Polymer Adsorption

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Outline

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1. Adsorption versus Depletion of polymer solutions
   - Single Chain Adsorption
   - Adsorption and Depletion of Semi-dilute solutions
2. Self-Similar Adsorption profile
   - Scaling theory of an adsorbed polymer layer
   - Colloid stabilization

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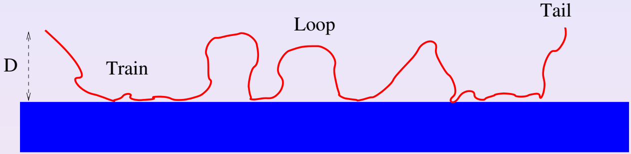
Flory Theory of Single Chain Adsorption



Flory Theory PGG

- Confinement Energy $F_{conf} \sim N(a/D)^{1/\nu}$
- Attraction Energy $F_{ads} = -N\epsilon(a/D)$
- Equilibrium Thickness $D \sim a\epsilon^{\frac{\nu}{\nu-1}}$
- Adsorption thickness independent of molecular weight

Proximal effects Eisenriegler et al.

- Diverging concentration profile. Only change in exponent.
- Connection to special transition

Mean Field Theory

Propagator Equation PGG 1969

- Diffusion Equation

$$-\frac{\partial G_N}{\partial N} = -\frac{a^2}{6}\nabla^2 G_N + U G_N$$

- Boundary condition $-\frac{1}{G_N}\frac{\partial G_N}{\partial z} = \kappa = \frac{1}{D}$
- Ground state dominance approximation

$$G_N(z,z') = \sum_n \exp -\epsilon_n N \quad \psi_n(z)\psi_n(z')$$

- Sum dominated by the first term, exponential concentration profile

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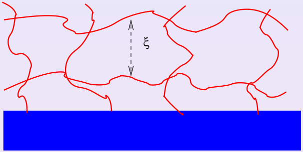
Semidilute solutions close to a wall



Free energy

- Ground state dominance approximation, $c(z) = \psi^2(z)$
- Excluded volume interaction v, Free energy

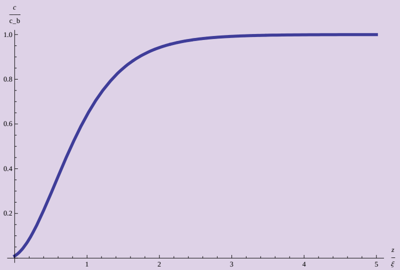
$$\mathcal{F}/kT = \int dz \left(\frac{a^2}{6} (\frac{d\psi}{dz})^2 + \frac{1}{2} v c^2 + \epsilon c \right)$$

- Lagrange multiplier $\epsilon = -v c c_b$ insures the imposed bulk concentration c_b
- Bulk correlation length $\xi = a/(12 v c_b)^{1/2}$
- Boundary condition $-\frac{1}{\psi}\frac{\partial \psi}{\partial z} = \kappa = \frac{1}{D}$

Adsorption and depletion

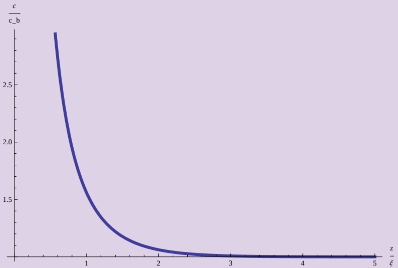
Polymer depletion $\kappa < 0$

Leibler, JF, PGG 1978



- Concentration profile
  $c = c_b \tanh^2 \frac{z+D}{2\xi}$
- Positive Interfacial tension
  $\gamma \sim kTc_b^{3/2}$

Polymer adsorption $\kappa > 0$



- Concentration Profile
  $c = c_b \tanh^{-2} \frac{z+D}{2\xi}$
- Adorbed amount
  $\Gamma = \kappa a^2/(3v)$
- Adsorbed layer thickness ξ
- Dilute solutions

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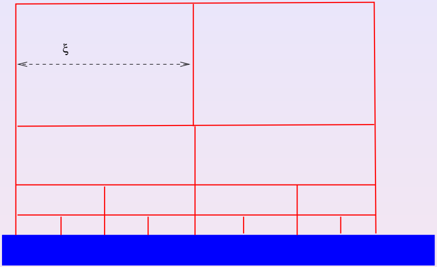
Self-similar concentration profile PGG 1981



Concentration profile

- Central Region: local structure of a semidilute solution, $\xi \sim z$

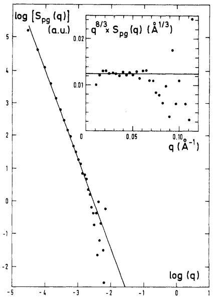
$$\xi \sim c^{-3/4} \qquad c \sim 1/z^{4/3}$$

- Proximal region: $z < D$ single chain behavior.
- Distal region: exponential decay over correlation length (or the radius)

Properties of polymer layers adsorbed from dilute solution

- Self-similar grid with largest size $R \sim N^{3/5}$. Adsorbed amount weakly dependent on N: $\Gamma = \Gamma_0(1 - N^{-1/5})$.
- Hydrodynamic thickness R
- Ellipsometric thickness $R \sim \int dz c(z) z dz \sim N^{2/5}$ Takahashi

Neutron scattering Auvray



- Power law decay of structure factor $S(q) \sim q^{-8/3}$
- Many experiments lead to exponential decay Cosgrove
- Separation of length scales

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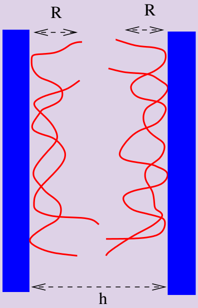
Interaction between polymer layers

Interactions between surfaces



- Excluded volume: repulsive
- Bridging: attractive

Mean Field theory

- Equilibrium interaction attractive ($h < R$) $W \sim -kT/h^3$
- Exponentially decaying tail
- Interaction between irreversibly adsorbed layers $W = 0$

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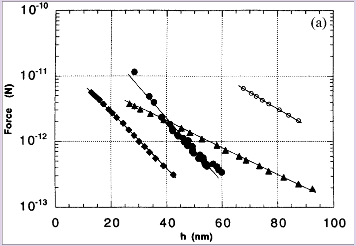
Interaction between polymer layers

Scaling theory PGG 1981

- Interaction energy $W \sim \pm kT/h^2$
- Free energy description Widom
- Equilibrium interaction : attractive
- Non equilibrium interaction between saturated layers repulsive

Experimental results

- Surface forces apparatus Klein
- Non saturated Layers
- Other techniques Bibette



Colloid Stabilization Klein, Pincus

- Polymer adsorption
- Good solvent
- Irreversible adsorption (Glassy Layers)
- Saturated layers
- Depends on History

Distributions of tails and loops sizes

Tails and Loops partition function Semenov, JF

- Loops
  - Obtained by reconstructing the self similar profile with loops
  - Partition function $Z_l(n) \sim n^{-(2\nu+1)}$
  - Dominated by short loops (trains)
- Tails
  - Obtained by cutting a loop into two tails
  - Partition function $Z_t \sim n^{-(\gamma-\nu)/2-1}$
  - Dominated by long tails
- Loops in the inside of the layer, tails on the outside
- Crossover length $z^* \sim N^{1/2}$

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Dynamics of adsorbed layers

Penetration in a adsorbed layer PGG 1985

- End point penetration (no hairpin entrance)
- Analogy with a quantum tunneling problem
- Very weak (logarithmic) energy barrier
- Reptation of an entering chain through the self-similar layer
- Penetration time $T = T_0 N^{-x}, \quad x = 0.3$

Desorption and exchange

- Second order chemical Kinetics

$$\frac{d\Gamma}{dt} = -k\Gamma c_b$$

- no desorption (Saturation condition)
- Exchange between labelled and non-labelled chains

Summary

- Scaling theory of Polymer adsorption
  - Applications to colloidal stablization
  - Non-Equilibrium adsorption kinetics
  - Guizelin layers

- Other applications to technological problems
  - Friction
  - Adhesion

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