Polymers

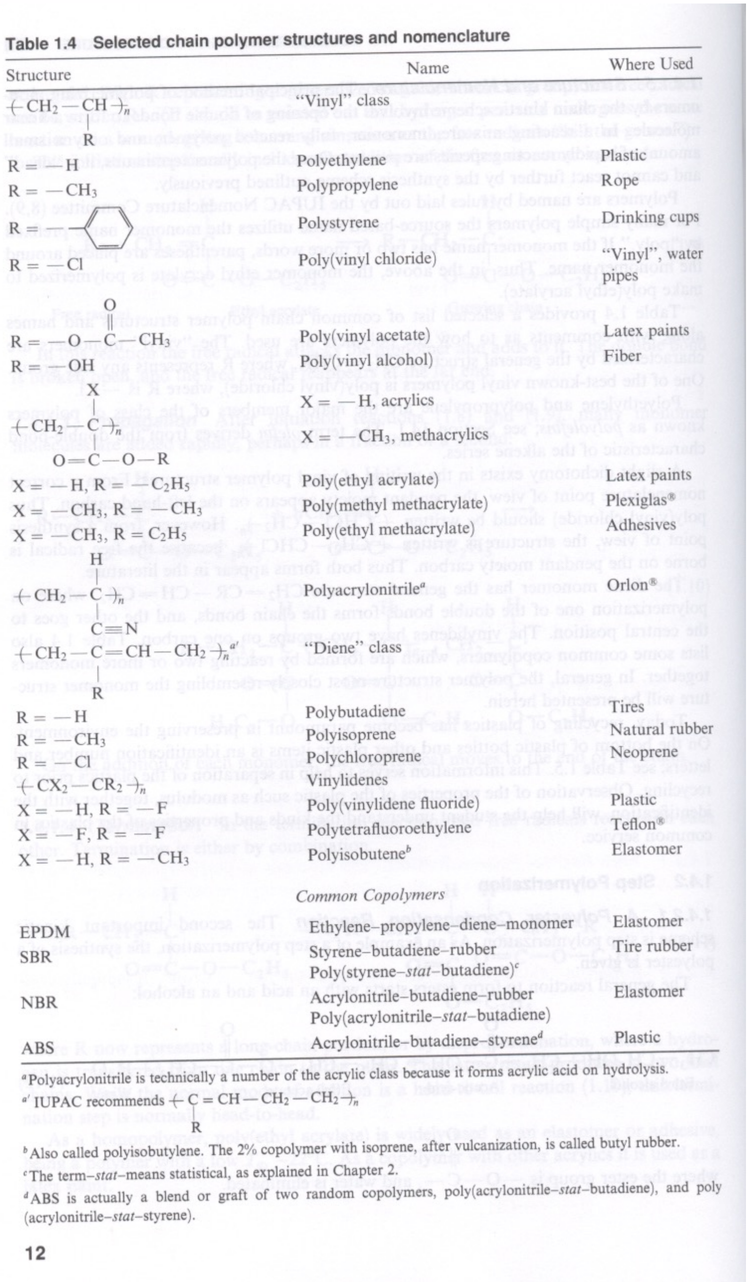


Table 1.4 Selected chain polymer structures and nomenclature

Structure	Name	Where Used
$\left(CH_2-\underset{\substack{\vert\\R}}{CH}\right)_n$	"Vinyl" class	
$R = -H$	Polyethylene	Plastic
$R = -CH_3$	Polypropylene	Rope
$R =$	Polystyrene	Drinking cups
$R = -Cl$	Poly(vinyl chloride)	"Vinyl", water pipes
$R = -O-\overset{\substack{O\\\Vert}}{C}-CH_3$	Poly(vinyl acetate)	Latex paints
$R = -OH$	Poly(vinyl alcohol)	Fiber
$\left(CH_2-\underset{\substack{\vert\\O=C-O-R}}{\overset{\substack{X\\\vert}}{C}}\right)_n$	$X = -H$, acrylics $X = -CH_3$, methacrylics	
$X = -H, R = -C_2H_5$	Poly(ethyl acrylate)	Latex paints
$X = -CH_3, R = -CH_3$	Poly(methyl methacrylate)	Plexiglas®
$X = -CH_3, R = C_2H_5$	Poly(ethyl methacrylate)	Adhesives
$\left(CH_2-\underset{\substack{\vert\\C\equiv N}}{\overset{\substack{H\\\vert}}{C}}\right)_n$	Polyacrylonitrile[a]	Orlon®
$\left(CH_2-\underset{\substack{\vert\\R}}{C}=CH-CH_2\right)_n$[a']	"Diene" class	
$R = -H$	Polybutadiene	Tires
$R = -CH_3$	Polyisoprene	Natural rubber
$R = -Cl$	Polychloroprene	Neoprene
$\left(CX_2-CR_2\right)_n$	Vinylidenes	
$X = -H, R = -F$	Poly(vinylidene fluoride)	Plastic
$X = -F, R = -F$	Polytetrafluoroethylene	Teflon®
$X = -H, R = -CH_3$	Polyisobutene[b]	Elastomer
	Common Copolymers	
EPDM	Ethylene–propylene–diene–monomer	Elastomer
SBR	Styrene–butadiene–rubber Poly(styrene–*stat*–butadiene)[c]	Tire rubber
NBR	Acrylonitrile–butadiene–rubber Poly(acrylonitrile–*stat*–butadiene)	Elastomer
ABS	Acrylonitrile–butadiene–styrene[d]	Plastic

[a] Polyacrylonitrile is technically a number of the acrylic class because it forms acrylic acid on hydrolysis.

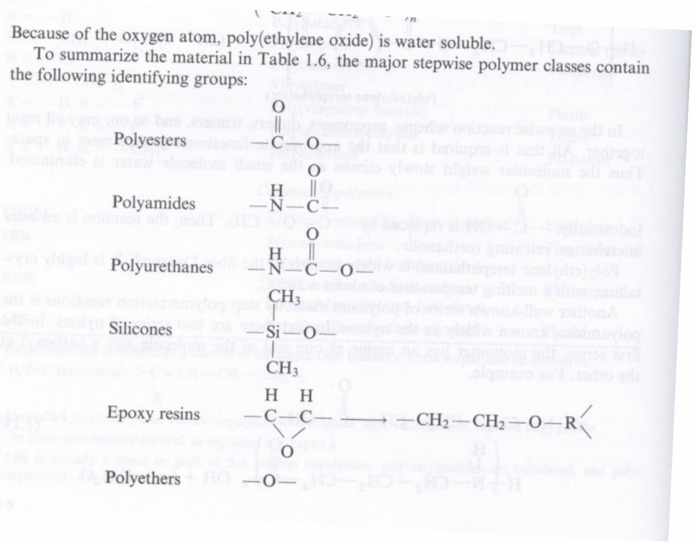
[a'] IUPAC recommends $\left(\underset{\substack{\vert\\R}}{C}=CH-CH_2-CH_2\right)_n$

[b] Also called polyisobutylene. The 2% copolymer with isoprene, after vulcanization, is called butyl rubber.

[c] The term–*stat*–means statistical, as explained in Chapter 2.

[d] ABS is actually a blend or graft of two random copolymers, poly(acrylonitrile–*stat*–butadiene), and poly (acrylonitrile–*stat*–styrene).

12



Because of the oxygen atom, poly(ethylene oxide) is water soluble.

To summarize the material in Table 1.6, the major stepwise polymer classes contain the following identifying groups:

Polyesters	$-\overset{\substack{O\\\Vert}}{C}-O-$
Polyamides	$-\overset{H}{N}-\overset{\substack{O\\\Vert}}{C}-$
Polyurethanes	$-\overset{H}{N}-\overset{\substack{O\\\Vert}}{C}-O-$
Silicones	$-\underset{\substack{\vert\\CH_3}}{\overset{\substack{CH_3\\\vert}}{Si}}-O-$
Epoxy resins	$\longrightarrow -CH_2-CH_2-O-R$
Polyethers	$-O-$

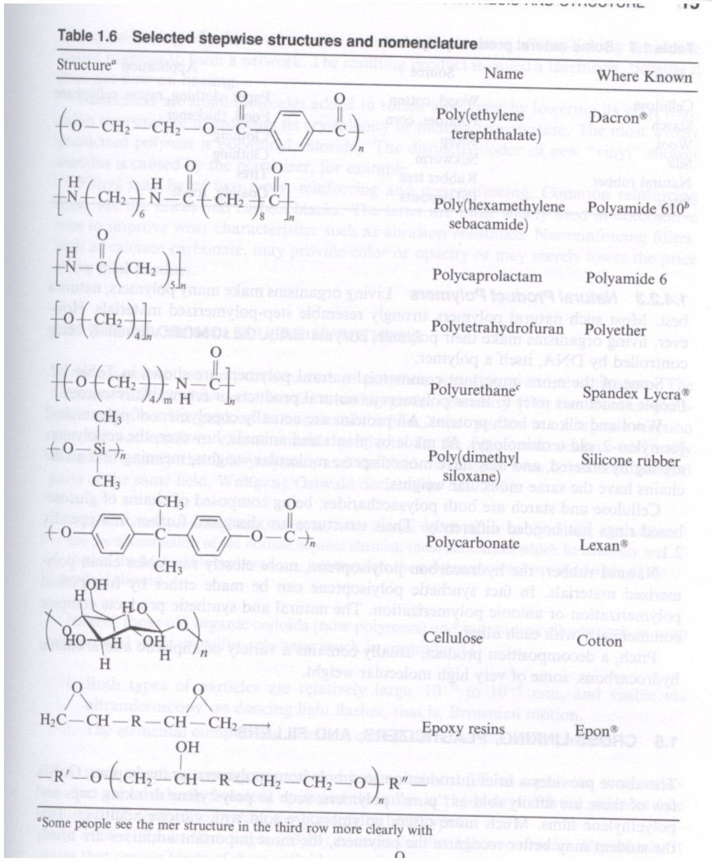


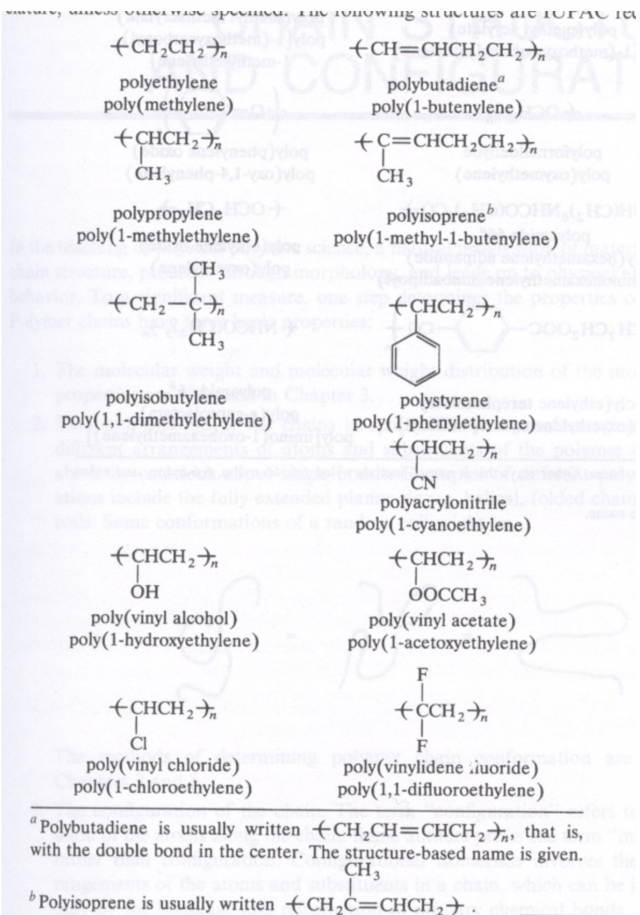
Table 1.6 Selected stepwise structures and nomenclature

Structure[a]	Name	Where Known
	Poly(ethylene terephthalate)	Dacron®
$\left[\overset{H}{N}\left(CH_2\right)_6\overset{H}{N}-\overset{\substack{O\\\Vert}}{C}\left(CH_2\right)_8\overset{\substack{O\\\Vert}}{C}\right]_n$	Poly(hexamethylene sebacamide)	Polyamide 610[b]
$\left[\overset{H}{N}-\overset{\substack{O\\\Vert}}{C}\left(CH_2\right)_5\right]_n$	Polycaprolactam	Polyamide 6
$\left[O\left(CH_2\right)_4\right]_n$	Polytetrahydrofuran	Polyether
$\left[\left(O\left(CH_2\right)_4\right)_m\underset{H}{N}-\overset{\substack{O\\\Vert}}{C}\right]_n$	Polyurethane[c]	Spandex Lycra®
$\left(O-\underset{\substack{\vert\\CH_3}}{\overset{\substack{CH_3\\\vert}}{Si}}\right)_n$	Poly(dimethyl siloxane)	Silicone rubber
	Polycarbonate	Lexan®
	Cellulose	Cotton
	Epoxy resins	Epon®

[a] Some people see the mer structure in the third row more clearly with

http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PolymerChemicalStructure.html

Polymers



clature, unless otherwise specified. The following structures are IUPAC rec

$-(CH_2CH_2)_n-$
polyethylene
poly(methylene)

$-(CH=CHCH_2CH_2)_n-$
polybutadiene[a]
poly(1-butenylene)

$-(\underset{CH_3}{CH}CH_2)_n-$
polypropylene
poly(1-methylethylene)

$-(\underset{CH_3}{C}=CHCH_2CH_2)_n-$
polyisoprene[b]
poly(1-methyl-1-butenylene)

$-(CH_2-\overset{CH_3}{\underset{CH_3}{C}})_n-$
polyisobutylene
poly(1,1-dimethylethylene)

polystyrene
poly(1-phenylethylene)

$-(\underset{CN}{CH}CH_2)_n-$
polyacrylonitrile
poly(1-cyanoethylene)

$-(\underset{OH}{CH}CH_2)_n-$
poly(vinyl alcohol)
poly(1-hydroxyethylene)

$-(\underset{OOCCH_3}{CH}CH_2)_n-$
poly(vinyl acetate)
poly(1-acetoxyethylene)

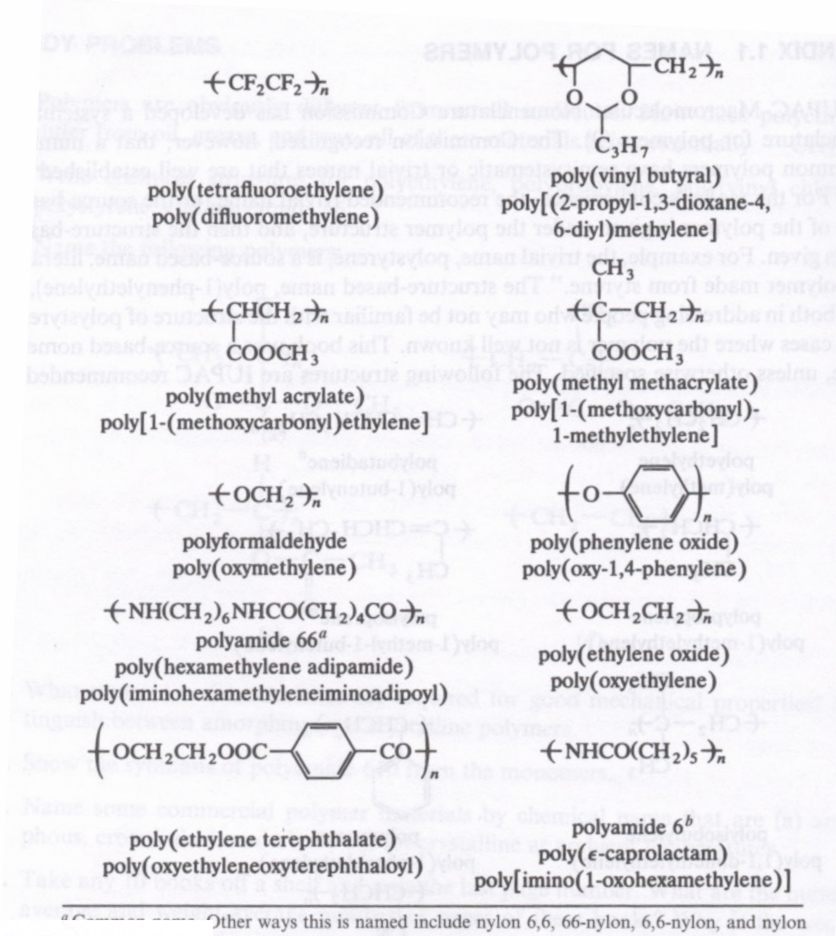
$-(\underset{Cl}{CH}CH_2)_n-$
poly(vinyl chloride)
poly(1-chloroethylene)

$-(\overset{F}{\underset{F}{C}}CH_2)_n-$
poly(vinylidene fluoride)
poly(1,1-difluoroethylene)

---

[a] Polybutadiene is usually written $-(CH_2CH=CHCH_2)_n-$, that is, with the double bond in the center. The structure-based name is given.

[b] Polyisoprene is usually written $-(CH_2\overset{CH_3}{C}=CHCH_2)_n-$



$-(CF_2CF_2)_n-$
poly(tetrafluoroethylene)
poly(difluoromethylene)

poly(vinyl butyral)
poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene]

$-(\underset{COOCH_3}{CH}CH_2)_n-$
poly(methyl acrylate)
poly[1-(methoxycarbonyl)ethylene]

$-(\overset{CH_3}{\underset{COOCH_3}{C}}-CH_2)_n-$
poly(methyl methacrylate)
poly[1-(methoxycarbonyl)-1-methylethylene]

$-(OCH_2)_n-$
polyformaldehyde
poly(oxymethylene)

poly(phenylene oxide)
poly(oxy-1,4-phenylene)

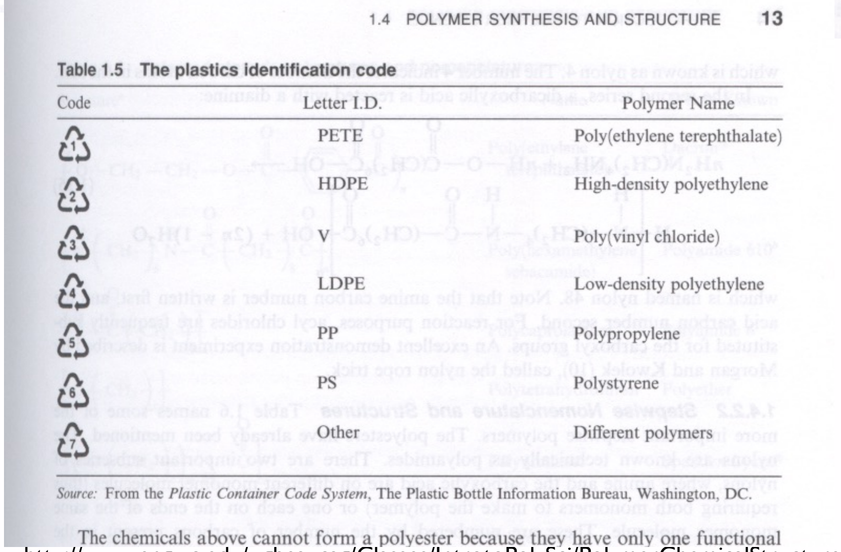
$-(NH(CH_2)_6NHCO(CH_2)_4CO)_n-$
polyamide 66[a]
poly(hexamethylene adipamide)
poly(iminohexamethyleneiminoadipoyl)

$-(OCH_2CH_2)_n-$
poly(ethylene oxide)
poly(oxyethylene)

poly(ethylene terephthalate)
poly(oxyethyleneoxyterephthaloyl)

$-(NHCO(CH_2)_5)_n-$
polyamide 6[b]
poly(ε-caprolactam)
poly[imino(1-oxohexamethylene)]

[a] Common name. Other ways this is named include nylon 6,6, 66-nylon, 6,6-nylon, and nylon



1.4 POLYMER SYNTHESIS AND STRUCTURE 13

Table 1.5 The plastics identification code

Code	Letter I.D.	Polymer Name
1	PETE	Poly(ethylene terephthalate)
2	HDPE	High-density polyethylene
3	V	Poly(vinyl chloride)
4	LDPE	Low-density polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	Other	Different polymers

Source: From the *Plastic Container Code System*, The Plastic Bottle Information Bureau, Washington, DC.

The chemicals above cannot form a polyester because they have only one functional

http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PolymerChemicalStructure.html

Polymers

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids, Vol. I"

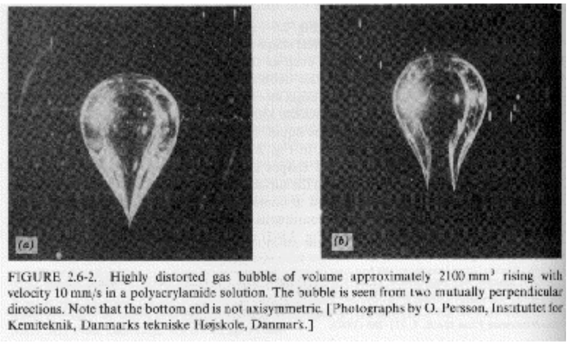
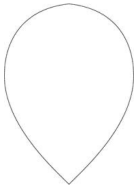
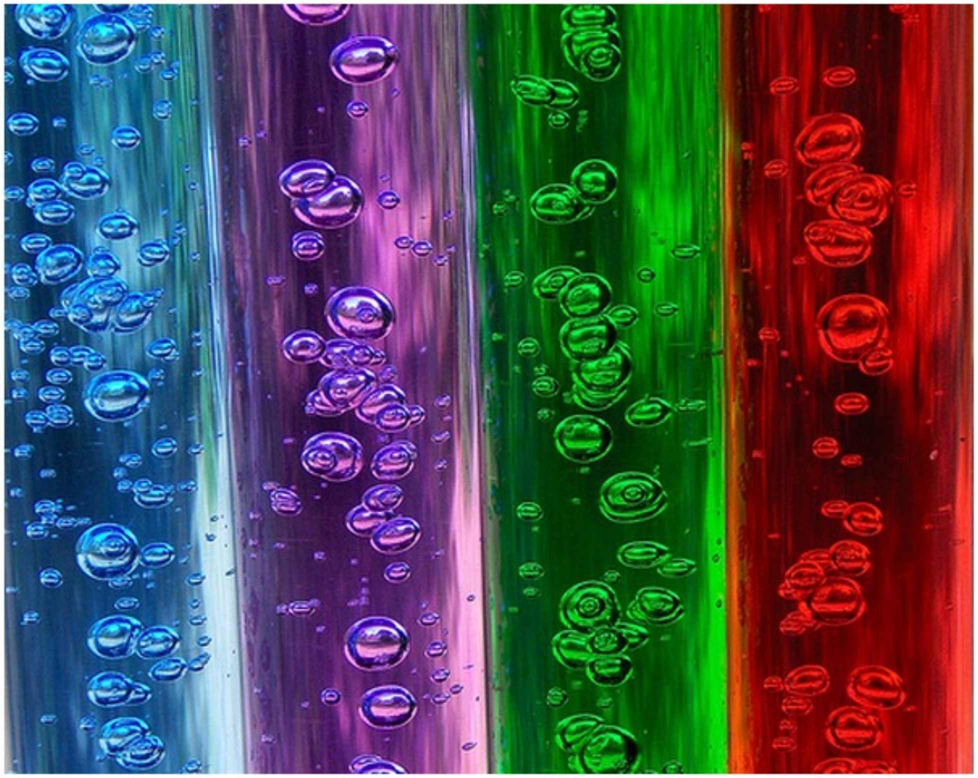


FIGURE 2.6-2. Highly distorted gas bubble of volume approximately 2100 mm^3 rising with velocity 10 mm/s in a polyacrylamide solution. The bubble is seen from two mutually perpendicular directions. Note that the bottom end is not axisymmetric. [Photographs by O. Persson, Instituttet for Kemiteknik, Danmarks tekniske Højskole, Danmark.]

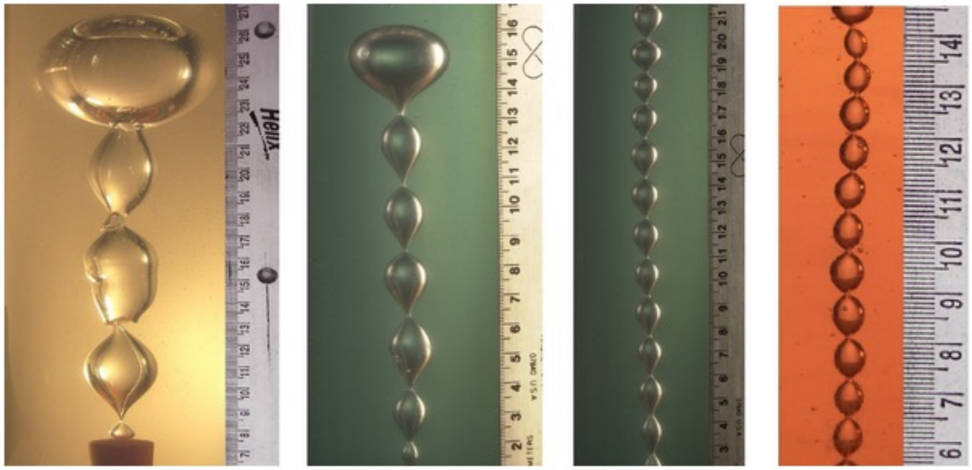


U. S. Navy Photograph

Transosonde balloon ready for launching.



Newtonian Fluid Bubbles



Bubbles in Polymer Solution

[Polymer Rheology](http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PolymerChemicalStructure.html)

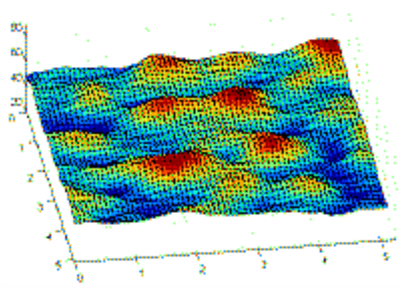
http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PolymerChemicalStructure.html

Polymers

Paul Flory [1] states that "…*perhaps the most significant structural characteristic of a long polymer chain… (is) its capacity to assume an enormous array of configurations.*"

Which are Polymers?

http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PicturesDNA.html



http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/What Does Searching Configurational Space Mean for Polymers.html

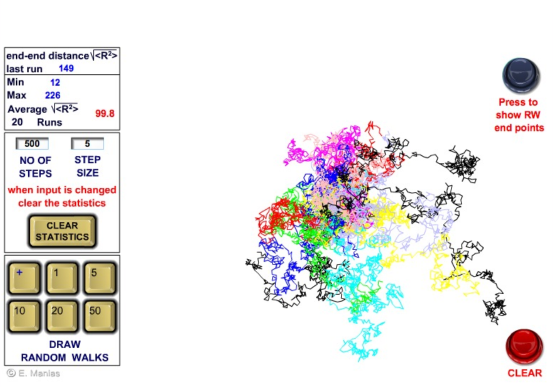
1) Principles of Polymer Chemistry, Flory PJ, (1953).

ww.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/WhatIsAPolymerPlastic.html

http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/MacroMolecularMaterials.html

Random Walk Generator (Manias Penn State)

http://zeus.plmsc.psu.edu/~manias/MatSE443/Study/7.html



end-end distance $\sqrt{<R^2>}$

last run 149

Min 12

Max 226

Average $\sqrt{<R^2>}$ 99.8

20 Runs

500 NO OF STEPS

5 STEP SIZE

when input is changed clear the statistics

-Polymers do not have a discrete size, shape or conformation.

-Looking at a single simulation of a polymer chain is of no use.

-We need to consider average features.

-Every feature of a polymer is subject to a statistical description.

-Scattering is a useful technique to quantify a polymer since it describes structure from a statistically averaged perspective.

Polymers

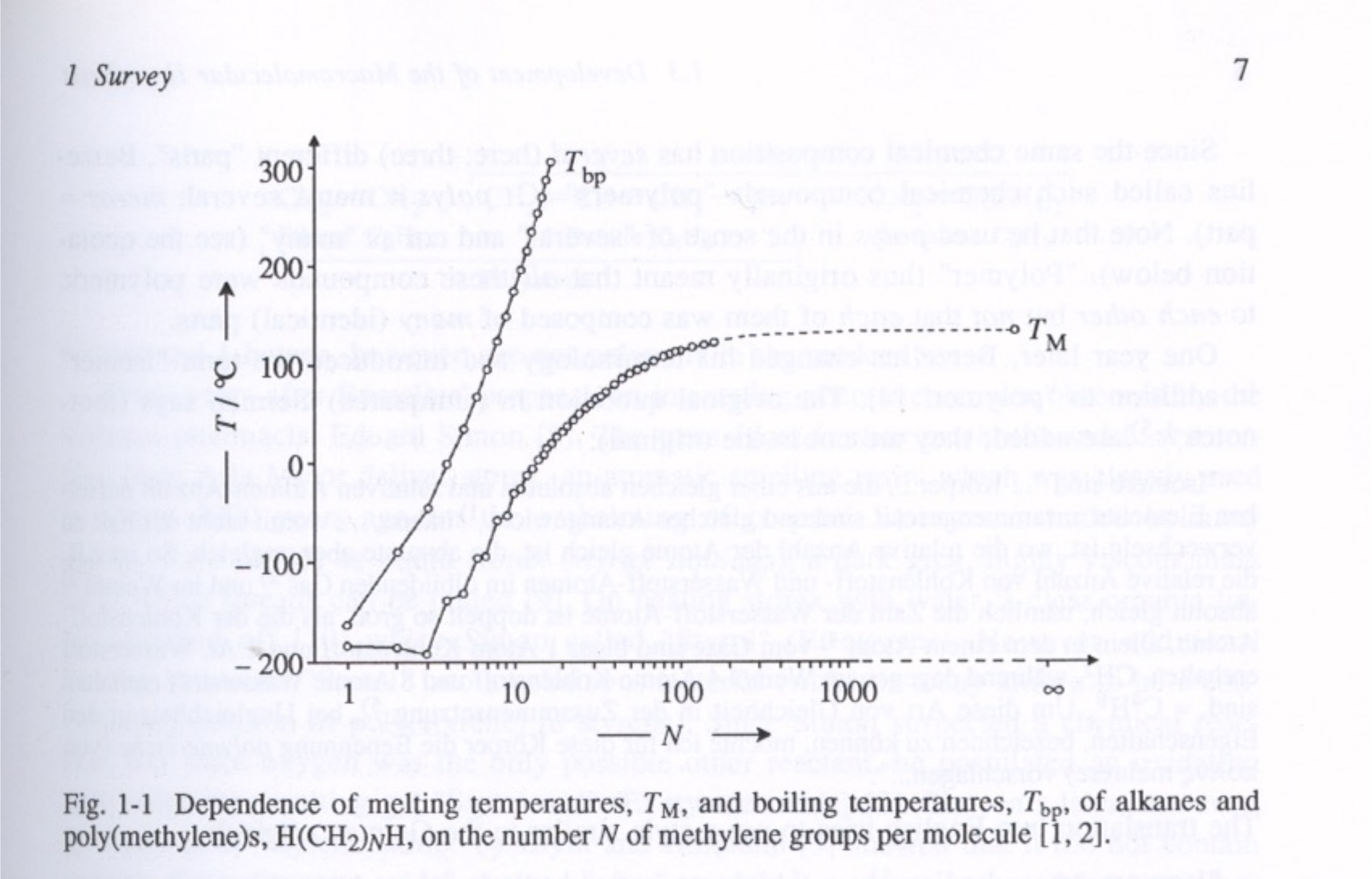

1 Survey 7

Fig. 1-1 Dependence of melting temperatures, T_M, and boiling temperatures, T_{bp}, of alkanes and poly(methylene)s, $H(CH_2)_NH$, on the number N of methylene groups per molecule [1, 2].

Polymers

Viscosity versus Rate of Strain

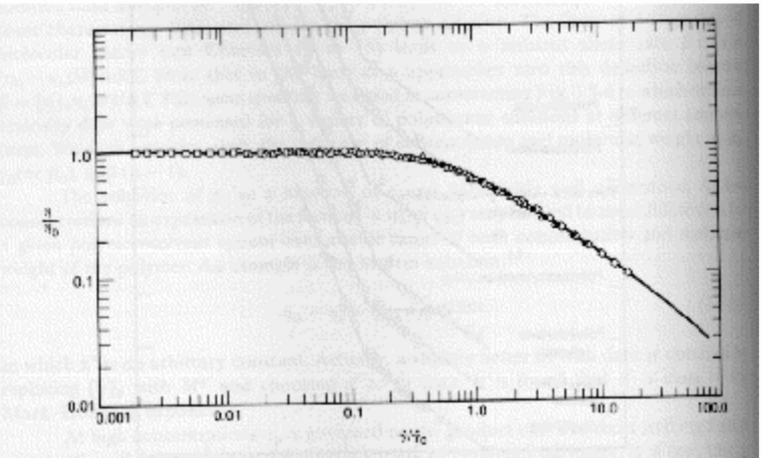


FIGURE 3.6-5. Composite plot of dimensionless viscosity η/η_0 versus dimensionless shear rate $\dot\gamma/\dot\gamma_0$, for several different concentrated polystyrene-*n*-butyl benzene solutions. Molecular weights varied from 1.6×10^5 to 2.4×10^6, concentrations from 0.255 to 0.55 g/cm^3, and temperatures from 303 to 333 K. [W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1-179 (1974).]

Zero Shear Rate Viscosity versus Concentration for Solutions

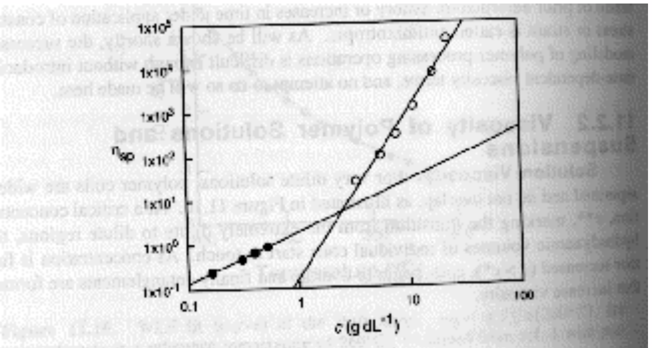


Figure 11.17. Concentration dependence of the specific viscosity of dilute and moderately concentrated solutions of cellulose acetate in dimethyl sulfoxide.^{3} The intersection of straight lines that are drawn through the dilute-solution (●) and concentrated-solution (○) data marks the critical concentration, c^* (ca. 3.7 g dL^{-1} in this case).

Zero Shear Rate Viscosity versus Molecular Weight

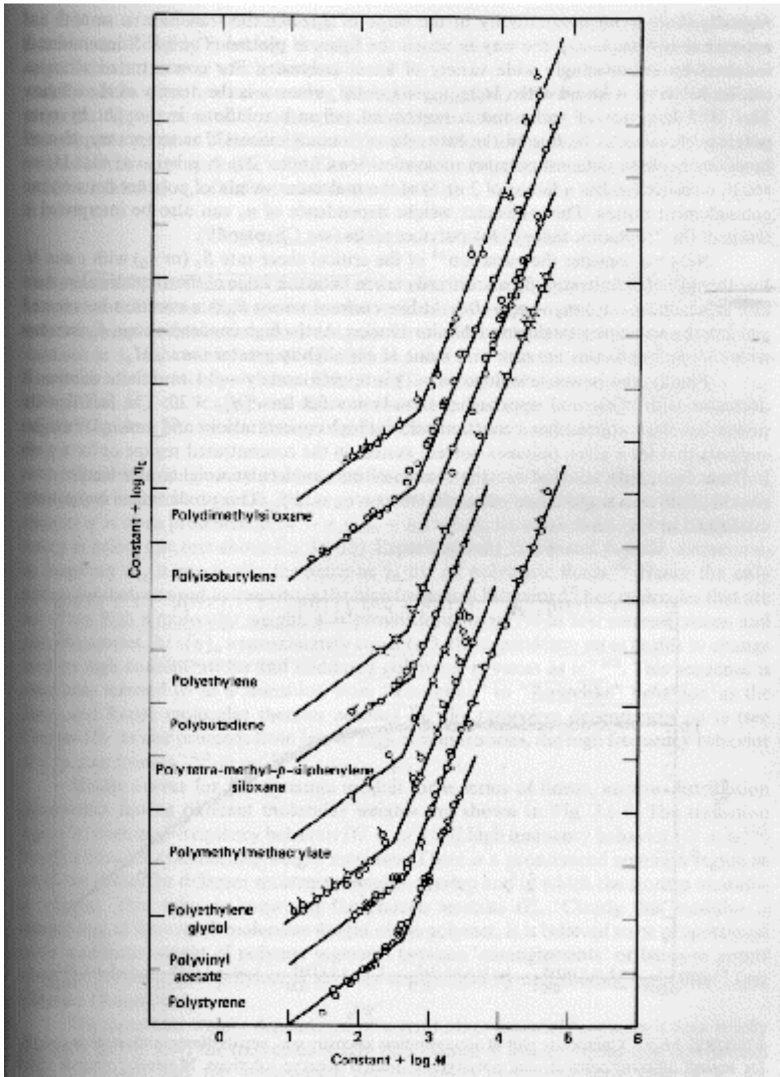


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261–357 (1968).]

From J. R. Fried,
"Polymer Science and Technology"

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids Vol. 1"

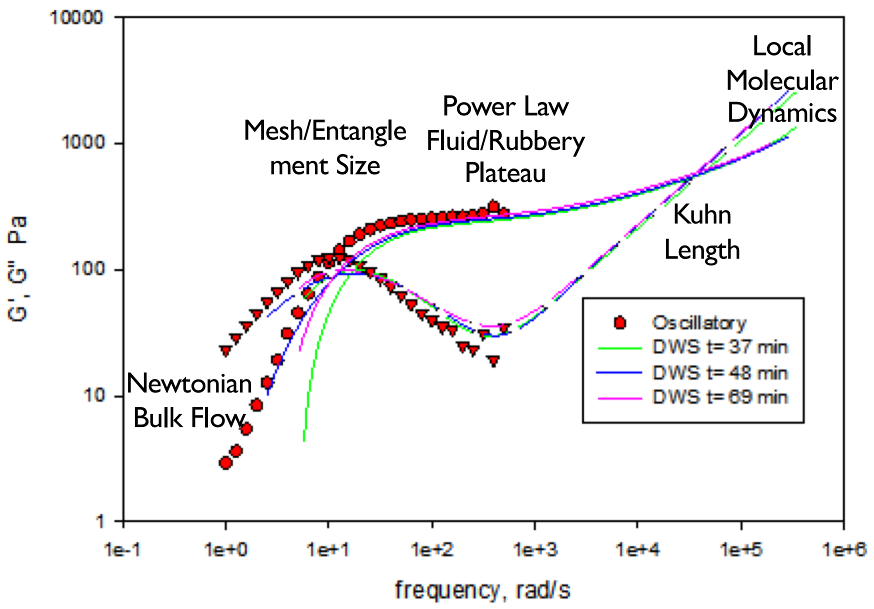
Polymers

If polymers are defined by dynamics why should we consider first statics?

Statistical Mechanics: Boltzmann (1896)
Statistical Thermodynamics: Maxwell, Gibbs (1902)

We consider the statistical average of a thermally determined structure, an equilibrated structure

Polymers are a material defined by dynamics and described by statistical thermodynamics



In a polymer melt, the viscous properties of Newtonian liquids combine with elastic forces. The latter contribute a real part to the dynamic shear compliance, to be identified with J_{e}^{0}:

$$J'(\omega \to 0) = J_{\mathrm{e}}^{0} \, . \tag{6.102}$$

Combining Eqs. (6.99) and (6.102) gives the dynamic shear compliance of polymeric fluids in the limit of low frequencies

$$J(\omega \to 0) = J_{\mathrm{e}}^{0} + \mathrm{i}\frac{1}{\eta_0 \omega} \, . \tag{6.103}$$

As we can see, η_0 and J_{e}^{0} show up directly and separately, in the limiting behavior of J' and J''.

The dynamic shear modulus follows as

$$\begin{aligned} G(\omega \to 0) &= \frac{1}{J(\omega \to 0)} = \frac{\eta_0 \omega}{\eta_0 \omega J_{\mathrm{e}}^{0} + \mathrm{i}} \\ &= \frac{\eta_0^2 \omega^2 J_{\mathrm{e}}^{0} - \mathrm{i}\eta_0 \omega}{(\eta_0 \omega J_{\mathrm{e}}^{0})^2 + 1} \, , \end{aligned} \tag{6.104}$$

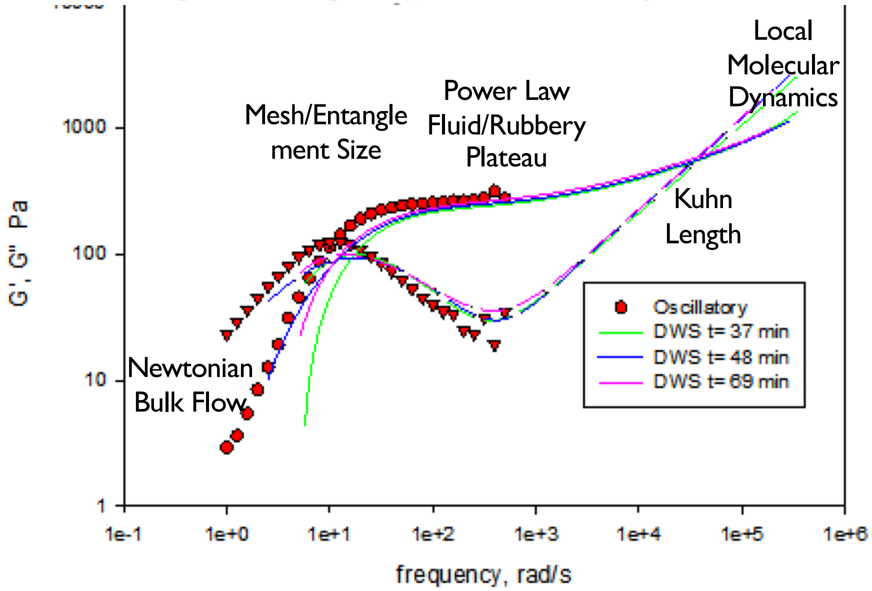
giving

$$G'(\omega \to 0) = J_{\mathrm{e}}^{0} \eta_0^2 \omega^2 \tag{6.105}$$

in agreement with Fig. 6.16, and

$$G''(\omega \to 0) = \eta_0 \omega \, . \tag{6.106}$$

We thus find characteristic power laws also for the storage and the loss modulus that again include J_{e}^{0} and η_0 in a well-defined way.



Synthetic Polymer Chain Structure
(A Statistical Hierarchy)

Synthetic Polymer Chain Structure
(A Statistical Hierarchy)

Consider that all linear polymer chains can be reduced to a step length and a free, universal joint
This is the Kuhn model, and the step length is called the Kuhn length, l_K

This is extremely easy to simulate
1)Begin at the origin, (0,0,0)
2)Take a step in a random direction to (i, j, k)
3)Repeat for N steps

On average for a number of these “random walks” we will find that the final position tends towards (0,0,0) since there is no preference for direction in a “random” walk

The walk does have a breadth (standard deviation), i.e. depending on the number of steps, N, and the step length l_K, the breadth of the walk will change.

l_K just changes proportionally the scale of the walk so
$<R^2>^{1/2} \sim l_K$

https://www.doitpoms.ac.uk/tlplib/polymerbasics/HTML5/Kuhn_randomwalk2.html

Synthetic Polymer Chain Structure
(A Statistical Hierarchy)

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l_K just changes proportionally the scale of the walk so
$<R^2>^{1/2} \sim l_K$

The chain is composed of a series of steps with no orientational relationship to each other.
So $<R> = 0$
$<R^2>$ has a value:

$$\langle R^2 \rangle = \sum_i \sum_j r_i \bullet r_j = \sum_i r_i \bullet r_i + \sum_i \sum_{j \neq i} r_i \bullet r_j$$

We assume no long-range interactions so that the second term can be 0.

$$\langle R^2 \rangle = N r^2$$

$<R^2>^{1/2} \sim N^{1/2}\, l_K$

https://www.doitpoms.ac.uk/tlplib/polymerbasics/HTML5/Kuhn_randomwalk2.html

Synthetic Polymer Chain Structure
(A Statistical Hierarchy)

$$<R^2>^{1/2} \sim N^{1/2}\, l_K$$

This function has the same origin as the function describing the root mean square distance of a diffusion pathway

$$<R^2>^{1/2} \sim t^{1/2}(2D)^{1/2}$$

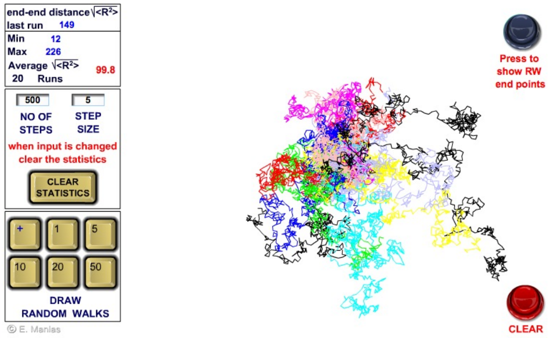
So, the Kuhn length bears some resemblance to the diffusion coefficient

And the random walk polymer chain bears some resemblance to Brownian Motion

The random chain is sometimes called a "Brownian Chain", a drunken walk, a random walk, a Gaussian Coil or Gaussian Chain among other names.

Random Walk Generator (Manias Penn State)

http://zeus.plmsc.psu.edu/~manias/MatSE443/Study/7.html



end-end distance $\sqrt{<R^2>}$
last run 149
Min 12
Max 226
Average $\sqrt{<R^2>}$ 99.8
20 Runs

NO OF STEPS: 500
STEP SIZE: 5

when input is changed clear the statistics

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The Primary Structure for Synthetic Polymers

Worm-like Chain
Freely Jointed Chain
Freely Rotating Chain
Rotational Isomeric State Model Chain (RISM)
Persistent Chain
Kuhn Chain

These refer to the local state of the polymer chain.

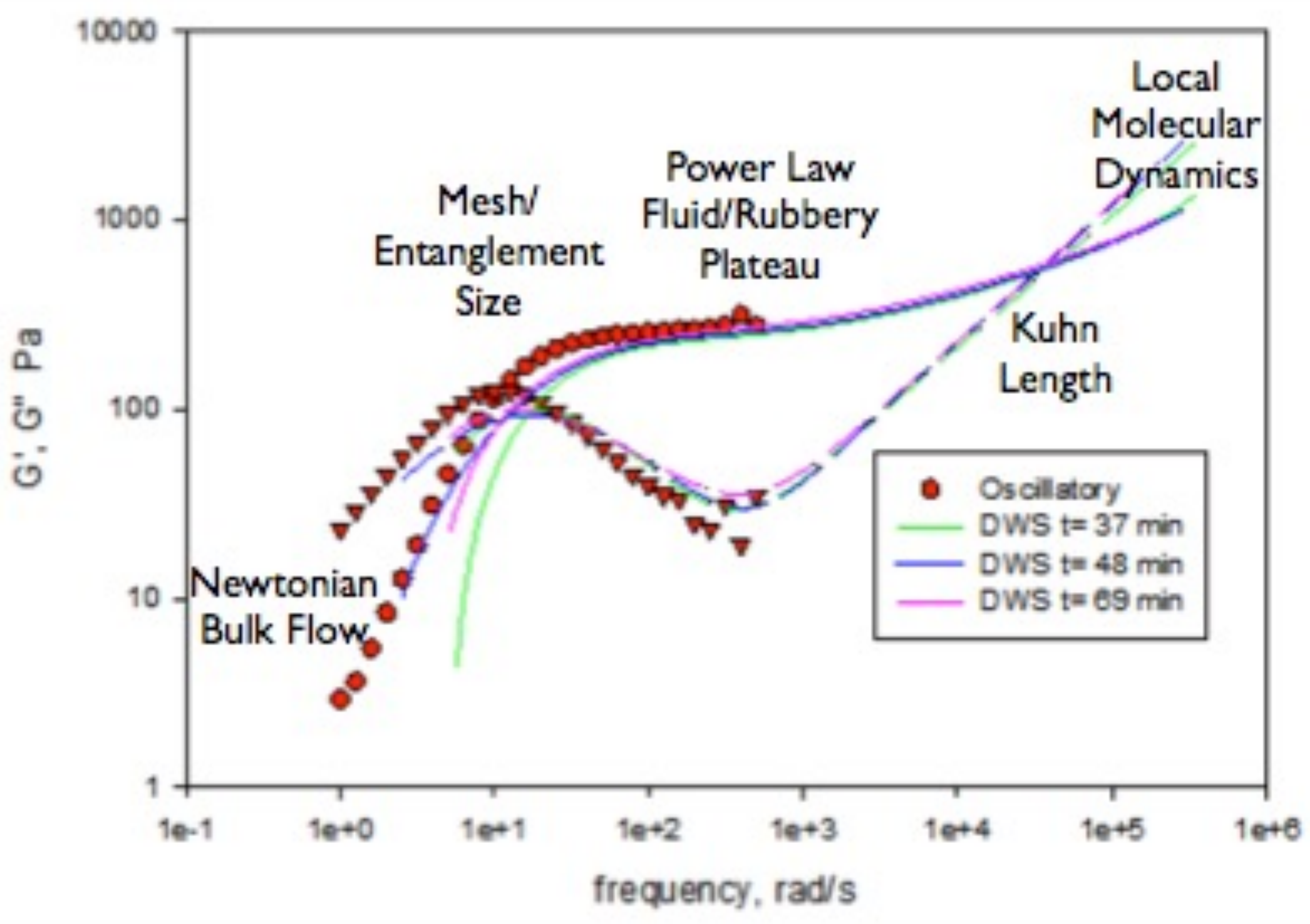
Generally, the chain is composed of chemical bonds that are directional, that is they are rods connected at their ends.

These chemical steps combine to make an effective rod-like base unit, the persistence length, for any synthetic polymer chain (this is larger than the chemical step).

The persistence length can be measured in scattering or can be inferred from rheology through the Kuhn length

$$l_K = 2\ l_P$$

The Primary Structure for Synthetic Polymers



The synthetic polymer is composed of linear bonds, covalent or ionic bonds have a direction.

Coupling these bonds into a chain involves some amount of memory of this direction for each coupled bond.

Cumulatively this leads to a persistence length that is longer than an individual bond.

Observation of a persistence length requires that the persistence length is much larger than the diameter of the chain. Persistence can be observed for worm-like micelles, synthetic polymers, DNA but not for chain aggregates of nanoparticles, strings or fibers where the diameter is on the order of the persistence length.

http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/PicturesDNA.html

The Gaussian Chain

Boltzman Probability
For a Thermally Equilibrated System

$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability
For a Chain of End-to-End Distance *R*

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

By Comparison, The Energy to stretch a Thermally Equilibrated Chain Can be Written

$$E = kT\frac{3R^2}{2nl_K^2}$$

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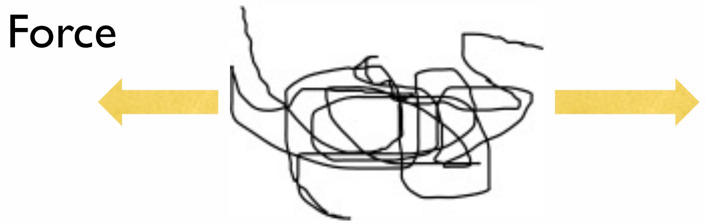


$$F = \frac{dE}{dR} = \frac{3kT}{nl_K^2}R = k_{spr}R$$

Assumptions:
-Gaussian Chain
-Thermally Equilibrated
-Small Perturbation of Structure (so it is still Gaussian after the deformation)

The Gaussian Chain

Boltzman Probability
For a Thermally Equilibrated System

$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability
For a Chain of End to End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

Use of P(*R*) to Calculate Moments:

$$\left\langle R^n \right\rangle = \int_{-\infty}^{\infty} R^n P(R)\,dR$$

Mean is the 1’st Moment:

$$\left\langle R \right\rangle = \int_{-\infty}^{\infty} R P(R)\,dR = 0$$

The Gaussian Chain

Boltzman Probability
For a Thermally Equilibrated System

$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability
For a Chain of End-to-End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

Use of P(*R*) to Calculate Moments:

$$\left\langle R^n \right\rangle = \int_{-\infty}^{\infty} R^n P(R)\, dR$$

Mean is the 1’st Moment:

$$\left\langle R \right\rangle = \int_{-\infty}^{\infty} R P(R)\, dR = 0$$

This is a consequence of symmetry of the
Gaussian function about 0.

The Gaussian Chain

Boltzman Probability
For a Thermally Equilibrated System

$$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability
For a Chain of End-to-End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

Use of P(R) to Calculate Moments:

$$\left\langle R^n \right\rangle = \int_{-\infty}^{\infty} R^n P(R)\, dR$$

Mean Square is the 2'ndMoment:

$$\left\langle R^2 \right\rangle = \int_{-\infty}^{\infty} R^2 P(R)\, dR \equiv \sum_{i=0}^{N} \sum_{j=0}^{N} r_i \bullet r_j = N r^2$$

The Gaussian Chain

Gaussian Probability
For a Chain of End-to-End Distance *R*

$$P(R)=\left(\frac{3}{2\pi\sigma^2}\right)^{3/2}\exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

Mean Square is the 2’ndMoment:

$$\left\langle R^2\right\rangle=\left(\frac{3}{2\pi\sigma^2}\right)^{3/2}\int_{-\infty}^{\infty}R^2\exp\left(-\frac{3R^2}{2\sigma^2}\right)dR$$

There is a problem to solve this integral since we can solve
an integral of the form k exp(k*R*) d*R*
R exp(kR^2) d*R* but not R^2 exp(kR^2) d*R*

There is a trick to solve this integral that is of importance
to polymer science and to other random systems that
follow the Gaussian distribution.

$$\left\langle R^2 \right\rangle = \frac{\int_{-\infty}^{\infty} R^2 P_G(R)dR}{\int_{-\infty}^{\infty} P_G(R)dR} = \frac{\int_{-\infty}^{\infty} R^2 \exp\left(\frac{R^2}{k^2}\right)dR}{\int_{-\infty}^{\infty} \exp\left(\frac{R^2}{k^2}\right)dR} \qquad (3)$$

These integrals require a trick to solve. First the integral is squared in x and y:

$$G(\alpha) = \int_{-\infty}^{\infty} \exp\left(-\alpha x^2\right)dx$$

$$\left(G(\alpha)\right)^2 = \int_{-\infty}^{\infty} \exp\left(-\alpha x^2\right)dx \int_{-\infty}^{\infty} \exp\left(-\alpha y^2\right)dy = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp\left(-\alpha\left(y^2 + x^2\right)\right)dy$$

Then Cartesian coordinates are replaced with circular coordinates, r and θ,

$$\left(G(\alpha)\right)^2 = \int_0^{\infty} rdr \int_0^{2\pi} d\theta \exp\left(-\alpha r^2\right) = 2\pi \int_0^{\infty} rdr \exp\left(-\alpha r^2\right)$$

$$= \frac{-2\pi}{2\alpha} \int_0^{\infty} -2\alpha r dr \exp\left(-\alpha r^2\right) = \frac{-\pi}{\alpha}\left[\exp\left(-\alpha r^2\right)\right]_0^{\infty} = \frac{\pi}{\alpha}$$

The integral in the numerator can be solved by another trick,

$$H(\alpha) = \int_{-\infty}^{\infty} x^2 \exp\left(-\alpha x^2\right)dx = -\frac{dG(\alpha)}{d\alpha}$$

and since $G(\alpha) = (\pi/\alpha)^{1/2}$, then $H(\alpha) = \frac{\pi^{1/2}}{2\alpha^{3/2}}$ so, with $\alpha = 1/k^2$ and $x = R$,

$$\left\langle R^2 \right\rangle = \frac{\int_{-\infty}^{\infty} R^2 \exp\left(\frac{R^2}{k^2}\right)dR}{\int_{-\infty}^{\infty} \exp\left(\frac{R^2}{k^2}\right)dR} = \frac{H(\alpha)}{G(\alpha)} = \frac{k^3\pi^{1/2}/2}{k\pi^{1/2}} = \frac{k^2}{2} \qquad (4)$$

http://www.eng.uc.edu/~gbeaucag/Classes/Properties/GaussianProbabilityFunctionforEnd.pdf

The Gaussian Chain

Gaussian Probability
For a Chain of End to End Distance R

$$P(R)=\left(\frac{3}{2\pi\sigma^2}\right)^{3/2}\exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

Mean Square is the 2'nd Moment:

$$\langle R^2\rangle=\left(\frac{3}{2\pi\sigma^2}\right)^{3/2}\int_{-\infty}^{\infty}R^2\exp\left(-\frac{3R^2}{2\sigma^2}\right)dR=\sigma^2\equiv nl_K^2$$

So, the Gaussian function for a polymer coil is:

$$\langle R^2\rangle=\left(\frac{3}{2\pi nl_K^2}\right)^{3/2}\int_{-\infty}^{\infty}R^2\exp\left(-\frac{3R^2}{2nl_K^2}\right)dR$$

The Gaussian Chain

$$\left\langle R^2 \right\rangle = n l_K^2$$

Means that the coil size scales with $n^{1/2}$

Or

Mass ~ n ~ Size^2

Generally, we say that

Mass ~ Size^{df}

Where d_f is the mass fractal dimension

A Gaussian Chain is a kind of 2-dimensional object like a disk.

The Gaussian Chain

$$\left\langle R^2 \right\rangle = n l_K^2$$

A Gaussian Chain is a kind of 2-dimensional object like a disk.

The difference between a Gaussian Chain and a disk lies in other dimensions of the two objects.

Consider an electric current flowing through the chain, it must follow a path of n steps. For a disk, the current follows a path of $n^{1/2}$ steps since it can short circuit across the disk. If we call this short circuit path p we have defined a connectivity dimension c such that:

$$p^c \sim n$$

And c has a value of 1 for a linear chain and 2 for a disk

The Gaussian Chain

$$\left\langle R^2 \right\rangle = n l_K^2$$

A Gaussian Chain is a kind of 2-dimensional object like a disk.
A linear Gaussian Chain has a connectivity dimension of 1 while
the disk has a connectivity dimension of 2.

The minimum path p is a fractal object and has a dimension, $d_{\min}$ so that,

$$p \sim R^{d_{\min}}$$

For a Gaussian Chain $d_{\min} = 2$ since p is the path n
For a disk $d_{\min} = 1$ since the short circuit is a straight line.

We find that $d_f = c\, d_{\min}$

There are other scaling dimensions, but they can all be related to two
independent structural scaling dimensions such as c and $d_{\min}$
or $d_{\min}$ and d_f

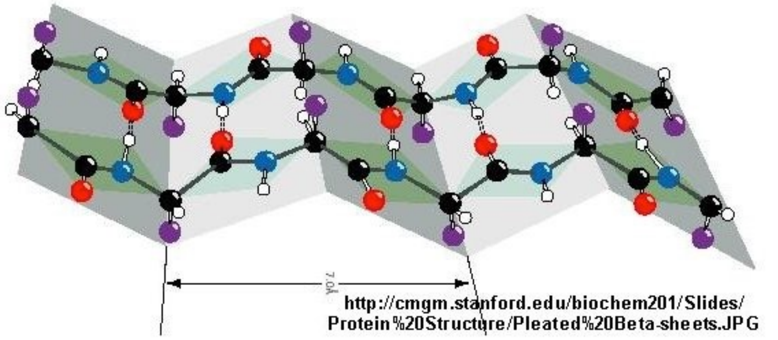
Disk

$$d_f = 2$$

$$d_{\min} = 1$$

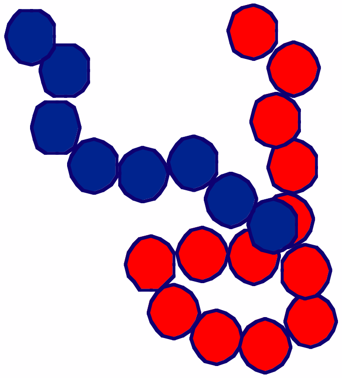
$$c = 2$$

Extended β-sheet
(misfolded protein)



http://cmgm.stanford.edu/biochem201/Slides/Protein%20Structure/Pleated%20Beta-sheets.JPG

Random Coil

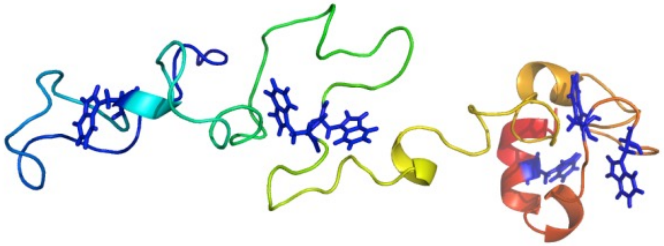


$$d_f = 2$$

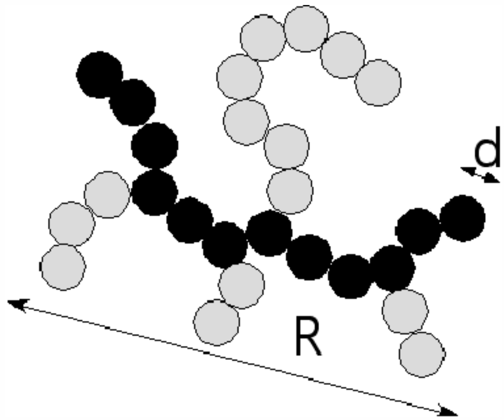
$$d_{\min} = 2$$

$$c = 1$$

Unfolded Gaussian chain

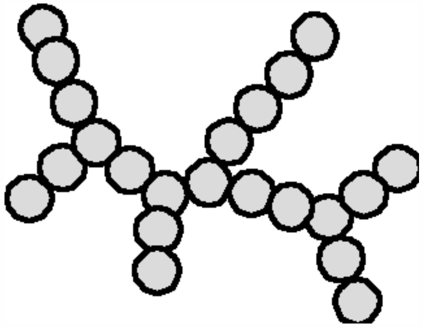


How Complex Mass Fractal Structures Can be Decomposed



Tortuosity

Connectivity



$$z \sim \left(\frac{R}{d}\right)^{d_f} \sim p^c \sim s^{d_{\min}}$$

$$p \sim \left(\frac{R}{d}\right)^{d_{\min}}$$

$$s \sim \left(\frac{R}{d}\right)^{c}$$

$$d_f = d_{\min} c$$

z	d_f	p	$d_{\min}$	s	c	R/d
27	1.36	12	1.03	22	1.28	11.2

Journal of Polymer Science: Part B: Polymer Physics, Vol. 36, 3147–3154 (1998)

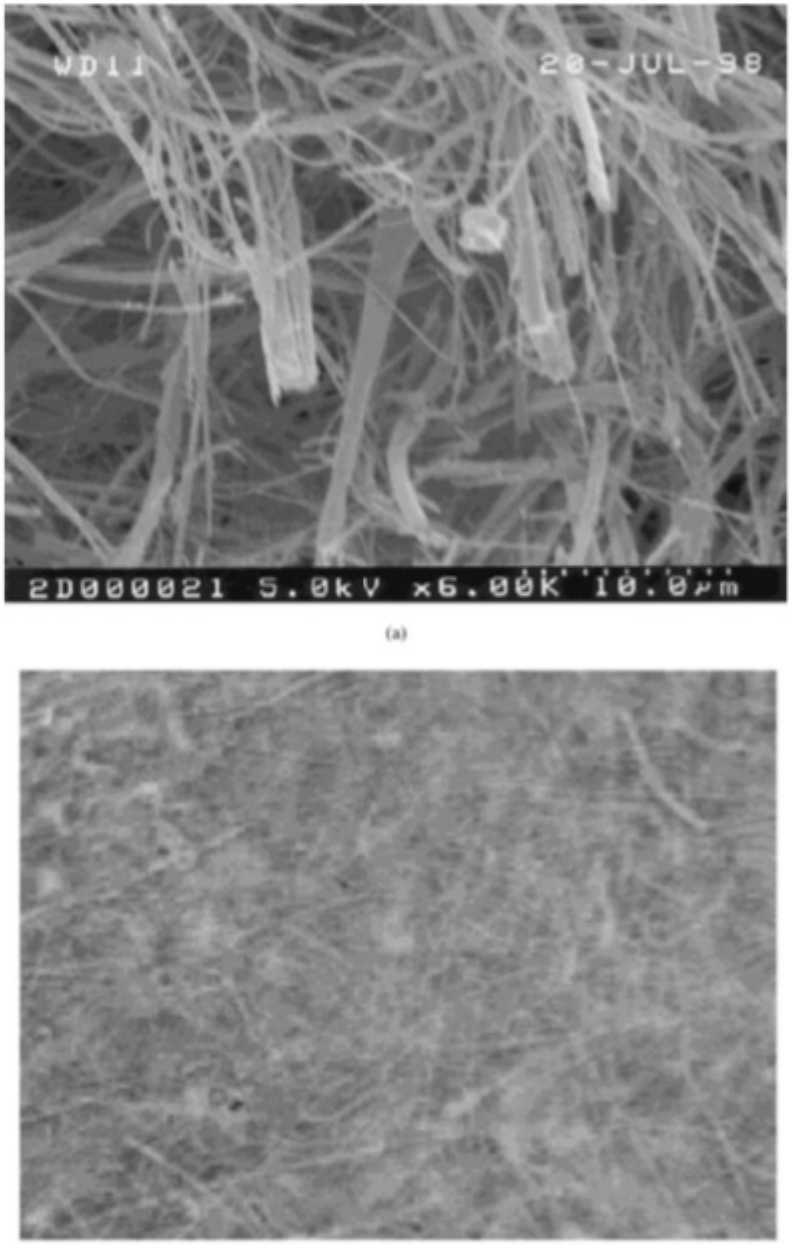


Figure 1. Micrographs of GMF sample showing micron-scale silica glass fibers in a polymer-like mat. (a) SEM micrograph after gold coating. This size scale corresponds to the persistence regime and the high-q end of the scaling regime. (b) Optical micrograph at 20×. This size scale would correspond to the scaling regime of Figure 2 below.

Fibers follow either Gaussian or Self-avoiding structure depending on binding of fibers

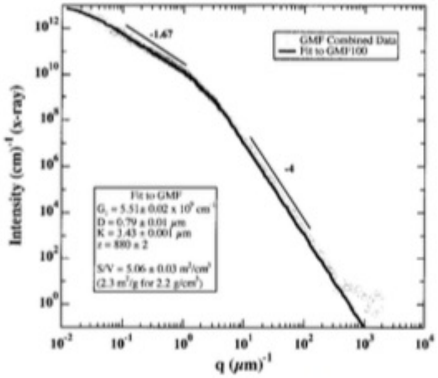


Figure 2. Log I vs. log q plot for GMF with an incident beam normal to the sample plane. Scaling regime at low-q follows good solvent scaling. High-q scaling follows Porod's law. Fit uses the unified equation with four free parameters and a model based on a polymer-like structure.

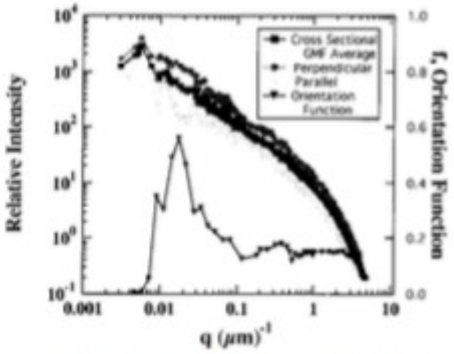


Figure 5. Orientation function and SALS data for GMF in cross-section as a function of q. Perpendicular and parallel are with respect to the plane of the mat.

Orientation partly governs separation

Pore size and fractal structure govern wicking

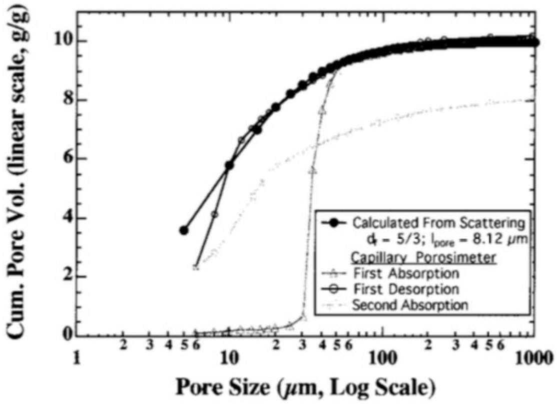


Figure 6. Cumulative pore volume vs. pore size from SALS and from capillary porosimetry.

The Primary Structure for Synthetic Polymers

Short-Range Interactions

The persistence length is created due to interactions between units of the chain that have similar chain indices

These interactions are termed “short-range interactions” because they involve short distances along the chain minimum path

Short-range interactions lead to changes in the chain persistence. For example, restrictions to bond rotation such as by the addition of short branches can lead to increases in the persistence length in polymers like polyethylene. Short-range interactions can be more subtle. For instance, short branches in a polyester can disrupt a natural tendency to form a helix leading to a reduction in the persistence length, that is making the chain more flexible.

All interactions occur over short spatial distances, short-range interactions occur over short-distances but the distinguishing feature is that they occur over short differences in chain index.

Short-range interactions do not influence the chain scaling.

The Primary Structure for Synthetic Polymers

Short-Range Interactions

Consider the simplest form of short-range interaction
We forbid the chain from the preceding step

Consider a chain as a series of steps r_i
r_i is a vector of length r and there are n such vectors in the chain

The mean value for r_{i+1} is 0

$$\langle r_{i+1} \rangle = \sum_{k=1}^{k=z} b_k = 0$$

b_k is a unit vector in a coordinate system,
6 of these vectors in a cubic system

The Primary Structure for Synthetic Polymers

Short-Range Interactions

$$\langle r_{i+1} \rangle = \sum_{k=1}^{k=z} b_k = 0$$

For exclusion of the previous step this sum
does not equal 0

$$\langle r_{i+1} \rangle_{Random} = \sum_{k=1}^{k=z} b_k = 0 = (z-1)\langle r_{i+1} \rangle_{ShortRangeInteraction} - r_i$$

So,

$$\langle r_{i+1} \rangle_{ShortRangeInteraction} = \frac{r_i}{(z-1)}$$

The Primary Structure for Synthetic Polymers

Short-Range Interactions

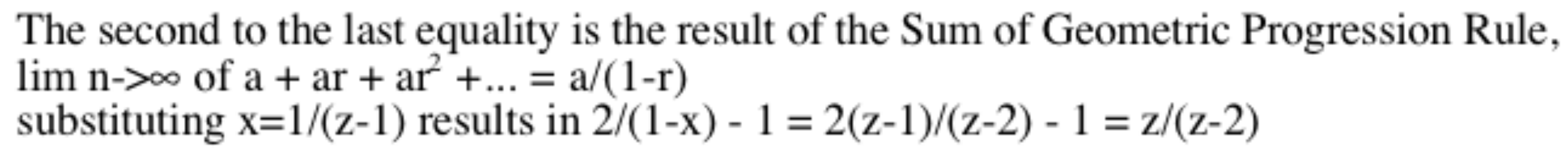
$$\left\langle r_{i+1} \right\rangle_{ShortRangeInteraction} = \frac{r_i}{(z-1)}$$

For Gaussian Chain

$$\left\langle R^2 \right\rangle = \sum_i \sum_j r_i \bullet r_j = \sum_i r_i \bullet r_i + \sum_i \sum_{j \neq i} r_i \bullet r_j \qquad \text{yields} \qquad \left\langle R^2 \right\rangle = N r^2$$

For SRI Chain the second term is not 0.

$$\left\langle r_i \bullet r_j \right\rangle = \frac{b^2}{(z-1)^{|i-j|}} \qquad \text{and} \qquad \left\langle R^2 \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \left\langle r_i \bullet r_j \right\rangle \cong \sum_{i=1}^{n} \sum_{k=-\infty}^{\infty} \frac{b^2}{(z-1)^{|k|}} = nb^2 \frac{z}{z-2} = nb^2_{effective}$$



The second to the last equality is the result of the Sum of Geometric Progression Rule,
lim n->∞ of $a + ar + ar^2 + \ldots = a/(1-r)$
substituting $x=1/(z-1)$ results in $2/(1-x) - 1 = 2(z-1)/(z-2) - 1 = z/(z-2)$

For Cartesian simulation $z = 6$ and b_{eff} is 1.22 b so about a 25% increase for one step self-avoidance.

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

The Primary Structure for Synthetic Polymers

Short-Range Interactions

Short-Range Interactions
Increase the persistence length

Chain scaling is not affected by short-range interactions.

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction
-Steric interactions
-Tacticity
-Charge (poly electrolytes)
-Hydrogen bonds
-Helicity

The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction

Characteristic Ratio, C_∞

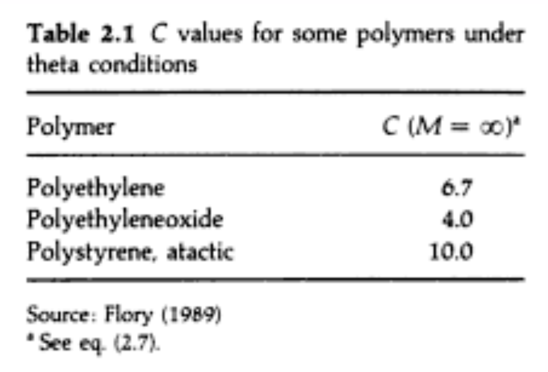


Table 2.1 *C* values for some polymers under theta conditions

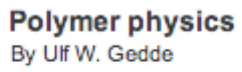
Polymer	$C\ (M = \infty)^a$
Polyethylene	6.7
Polyethyleneoxide	4.0
Polystyrene, atactic	10.0

Source: Flory (1989)
^{a} See eq. (2.7).

$$\left\langle R^2 \right\rangle = n_{Kuhn} l_{Kuhn}^2 = L l_{Kuhn} = C_\infty n_{Bond} l_{Bond}^2 = C_\infty L l_{Bond}$$

$$l_{Kuhn} \sim b_{Effective}$$

$$C_\infty = \frac{l_{Kuhn}}{l_{Bond}}$$



Polymer physics
By Ulf W. Gedde

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
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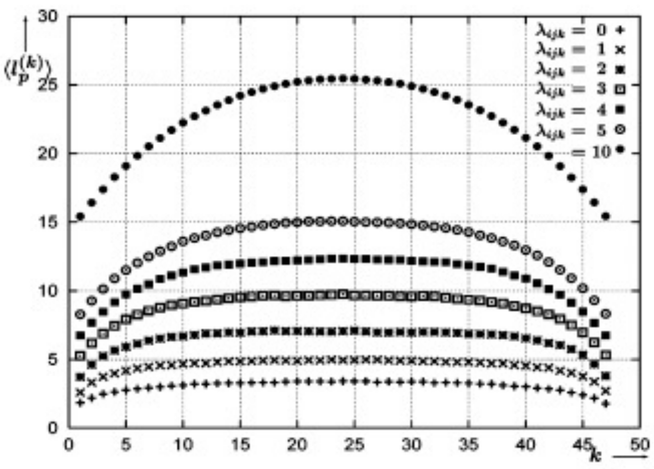


Figure 7. The persistence length plots, $\langle l_p^{(k)} \rangle$, obtained via eq 10, versus segment number, k, for various semiflexible, linear polymers, each of length 48. The strength of the intrinsic stiffness is varied between polymers by increasing the strength of the bending penalty, λ_{ijk} from 0 (bottom)...5, 10 (top).

Macromolecules **2005,** *38,* 5288–5299

"Intrinsic" and "Topological" Stiffness in Branched Polymers

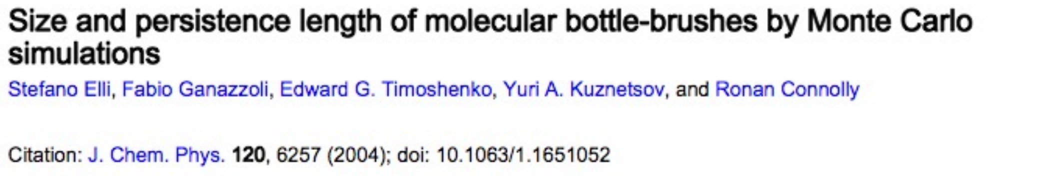
Ronan Connolly,[†] Giovanni Bellesia,[†] Edward G. Timoshenko,[*,†,‡] Yuri A. Kuznetsov,[§] Stefano Elli,[∥] and Fabio Ganazzoli[∥]

$$C_\infty = \frac{l_{Kuhn}}{l_{Bond}}$$

The Characteristic Ratio varies with *N* due to chain end effects. There is generally an increase in *C* with *N*, and it plateaus at high molecular weight.

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

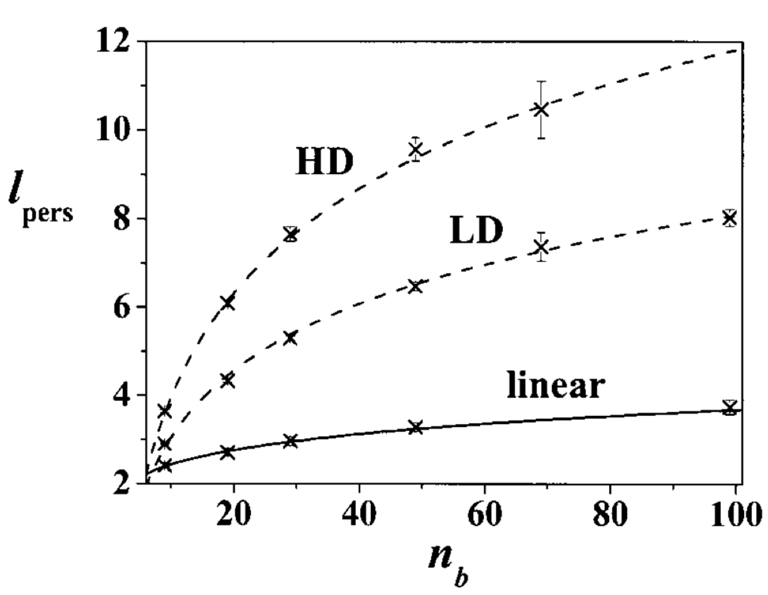
Molecular weight dependence of persistence length

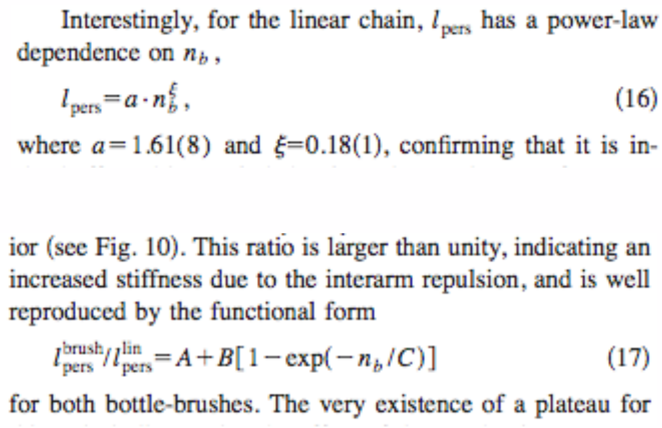


Size and persistence length of molecular bottle-brushes by Monte Carlo simulations

Stefano Elli, Fabio Ganazzoli, Edward G. Timoshenko, Yuri A. Kuznetsov, and Ronan Connolly

Citation: J. Chem. Phys. **120**, 6257 (2004); doi: 10.1063/1.1651052





Interestingly, for the linear chain, l_{pers} has a power-law dependence on n_b,

$$l_{\text{pers}} = a \cdot n_b^{\xi}, \qquad (16)$$

where $a = 1.61(8)$ and $\xi = 0.18(1)$, confirming that it is in-

ior (see Fig. 10). This ratio is larger than unity, indicating an increased stiffness due to the interarm repulsion, and is well reproduced by the functional form

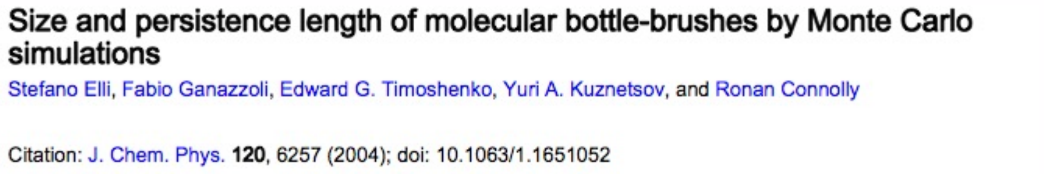
$$l_{\text{pers}}^{\text{brush}}/l_{\text{pers}}^{\text{lin}} = A + B[1 - \exp(-n_b/C)] \qquad (17)$$

for both bottle-brushes. The very existence of a plateau for

LD = Low branch density
HD = High branch density

This is a 5-parameter model for persistence length!
(used to model 5 or 6 data points!!!)

Molecular weight dependence of persistence length



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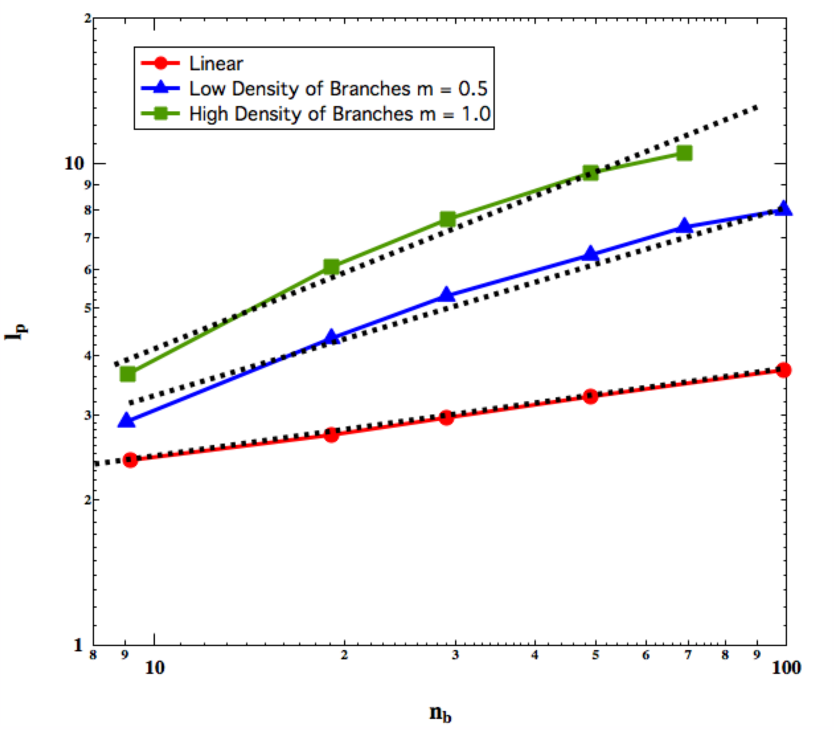

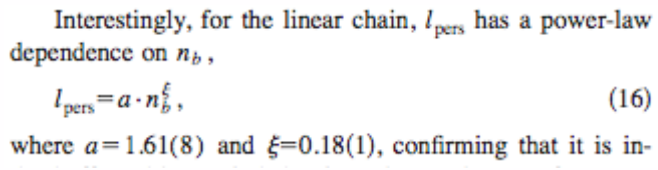

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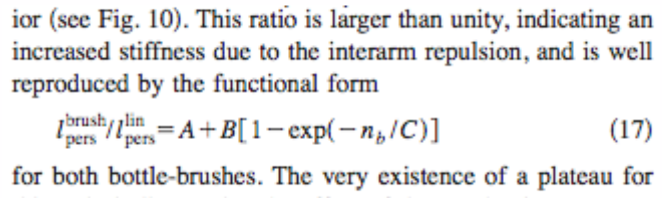

ior (see Fig. 10). This ratio is larger than unity, indicating an increased stiffness due to the interarm repulsion, and is well reproduced by the functional form

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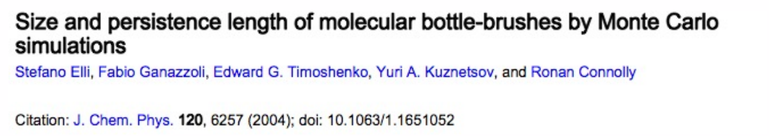
for both bottle-brushes. The very existence of a plateau for

This is a 5-parameter model for persistence length!
(used to model 5 or 6 data points!!!)

(Also, this model fails to predict an infinite molecular weight persistence length.)

Molecular weight dependence of persistence length



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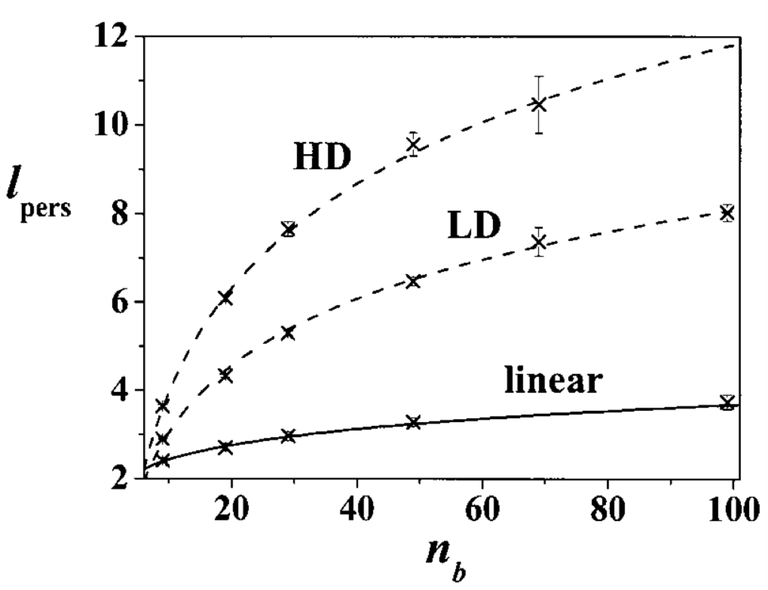
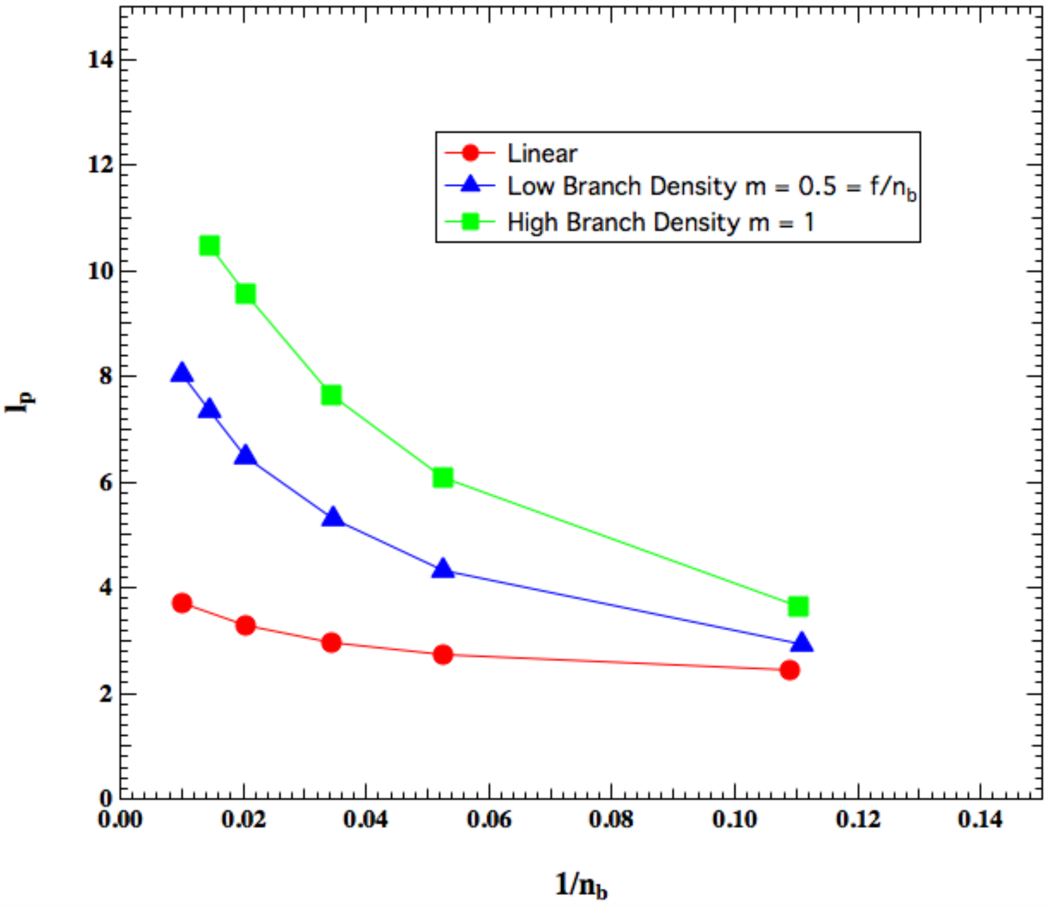


LD = Low branch density

HD = High branch density

Proposed End Group Functionality

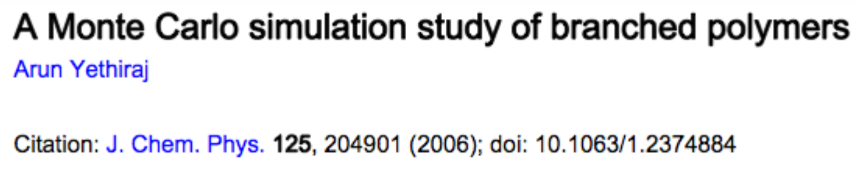
$$l_p = l_{p,\infty} - \left(\frac{2K}{M}\right)$$



This works better for Yethiraj’s data.
(Except that the infinite persistence length is not monotonic in branch length)

Proposed End Group Functionality

$$l_p = l_{p,\infty} - \left(\frac{2K}{M}\right)$$



A Monte Carlo simulation study of branched polymers

Arun Yethiraj

Citation: J. Chem. Phys. **125**, 204901 (2006); doi: 10.1063/1.2374884

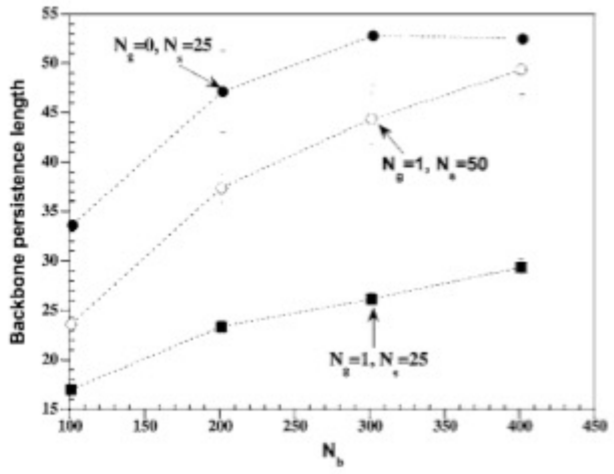
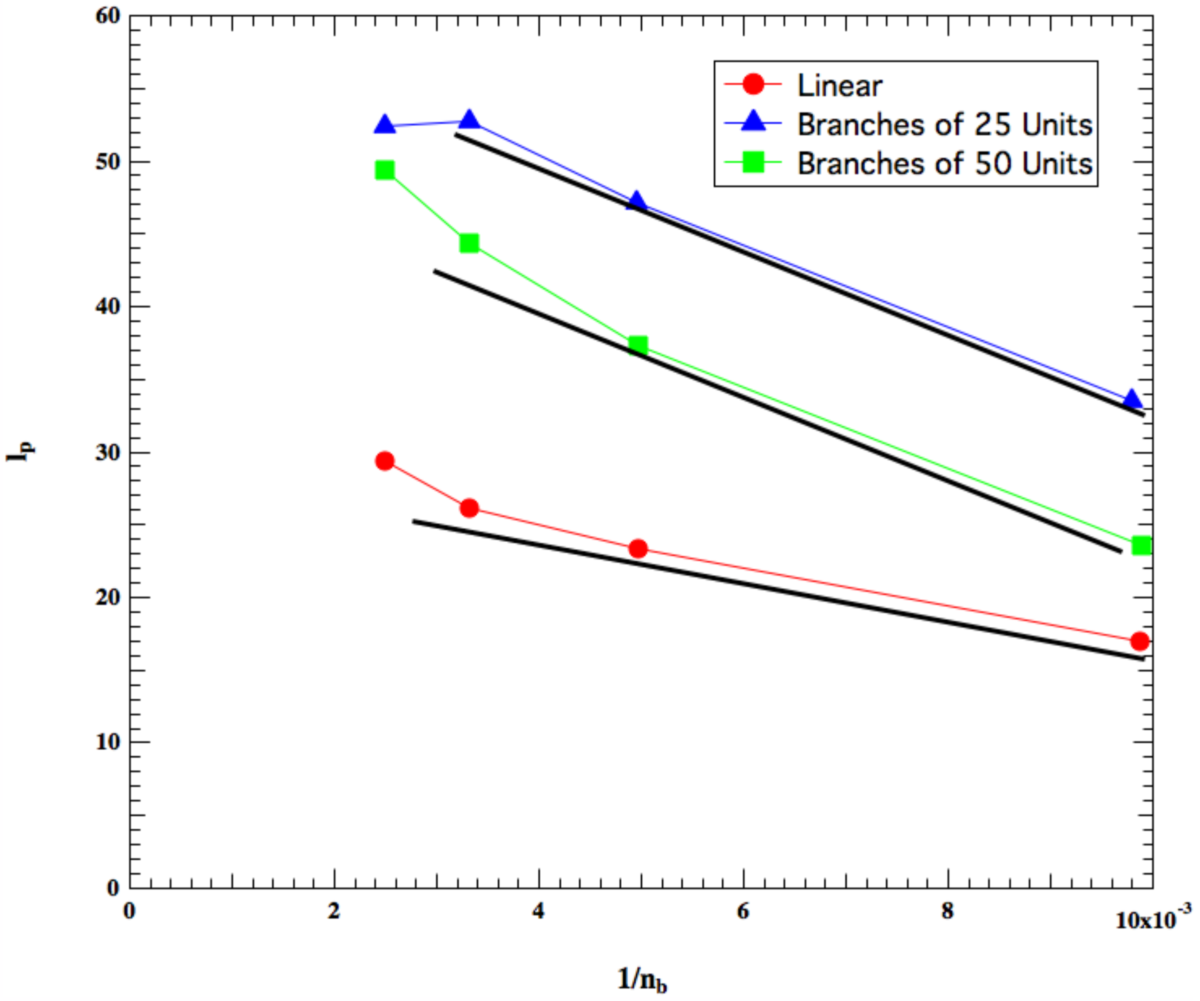
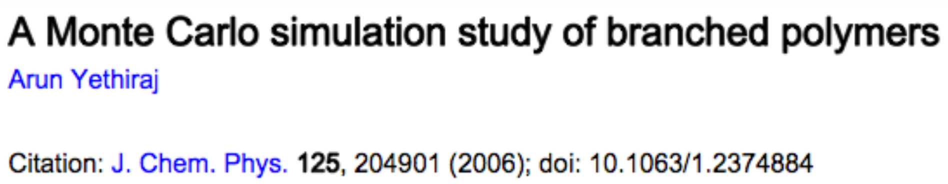


FIG. 2. Persistence length of the backbone as a function of number of backbone beads for various values of the branch length (N_s) and the number of beads between branch points (N_g) and for $\varepsilon_S=\varepsilon_B=0$. The lines are meant to guide the eye.





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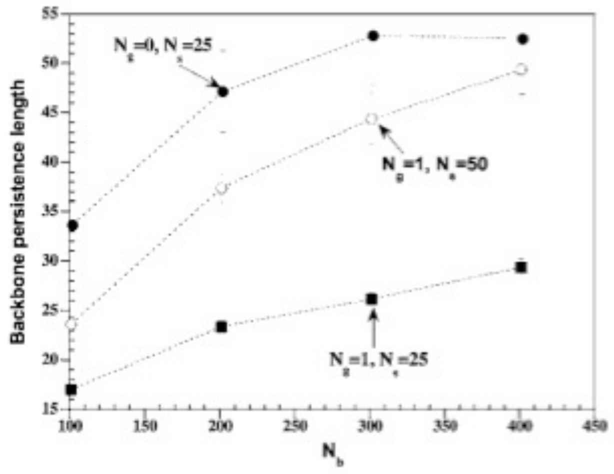
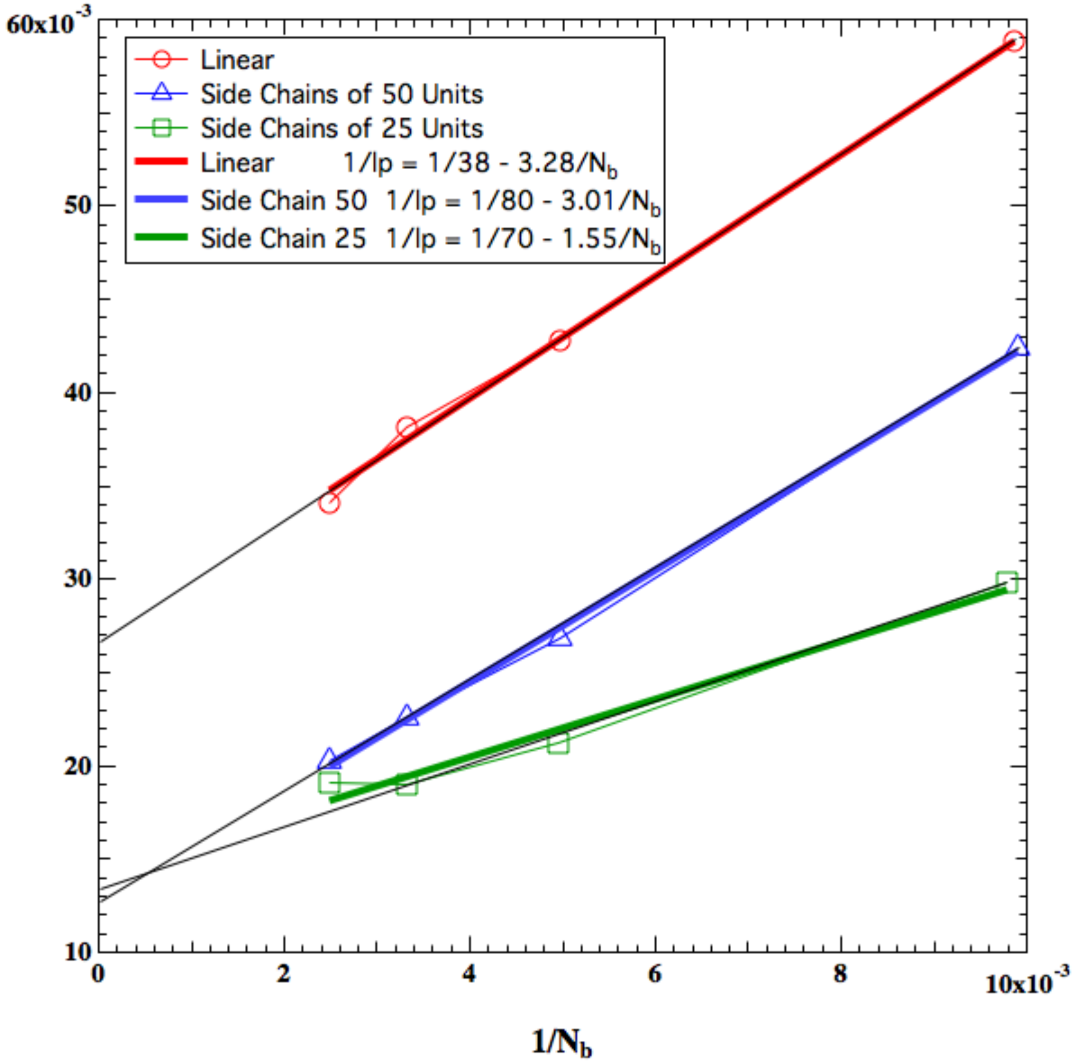


FIG. 2. Persistence length of the backbone as a function of number of backbone beads for various values of the branch length (N_s) and the number of beads between branch points (N_g) and for $\varepsilon_S=\varepsilon_B=0$. The lines are meant to guide the eye.

Alternative Functionality
based on increase in chain flexibility

$$\left(\frac{1}{l_p}\right)=\left(\frac{1}{l_{p,\infty}}\right)+\left(\frac{2K}{M}\right)$$



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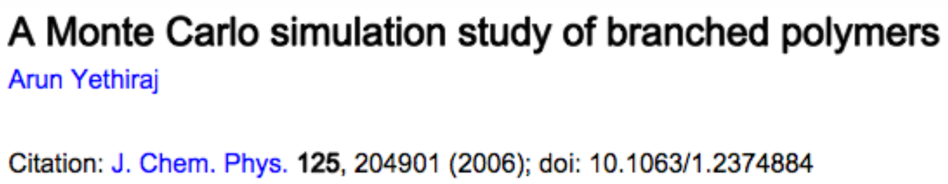
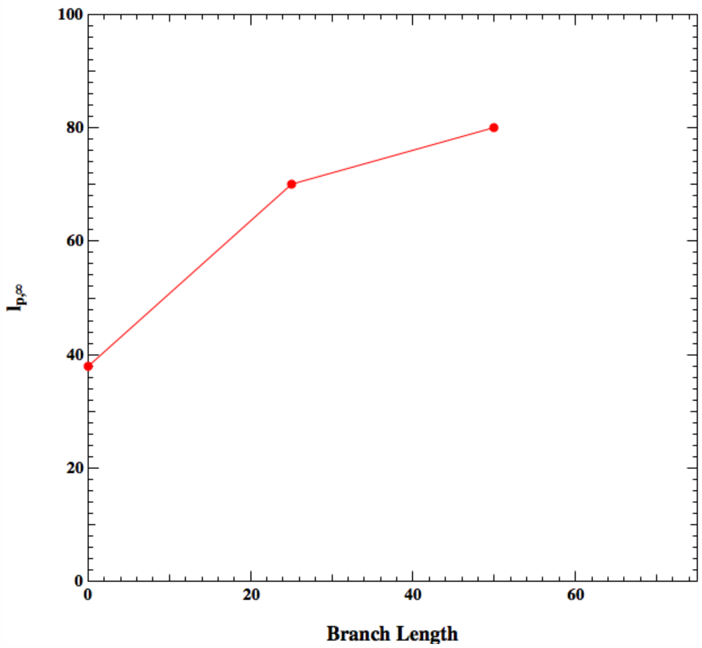
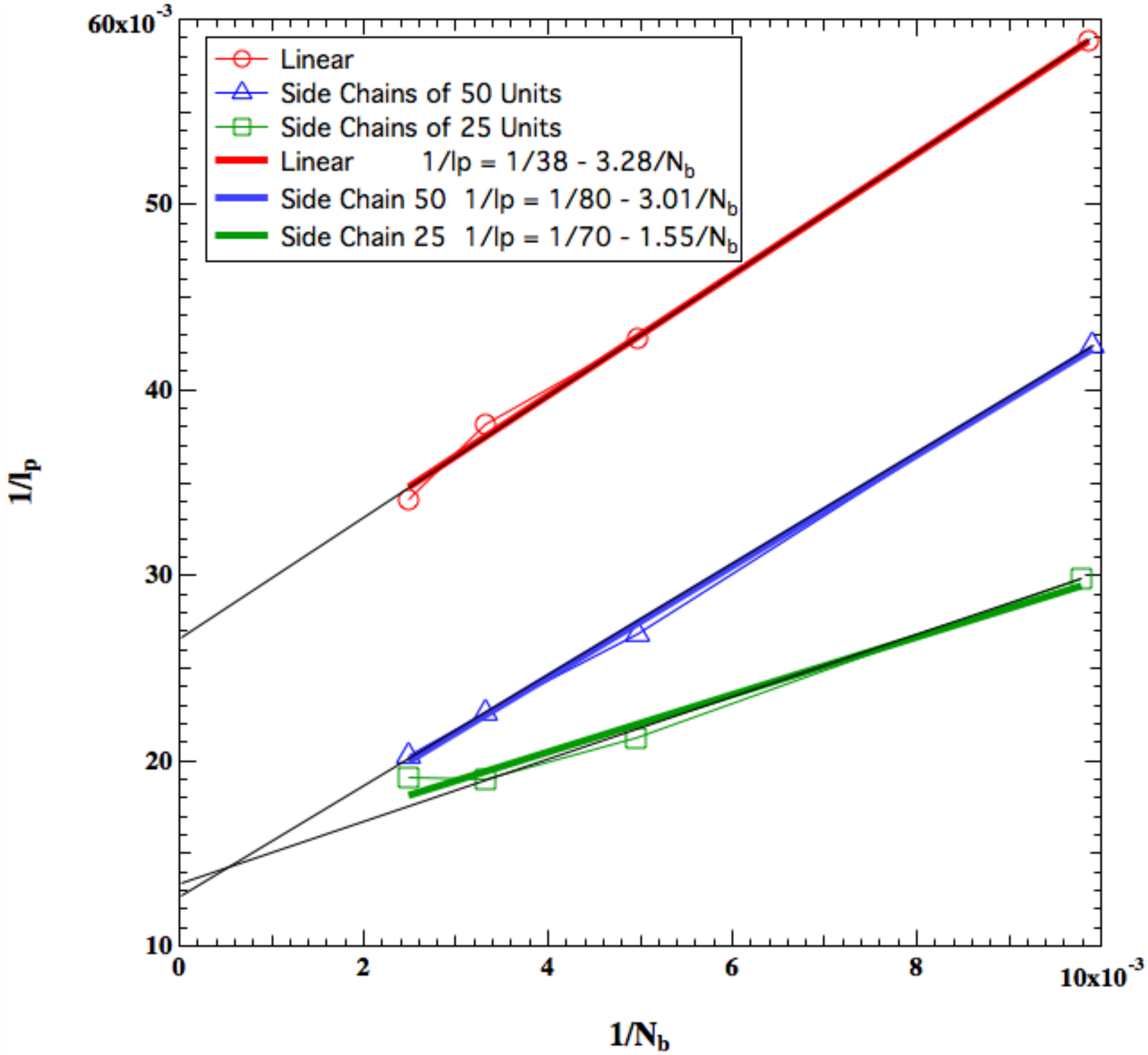


A Monte Carlo simulation study of branched polymers

Arun Yethiraj

Citation: J. Chem. Phys. **125**, 204901 (2006); doi: 10.1063/1.2374884





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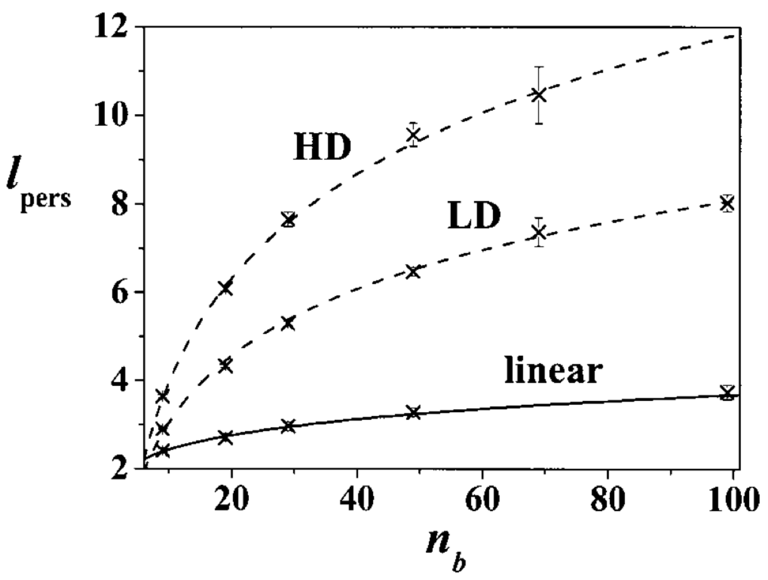
$$\left(\frac{1}{l_p}\right)=\left(\frac{1}{l_{p,\infty}}\right)+\left(\frac{2K}{M}\right)$$

Size and persistence length of molecular bottle-brushes by Monte Carlo simulations

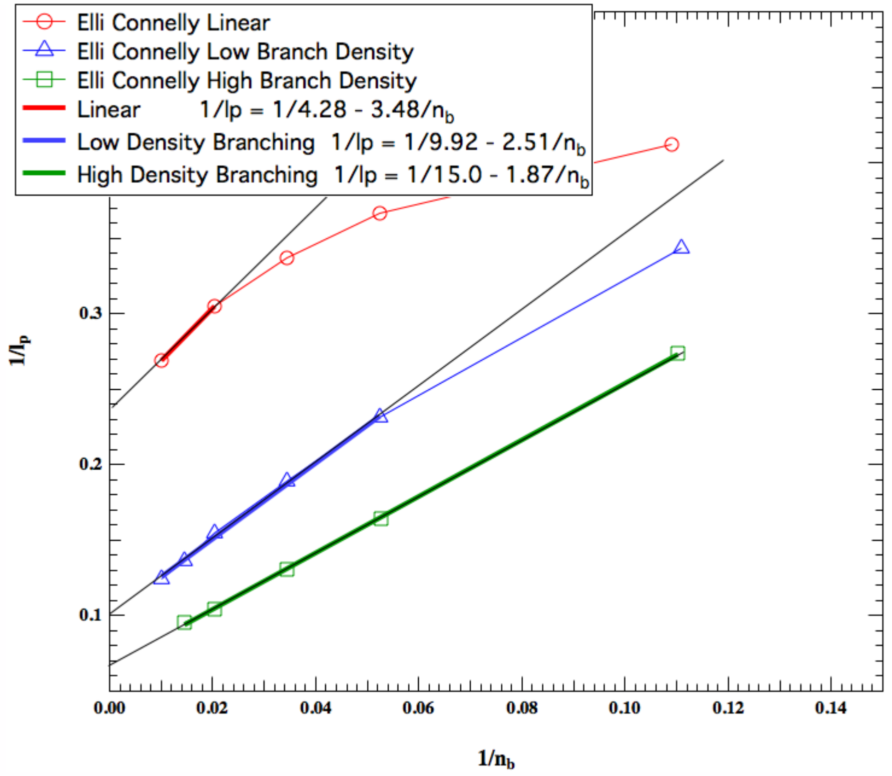
Stefano Elli, Fabio Ganazzoli, Edward G. Timoshenko, Yuri A. Kuznetsov, and Ronan Connolly

Citation: J. Chem. Phys. **120**, 6257 (2004); doi: 10.1063/1.1651052



LD = Low branch density

HD = High branch density



Alternative Functionality based on increase in chain flexibility

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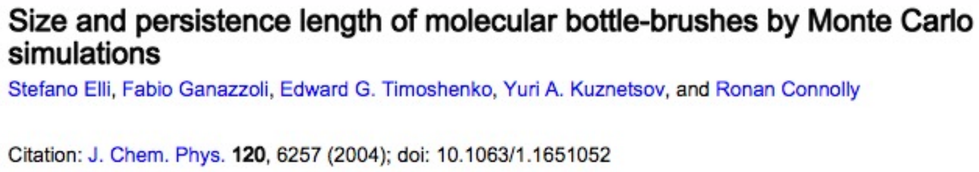

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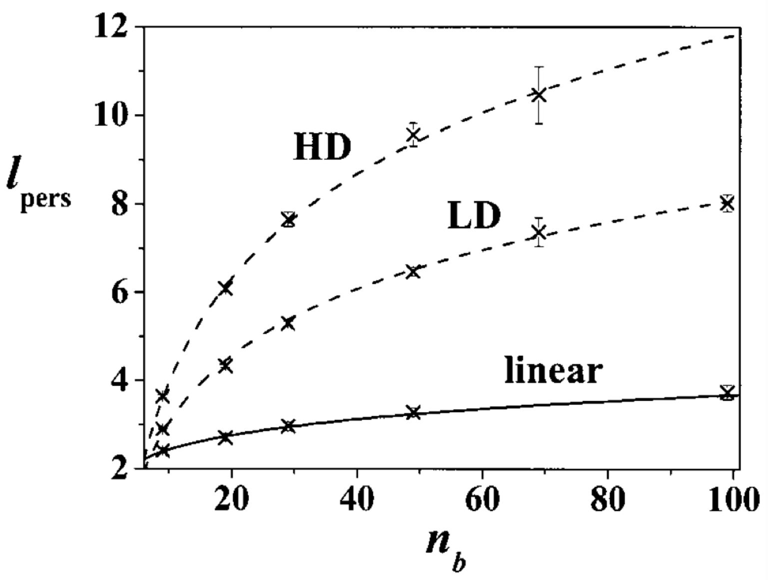

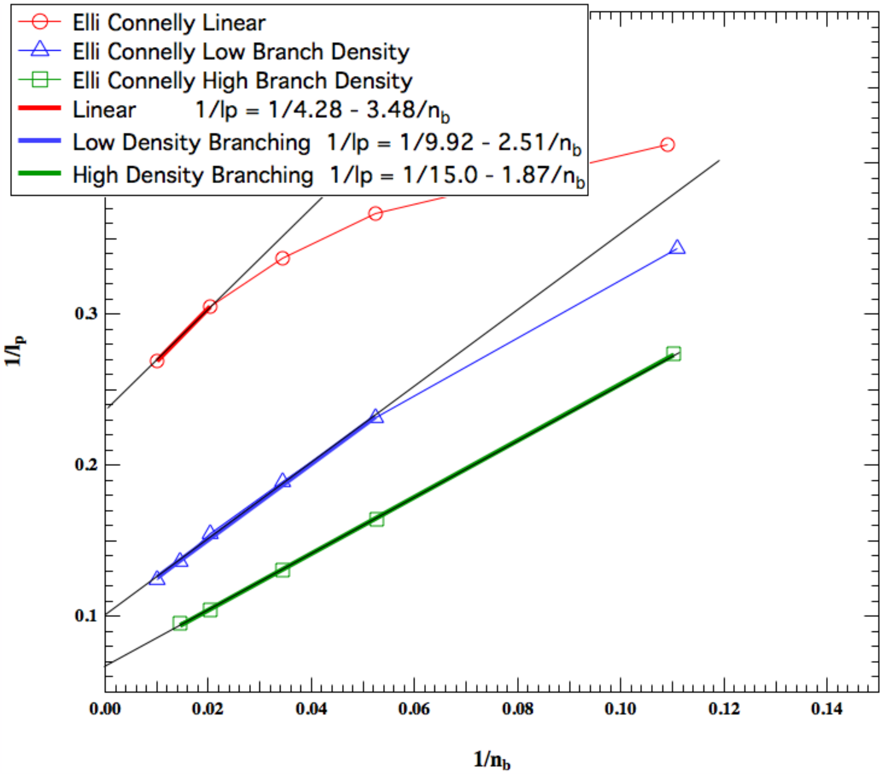

LD = Low branch density
HD = High branch density

Equation fails at low n_b since it predicts l_p => when n_b => 0

Alternative Functionality
based on increase in chain flexibility

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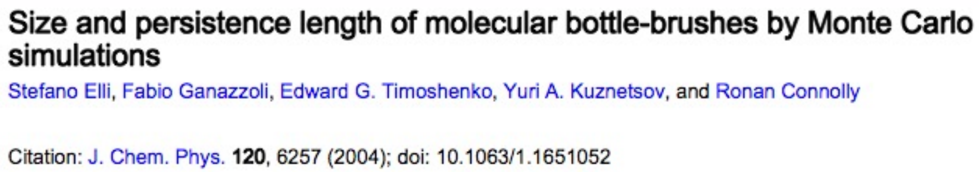

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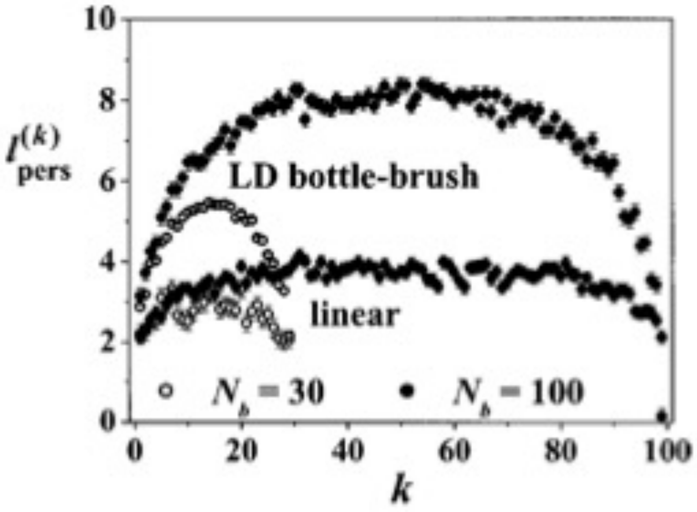
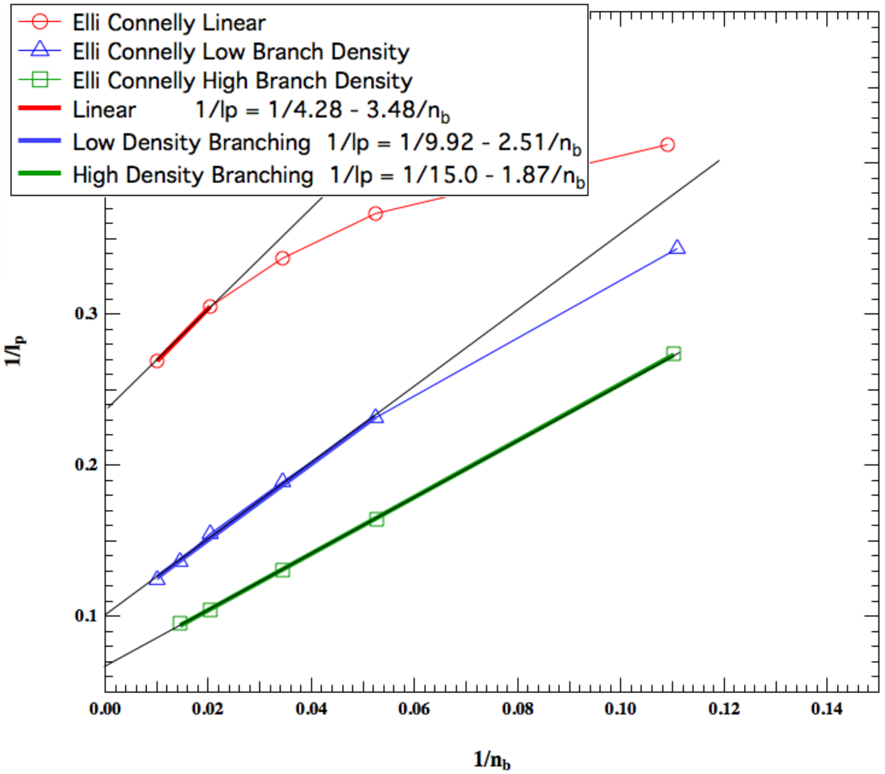


FIG. 8. The persistence length $l^{(k)}_{\text{pers}}$ obtained through Eq. (5) for the linear chain (lower data points) and the LD bottle-brushes with $N_a = 5$ beads per arm (upper data points) as a function of the spring location k within the chain ($k=1$ and $k=N_b-1$ are the terminal spring) for different backbone lengths.



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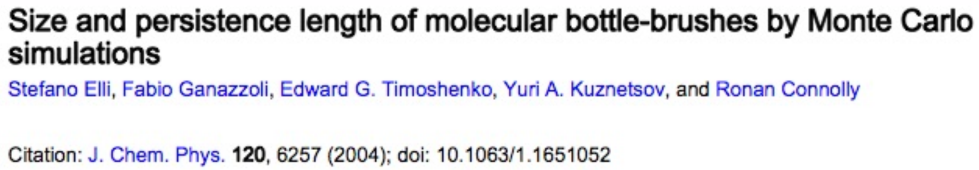

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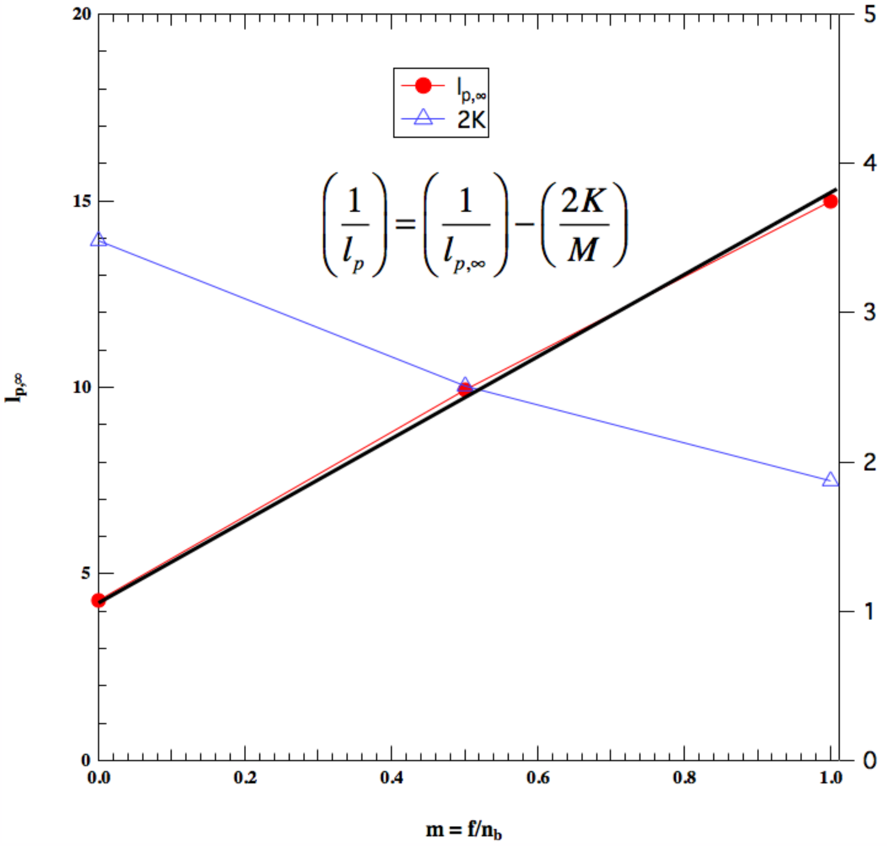

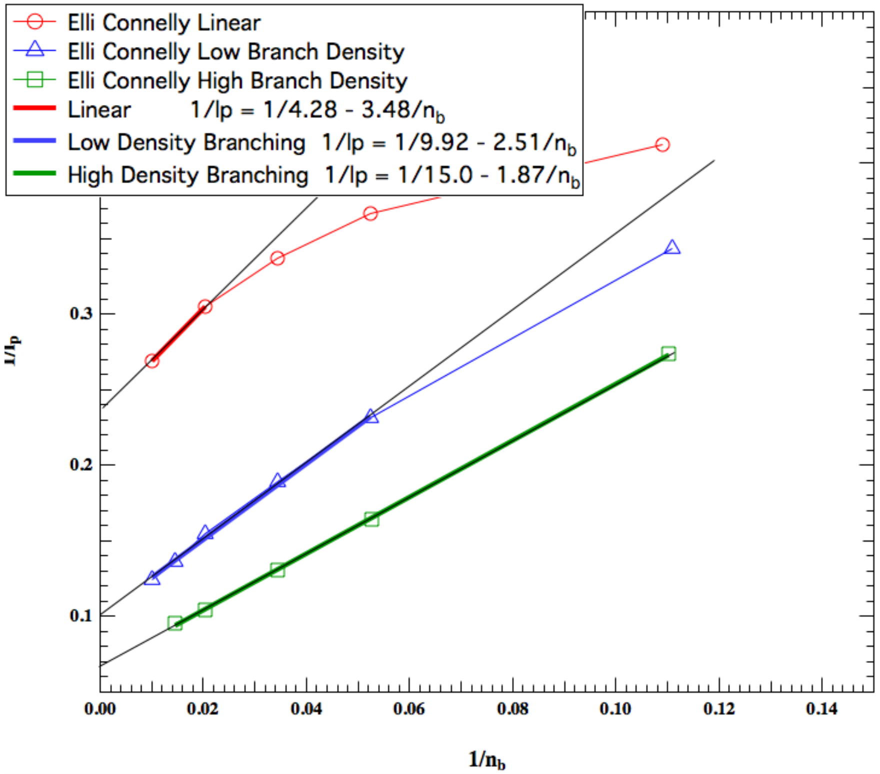

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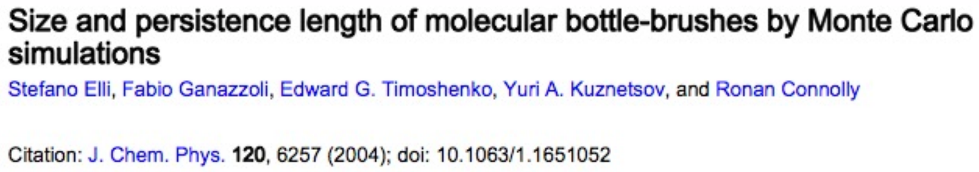

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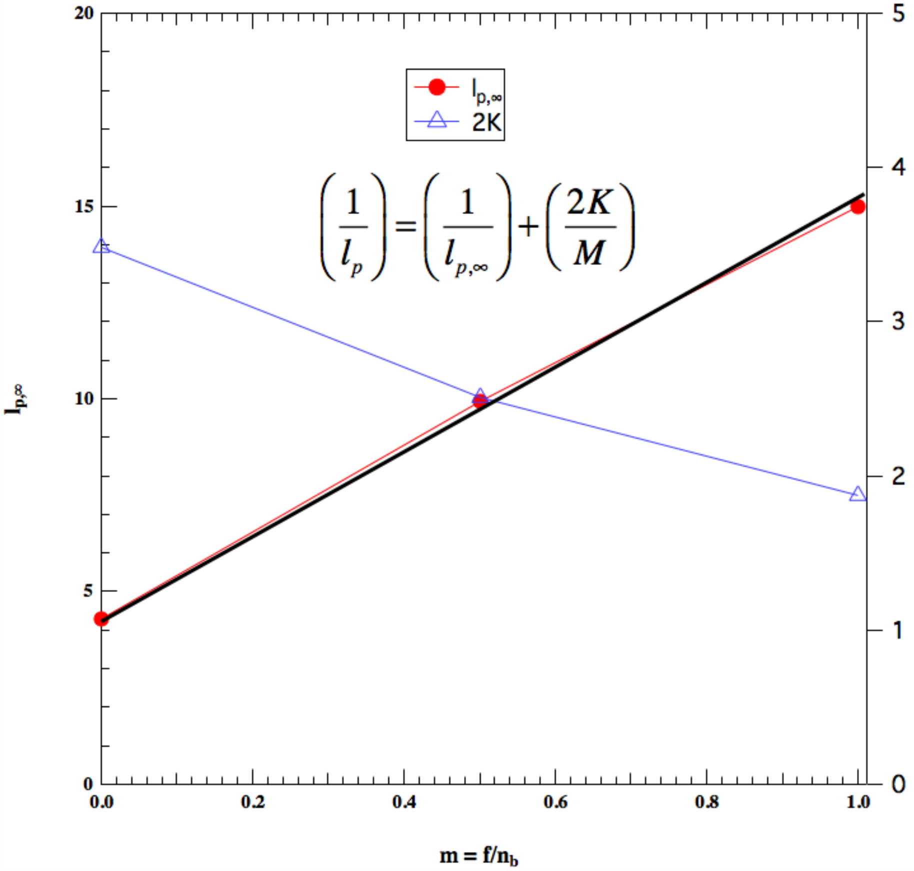
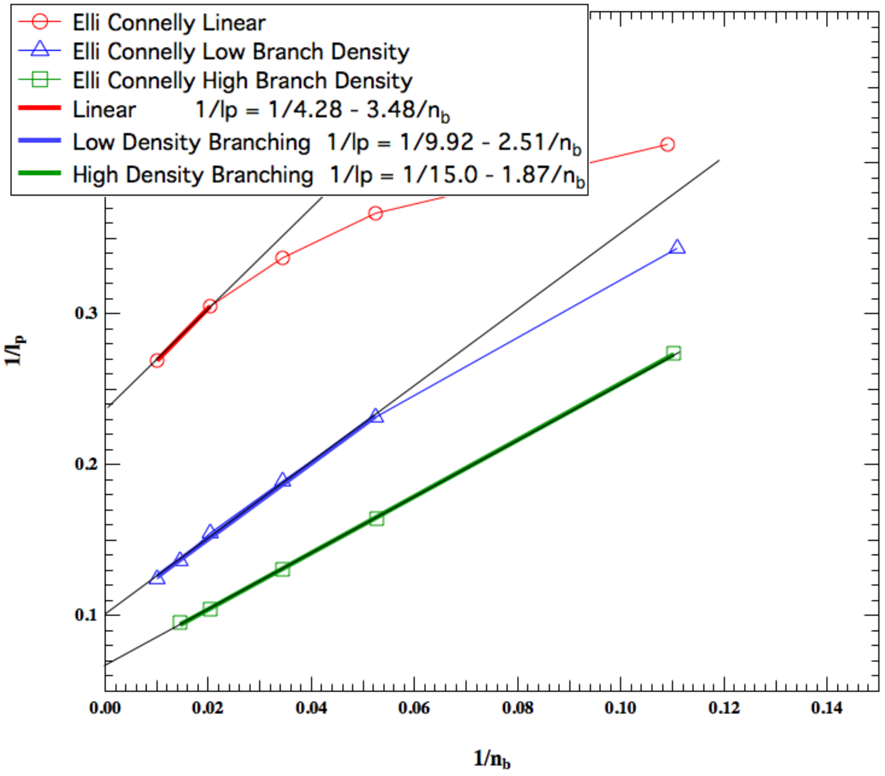




The 2K values imply that end groups become less important for more rigid chains

The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction
-Steric interactions
-Tacticity
-Charge (poly electrolytes)
-Hydrogen bonds
-Helicity

The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction

Figure 1.1: A simple polymer in the trans conformation.

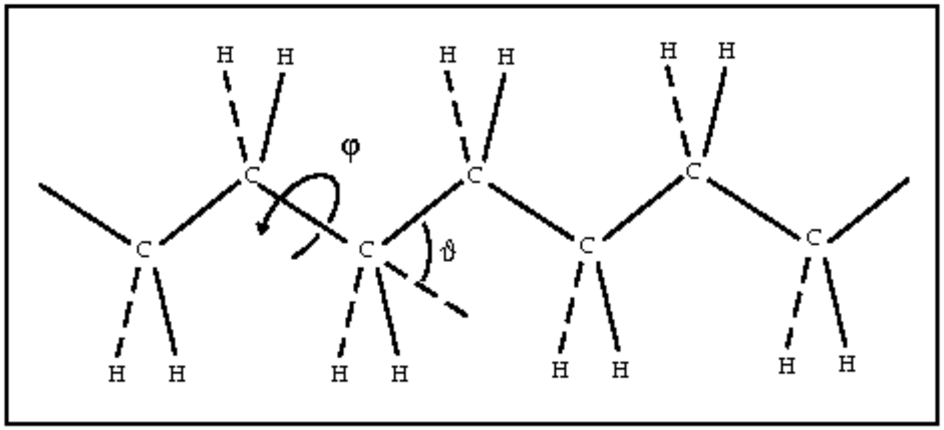
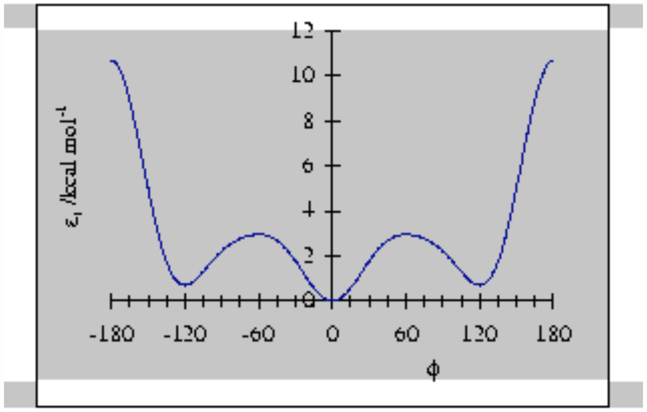
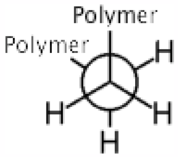


Figure 1.2: Dihedral angle energy of n-butane.



http://cbp.tnw.utwente.nl/PolymeerDictaat/node4.html



Polyethylene

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction

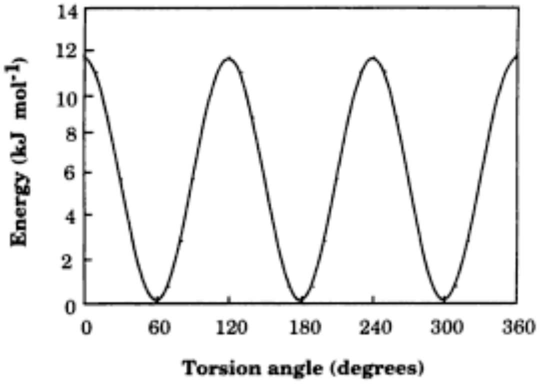


Figure 2.2 Conformational energy of ethane as a function of torsion angle.

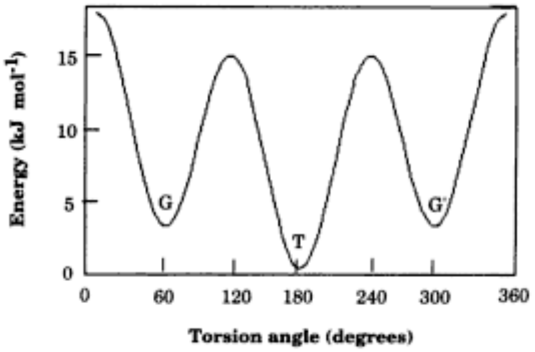
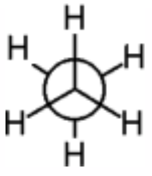
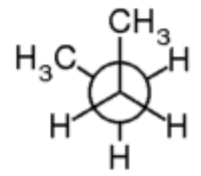


Figure 2.4 Conformational energy of *n*-butane as a function of torsion angle of the central carbon–carbon bond. The outer carbon–carbon bonds are assumed to be in their minimum energy states (staggered positions).



Ethane



Butane

Polymer physics
By Ulf W. Gedde

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction

Characteristic Ratio, C_∞

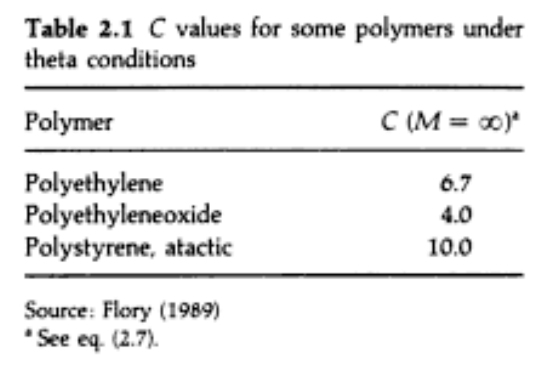


Table 2.1 *C* values for some polymers under theta conditions

Polymer	$C\ (M=\infty)^a$
Polyethylene	6.7
Polyethyleneoxide	4.0
Polystyrene, atactic	10.0

Source: Flory (1989)
^{a} See eq. (2.7).

$$\langle R^2\rangle = n_{Kuhn} l_{Kuhn}^2 = L l_{Kuhn} = C_\infty n_{Bond} l_{Bond}^2 = C_\infty L l_{Bond}$$

$$l_{Kuhn} \sim b_{Effective}$$

$$C_\infty = \frac{l_{Kuhn}}{l_{Bond}}$$

Polymer physics
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The Primary Structure for Synthetic Polymers

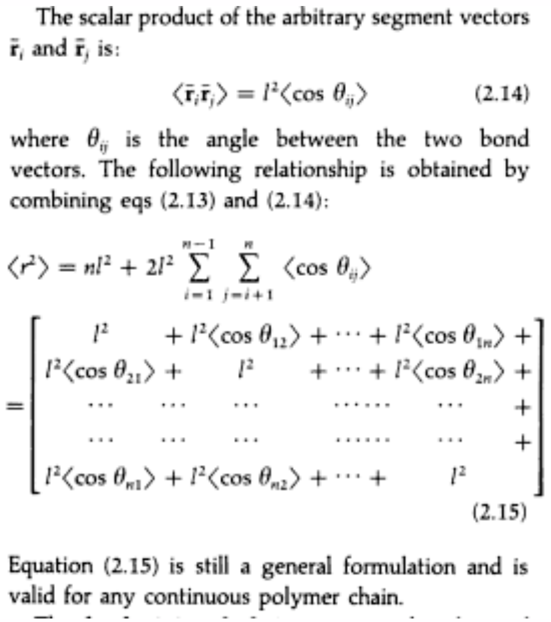
Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction

$$C_\infty = \frac{l_{Kuhn}}{l_{Bond}}$$

Consider a freely rotating chain that has a bond angle restriction of 109.5 °



The scalar product of the arbitrary segment vectors $\bar{\mathbf{r}}_i$ and $\bar{\mathbf{r}}_j$ is:

$$\langle \bar{\mathbf{r}}_i \bar{\mathbf{r}}_j \rangle = l^2 \langle \cos \theta_{ij} \rangle \qquad (2.14)$$

where θ_{ij} is the angle between the two bond vectors. The following relationship is obtained by combining eqs (2.13) and (2.14):

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \cos \theta_{ij} \rangle$$

$$= \begin{bmatrix} l^2 & + l^2\langle \cos \theta_{12} \rangle & + \cdots + & l^2\langle \cos \theta_{1n} \rangle & + \\ l^2\langle \cos \theta_{21} \rangle + & l^2 & + \cdots + & l^2\langle \cos \theta_{2n} \rangle & + \\ \cdots \quad \cdots & \cdots & \cdots\cdots & \cdots & + \\ \cdots \quad \cdots & \cdots & \cdots\cdots & \cdots & + \\ l^2\langle \cos \theta_{n1} \rangle + & l^2\langle \cos \theta_{n2} \rangle & + \cdots + & l^2 & \end{bmatrix} \qquad (2.15)$$

Equation (2.15) is still a general formulation and is valid for any continuous polymer chain.

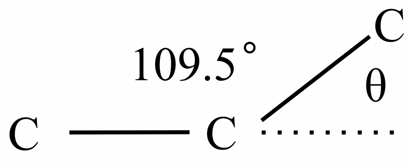
Polymer physics
By Ulf W. Gedde

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf

The Primary Structure for Synthetic Polymers

Short-Range Interactions

Consider a freely rotating chain that has a bond angle restriction of 109.5 ° $= \tau$



$$\langle \bar{\mathbf{r}}_i \bar{\mathbf{r}}_{i+1} \rangle = l^2 \cos(180 - \tau)$$

$$\langle \bar{\mathbf{r}}_i \bar{\mathbf{r}}_{i+2} \rangle = l^2 \cos^2(180 - \tau)$$

$$\langle \bar{\mathbf{r}}_i \bar{\mathbf{r}}_j \rangle = l^2[\cos(180 - \tau)]^{j-i}$$

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} [\cos(180 - \tau)]^{j-i}$$

$$= \left[\begin{array}{cccccc} l^2 & + \, l^2 \cos(180 - \tau) & + \cdots & + \, l^2[\cos(180 - \tau)]^{n-1} & + \\ l^2 \cos(180 - \tau) & + \quad l^2 & + \cdots & + \, l^2[\cos(180 - \tau]^{n-2} & + \\ \cdots & \cdots & \cdots & \cdots & + \\ \cdots & \cdots & \cdots & \cdots & + \\ l^2[\cos(180 - \tau)]^{n-1} + & \cdots & \cdots & l^2 & \end{array} \right] \qquad (2.17)$$

The summation can be performed over a single variable (k) by substituting $j - i$ by k:

$$\langle r^2 \rangle = nl^2 \left[1 + \frac{2}{n} \sum_{k=1}^{n-1} (n - k)\alpha^k \right] \qquad (2.18)$$

where $\alpha = \cos(180 - \tau)$.

Equation (2.18) can be simplified as follows:

$$\langle r^2 \rangle = nl^2 \left[1 + \frac{2}{n} \sum_{k=1}^{n-1} (n - k)\alpha^k \right]$$

$$= nl^2 \left[1 + 2 \sum_{k=1}^{n-1} \alpha^k - \frac{2}{n} \sum_{k=1}^{n-1} k\alpha^k \right]$$

$$= nl^2 \left[1 + \frac{2(\alpha - \alpha^n)}{1 - \alpha} - \frac{2}{n} \left(\frac{\alpha(1 - \alpha)^n}{(1 - \alpha)^2} - \frac{n\alpha^n}{1 - \alpha} \right) \right]$$

$$= nl^2 \left[1 + \frac{2\alpha}{1 - \alpha} - \frac{2\alpha}{n} \frac{(1 - \alpha)^n}{(1 - \alpha)^2} \right]$$

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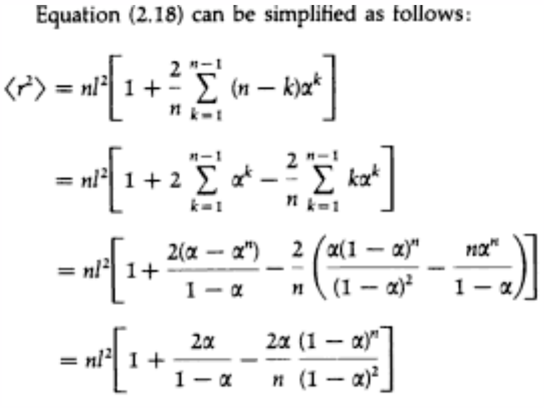
The Primary Structure for Synthetic Polymers

Short-Range Interactions

Consider a freely rotating chain that has a bond angle restriction of 109.5 ° = τ



Equation (2.18) can be simplified as follows:

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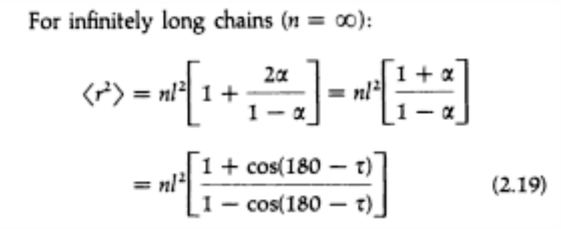
$$= nl^2\left[1+\frac{2(\alpha-\alpha^n)}{1-\alpha}-\frac{2}{n}\left(\frac{\alpha(1-\alpha)^n}{(1-\alpha)^2}-\frac{n\alpha^n}{1-\alpha}\right)\right]$$

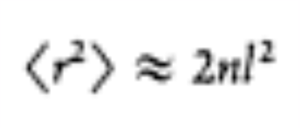
$$= nl^2\left[1+\frac{2\alpha}{1-\alpha}-\frac{2\alpha}{n}\frac{(1-\alpha)^n}{(1-\alpha)^2}\right]$$



For infinitely long chains ($n = \infty$):

$$\langle r^2\rangle = nl^2\left[1+\frac{2\alpha}{1-\alpha}\right] = nl^2\left[\frac{1+\alpha}{1-\alpha}\right]$$

$$= nl^2\left[\frac{1+\cos(180-\tau)}{1-\cos(180-\tau)}\right] \qquad (2.19)$$



$$\langle r^2\rangle \approx 2nl^2$$

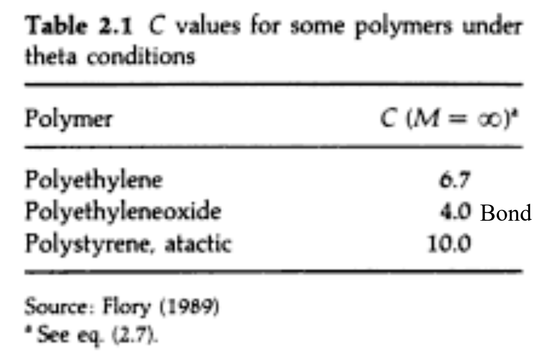


Table 2.1 *C* values for some polymers under theta conditions

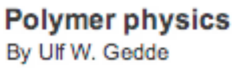
	Polymer	$C\ (M = \infty)^a$	
Moderate Flexibility	Polyethylene	6.7	
High Rotational Flexibility	Polyethyleneoxide	4.0	Bond angles 109.5° : 104.5°
Lower Rot. Flexibility	Polystyrene, atactic	10.0	

Source: Flory (1989)

[a] See eq. (2.7).

$$C_\infty = \frac{l_{Kuhn}}{l_{Bond}} = 1.40$$

For a Freely Rotating Polyethylene Chain



Polymer physics

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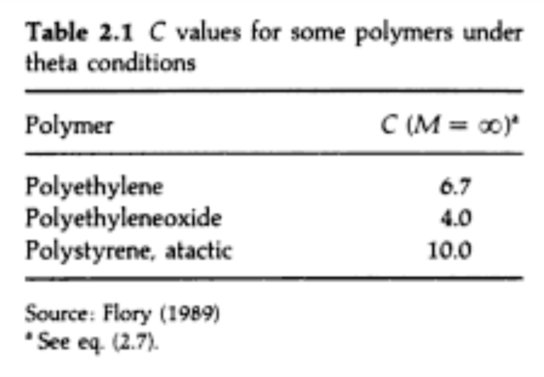
http://books.google.com/books?id=Iem3fC7XdnkC&pg=PA23&lpg=PA23&dq=coil+expansion+factor &source=bl&ots=BGjRfhZYaU&sig=I0OPb2VRuf8Dm8qnrmrhyjXyEC8&hl=en&sa=X&ei=fSV0T-XqMMHW0QHi1-T_Ag&ved=0CF0Q6AEwBw#v=onepage&q=coil%20expansion%20factor&f=false

The Primary Structure for Synthetic Polymers

Short-Range Interactions

Consider a freely rotating chain that has a bond angle restriction of 109.5 ° = τ



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Source: Flory (1989)

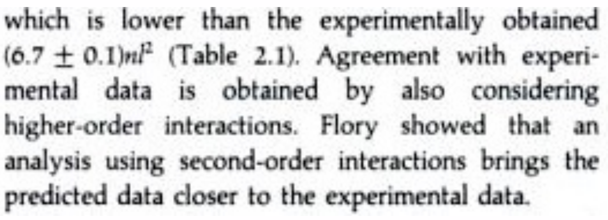
^{a} See eq. (2.7).

$$\langle r^2 \rangle \approx 2nl^2$$

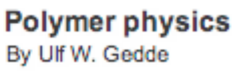
$$C_\infty = \frac{l_{Kuhn}}{l_{Bond}}$$

If we consider restrictions to bond rotation for first order interactions

$$C_\infty = \frac{l_{Kuhn}}{l_{Bond}} => 3.4$$



which is lower than the experimentally obtained $(6.7 \pm 0.1)nl^2$ (Table 2.1). Agreement with experimental data is obtained by also considering higher-order interactions. Flory showed that an analysis using second-order interactions brings the predicted data closer to the experimental data.



Polymer physics

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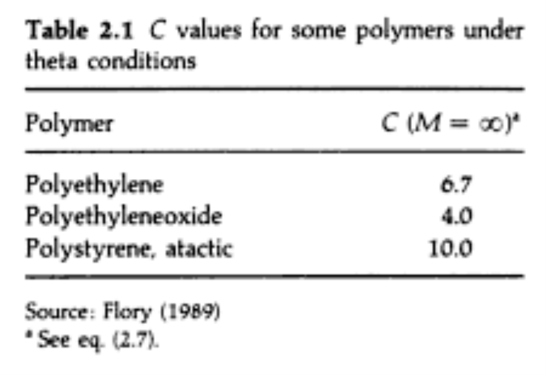
http://books.google.com/books?id=Iem3fC7XdnkC&pg=PA23&lpg=PA23&dq=coil+expansion+factor&source=bl&ots=BGjRfhZYaU&sig=I0OPb2VRuf8Dm8qnrmrhyjXyEC8&hl=en&sa=X&ei=fSV0T-XqMMHW0QHi1-T_Ag&ved=0CF0Q6AEwBw#v=onepage&q=coil%20expansion%20factor&f=false

The Primary Structure for Synthetic Polymers

Short-Range Interactions



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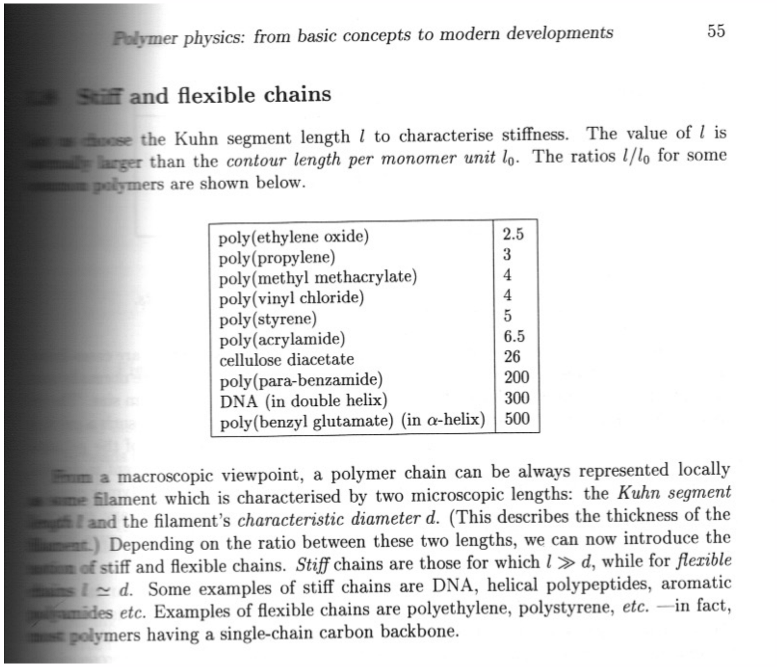
Polymer	$C\ (M = \infty)^a$
Polyethylene	6.7
Polyethyleneoxide	4.0
Polystyrene, atactic	10.0

Source: Flory (1989)
^{a} See eq. (2.7).

Polymer physics
By Ulf W. Gedde



Polymer physics: from basic concepts to modern developments 55

[illegible] Stiff and flexible chains

Let us choose the Kuhn segment length l to characterise stiffness. The value of l is normally larger than the *contour length per monomer unit* l_0. The ratios l/l_0 for some common polymers are shown below.

poly(ethylene oxide)	2.5
poly(propylene)	3
poly(methyl methacrylate)	4
poly(vinyl chloride)	4
poly(styrene)	5
poly(acrylamide)	6.5
cellulose diacetate	26
poly(para-benzamide)	200
DNA (in double helix)	300
poly(benzyl glutamate) (in α-helix)	500

From a macroscopic viewpoint, a polymer chain can be always represented locally as some filament which is characterised by two microscopic lengths: the *Kuhn segment length* l and the filament's *characteristic diameter* d. (This describes the thickness of the filament.) Depending on the ratio between these two lengths, we can now introduce the notion of stiff and flexible chains. *Stiff* chains are those for which $l \gg d$, while for *flexible* chains $l \simeq d$. Some examples of stiff chains are DNA, helical polypeptides, aromatic polyamides *etc.* Examples of flexible chains are polyethylene, polystyrene, *etc.* —in fact, most polymers having a single-chain carbon backbone.

$$C_\infty = \frac{l_{Kuhn}}{l_{Bond}}$$

Alexei Khokhlov in Soft and Fragile Matter (2000)

Contour length per monomer is 2 * bond length

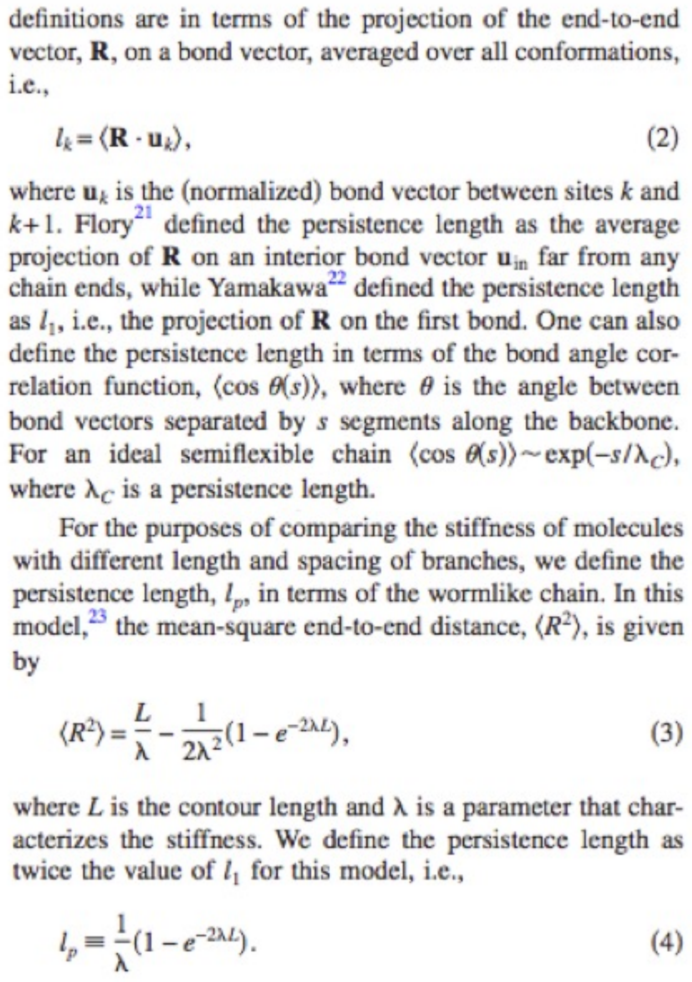
The Primary Structure for Synthetic Polymers

Short-Range Interactions

Persistence Length, lp

(Arun Yethiraj J. Chem. Phys. 125, 204901 (2006))

Several Definitions



definitions are in terms of the projection of the end-to-end vector, **R**, on a bond vector, averaged over all conformations, i.e.,

$$l_k = \langle \mathbf{R} \cdot \mathbf{u}_k \rangle, \qquad (2)$$

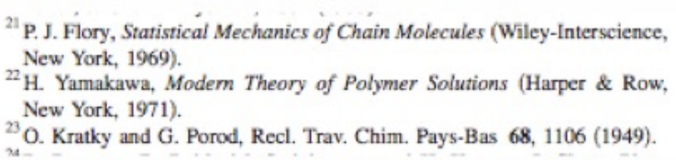
where $\mathbf{u}_k$ is the (normalized) bond vector between sites k and $k+1$. Flory[21] defined the persistence length as the average projection of **R** on an interior bond vector $\mathbf{u}_{\text{in}}$ far from any chain ends, while Yamakawa[22] defined the persistence length as l_1, i.e., the projection of **R** on the first bond. One can also define the persistence length in terms of the bond angle correlation function, $\langle \cos \theta(s) \rangle$, where θ is the angle between bond vectors separated by s segments along the backbone. For an ideal semiflexible chain $\langle \cos \theta(s) \rangle \sim \exp(-s/\lambda_C)$, where λ_C is a persistence length.

For the purposes of comparing the stiffness of molecules with different length and spacing of branches, we define the persistence length, l_p, in terms of the wormlike chain. In this model,[23] the mean-square end-to-end distance, $\langle R^2 \rangle$, is given by

$$\langle R^2 \rangle = \frac{L}{\lambda} - \frac{1}{2\lambda^2}(1 - e^{-2\lambda L}), \qquad (3)$$

where L is the contour length and λ is a parameter that characterizes the stiffness. We define the persistence length as twice the value of l_1 for this model, i.e.,

$$l_p \equiv \frac{1}{\lambda}(1 - e^{-2\lambda L}). \qquad (4)$$



[21] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley-Interscience, New York, 1969).

[22] H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971).

[23] O. Kratky and G. Porod, Recl. Trav. Chim. Pays-Bas **68**, 1106 (1949).

-Appendix of Flory's book, **lin**.
-Yamakawa's book is online, **l1**.
-Bond Angle Correlation, λC.
-Kratky-Porod Worm-like Chain Model, **lp**.

The Primary Structure for Synthetic Polymers

Scattering Observation of the Persistence Length

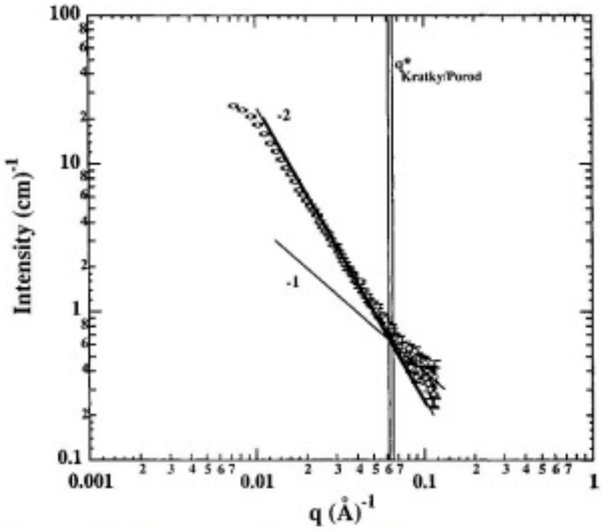
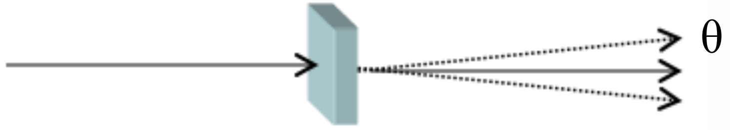


Figure 2. *Kratky/Porod graphical analysis in a log-log plot of corrected SANS data from a 5% by volume d-PHB sample in h-PHB. The lower power -2 line is the best visual estimate; the upper line is shifted to match a global unified fit. Key: left, q* corresponds to best visual estimate; right, plot to match global unified fit. The statistical error in the data is shown [3].*

$$I(q) = Bq^{-d_f}$$

$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) \qquad d = \frac{2\pi}{q}$$



A power-law decay of -1 slope has only one structural interpretation.

The Primary Structure for Synthetic Polymers

Consider a Brownian path with an index or continuous postion variable "s". For the simulated walks "s" is the time. For a polymer chain "s" is the chain index. Next consider an arbitrary origin of a coordinate system (0,0,0) and vectors to positions of the walk **r**(s). The unit tangent vector to the walk, **t**(s), is defined by,

$$\bar{t}(s) = \frac{\partial \bar{r}(s)}{\partial s} \quad (1)$$

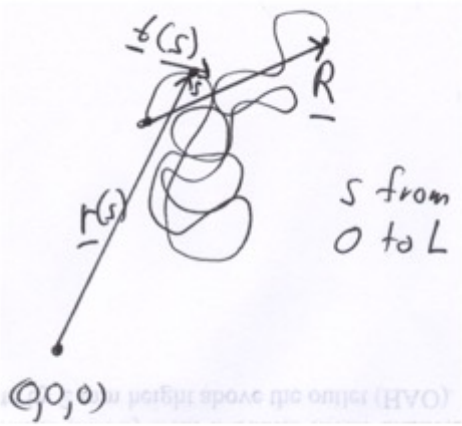
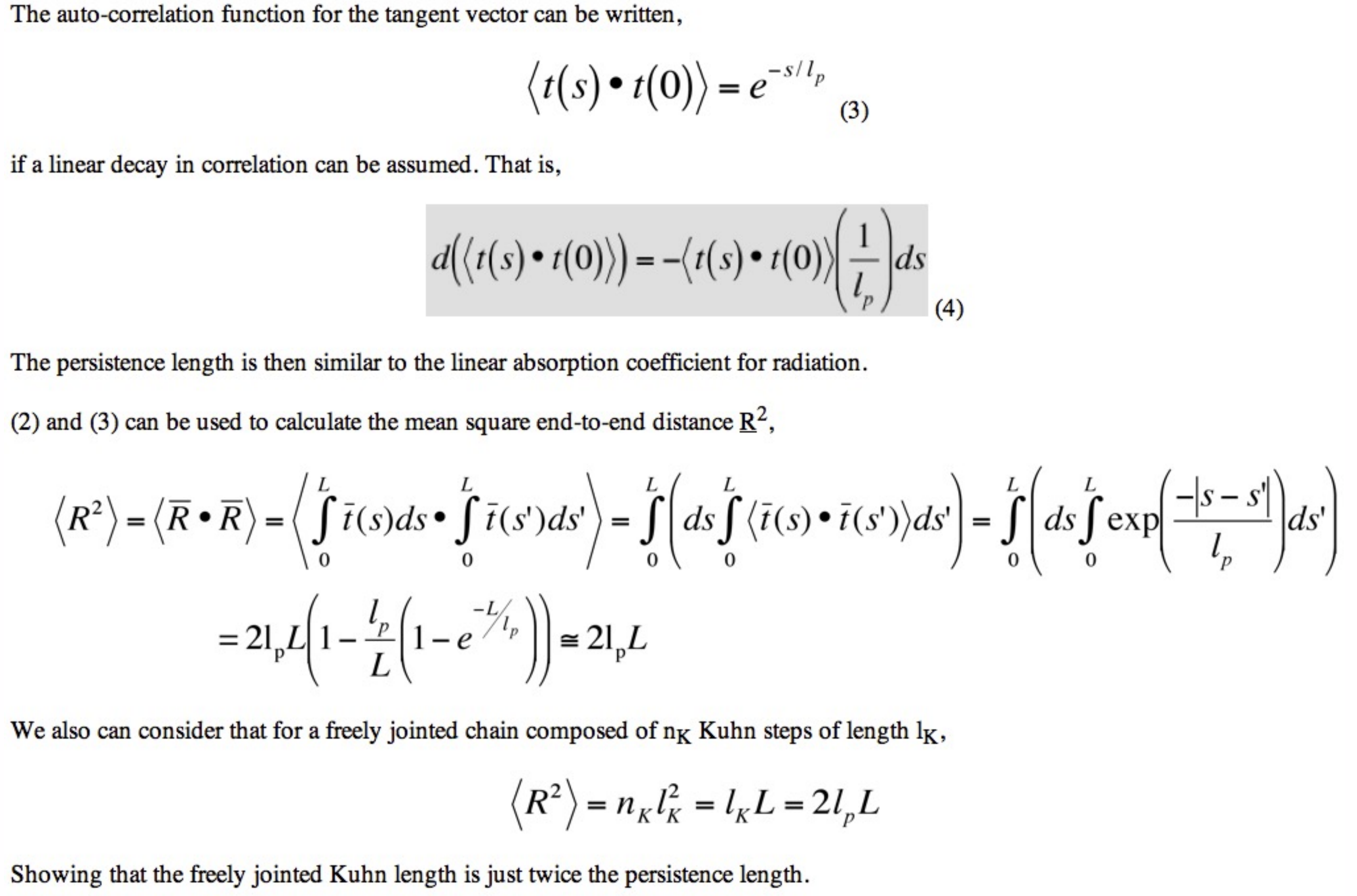


Figure 1. Brownian Path.

The end-to-end distance for the Brownian path is given by,

$$\bar{R} = \int_0^L \bar{t}(s)\,ds \quad (2)$$

http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/Persistence/Persistence.h
ml



The auto-correlation function for the tangent vector can be written,

$$\langle t(s) \bullet t(0) \rangle = e^{-s/l_p} \quad (3)$$

if a linear decay in correlation can be assumed. That is,

$$d\left(\langle t(s) \bullet t(0) \rangle\right) = -\langle t(s) \bullet t(0) \rangle \left(\frac{1}{l_p}\right) ds \quad (4)$$

The persistence length is then similar to the linear absorption coefficient for radiation.

(2) and (3) can be used to calculate the mean square end-to-end distance $\underline{R}^2$,

$$\langle R^2 \rangle = \langle \overline{R} \bullet \overline{R} \rangle = \left\langle \int_0^L \bar{t}(s) ds \bullet \int_0^L \bar{t}(s') ds' \right\rangle = \int_0^L \left(ds \int_0^L \langle \bar{t}(s) \bullet \bar{t}(s') \rangle ds' \right) = \int_0^L \left(ds \int_0^L \exp\left(\frac{-|s-s'|}{l_p} \right) ds' \right)$$

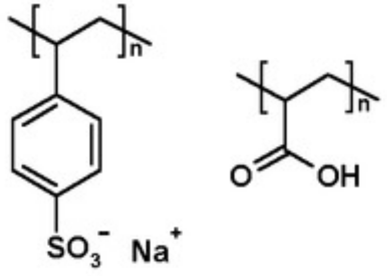
$$= 2 \mathrm{l_p} L \left(1 - \frac{l_p}{L} \left(1 - e^{-L/l_p} \right) \right) \cong 2 \mathrm{l_p} L$$

We also can consider that for a freely jointed chain composed of n_K Kuhn steps of length l_K,

$$\langle R^2 \rangle = n_K l_K^2 = l_K L = 2 l_p L$$

Showing that the freely jointed Kuhn length is just twice the persistence length.

Polyelectrolytes (proteins, charged polymers, polyethylene oxide, polypropylene oxide, poly nucleic acids, etc.)



SCPE WCPE

Strongly charged polyelectrolytes = each monomer unit is charged
Weakly charged polyelectrolytes = some monomers are charged
This can depend on the counter ion concentration

For SCPE the electrostatic persistence length dominates, for WCPE there is a competition between Coulombic and non-electrostatic persistence.

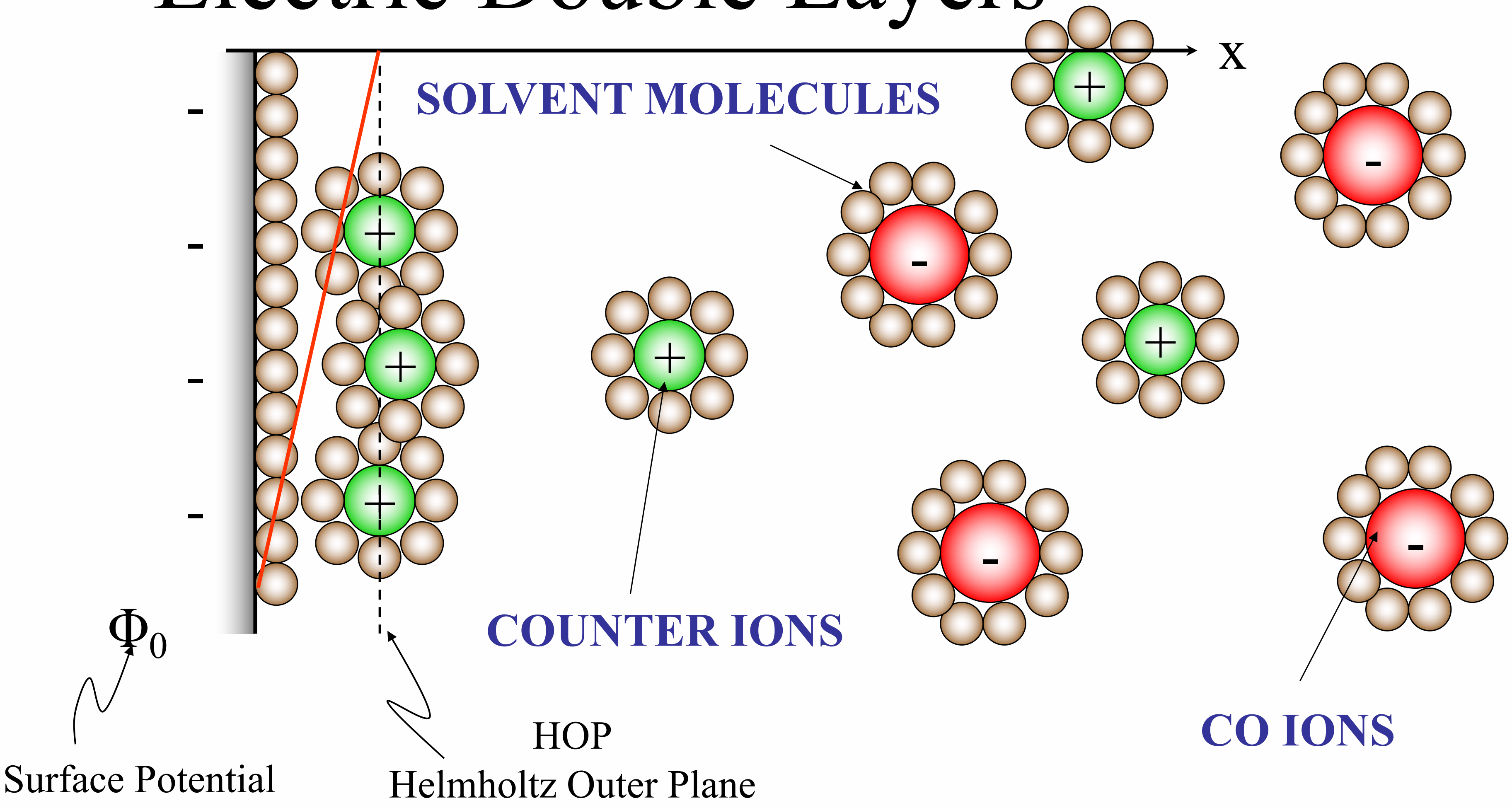
Debye-Hückel Potential (U(r)) between two charges (e) separated by a distance r,

$$U(r) = \frac{e^2}{\varepsilon r} \exp\left(-\frac{r}{r_D}\right) \qquad r_D = \left(\frac{\varepsilon k T}{4\pi n e^2}\right)^{1/2}$$

r_D is the Debye screening length, n is the counter ion (salt) concentration, r_D determines how quickly the electrostatic potential decays

Soft and Fragile Matter, M. E. Cates, M.R. Evans Chapter 3 Alexi Khokhlov (2000); Chines review of polyelectrolytes from web

Electric Double Layers



SOLVENT MOLECULES

COUNTER IONS

CO IONS

Surface Potential

HOP

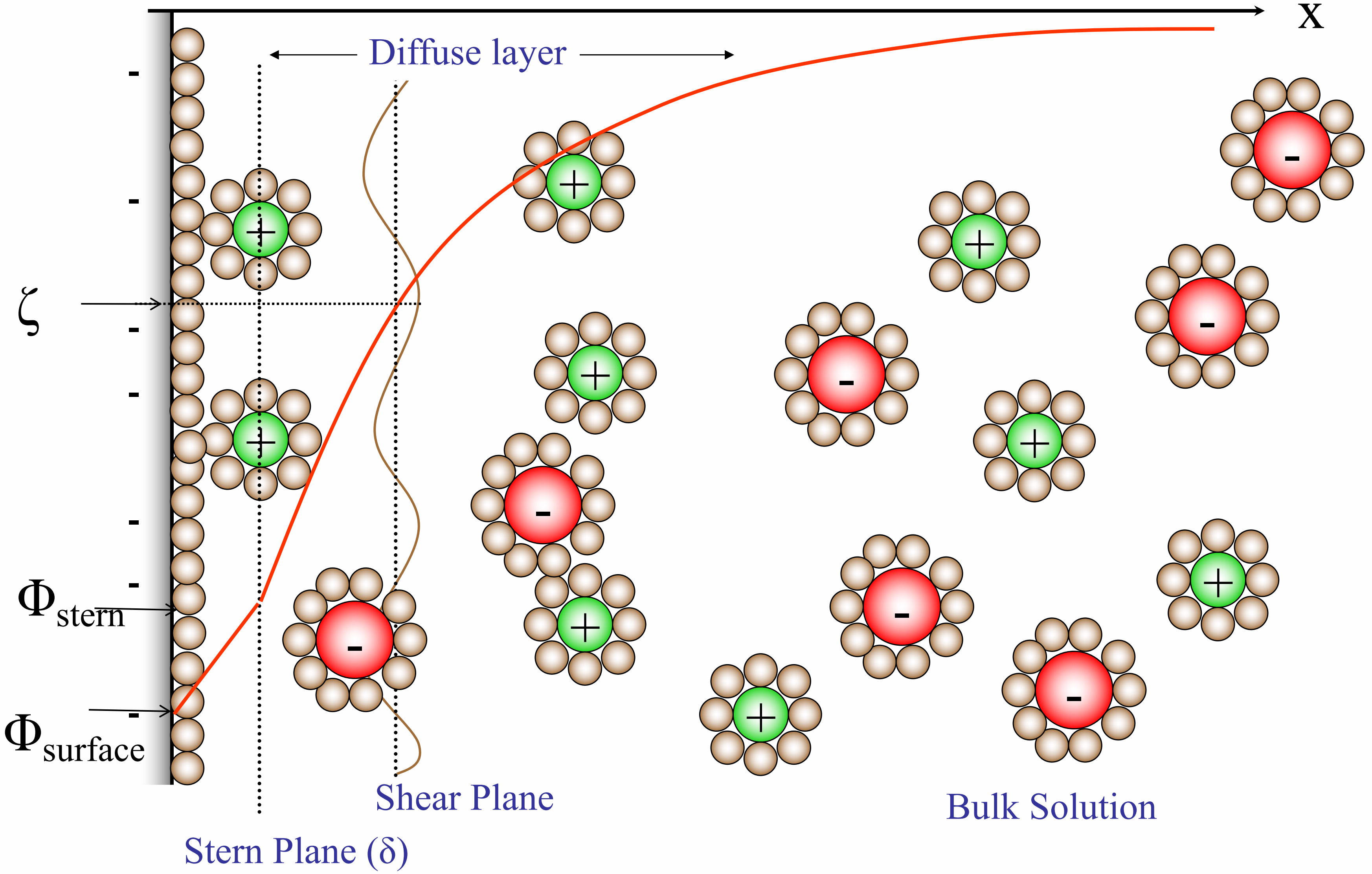
Helmholtz Outer Plane

Helmholtz (100+ years ago) proposed that surface charge is balanced by a layer of oppositely charged ions.

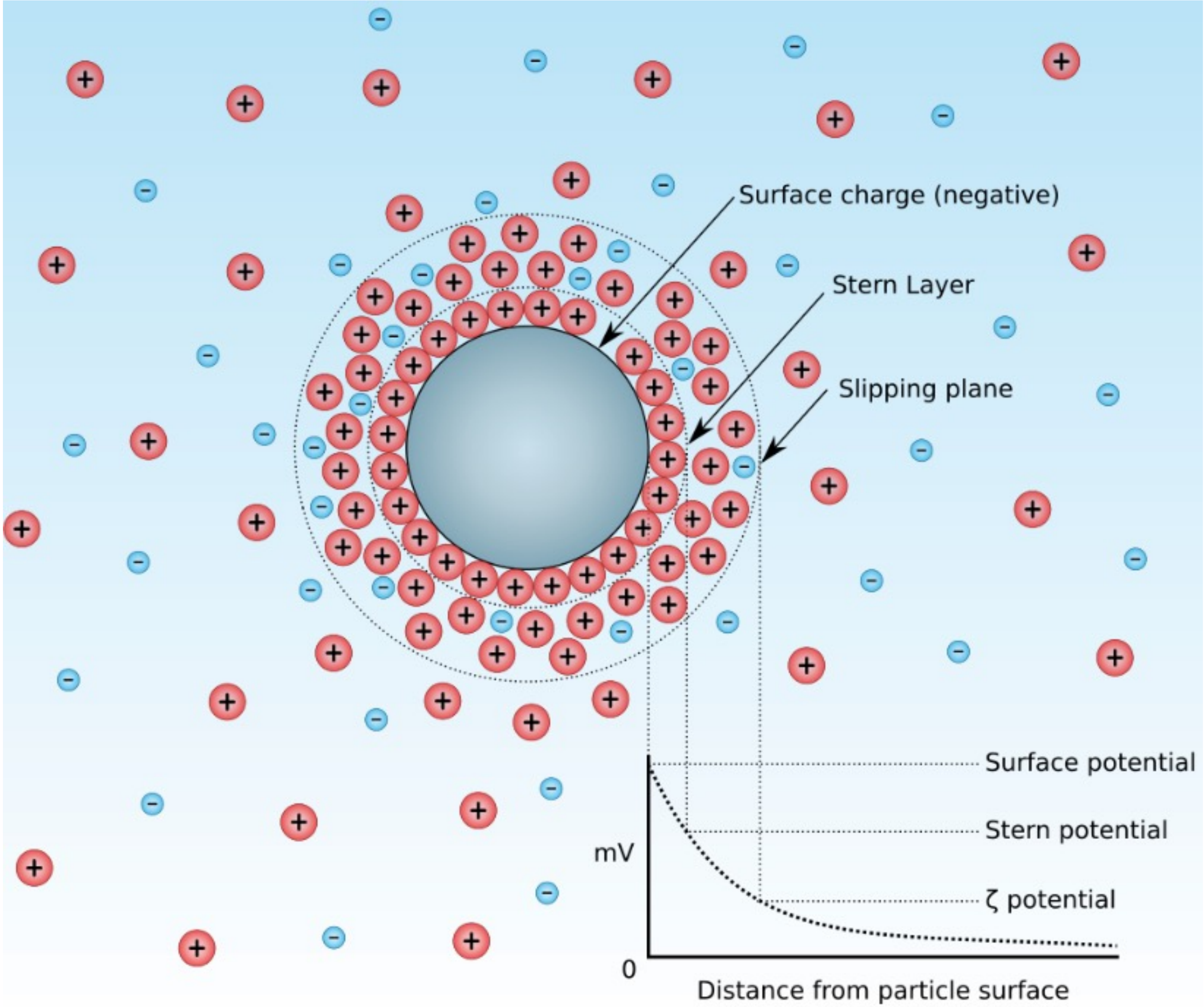
All colloids should flocculate.

Zeta (ζ) Potential

Gouy/Chapman diffuse double layer + layer of adsorbed charge.



Φ = electrostatic potential (Volt = J/coulomb)


Surface charge (negative)
Stern Layer
Slipping plane
Surface potential
Stern potential
mV
ζ potential
0
Distance from particle surface

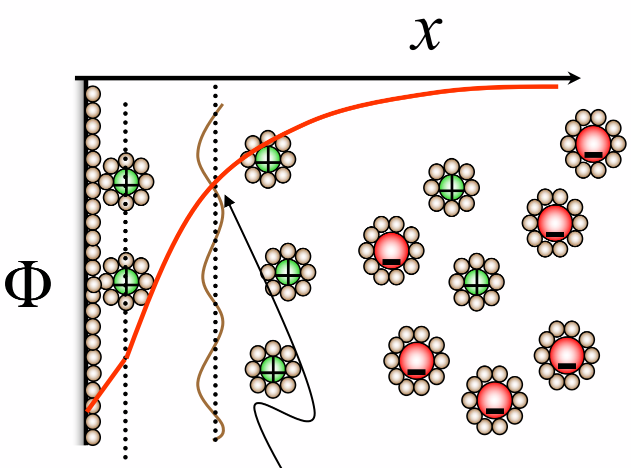
Debye-Hückel approximation for Φ(x)

$$\frac{ze\Phi_o}{kT} << 1 \quad \text{Debye} - \text{Hückel Approximation}$$

$$\Phi(x) = \Phi_0 \exp(-\kappa x)$$

$$\kappa = \left(\frac{2e^2 n_0 z^2}{\varepsilon_r \varepsilon_o kT}\right)^{1/2} \qquad \kappa^{-1} = \text{Debye screening length}$$

Gouy-Chapman Model



Exponential function

Dale Schaefer Slides 2010

http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/Persistence/Persistence.
ml

Polyelectrolytes (proteins, charged polymers, polyethylene oxide, polypropylene oxide, poly nucleic acids, etc.)

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Weakly charged polyelectrolytes = some monomers are charged
This can depend on the counter ion concentration

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r_D is the Debye screening length, n is the counter ion (salt) concentration, r_D determines how quickly the electrostatic potential decays

Soft and Fragile Matter, M. E. Cates, M.R. Evans Chapter 3 Alexi Khokhlov (2000); Chines review of polyelectrolytes from web

http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/Persistence/Persistence.
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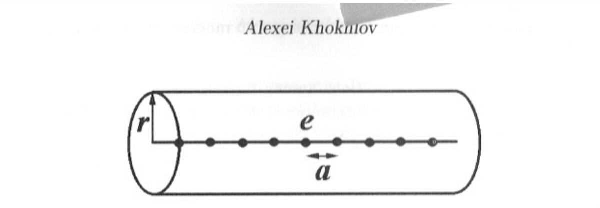

Figure 13. *Illustration of the phenomenon of counterion condensation.*

-Counterion Condensation

A counter ion has translational entropy that drives it away from a chain of charged monomers

$$\Delta G_1 = kT\ln\frac{V_2}{V_1} = kT\ln\frac{V_2}{V_1}$$

V_2 and V_1 are the initial and final cylinders

A counter ion has an enthalpy that attracts it to a chain of charged monomers (a = charge separation on chain)

$$\Delta G_2 = -\frac{e\rho}{\varepsilon}\ln\frac{r_2}{r_1} = -\frac{e^2}{\varepsilon a}\ln\frac{V_2}{V_1} \qquad \rho = \frac{e}{a}$$

Balancing these two we have the parameter u,

$$u \equiv \frac{e^2}{\varepsilon a kT}$$

u < 1 entropy is favored, and counter ions move out (disperse into solution),
u > 1 enthalpy favored and c. i. move in (condense on chain)

Counter ions condense until the chain charge is neutralized, when

$$u_{eff} = \frac{\rho_{eff} e^2}{\varepsilon kT} = 1$$

ρ_{eff} is the chain charge and condensed counter ion charge

Soft and Fragile Matter, M. E. Cates, M.R. Evans Chapter 3 Alexi Khokhlov (2000); Chines review of polyelectrolytes from web

http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/Persistence/Persistence.
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Polyelectrolytes (proteins, charged polymers, polyethylene oxide, polypropylene oxide, poly nucleic acids, etc.)

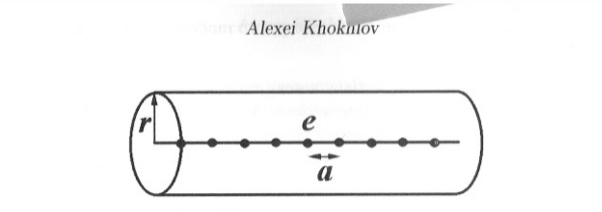


Figure 13. *Illustration of the phenomenon of counterion condensation.*

-Electrostatic Persistence Length

Persistence is increased by electrostatic charge. $l_{per} = l_o + l_e$

For $a << l_{per} << r_D$

Interaction between charges separated by distance less than r_D, short range repulsion increases persistence length

Interaction between charges separated by a distance > l_{per} effect chain scaling

When $u_{eff} = \frac{\rho_{eff} e}{\varepsilon kT} = 1$ charge condensation stops since all charge on the chain is neutralized

and a maximum effective linear charge density is reached $\rho_{eff,\max} = \frac{\varepsilon kT}{e}$

Soft and Fragile Matter, M. E. Cates, M.R. Evans Chapter 3 Alexi Khokhlov (2000); Chines review of polyelectrolytes from web

Alexei Khokhlov

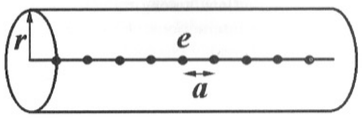


Figure 13. *Illustration of the phenomenon of counterion condensation.*

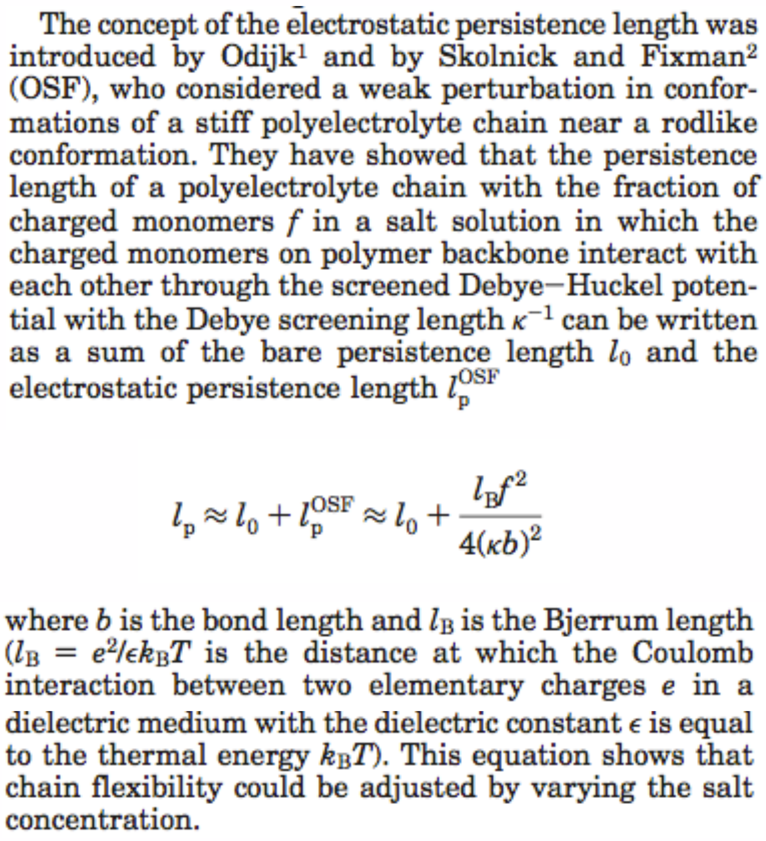
Summary of Polyelectrolyte Persistence Length

3 size scales are important,

- "a" spacing of charge groups on the chain
- r_D or κ^{-1} Debye Screening length
- $l_{p,0}$ bare persistence length with no charge

"a" must be smaller than r_D for there to be a change in persistence, this is so that neighboring charges can interact
r_D must be smaller than $l_{p,0}$ for there to be a change in persistence

The parameter "u" enthalpy of attraction divided by T*entropy of dispersion of charge governs u>1 charge condense; u<1 charges disperse



The concept of the electrostatic persistence length was introduced by Odijk[1] and by Skolnick and Fixman[2] (OSF), who considered a weak perturbation in conformations of a stiff polyelectrolyte chain near a rodlike conformation. They have showed that the persistence length of a polyelectrolyte chain with the fraction of charged monomers f in a salt solution in which the charged monomers on polymer backbone interact with each other through the screened Debye–Huckel potential with the Debye screening length κ^{-1} can be written as a sum of the bare persistence length l_0 and the electrostatic persistence length l_p^{OSF}

$$l_p \approx l_0 + l_p^{OSF} \approx l_0 + \frac{l_B f^2}{4(\kappa b)^2}$$

where b is the bond length and l_B is the Bjerrum length ($l_B = e^2/\epsilon k_B T$ is the distance at which the Coulomb interaction between two elementary charges e in a dielectric medium with the dielectric constant ϵ is equal to the thermal energy k_BT). This equation shows that chain flexibility could be adjusted by varying the salt concentration.

Dobrynin AV *Macro.* **38** 9304 (2005)

Other measures of Local Structure

Kuhn Length, Persistence Length: Static measure of step size

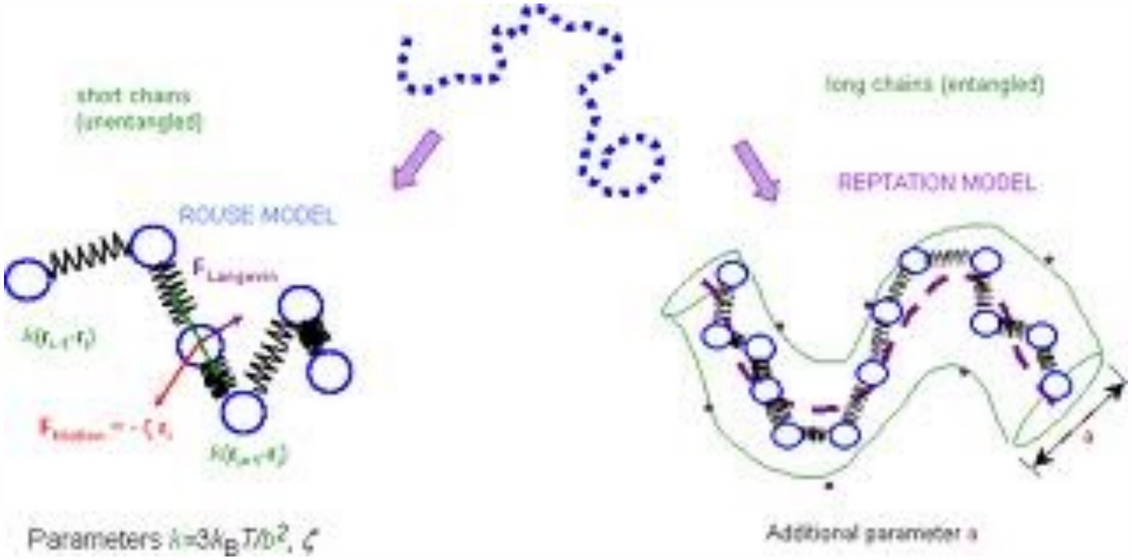
Tube Diameter: Dynamic measure of chain lateral size

Packing Length: Combination of static and dynamic measure of local structure

Packing Length and Tube Diameter

Chain dynamics in the melt can be described by a small set of “physically motivated, material-specific paramters”

Tube Diameter d_T
Kuhn Length l_K
Packing Length p



Larson Review of Tube Model for Rheology

http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/SukumaranScience.pdf

Strobel Chapter 8

$$u = q^2 a_{\mathrm{R}}^2 \left(\frac{t}{\tau(\delta = \pi)} \right)^{1/2} = q^2 \left(\frac{12kTa_{\mathrm{R}}^2 t}{\zeta_{\mathrm{R}}} \right)^{1/2}$$

u reflects Rouse behavior. In plots versus u, deviations from ideal Rouse Behavior indicate tube constraints.

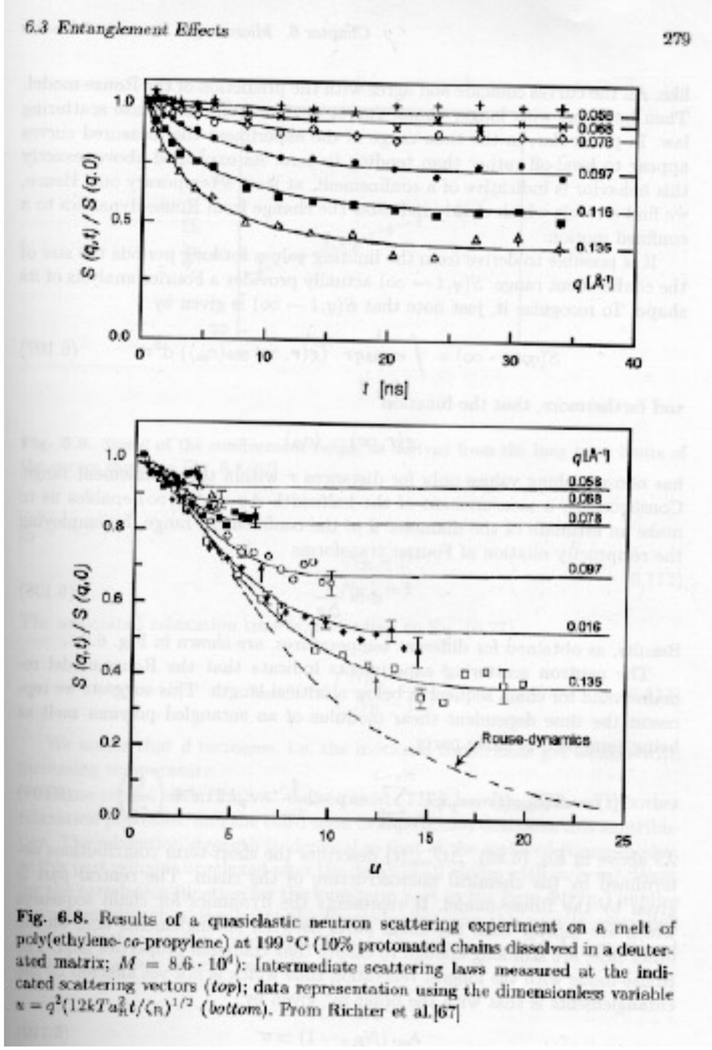

6.3 Entanglement Effects 279

Fig. 6.8. Results of a quasielastic neutron scattering experiment on a melt of poly(ethylene-*co*-propylene) at 199 °C (10% protonated chains dissolved in a deuterated matrix; $M = 8.6 \cdot 10^4$): Intermediate scattering laws measured at the indicated scattering vectors (*top*); data representation using the dimensionless variable $u = q^2(12kTa_{\mathrm{R}}^2 t/\zeta_{\mathrm{R}})^{1/2}$ (*bottom*). From Richter et al.[67]

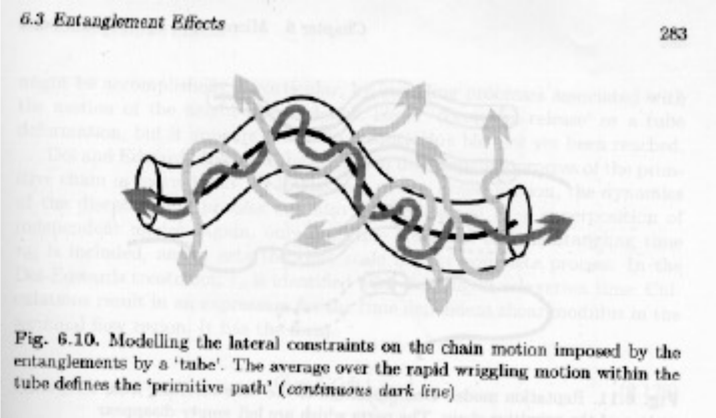

6.3 Entanglement Effects 283

Fig. 6.10. Modelling the lateral constraints on the chain motion imposed by the entanglements by a 'tube'. The average over the rapid wriggling motion within the tube defines the 'primitive path' (*continuous dark line*)

Quasi-elastic neutron scattering data demonstrating the existence of the tube

Unconstrained motion => S(q) goes to 0 at very long times

Each curve is for a different q = 1/size

At small size there are less constraints (within the tube)

At large sizes there is substantial constraint (the tube)

By extrapolation to high times
a size for the tube can be obtained
d_T

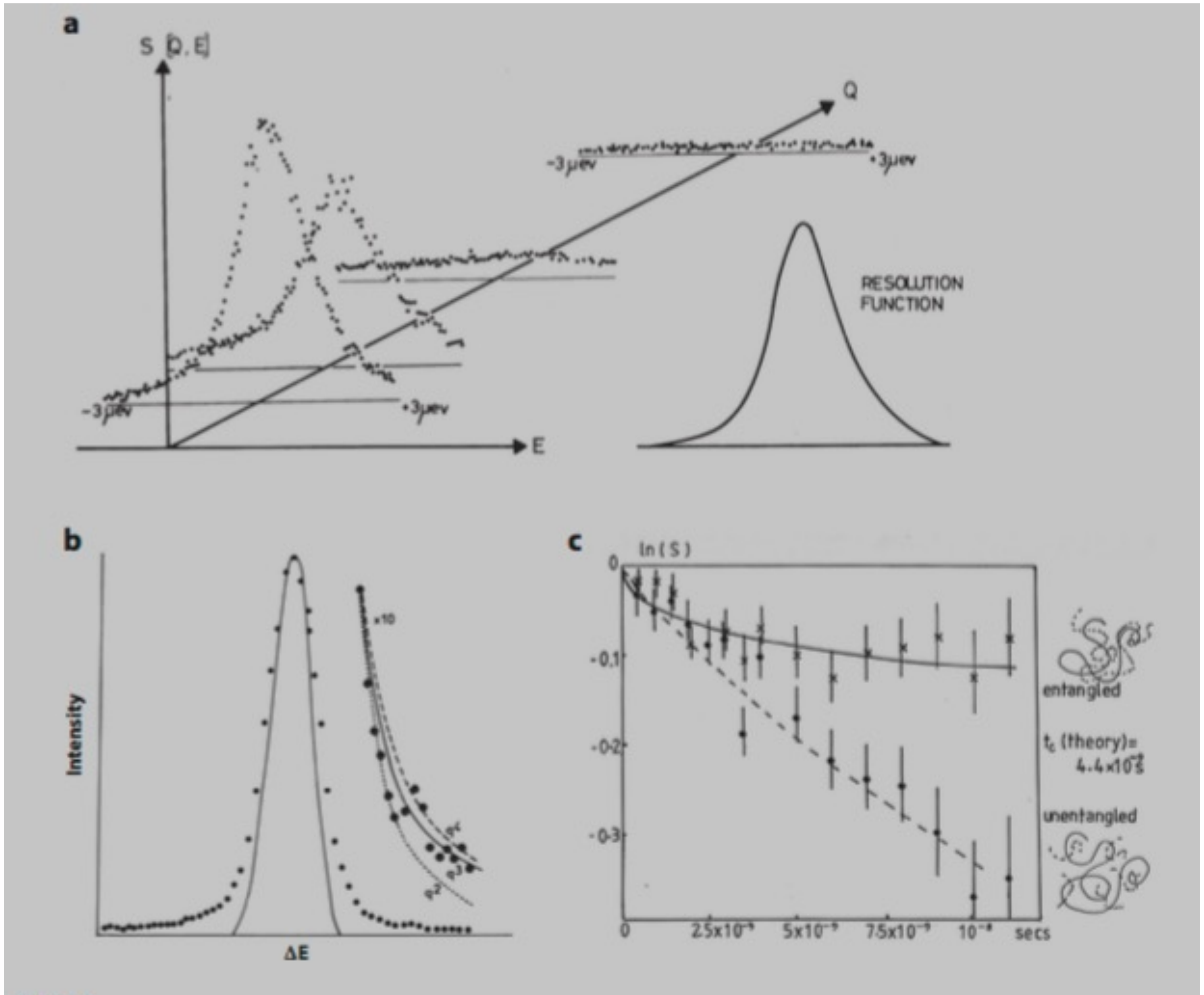


Figure 2

Quasi-elastic scattering from (*a*) poly-(dimethyl siloxane) using the back scattering spectrometer, IN10, as described in Reference 17; (*b*) expanded section of the wings of the Q-E scattering showing the difficulty of distinguishing between different models; (*c*) adapted from Reference 28 with permission from the Royal Society of Chemistry showing the IN11 (spin-echo) data for two mixtures of high–molecular weight polytetrahydrofuran (PTHF) entangled in a matrix of high–molecular weight deuterated PTHF and unentangled in a low–molecular weight matrix.

Julia Higgins Review Article (2016)

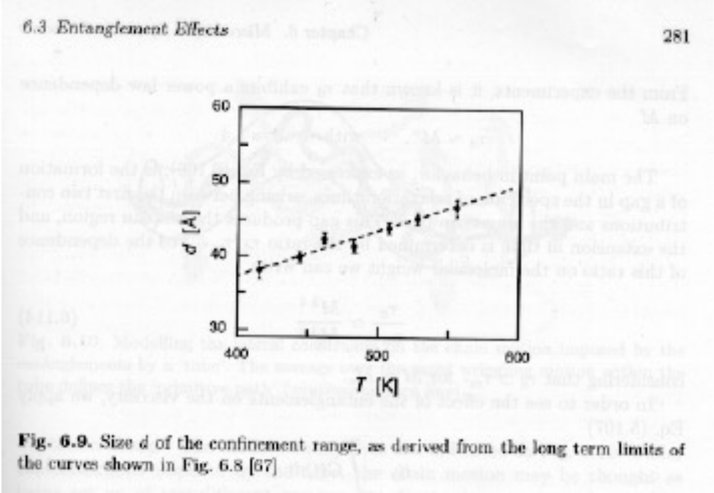


Fig. 6.9. Size d of the confinement range, as derived from the long term limits of the curves shown in Fig. 6.8 [67]

There are two regimes of hierarchy in time dependence
Small-scale unconstrained Rouse behavior
Large-scale tube behavior

We say that the tube follows a “primitive path”
This path can “relax” in time = Tube relaxation or **Tube Renewal**

A model called **Tube Dilation** also exists to describe deviations between the tube model and experiment

Without tube renewal the Reptation model predicts that viscosity follows N^3 (observed is $N^{3.4}$)

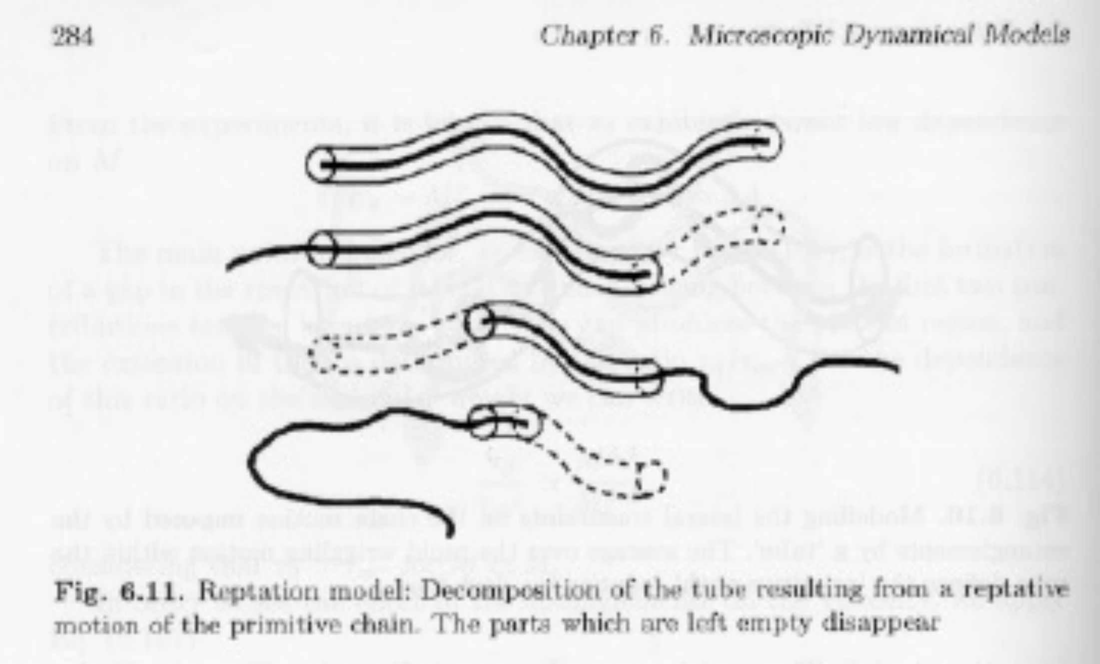


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Fig. 6.11. Reptation model: Decomposition of the tube resulting from a reptative motion of the primitive chain. The parts which are left empty disappear

Without tube renewal the Reptation model predicts that viscosity follows N^3 (observed is $N^{3.4}$)

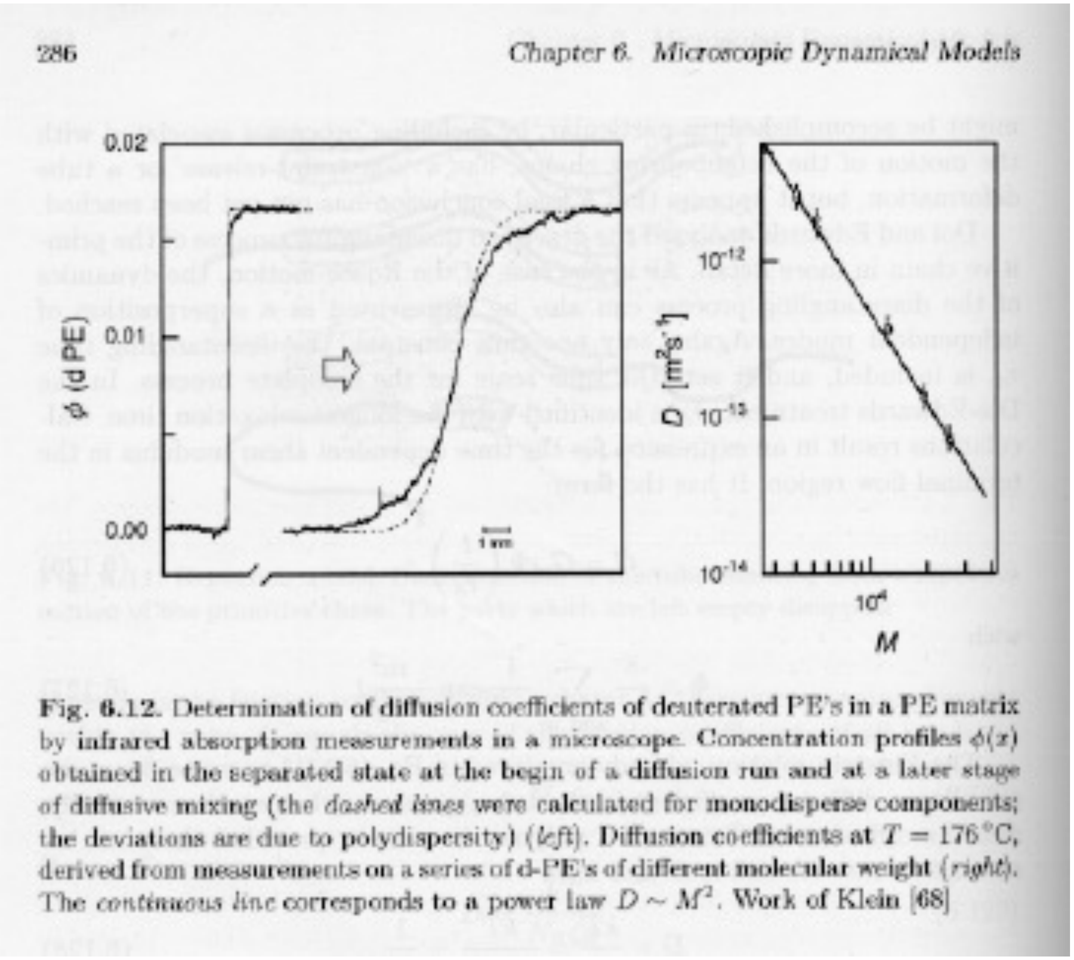


Fig. 6.12. Determination of diffusion coefficients of deuterated PE's in a PE matrix by infrared absorption measurements in a microscope. Concentration profiles $\phi(x)$ obtained in the separated state at the begin of a diffusion run and at a later stage of diffusive mixing (the *dashed lines* were calculated for monodisperse components; the deviations are due to polydispersity) (*left*). Diffusion coefficients at $T = 176\,^{\circ}\mathrm{C}$, derived from measurements on a series of d-PE's of different molecular weight (*right*). The *continuous line* corresponds to a power law $D \sim M^{-2}$. Work of Klein [68]

Fick's Second Law

$$\frac{\partial \varphi}{\partial t} = D\,\frac{\partial^2 \varphi}{\partial x^2}$$

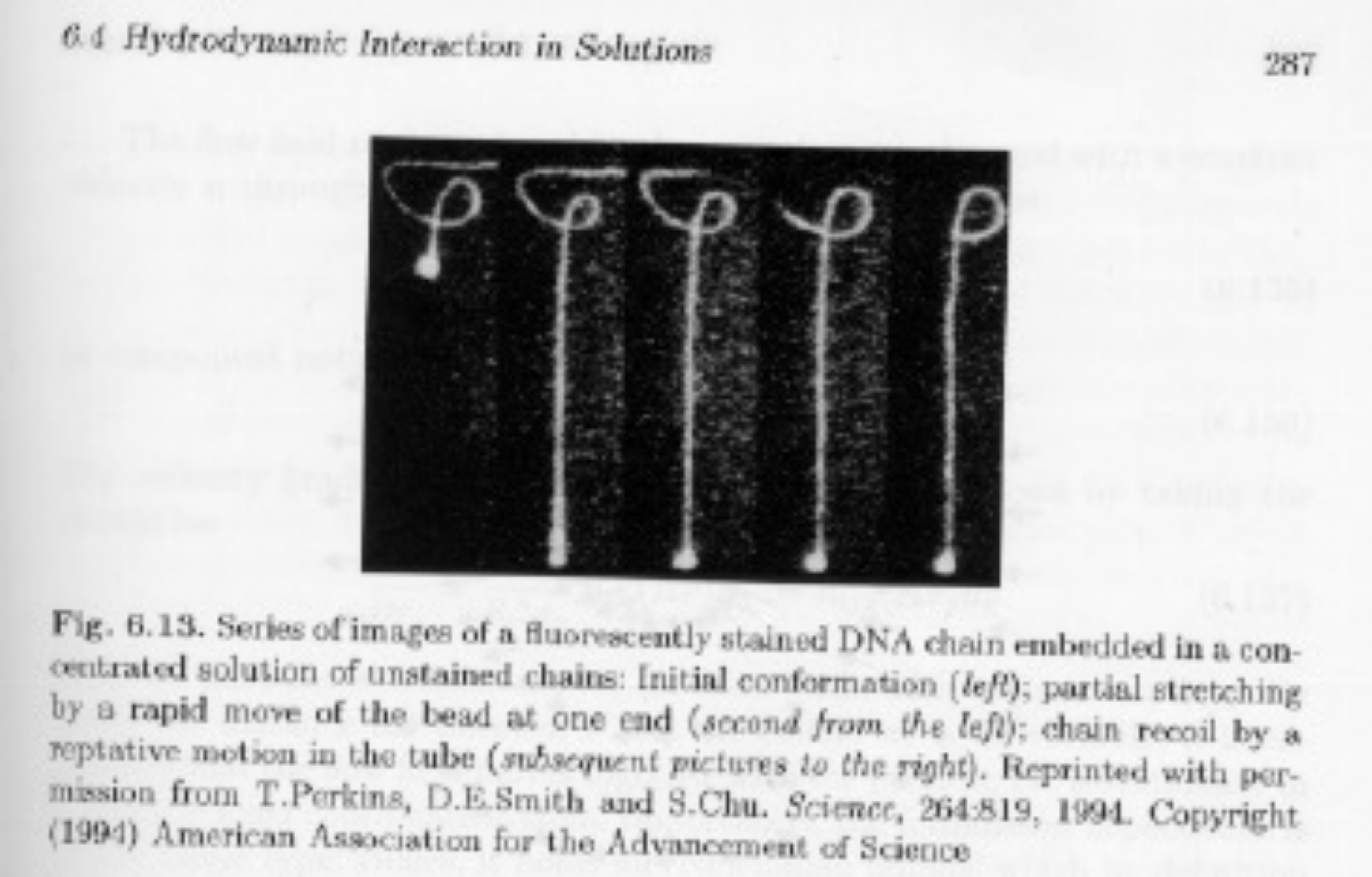
$$n\left(x,t\right) = n_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$n\left(x,t\right) = n_0\left[1 - 2\left(\frac{x}{2\sqrt{Dt\pi}}\right)\right]$$

Reptation predicts that the diffusion coefficient will follow N^2 (Experimentally it follows N^2)
Reptation has some experimental verification
Where it is not verified we understand that tube renewal is the main issue.

(Rouse Model predicts D ~ 1/N)

Reptation of DNA in a concentrated solution



6.4 Hydrodynamic Interaction in Solutions 287

Fig. 6.13. Series of images of a fluorescently stained DNA chain embedded in a concentrated solution of unstained chains: Initial conformation (*left*); partial stretching by a rapid move of the bead at one end (*second from the left*); chain recoil by a reptative motion in the tube (*subsequent pictures to the right*). Reprinted with permission from T.Perkins, D.E.Smith and S.Chu. *Science*, 264:819, 1994. Copyright (1994) American Association for the Advancement of Science

Simulation of the tube

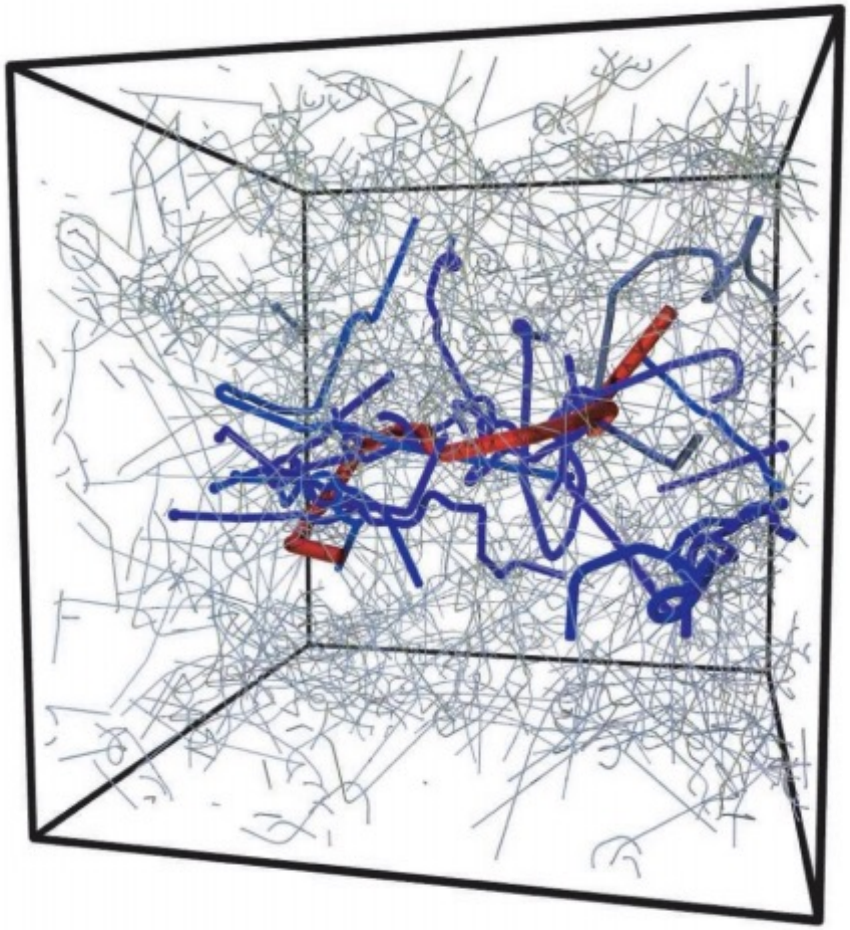


Fig. 3. Result of the primitive-path analysis of a melt of 200 chains of $N + 1 = 350$ beads. We show the primitive path of one chain (red) together with all of those it is entangled with (blue). The primitive paths of all other chains in the system are shown as thin lines.

Simulation of the tube

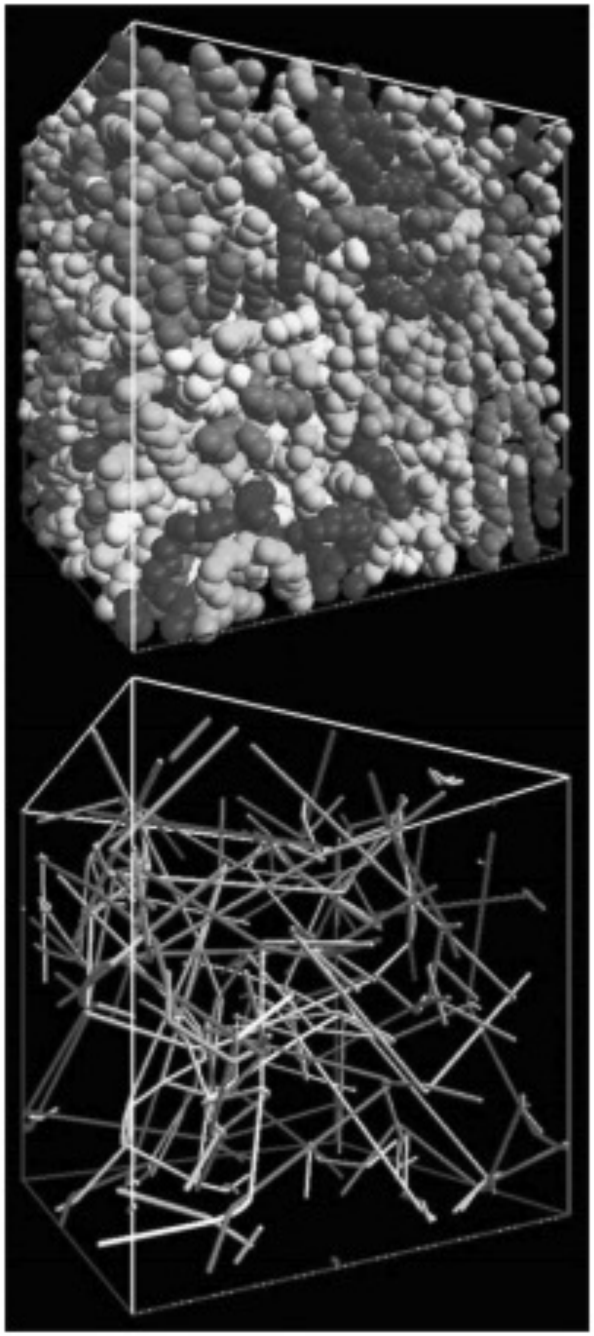


Fig. 3. A representative amorphous polymer sample and the corresponding network of primitive paths.

Packing Length

Origin of the Packing Length:

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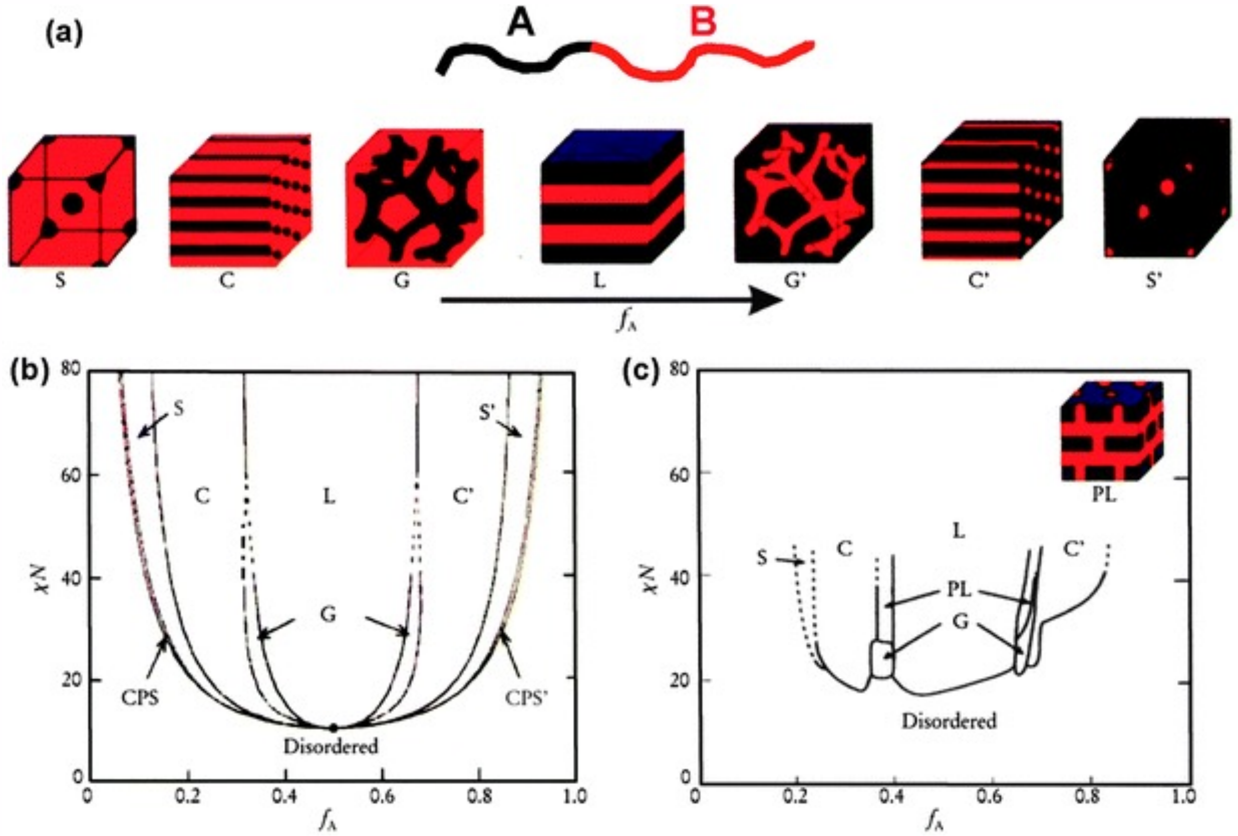
Consider a di-block copolymer domain interface
(and blends with homopolymers as a compatibilizer)



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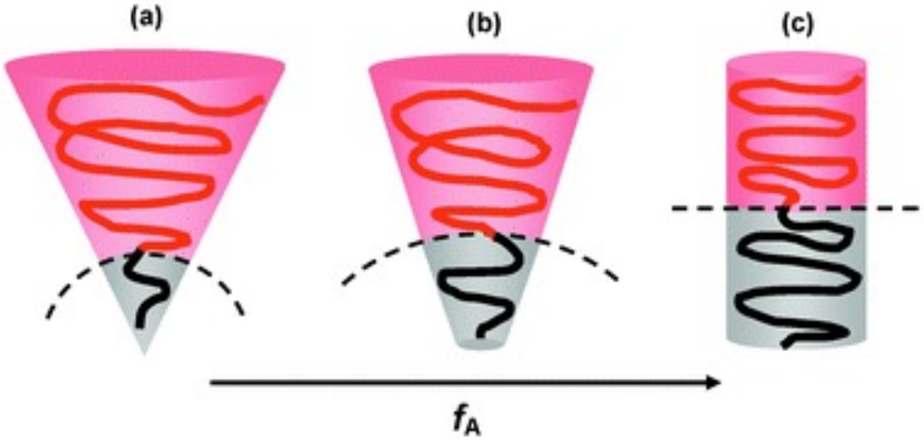

Fig. 3 Schematic illustration of the possible polymer chain arrangements in different morphologies of AB diblocks changing from sphere (a) to cylinder (b) and to lamella (c), as the volume fraction (f_A) of the A block (black) increases to ~0.5. The dash curve in each morphology represents a part of the interface between A and B domains. The concept of this figure originates from ref. 24. This reference contributes to BCP self-assembly in solution, and is cited accordingly in Section 3.1.

http://pubs.rsc.org/en/content/articlehtml/2012/cs/c2cs35115c

Free Energy Contributions:

Interfacial Energy Proportional to the Total Surface Area

(makes domains large to reduce surface area)

Sur = $\chi kTAd_t/V_c$

d_t is the thickness of the interfacial layer where the A-B junction is located

A is the cross sectional area of a polymer chain

V_c is the occupied volume of a unit segment of a polymer chain

The total occupied volume of a block copolymer chain is $V_{occupied} = N_{AB} V_c$;

This occupied volume is also given by $V_{occupied} = d_{AB} A$ where d_{AB} is the length of the block copolymer chain assuming it forms a cylindrical shaped object and the block copolymer domain spacing.

Energy of Elongation of Polymer Chains, Elastic Energy

(makes domains small)

Assumes that one end is at the interface and the other end must fill the space.

Chain = $-3kT\, d_{AB}^2/(2\langle R^2\rangle) = -3kT\, N_{AB}V_c^2/(l_K^2A^2)$

$d_{AB} = N_{AB} V_c/A$ from above and $\langle R^2\rangle = N_{AB}l_K^2$

The free energy will be minimized in A to obtain the optimum phase size d_{AB}. So it is the packing of the chains at the interface that governs the phase behavior of BCP's.

$\Delta G/kT = \chi kTAd_t/V_c - 3kT\, N_{AB}V_c^2/(2(l_KA)^2$

$d(\Delta G/kT)/dA = \chi d_t/V_c + 3\, N_{AB}V_c^2/(l_K^2A^3) = 0$

$A = \{3\, N_{AB}V_c^3/(l_K^2\chi d_t)\}^{1/3}$

$d_{AB} = N_{AB} V_c/A = N_{AB}^{2/3}/(3l_K^2\chi d_t)^{1/3}$ This is verified by experiment (Hashimoto papers)

Three terms arise from the consideration of microphase separation

A is the cross-sectional area of a polymer chain
V_c is the occupied volume of a unit segment of a polymer chain
$V_{occupied} = N_{AB} V_c$ The total occupied volume of a block copolymer chain

Witten defines a term "a" that he calls the intrinsic elasticity of a polymer chain
Elastic Energy/(3kT) = $a <R^2>/(2V_{occupied})$ where $a = V_{occupied}/<R_0^2> = V_{occupied}/(N_K\ l_K^2)$
(Previously we had the spring constant $k_{spr}/kT = 3/<R_0^2> = 3a/V_{occupied}$; $a = k_{spr}\ V_{occupied}/3$)

"a" has units of length and is termed by Witten the "***packing length***" since it relates to the packing or occupied volume for a chain unit, $V_{occupied}$. "a" is a ratio between the packing volume and the molar mass as measured by $<R_0^2>$.

Since $V_{occupied} = N_K V_c$, and $<R_0^2> = N_K\ l_K^2$, then $a = V_c/l_K^2$, so the packing length relates to the lateral occupied size of a Kuhn unit, the lateral distance to the next chain. This is a kind of "***mesh size***" for the polymer melt. The cross-sectional area, A, is defined by "a", $A = \pi a^2$, and $V_c = a\ l_K^2$, so the BCP phase size problem can be solved using only the parameter "a".

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Other uses for the packing length

The packing length is a fundamental parameter for calculation of dynamics for a polymer melt or concentrated solution.

Plateau modulus of a polymer melt $G \sim 0.39\ kT/a^3$

Structural Control of "a"

$a = m_0/(\rho\ l_K\ l_0)$

Vary mass per chain length, m_0/l_0

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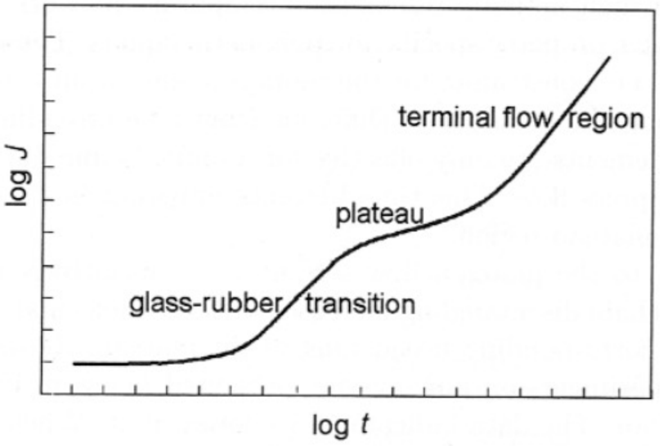

Fig. 5.12. General shape of the complete creep curve of PS, as suggested by the appearance of the different parts shown in Fig. 5.11

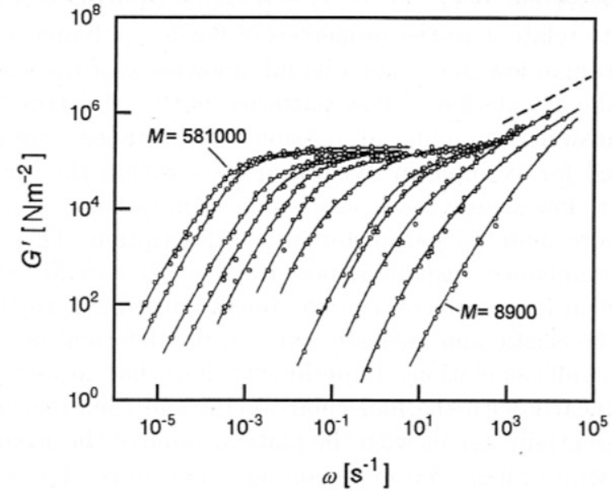

Fig. 5.15. Storage shear moduli measured for a series of fractions of PS with different molecular weights in the range $M = 8.9 \cdot 10^3$ to $M = 5.81 \cdot 10^5$. The *dashed line* in the upper right corner indicates the slope corresponding to the power law Eq. (6.81) derived for the Rouse-model of the glass-transition. Data from Onogi et al.[54]

$$J^*(\omega \to 0) = J_e^0 - i\frac{1}{\eta_0\omega} \qquad (5.103)$$

As we see, η_0 and J_e^0 show up directly and separately, in the limiting behavior of J' and J''.

The dynamic shear modulus follows as

$$\begin{aligned} G^*(\omega \to 0) &= \frac{1}{J^*(\omega \to 0)} = \frac{\eta_0\omega}{\eta_0\omega J_e^0 - i} \\ &= \frac{\eta_0^2\omega^2 J_e^0 + i\eta_0\omega}{(\eta_0\omega J_e^0)^2 + 1} \end{aligned} \qquad (5.104)$$

giving

$$G'(\omega \to 0) = J_e^0\eta_0^2\omega^2 \qquad (5.105)$$

in agreement with Fig. 5.15, and

$$G''(\omega \to 0) = \eta_0\omega \qquad (5.106)$$

We thus find characteristic power laws also for the storage and the loss modulus which again include J_e^0 and η_0 in a well-defined way.

One may wonder if η_0 and J_e^0 can also be deduced from the time dependent response functions, as for example from $G(t)$. Indeed, direct relationships exist, expressed by the two equations

Low Frequency G' ~ ω^2
From definition of viscoelastic

High Frequency G' ~ $\omega^{1/2}$
From Rouse Theory for T_g

Plateau follows rubber elasticity
G' ~ $3kT/(N_{K,e}\, l_K^2)$

Plateau Modulus

Not Dependent on N, Depends on T and concentration

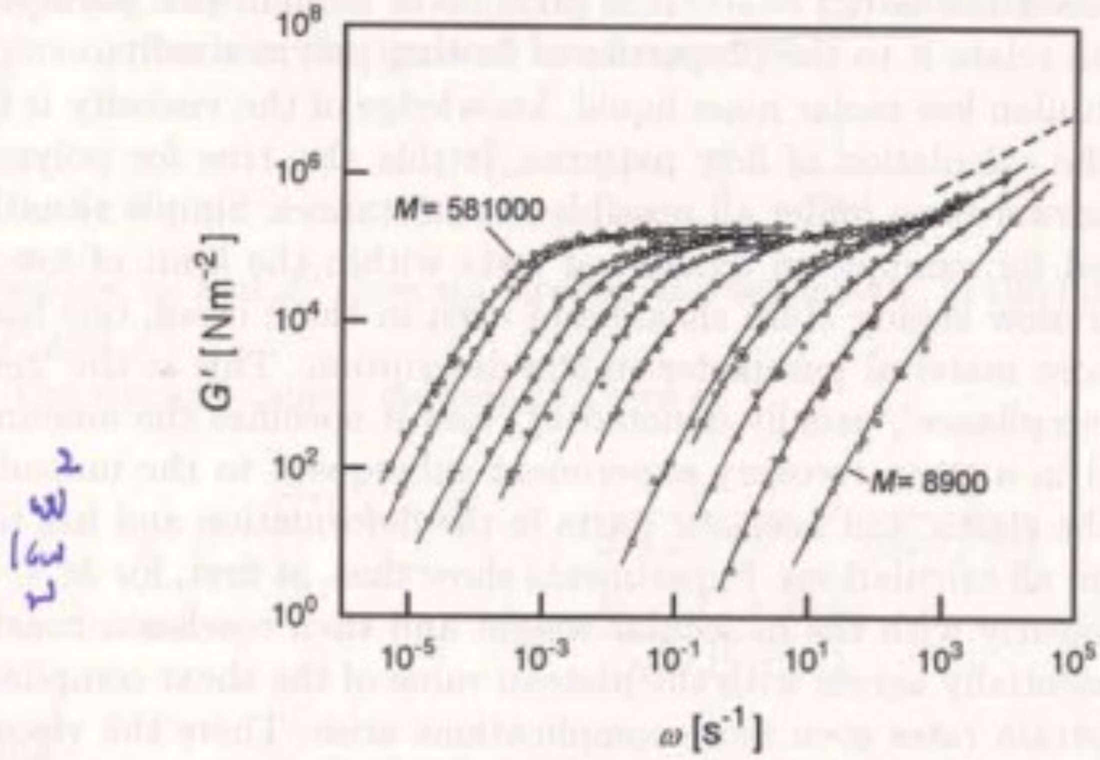

Fig. 5.15. Storage shear moduli measured for a series of fractions of PS with different molecular weights in the range $M = 8.9 \cdot 10^3$ to $M = 5.81 \cdot 10^5$. The *dashed line* in the upper right corner indicates the slope corresponding to the power law Eq. (6.81) derived for the Rouse-model of the glass-transition. Data from Onogi et al.[54]

$$G_0 = \frac{4\rho RT}{5M_e} = \frac{4RT}{5p^3}$$

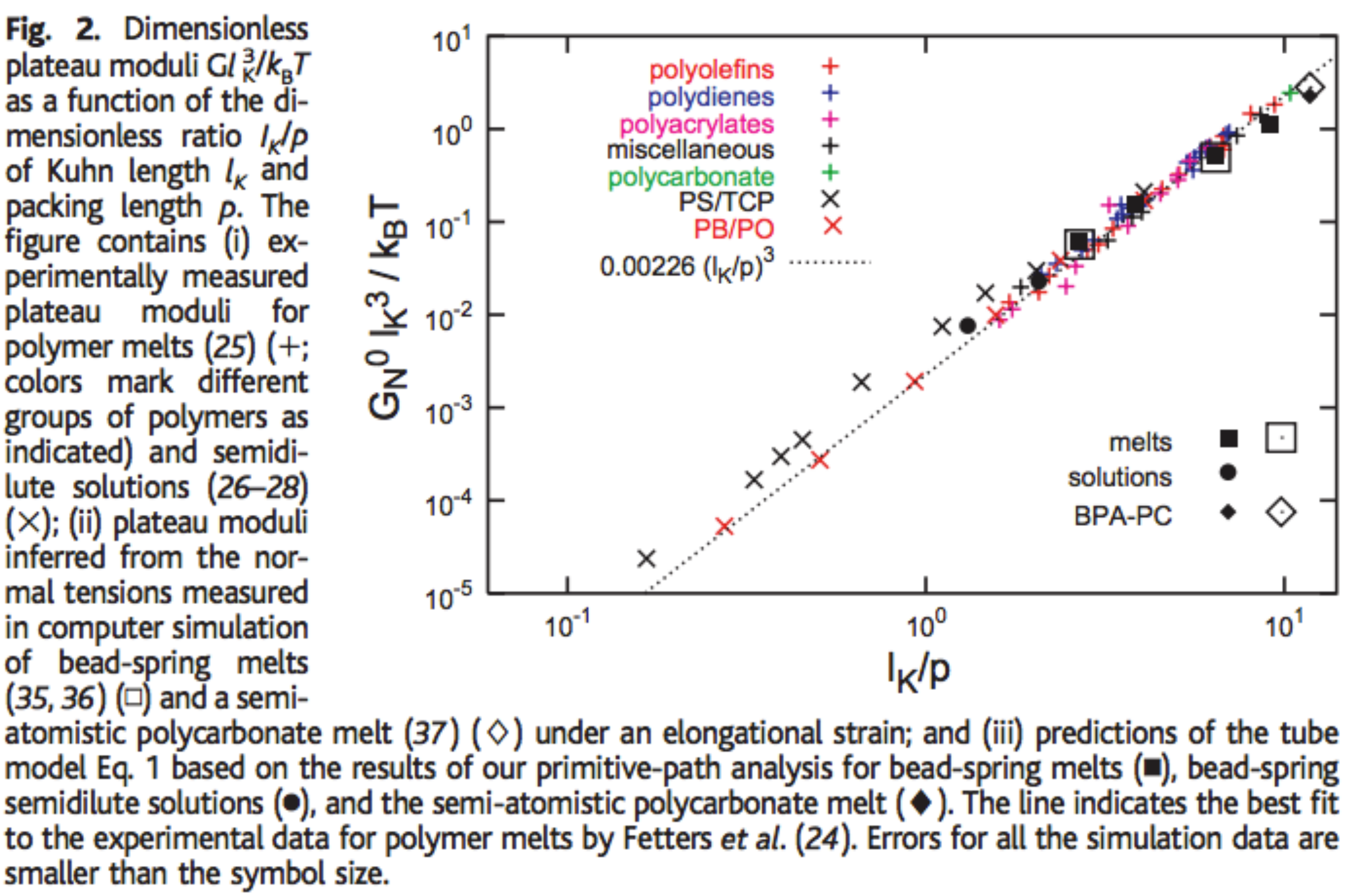

Fig. 2. Dimensionless plateau moduli Gl_K^3/k_BT as a function of the dimensionless ratio l_K/p of Kuhn length l_K and packing length p. The figure contains (i) experimentally measured plateau moduli for polymer melts (*25*) (+; colors mark different groups of polymers as indicated) and semidilute solutions (*26–28*) (×); (ii) plateau moduli inferred from the normal tensions measured in computer simulation of bead-spring melts (*35, 36*) (□) and a semi-atomistic polycarbonate melt (*37*) (◇) under an elongational strain; and (iii) predictions of the tube model Eq. 1 based on the results of our primitive-path analysis for bead-spring melts (■), bead-spring semidilute solutions (●), and the semi-atomistic polycarbonate melt (◆). The line indicates the best fit to the experimental data for polymer melts by Fetters *et al.* (*24*). Errors for all the simulation data are smaller than the symbol size.

this implies that $d_T \sim p$

Kuhn Length- conformations of chains $\langle R^2 \rangle = l_K L$

Packing Length-length where polymers interpenetrate $p = 1/(\rho_{chain} \langle R^2 \rangle)$
where ρ_{chain} is the number density of monomers