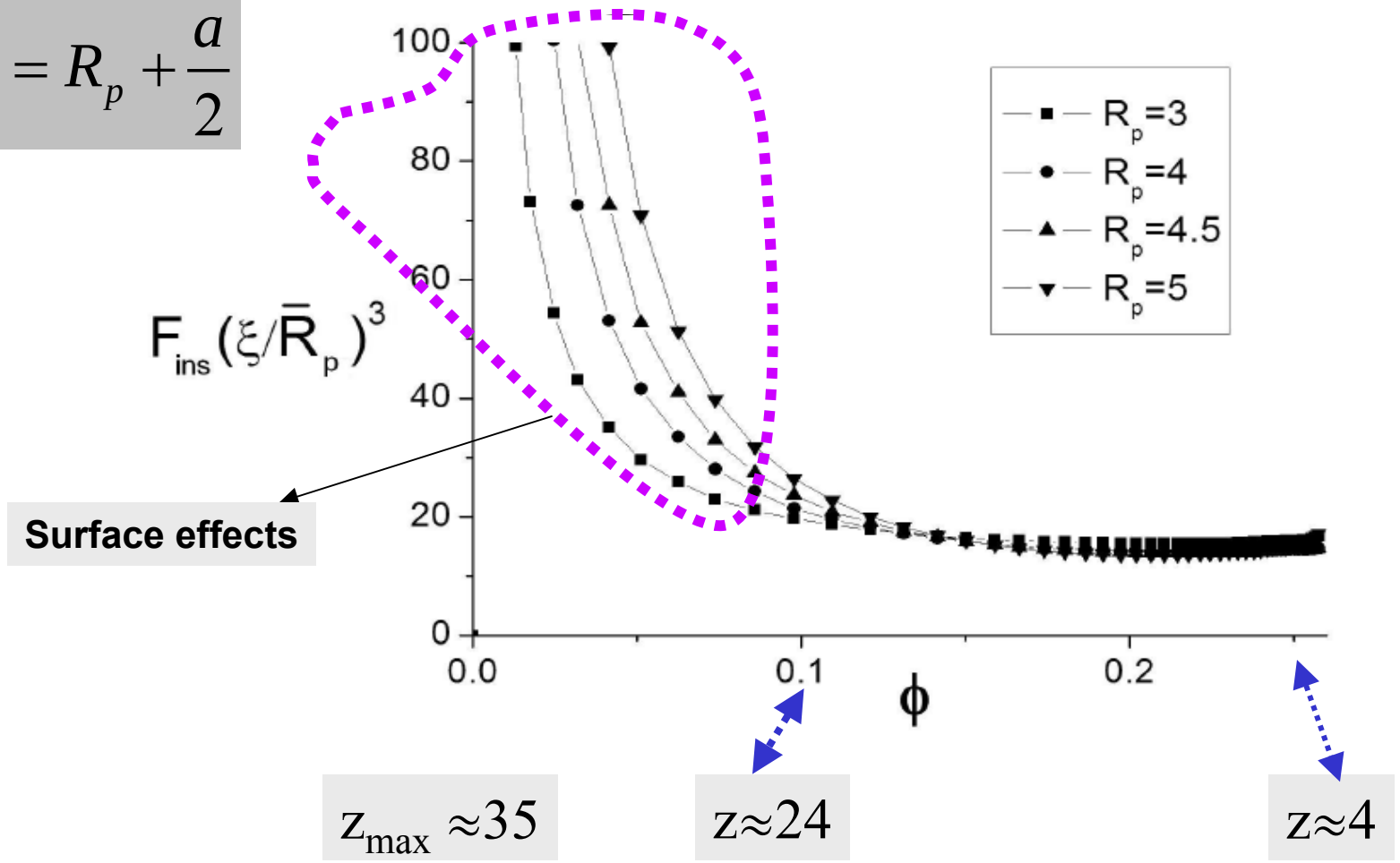
- $\approx$ sphere/globular protein — approx'

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



Insertion of a Sphere: Osmotic Penalty

$$\bar{R}_p = R_p + \frac{a}{2}$$



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

V. Ermilov, A. Lazutin & AH: Macromolecules (2010)

The Osmotic Penalty - Comments

Bulk vs. Brush

Brush

$\Pi(z)$ anisotropic

$F_{ins}(z) \approx \Pi(z)\, V \quad R \ll H,\ z \ll H$

Elastic & Interaction free energies

Bulk

Π isotropic

$F_{ins} = \Pi\, V \quad$ any R, z

Interaction free energy

F_{ins} : effect of density

Decreasing Σ at constant T ➡ Increase $\Pi(z)$ & F_{ins}

Brush collapse via T tuning at constant Σ ➡ Decrease $\Pi(z)$ & F_{ins}

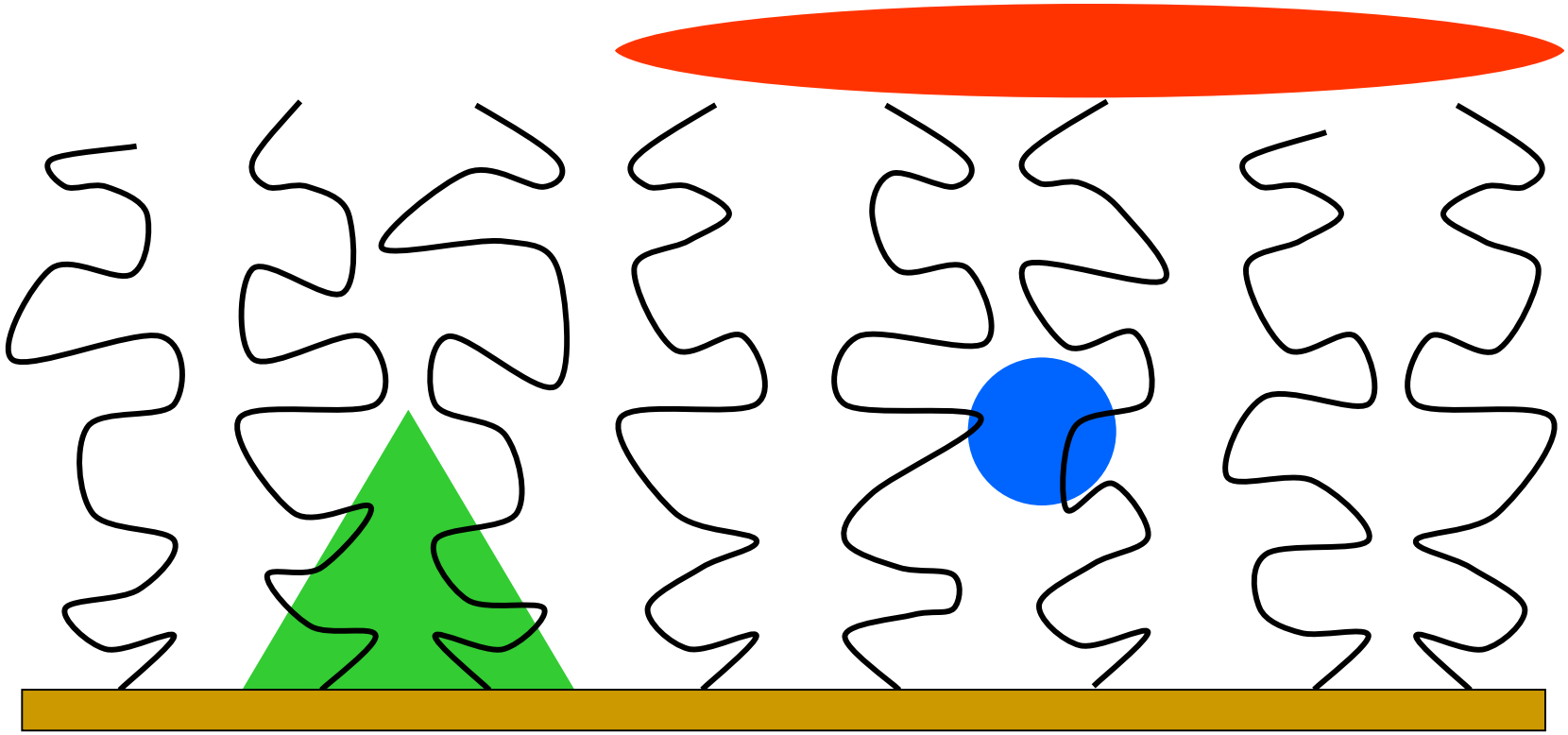
Σ area per chain

F_{ins} ➡ **"Osmotic Archimedes Principle"**

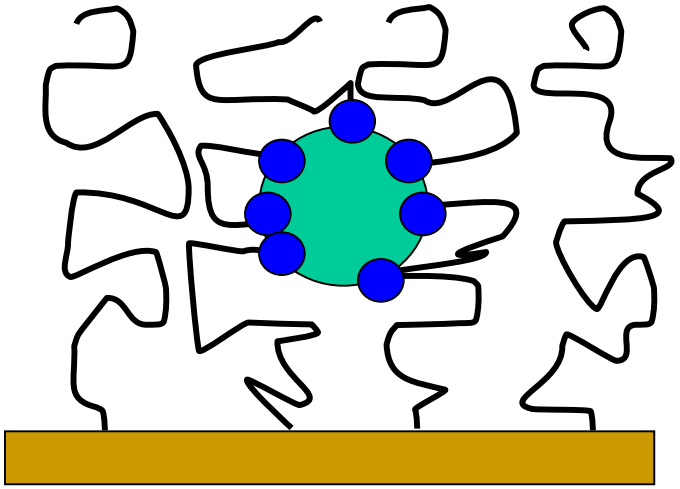
"Osmotic buoyancy"

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
- -εkT per monomer in contact
- ε<<1 below adsorption threshold
  - ⟶ no bulk complexation
  - ⟶ weak perturbation

$$F_{att} \approx -\varepsilon kTc(z)A_p a$$

Proposed for proteins but more suitable for colloids

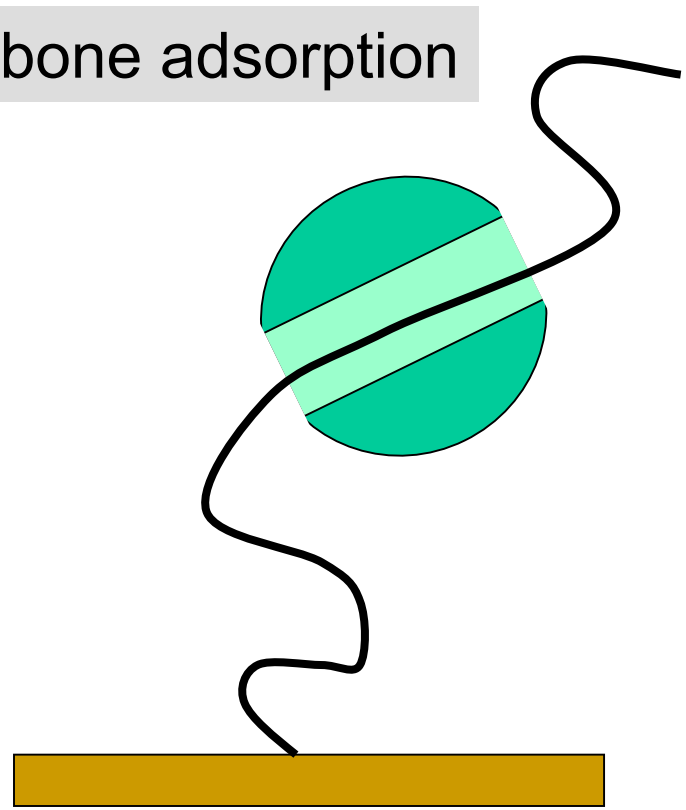
Strong Specific Ternary Adsorption: 2 Cases

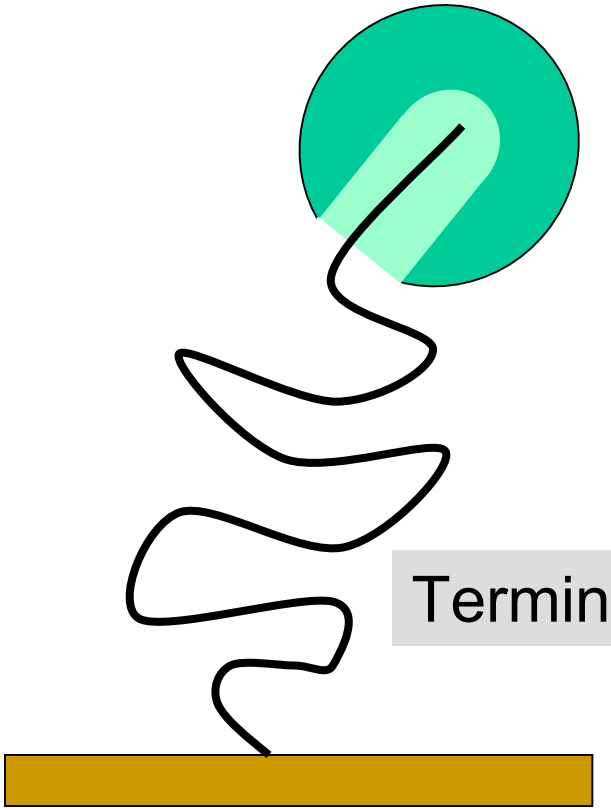
$F_{attraction} >> kT$
Specific Adsorption Site
Binds definite number of monomers

Strong Adsorption
⇒Weak Perturbation

Antibodies - 2 types of binding sites:

Backbone adsorption





Terminal adsorption

The Insertion Mode

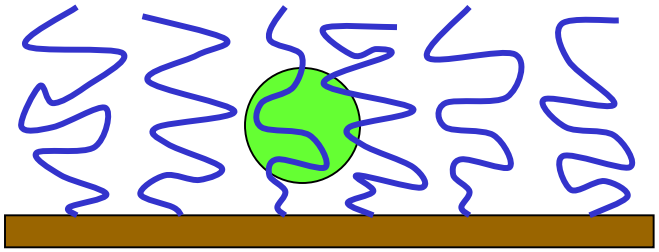
Open (?) Questions:

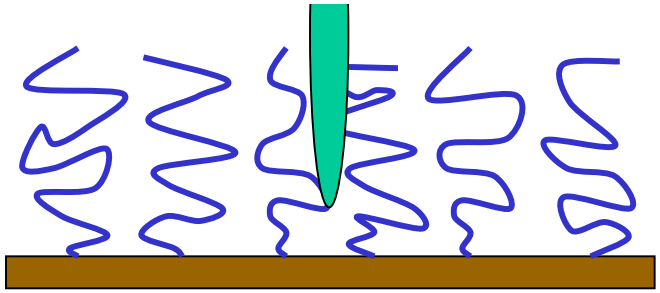
- What is small?
- The cross-over between small and big?
- Surface & edge effects?
- Shape effects?

In any case

physically transparent & simple approximation complementing the "compression + Derjaguin's'" approximation for "large" particles

INSERTION INTO BRUSHES: 3 DIRECTIONS



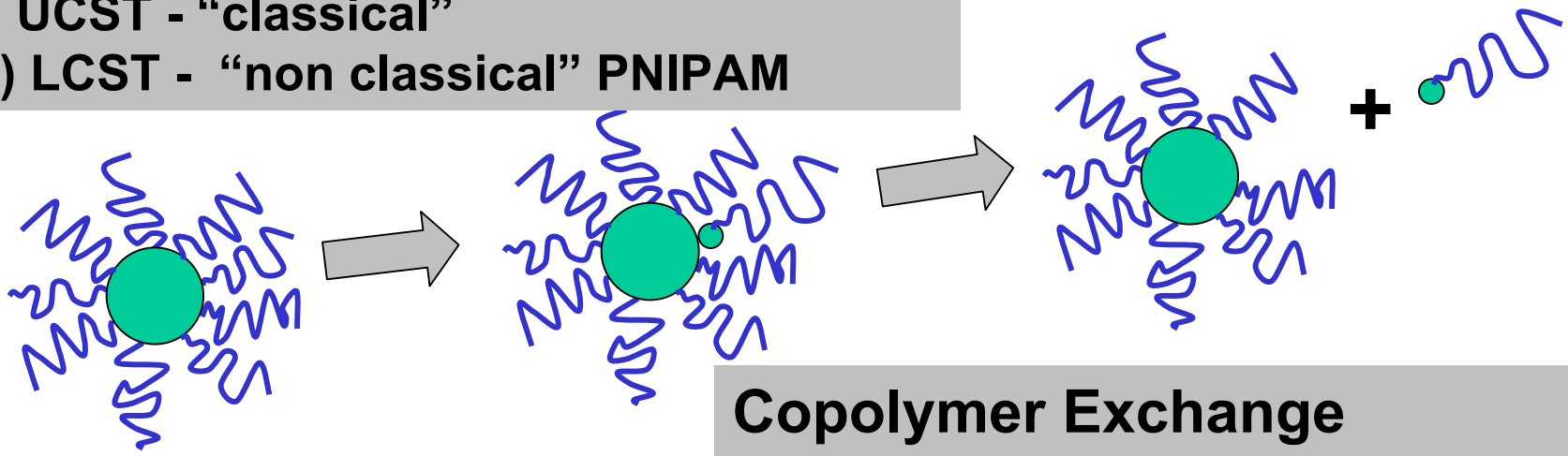


Colloids/Proteins (primary, ternary X3)

- Adsorption isotherms-SCF
- Concentration profiles-SCF
- F_{ins} - simulation: MC+Umbrella sampling
- Collapse effects-SCF
- (I) UCST - "classical"
- (II) LCST - "non classical" PNIPAM

AFM-sharp tips

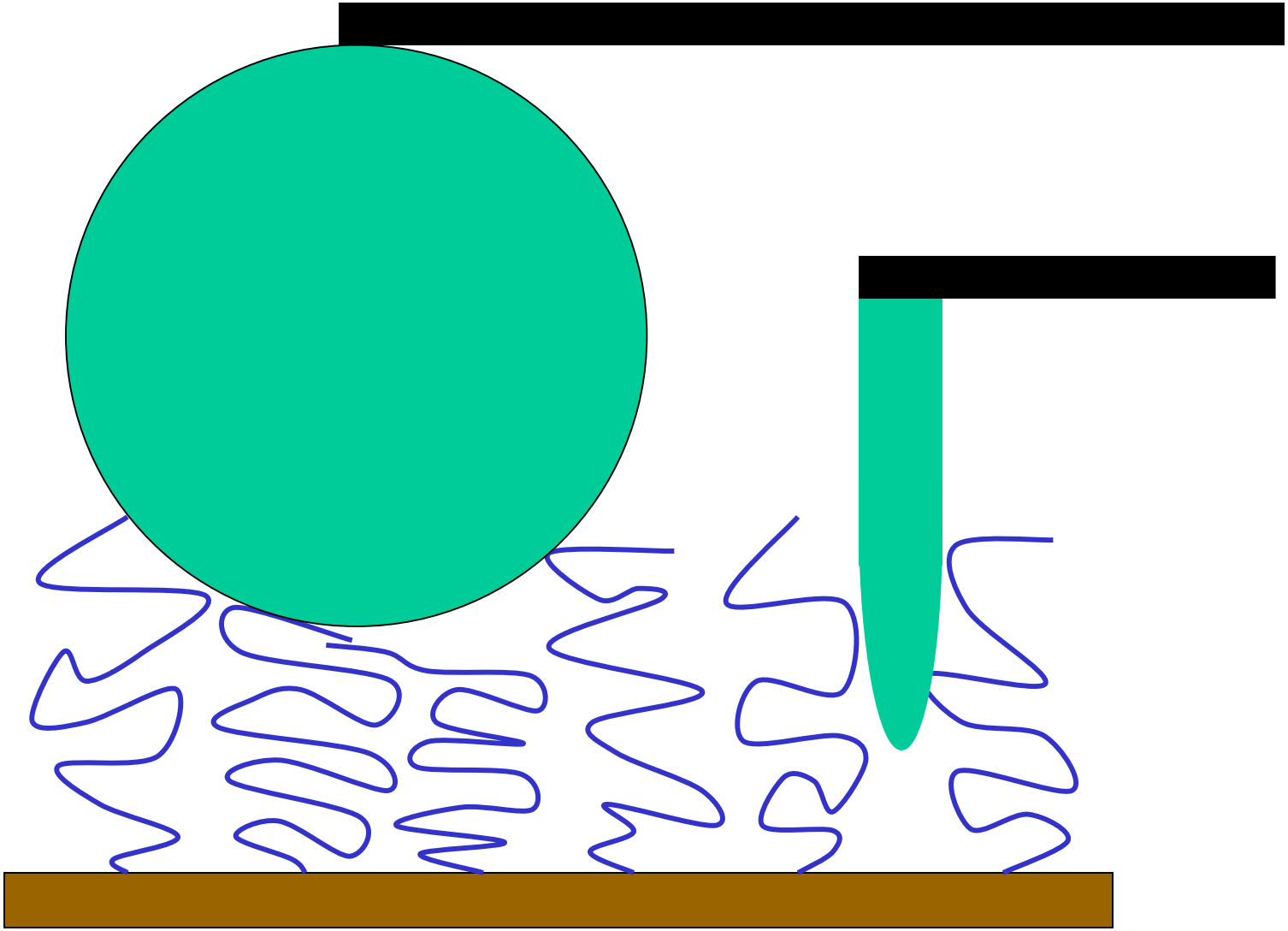
- Force laws



Copolymer Exchange

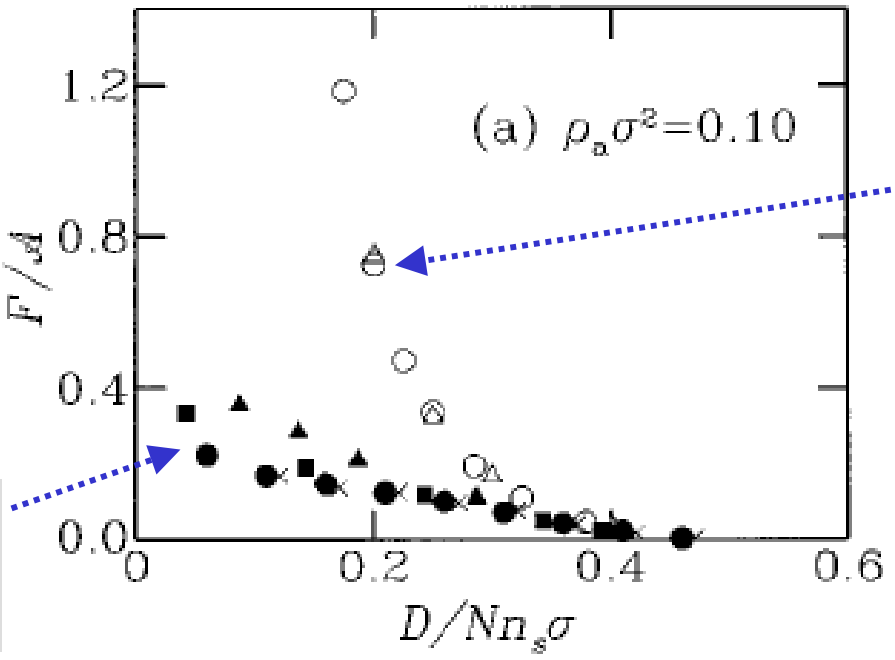
- Rate Constants
- Concentration Effects (slow down)

AFM force laws: Colloidal vs. Sharp tips



Simulation: Sharp Tip vs. "Planar Piston"

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



planar piston = cylindrical tip within Derjaguin's approx'

sharp tip: ≈cylindrical

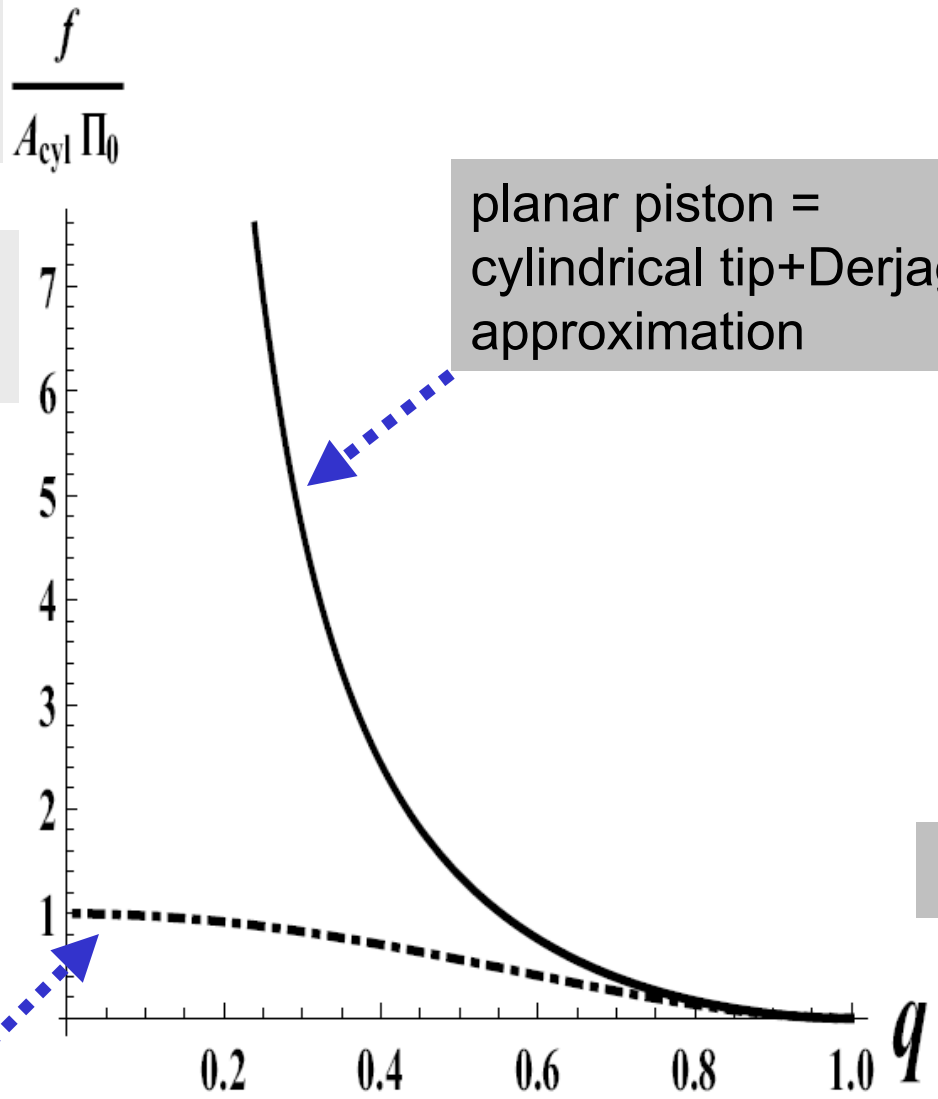
Figure 1. Force–displacement curves for a brush with grafting density (a) $\rho_a = 0.1\sigma^{-2}$ and (b) $0.07\sigma^{-2}$ for chain length $N = 100$, compressed by an identical brush (○), an infinite, bare surface (△), and an AFM tip. The radii (r_{cyl}/σ, r_{sph}/σ) of the tip are (7, 10) (×), (10, 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_s.

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 $\Pi_0 \simeq 0.12kT/a^3$



planar piston = cylindrical tip+Derjaguin's approximation

cylindrical tip:osmotic penalty

$$F_{ins} \approx \int_D^{H_0} \Pi(z) A(z) dz$$

$q=D/H_0$

AH & EB Zhulina:Langmuir (2010)

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

$$f_{ins} = A_{cyl}\Pi = const'$$

Alexander model

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

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:

Why PEG works?

(1) Surface contact: U_{ads}

(2) Osmotic Penalty at the surface

$$\Pi \approx \frac{kT}{\xi^3} \quad \& \quad \xi \approx \Sigma^{1/2} \quad \Rightarrow \quad \frac{F_{ins}}{kT} \approx \frac{V_{protein}}{\Sigma^{3/2}}$$

Adsorption isotherm:

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

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

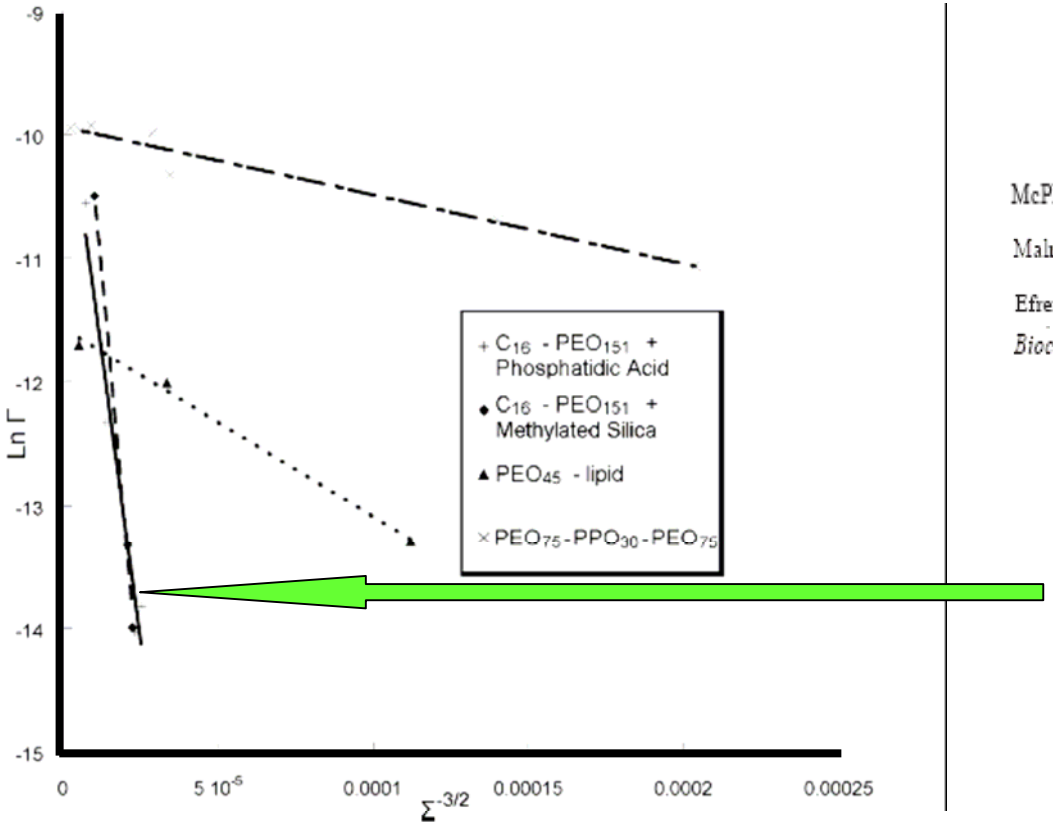
$$\ln\Gamma \approx \ln c_{protein} + \frac{U_{ads}}{kT} - \frac{V_{protein}}{\Sigma^{3/2}}$$

⇒ **Dense brushes repress protein adsorption**

Fibrinogen: Primary Adsorption?

Why PEG works?

$$\ln\Gamma \approx const' - \frac{V_{protein}}{\Sigma^{3/2}}$$



McPherson, T.; Kidane, A.; Szleifer, I.; Park, K. *Langmuir* **1998**, *14*, 176.

Malmsten, M.; van Alstine, J. M. *J. Colloid Interface Sci.* **1996**, *177*, 502–512.

Efremova, N. V.; Bondurant, B.; O'Brien, D. F.; Leckband, D. E. *Biochemistry* **2000**, *39*, 3441–3451.

fit: $V_{protein} \approx 2 \times 10^5 \ \overset{o}{A}^3$

literature: anhydrous fibrinogen

$V_{protein} \approx 4.8 \times 10^5 \ \overset{o}{A}^3$