



# Theory of Polymer Brushes

Andreas Dahlin  
Lecture: 4/6

[adahlin@chalmers.se](mailto:adahlin@chalmers.se)  
<http://www.adahlin.com/>

2021-02-01

Surface Engineering

1



## Outline

What you might know from before: Polymers are entropic springs where the end-to-end distance probability follows a Gaussian distribution.

Now we will extend this model to take two more things into account:

- The self-avoidance effect (excluded volume).
- The influence from a solvent around the polymer.

Then we look at polymer *brushes*, i.e. polymers with one end attached to a surface.

There is mostly theory in this lecture, more about applications later!

2021-02-01

Surface Engineering

2



## Repetition: Conformational Entropy

From the freely jointed chain model, the entropy as function of end-to-end distance is given by:

$$S(r) = \text{constant} - \frac{3k_B r^2}{2abN}$$

The expected value  $R$  for end-to-end distance is given from the “random walk” behavior:

$$\langle |r| \rangle = R = [abN]^{1/2}$$

Thus, to predict  $R$  we need:

- Monomer size  $a$ .
  - Number of monomers  $N$ .
  - Kuhn-length  $b$  (twice the *persistence length*).
- } or contour length



## Repetition: Polymers as Entropic Springs

When the entropy is known as a function of chain elongation, we can get the free energy as a function of  $r$  for the random walk model:

$$G(r) = -TS(r) = \frac{3k_B T r^2}{2abN} + \text{constant}$$

The force required to stretch the chain is:

$$F(r) = \frac{\partial G}{\partial r} = \frac{3k_B T r}{abN}$$

The “spring constant” is:

$$\frac{\partial^2 G}{\partial r^2} = \frac{\partial F}{\partial r} = \frac{3k_B T}{abN}$$



Wikipedia: Spring

Note that it is easier to pull long and stiff polymers (counterintuitive).

Here all is based on conformational entropy, no interaction energies accounted for!



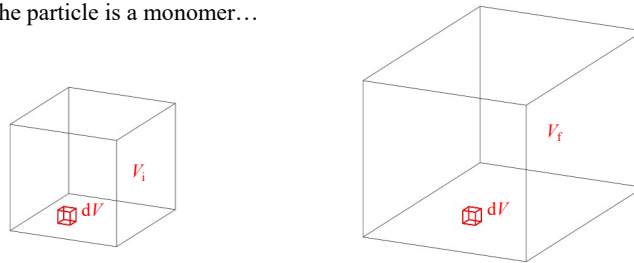
## Repetition: Volumes and Entropy

Consider volume expansion from the viewpoint of statistical mechanics.

We can discretize the space available into a certain number of positions, each with volume  $dV$ , where a particle can be located. The entropy change is then:

$$\Delta S = k_B \log(W_f) - k_B \log(W_i) = k_B \log\left(\frac{W_f}{W_i}\right) = k_B \log\left(\frac{\frac{V_f}{dV}}{\frac{V_i}{dV}}\right) = k_B \log\left(\frac{V_f}{V_i}\right)$$

Now imagine the particle is a monomer...



2021-02-01

Surface Engineering

5



## Self Avoiding Chains

Assume we have our  $N$  chain segments, each with volume  $v$ , in a total volume  $V$ . The *excluded volume* occupied by the coil is  $Nv$ .

We can now do a *mean field approximation*: We assume that the segment density is homogenous throughout the volume that the coil occupies.

The entropy loss per segment is then:

$$\Delta S_{\text{seg}} = k_B \log\left(\frac{V_f}{V_i}\right) = k_B \log\left(\frac{V - Nv}{V}\right) = k_B \log\left(1 - \frac{Nv}{V}\right) \approx -\frac{k_B Nv}{V}$$

for small polymer volume fractions ( $Nv/V$ )

We thus treat the polymer as a “gas” of monomers. Remember that the molecule is assumed to be long and flexible and it wobbles around (so the assumption is not crazy).

2021-02-01

Surface Engineering

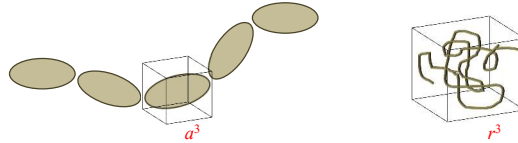
6



## Excluded Volume Entropy

We can assume that  $V \approx r^3$  and probably  $v \approx a^3$  but we just call it  $v$  for now:

$$\Delta S_{\text{seg}} = -\frac{k_B N v}{r^3}$$



We get the total free energy increase for the polymer due to the presence of itself by multiplying with  $N$  (all monomers) and temperature:

$$\Delta G_{\text{vol}}(r) = -NT\Delta S_{\text{seg}} = \frac{k_B T v N^2}{r^3}$$

The chain will want to expand to make  $\Delta G_{\text{vol}}$  smaller but we must not forget the conformational entropy cost of stretching the chain:

$$G(r) = \frac{3k_B T r^2}{2abN} + \frac{k_B T v N^2}{r^3} + \text{constant}$$



## Sanity Check: Osmotic Pressure?

Osmotic pressure  $\Pi$  with a second virial coefficient  $B$  is given by:

$$\Pi = k_B T [C + B C^2] \quad \text{"ideal" (dilute) behavior for } B = 0$$

Here  $C$  is concentration (inverse volume), which inside the coil is  $N/V$ :

$$\Pi = k_B T \left[ \frac{N}{V} + B \left[ \frac{N}{V} \right]^2 \right] \quad G = \Pi V = k_B T \left[ N + \frac{N^2}{V} \right]$$

The free energy increase due to the deviation from ideal behavior is:

$$\Delta G = \Pi V = k_B T \left[ N + B \frac{N^2}{V} \right] - k_B T N = \frac{k_B T B N^2}{V}$$

Again assuming  $V = r^3$ , we see that  $B = v$  so the osmotic pressure effect is equivalent.

We will look at energetic interactions soon...



## Example of the Excluded Volume Effect

As an example we can plot the free energies as a function of  $r$  for:

$$N = 1000$$

$$a = 1 \text{ nm}$$

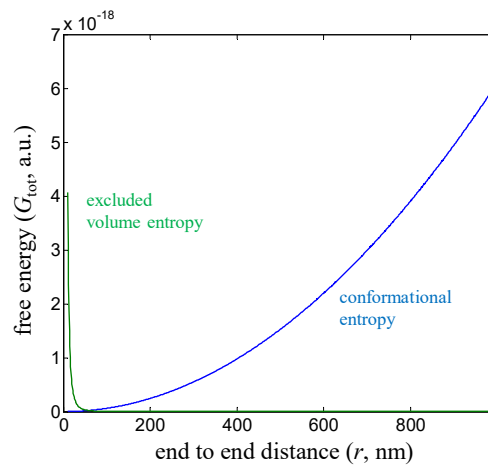
$$b = 1 \text{ nm}$$

$$v = 1 \text{ nm}^3$$

For small  $r$  the excluded volume effect dominates entirely, but disappears very fast with ( $r^{-3}$ ).

The conformational entropy loss increases steadily ( $r^2$ ).

Minimum for some value of  $r$ !



## The Flory Radius

We can minimize  $G_{\text{tot}}$  with respect to  $r$  by taking the derivative:

$$\frac{\partial G_{\text{tot}}}{\partial r} = \frac{3k_B T r}{abN} - \frac{3k_B T v N^2}{r^4}$$

Setting the derivative to zero will give the free energy minimum and thus the expected value of  $r$  (in other words  $R$ ) from:

$$\frac{3k_B T r}{abN} = \frac{3k_B T v N^2}{R^4}$$

This gives us:

$$R^5 = abvN^3$$

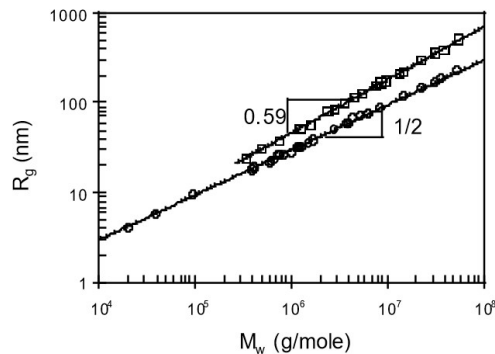
So we arrive at an exponent of 3/5 instead of 1/2. We can denote this as the Flory radius:

$$R_F = [abv]^{1/5} N^{3/5}$$



## Validity?

The “accurate” value of the exponent, based on the math of self-avoiding random walks, is 0.588... But experiments cannot discriminate this value from 3/5 (though from 1/2).



“radius of gyration” of polystyrene chains in a “theta-solvent” (cyclohexane at 34.5°C) and in a good solvent (benzene at 25°C)

Fetters et al.  
*Journal of Physical and Chemical Reference Data* **1994**, 23 (4), 619-640.

2021-02-01

Surface Engineering

11



## Who Cares About 1/2 or 3/5?

The value of the exponent is very important because  $N$  is a large number!

$$\frac{R_F}{R} = \frac{[abv]^{1/5} N^{3/5}}{[abN]^{1/2}} \approx N^{1/10}$$

Equal to 1.58 for  $N = 100$  and 2.00 for  $N = 1000$ .

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 3 MARCH, 1949

### The Configuration of Real Polymer Chains\*

PAUL J. FLORY  
*Department of Chemistry, Cornell University, Ithaca, New York*  
(Received August 23, 1948)

The average configuration of polymer molecules in solution is markedly influenced by the obvious requirement, ordinarily disregarded in problems relating to molecular configuration, that two elements of the molecule are forbidden from occupying the same location in space. The influence of spatial “interferences” between different segments of the molecule on its average configuration has been investigated by statistical and thermodynamic methods.

It is shown that if the average linear dimension of a polymer chain is to be taken proportional to a power of the chain length, that power must be greater than the value 0.50 previously deduced in the conventional “random flight” treatment of molecular configuration. This power should approach 0.60 for long chain molecules in good solvents. With increase in size of the solvent molecule, the influence of

interference on molecular configuration diminishes, vanishing entirely in the extreme case of a solvent which is also a high polymer. The effect of a heat of interaction between solvent and polymer may also be incorporated quantitatively in the theory. A positive heat of mixing (poor solvent) tends to offset the expansive influence of interference, and the exponent referred to above tends to approach 0.50. The results are of foremost significance in the interpretation of the intrinsic viscosity and its dependence on the polymer constitution and on the solvent. It is pointed out that the spatial dimensions of the irregularly coiled polymer molecule cannot be correlated directly with hindrance to rotation about chain bonds, unless the expansion of the configuration due to interference and the effects of the heat of dilution are first of all taken into account.

2021-02-01

Surface Engineering

12



## Nobel Prize in Chemistry 1974

For predicting the "spatial configuration of macromolecular chains".



Paul Flory

2021-02-01

Surface Engineering

13



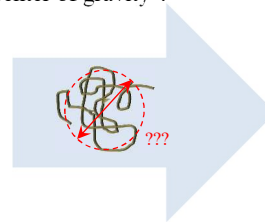
## The Size of a Coil

So what is now the size of a polymer molecule?

The physical size of a coil is often described by the *radius of gyration*  $R_g$ , which is "the mean squared distance of each point on the object from its center of gravity".

For a random walk, one can relate  $R_g$  to  $R$  by:

$$R_g = R \left[ \frac{1}{6} \right]^{1/2}$$



Note that  $R_g$  is indeed a radius, so the diameter is  $2R_g$ .

Experimental data (like light scattering) will tend to give the *hydrodynamic radius*, which is not the same thing as  $R_g$  but similar in magnitude.

Whatever parameter we use it will be proportional to the end-to-end distance, so  $R$  (or  $R_F$ ) is a characteristic length that represents the size of the polymer!

2021-02-01

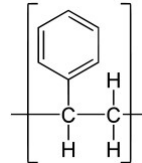
Surface Engineering

14



## Demonstration: Good Solvent

How much polystyrene can fit in a beaker?



2021-02-01

Surface Engineering

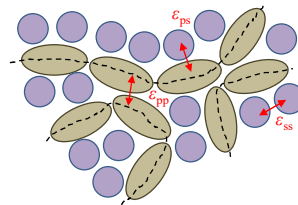
15



## Interactions with a Solvent

We looked at entropic effects of chain configuration and excluded volume. In a solvent we also need to consider the energy of the molecular interactions (non-covalent):

- Polymer and solvent ( $\epsilon_{ps}$ ).
- Polymer and polymer ( $\epsilon_{pp}$ ).
- Solvent and solvent ( $\epsilon_{ss}$ ).



Intuitively, it is clear that polymers will occupy a larger volume if they “like” the solvent. (Unless the solvent likes itself very much...)

If interactions between polymer and solvent are not favored (or if the polymer likes itself very much) we expect the polymer to occupy a smaller volume.

2021-02-01

Surface Engineering

16





## The Number of Interactions

Assume there are  $z$  “contact points” between a segment of a polymer or a solvent molecule and that only nearest neighbors count (regular solution model).

We have  $N$  segments (each with volume  $v$ ) within a volume  $r^3$ . Assume the probability that a neighbor of a polymer segment is another polymer segment is equal to the volume fraction of polymer segments  $Nv/r^3$ . We have  $Nz$  contact points to the polymer in total, so the number of polymer-polymer interactions is:

$$n_{pp} = \frac{Nz}{2} \times \frac{Nv}{r^3} = \frac{zvN^2}{2r^3}$$

We divide by two because otherwise we count the same interaction twice! The volume fraction of solvent is  $1 - Nv/r^3$  so the number of polymer-solvent interactions is:

$$n_{ps} = Nz \left[ 1 - \frac{Nv}{r^3} \right]$$

We can write the number of solvent-solvent interactions as:

$$n_{ss} = n_0 - n_{pp} - n_{ps} = n_0 - Nz \left[ 1 - \frac{Nv}{r^3} \right] - \frac{zvN^2}{2r^3}$$

Here  $n_0$  is the number of solvent-solvent interactions in the absence of the polymer.

2021-02-01

Surface Engineering

17



## A Single Solvent Interaction Parameter

Now we can write the total interaction energy:

$$\begin{aligned} U_{\text{int}} &= n_{pp}\epsilon_{pp} + n_{ps}\epsilon_{ps} + n_{ss}\epsilon_{ss} = \\ &= \frac{zvN^2}{2r^3}\epsilon_{pp} + zN \left[ 1 - \frac{vN}{r^3} \right] \epsilon_{ps} + \left[ n_0 - \frac{zvN^2}{2r^3} - zN \left[ 1 - \frac{vN}{r^3} \right] \right] \epsilon_{ss} = \\ &= \frac{zvN^2}{2r^3} [\epsilon_{pp} - 2\epsilon_{ps} + \epsilon_{ss}] + \underbrace{zN[\epsilon_{ps} - \epsilon_{ss}] + n_0\epsilon_{ss}}_{\text{constant}} \end{aligned}$$

Just as in the excluded volume argument by Flory, the critical parameter is  $r$ . Next, we introduce the dimensionless parameter:

$$\chi = -\frac{z}{2k_B T} [\epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps}]$$

So we can write the interaction energy as:

$$U_{\text{int}} = -\frac{k_B T v \chi N^2}{r^3} + \text{constant}$$

Note that higher  $\epsilon_{ps}$  makes  $\chi$  higher and that  $U_{\text{int}}$  is proportional to  $r^{-3}$ .

2021-02-01

Surface Engineering

18



## The Theta Solvent

Now recall Flory's excluded volume argument and introduce the solvent interactions as another parameter in the total free energy:

$$G(r) = \frac{3k_B T r^2}{2abN} + \frac{k_B T v N^2}{r^3} + \frac{k_B T v \chi N^2}{r^3} + \text{constant}$$

configurational  
entropy
excluded  
volume
solvent  
interactions

We can rewrite the excluded volume and solvent interaction terms as one:

$$G(r) = \frac{3k_B T r^2}{2abN} + \frac{k_B T v N^2}{r^3} [1 - \chi] + \text{constant}$$

For  $\chi = 1$  we can remove the entire second term! The result will be the random walk! The excluded volume effect perfectly compensates the solvent interaction energies. This is known as the *theta solvent* condition.

2021-02-01

Surface Engineering

19



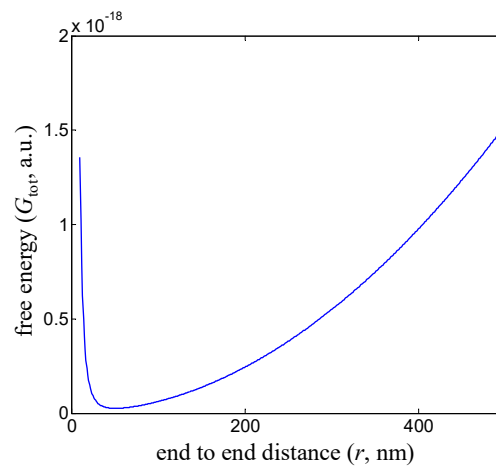
## The Solvent Effect

Plot of total free energy as a function of  $r$  for:

$$\begin{aligned} T &= 300 \text{ K} \\ N &= 1000 \\ a &= b = 1 \text{ nm} \\ v &= 1 \text{ nm}^3 \\ \chi &= 1/3 \end{aligned}$$

There is still an energy minimum at roughly the same value for  $r$ !

The solvent "does not do much" for modest values of  $\chi$ !



2021-02-01

Surface Engineering

20



## Energy Minimization in Solvent

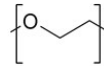
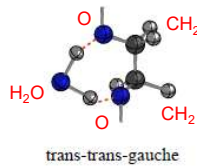
We can perform the same energy minimization calculation as for the Flory radius:

$$\frac{\partial G}{\partial r} = \frac{3k_B T r}{abN} - \frac{3k_B T v[1 - \chi]N^2}{r^4} \quad R_F = [abv[1 - \chi]]^{1/5} N^{3/5}$$

The “ordinary” Flory radius is clearly recovered for  $\chi = 0$ ! When  $\chi < 1$ , we still have the same scaling relation, that is  $R$  proportional to  $N^{3/5}$ .

So the solvent effectively changes the excluded volume effect. We can set  $\chi = 0$  as long as we keep in mind that  $v$  changes if you change solvent.

Actually even  $a$  and  $b$  can change with solvent! For instance, hydrogen bonding locks subsequent ether oxygens in poly(ethylene glycol) at  $a = 0.28$  nm.



Oosterhelt et al.  
*New Journal of Physics* **1999**, 1, 6.

2021-02-01

Surface Engineering

21



## Exercise 4.1

A polymer has monomer length 0.5 nm, Kuhn length 1 nm and excluded volume  $0.1 \text{ nm}^3$  in a good solvent. Estimate the polymer volume fraction inside a coil in solution for  $N = 100$  and  $N = 1000$ . (You need to somehow express the volume of monomers and estimate the total volume that the coil occupies.)

2021-02-01

Surface Engineering

22



## Exercise 4.1

The volume fraction of polymer inside its own coil is approximately:

$$\phi = \frac{Na^3}{R_F^3} = \frac{Na^3}{[abv]^{1/5}N^{3/5}]^3} = a^{12/5}[bv]^{-3/5}N^{-4/5}$$

Note that we use  $a^3$  for the physical size of the monomer, but not for the excluded volume parameter since that contains solvent effects. This is the most accurate way with the information available!

The answers for the different  $N$ :

$$\phi = 0.5^{12/5}[1 \times 0.1]^{-3/5}100^{-4/5} = 0.018 \dots$$

$$\phi = 0.5^{12/5}[1 \times 0.1]^{-3/5}1000^{-4/5} = 0.0030 \dots$$

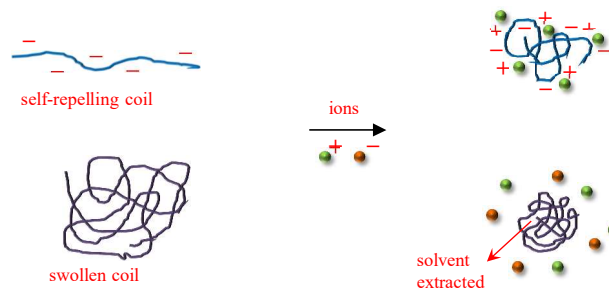
Important to note that the "density" of the coil decreases with  $N$ .



## Other Environmental Effects

The  $\chi$  parameter depends on environmental factors other than just solvent type!

One example is ionic strength: Self-repulsion of charged chains can be screened by counterions and hydrophilic polymers can be shrunk by osmotic pressure.



Some polymers can undergo chemical changes with pH (protonation), thereby changing their charge, so pH is another factor that can influence  $\chi$ .



## Globule States

When  $\chi > 1$  we cannot calculate  $R_F$  (negative number to the power of  $1/5$ ). The unfavorable interactions with the solvent overcome the excluded volume effect!

In essence this shows a phase transition: The polymer collapses into a compact *globule* state! The scaling relation for  $R$  is now to  $N^{1/3}$ .



coil ( $\chi < 1$ )

$$R \propto N^{3/5}$$



theta solvent ( $\chi = 1$ )

$$R \propto N^{1/2}$$



globule ( $\chi > 1$ )

$$R \propto N^{1/3}$$

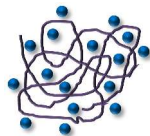
Consider the globule as spherical ball containing only polymer with volume  $V = Na^3$ . Since the end to end distance  $R$  must be proportional to the physical size we get  $R$  proportional to  $N^{1/3}$ .



## Critical Solution Temperatures

Higher temperature generally promotes mixing due to the entropy gain, but not if the solvent loses too much entropy due to limited bond configurations (hydrophobic effect).

The same holds for polymers: Some will go from solvated to collapsed upon increased temperature. They have a *lower critical solution temperature* instead of an upper temperature above which they are always solvated.



mixed phase



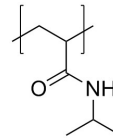
phase separated

Regardless, there will always be a *theta temperature* at which there is a transition and the solvent becomes a theta solvent.



## Demonstration: Thermoresponsive Polymer

Poly(N-isopropylacrylamide) undergoes a LCST transition at  $\sim 32^\circ\text{C}$  in water.



2021-02-01

Surface Engineering

27



## Polymers Attached to Surfaces

Consider a planar surface onto which the polymer can be attached in some way.

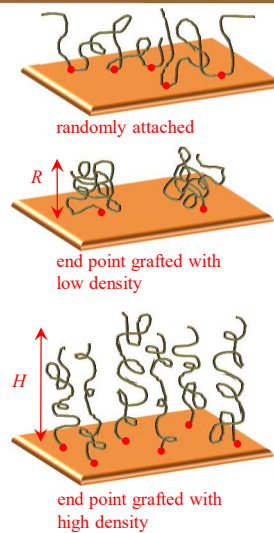
Randomly attached segments are hard to model...

Can we understand what happens when only the end point is attached? This is often the case in reality since the end group is chemically different!

Assume we have  $\Gamma$  polymers attached per unit area. (Same meaning of  $\Gamma$  as in previous lectures.)

If  $\Gamma < 1/R^2$  there is no interaction and the coils extend approximately a distance of  $R$ . Not so exciting...

But what happens when the grafting density is high so the coils overlap, i.e.  $\Gamma > 1/R^2$ ?



2021-02-01

Surface Engineering

28



## Finding the Brush Height

We start with the conformational entropy. Assume that the other endpoint is located just at the average extension  $H$ . We thus replace  $r$  with  $h$  in the free energy from stretching:

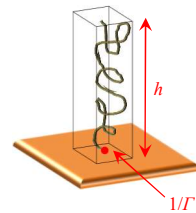
$$G_{\text{con}}(h) = \frac{3k_B T h^2}{2abN} + \text{constant}$$

Dealing with excluded volume is also quite simple. We can assume each coil occupies a volume of  $h/\Gamma$  (instead of  $r^3$ ). The grafting density  $\Gamma$  is fixed. The entropy loss from self avoidance is per segment:

$$\Delta S_{\text{seg}} = k_B \log \left( \frac{\frac{h}{\Gamma} - vN}{\frac{h}{\Gamma}} \right) = k_B \log \left( 1 - \frac{vN\Gamma}{h} \right) \approx - \frac{k_B v N \Gamma}{h}$$

So we get the free energy contribution as before:

$$G_{\text{vol}}(h) = \frac{k_B T v \Gamma N^2}{h}$$



2021-02-01

Surface Engineering

29



## The Solvent Effect for Brushes

Now recall the total interaction energy for solvent effects. Again, the only difference is that the volume is now  $h/\Gamma$  instead of  $r^3$ :

$$U_{\text{int}} = \frac{zv\Gamma N^2}{2h} [\epsilon_{\text{pp}} - 2\epsilon_{\text{ps}} + \epsilon_{\text{ss}}] + \underbrace{zN[\epsilon_{\text{ps}} - \epsilon_{\text{ss}}] + n_0\epsilon_{\text{ss}}}_{\text{constant with respect to } h}$$

We can define  $\chi$  just like before and write the interaction energy as:

$$U_{\text{int}} = - \frac{k_B T v \chi \Gamma N^2}{h} + \text{constant}$$

So we now have all three free energy terms for the brush:

$$G(h) = \frac{3k_B T h^2}{2abN} + \frac{k_B T v \Gamma N^2}{h} [1 - \chi] + \text{constant}$$

You should know what to do next...

2021-02-01

Surface Engineering

30



## The Alexander - de Gennes Brush

As before, we find the end to end distance that minimizes the free energy (now  $H$ ):

$$\frac{\partial G}{\partial h} = \frac{3k_B T h}{abN} - \frac{k_B T v \Gamma N^2}{h^2} [1 - \chi]$$

If we ignore the solvent parameter ( $\chi = 0$ ) we get the solution:

$$H = \left[ \frac{abv\Gamma}{3} \right]^{1/3} N$$

We see that  $H$  scales linearly with  $N$  (not like coils in solution).

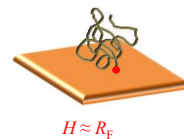
Also, we see that  $H$  is proportional to  $\Gamma^{1/3}$ , so brush height depends very weakly on grafting density (a bit counterintuitive).



## Sanity Check: Extreme Grafting Densities

Let us see what happens when the coils are barely overlapping:  $\Gamma = R_F^{-2}$

$$H = \left[ \frac{abv}{3[abv]^{1/5} N^{3/5}} \right]^{1/3} N = \left[ \frac{1}{3} \right]^{1/3} [abv]^{1/5} N^{3/5} = \left[ \frac{1}{3} \right]^{1/3} R_F$$



Almost  $H = R_F$  which makes sense, but different scaling with  $N$ .

Highest possible grafting density must correspond to monomer area:  $\Gamma = a^{-2}$

$$H = \left[ \frac{abv}{3a^2} \right]^{1/3} N = \left[ \frac{1}{3} \right]^{1/3} \left[ \frac{bv}{a} \right]^{1/3} N$$

As long as  $b$  is comparable to  $a$  and  $v$  comparable to  $a^3$  we get  $H$  comparable to  $aN$  (contour length) so everything seems fine.







## Brush Density

We can calculate the volume fraction  $\Phi$  inside the brush.

The volume of one strand is  $Na^3$ .

The volume occupied of one coil is  $H/\Gamma$  so:

$$\Phi = \frac{\Gamma Na^3}{H} = \frac{\Gamma Na^3}{\left[\frac{abv\Gamma}{3}\right]^{1/3} N} = \frac{a^{8/3}\Gamma^{2/3}}{\left[\frac{bv}{3}\right]^{1/3}}$$

Depends on grafting density but not  $N$ !

Completely different compared to the monomer density inside a coil in solution!

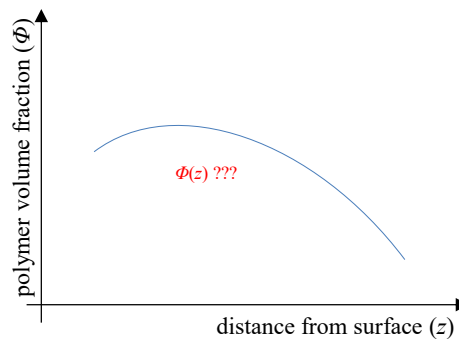


## Model Limits

The Alexander - de Gennes brush is *strongly stretched*. We assume the opposite end of the polymer is at the “top” of the brush! This leads to some problems:

- Scaling relation as proportional to  $N$  is only valid if  $\Gamma$  is high.
- Monomer *density profile* not accurate.

$$\int_0^\infty \frac{\Phi}{a^3} dz = \Gamma N$$

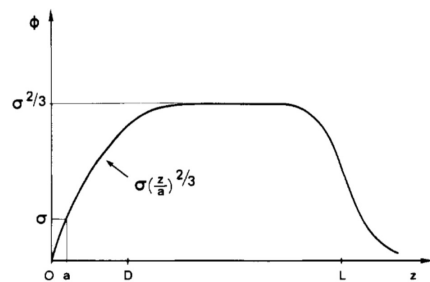




## Monomer Density Profiles

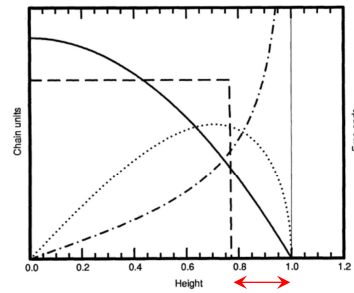
The de Gennes “step function” height multiplied by 1.3 gives the end point of the more accurate parabolic profile (derived by Milner).

Strictly speaking the brush height is not so easy to define...



**Figure 6.** Concentration profile for a grafted layer immersed in a good solvent in the overlapping regime.

de Gennes  
*Macromolecules* **1980**, 13 (5), 1069-1075.



**Fig. 2.** Chain-unit density profiles  $\phi(z)$  for a “parabolic” brush (that is,  $\phi \ll 1$  so  $\mu \approx \phi$ ), and the step-function ansatz at equal coverage  $\sigma$  and chain length  $N$ . Also shown are end-density profiles for brushes with (dotted) and without (dot-dashed) solvent.

Milner  
*Science* **1991**, 251 (4996), 905-914.

2021-02-01

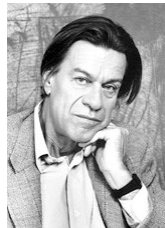
Surface Engineering

35



## Nobel Prize in Physics 1991

A guru in soft matter in general, especially known for his work with liquid crystals and polymer brushes.



Pierre-Gilles de Gennes

2021-02-01

Surface Engineering

36



## Reflections and Questions

---



2021-02-01

Surface Engineering

37



## Exercise 4.2

---

For a strongly stretched brush of poly(N-isopropylacrylamide) with  $M = 50 \text{ kg/mol}$ , each coil occupies  $500 \text{ \AA}^2$  on the surface. The monomer has length  $a = 3.0 \text{ \AA}$  (and can be written as  $\text{C}_6\text{H}_{10}\text{ON}$ ). The Kuhn length is  $5 \text{ nm}$  and you may assume  $\nu = a^3$ . What is the thickness of the brush?

→

62 nm

2021-02-01

Surface Engineering

38

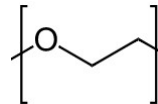


### Exercise 4.3

A brush of poly(ethylene glycol) with 20 kg/mol is 50 nm thick. The grafting density is  $0.28 \text{ nm}^{-2}$ . The monomer has length  $a = 0.28 \text{ nm}$  and the Kuhn length is 0.72 nm. What is the excluded volume parameter ( $v$ )? (Compare with  $a^3$ .)

→

$0.07 \text{ nm}^3$



### Exercise 4.4

A polymer brush has a thickness which is 80% of its maximum value. The grafting density is  $0.5 \text{ nm}^{-2}$  and the monomer length is 0.5 nm. You may assume that the excluded volume parameter is the cube of the monomer length. What is then the Kuhn length?

→

6.14 nm



### Exercise 4.5

One often says that when  $\Gamma < R_F^{-2}$  end point grafted polymers extend approximately a distance of  $R_F$ . Calculate the extension  $r$  from the surface under the assumption that the coil occupies a half-spherical volume and the free end is always on the surface on this sphere (express the answer in terms of  $R_F$ ).

→

$$[3/[2\pi]]^{1/5} R_F$$

