Polymer Physics

10:10 – 11:05
Baldwin 661

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https://www.eng.uc.edu/~beaucag/Classes/Properties.html

Zoom Meeting:
https://ucincinnati.zoom.us/j/85441549694?pwd=mktG1NStvD8zvoT8spbseBiWYOYUEO.1

General Descriptions
Overview

Physical description of an isolated polymer chain
Dimensionality and fractals
Short-range and long-range interactions
Packing length and tube diameter

Long-range interactions and chain scaling
Flory-Krigbaum theory
The semi-dilute and concentrated regimes
Blob theory (the tensile, concentration, and thermal blobs)
Coil collapse/protein folding

Analytic Techniques for Polymer Physics
Measurement of the size of a polymer chain
R_g, R_h, R_{eted}
Small-angle neutron, x-ray scattering and static light scattering
Intrinsic viscosity
Dynamic light scattering
Polymer melt rheology
DSC/DMTA/TGA

Polymers

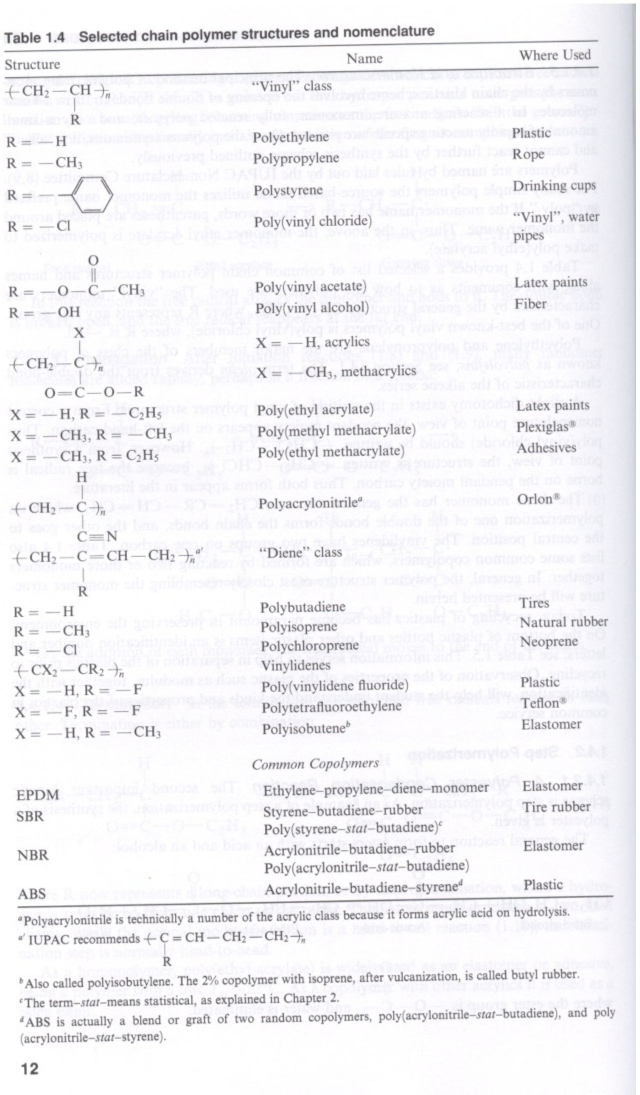


Table 1.4 Selected chain polymer structures and nomenclature

Structure	Name	Where Used
$\text{-(-}CH_2-\underset{\vert\atop R}{CH}\text{-)-}_n$	"Vinyl" class	
$R = -H$	Polyethylene	Plastic
$R = -CH_3$	Polypropylene	Rope
$R =$	Polystyrene	Drinking cups
$R = -Cl$	Poly(vinyl chloride)	"Vinyl", water pipes
$R = -O-\overset{O}{\overset{\Vert}{C}}-CH_3$	Poly(vinyl acetate)	Latex paints
$R = -OH$	Poly(vinyl alcohol)	Fiber
$\text{-(-}CH_2-\overset{X}{\overset{\vert}{C}}\text{-)-}_n$	$X = -H$, acrylics	
$O{=}C-O-R$	$X = -CH_3$, 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
$\text{-(-}CH_2-\overset{H}{\overset{\vert}{\underset{C\equiv N}{\underset{\vert}{C}}}}\text{-)-}_n$	Polyacrylonitrile[a]	Orlon®
$\text{-(-}CH_2-\underset{\vert\atop R}{C}{=}CH-CH_2\text{-)-}_n{}^{a'}$	"Diene" class	
$R = -H$	Polybutadiene	Tires
$R = -CH_3$	Polyisoprene	Natural rubber
$R = -Cl$	Polychloroprene	Neoprene
$\text{-(-}CX_2-CR_2\text{-)-}_n$	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 $\text{-(-}\underset{\vert\atop R}{C}=CH-CH_2-CH_2\text{-)-}_n$

[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).

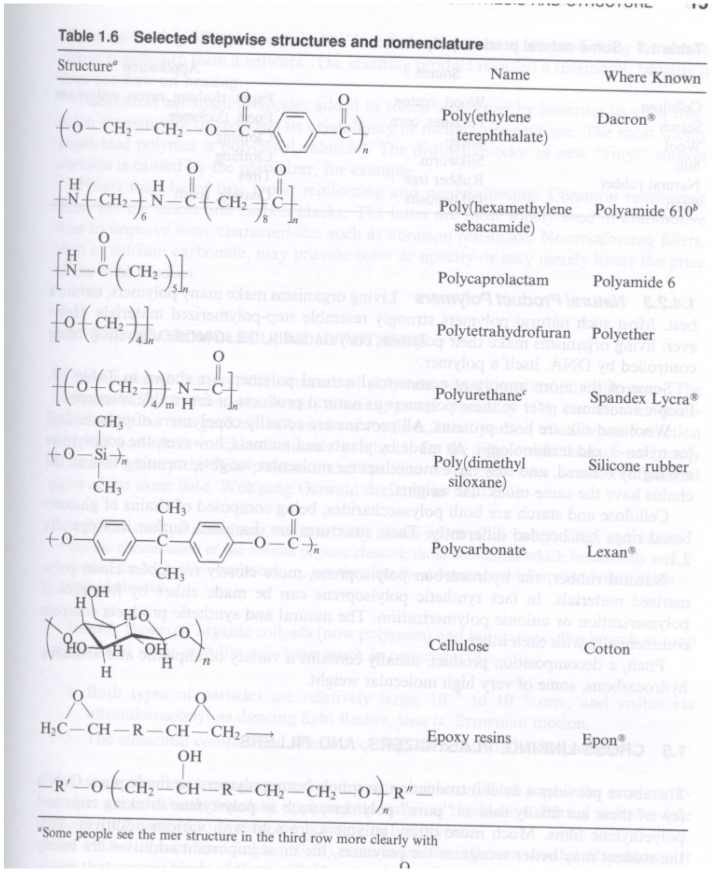
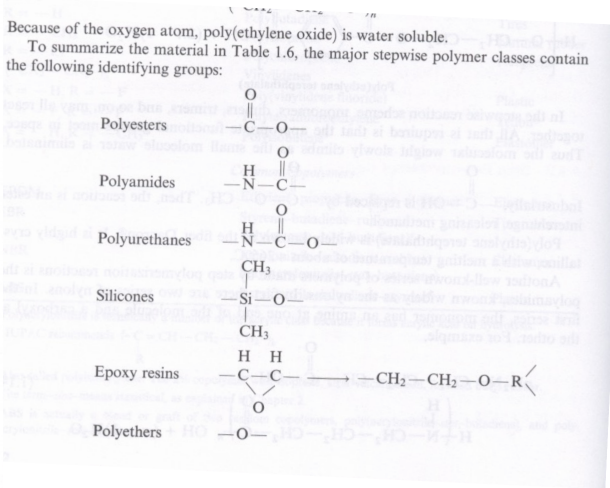


Table 1.6 Selected stepwise structures and nomenclature

Structure[a]	Name	Where Known
	Poly(ethylene terephthalate)	Dacron®
$\left[\overset{H}{N}\left(CH_2\right)_6\overset{H}{N}-\overset{O}{\overset{\Vert}{C}}\left(CH_2\right)_8\overset{O}{\overset{\Vert}{C}}\right]_n$	Poly(hexamethylene sebacamide)	Polyamide 610[b]
$\left[\overset{H}{N}-\overset{O}{\overset{\Vert}{C}}\left(CH_2\right)_5\right]_n$	Polycaprolactam	Polyamide 6
$\left[O\left(CH_2\right)_4\right]_n$	Polytetrahydrofuran	Polyether
$\left[\left(O\left(CH_2\right)_4\right)_m\underset{H}{N}-\overset{O}{\overset{\Vert}{C}}\right]_n$	Polyurethane[c]	Spandex Lycra®
$\text{-(-}O-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{Si}}}}\text{-)-}_n$	Poly(dimethyl siloxane)	Silicone rubber
	Polycarbonate	Lexan®
	Cellulose	Cotton
$H_2\overset{O}{C-CH}-R-\overset{O}{CH-CH_2}\longrightarrow$ $-R'-O\left(CH_2-\overset{OH}{\overset{\vert}{CH}}-R-CH_2-CH_2-O\right)_nR''-$	Epoxy resins	Epon®

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



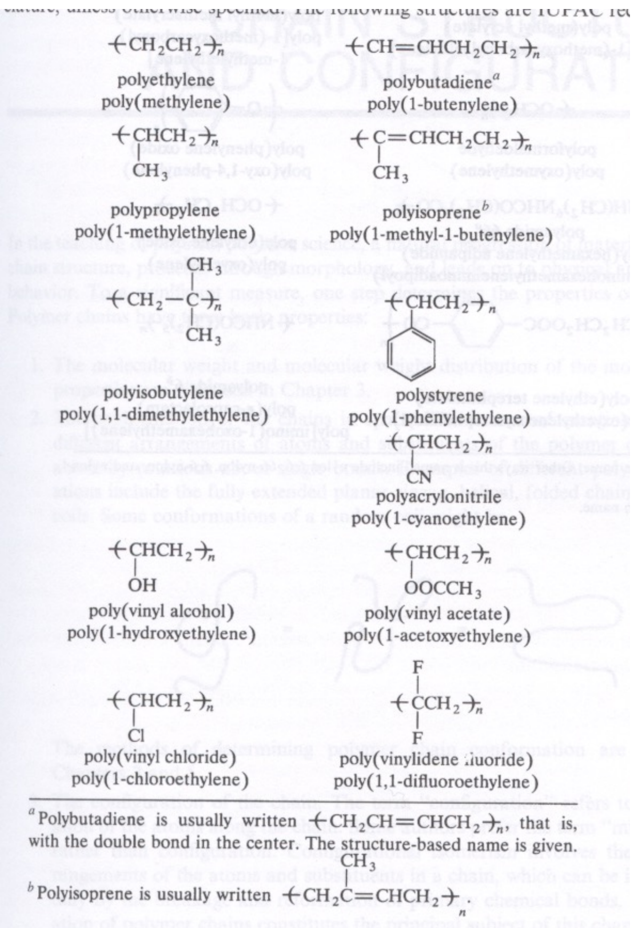
Because of the oxygen atom, poly(ethylene oxide) is water soluble.

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

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

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)

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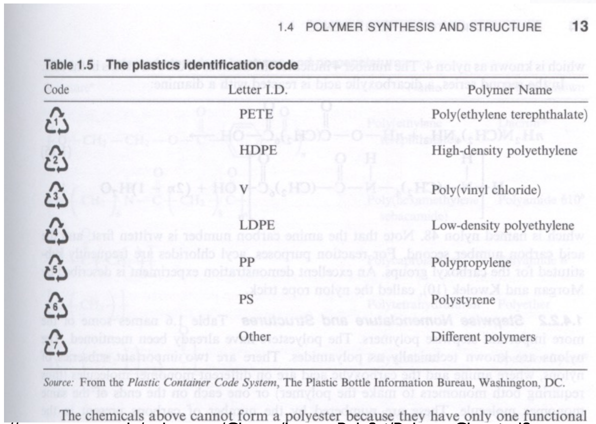
[a] Polybutadiene is usually written $(CH_2CH{=}CHCH_2)_n$, that is, with the double bond in the center. The structure-based name is given.

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



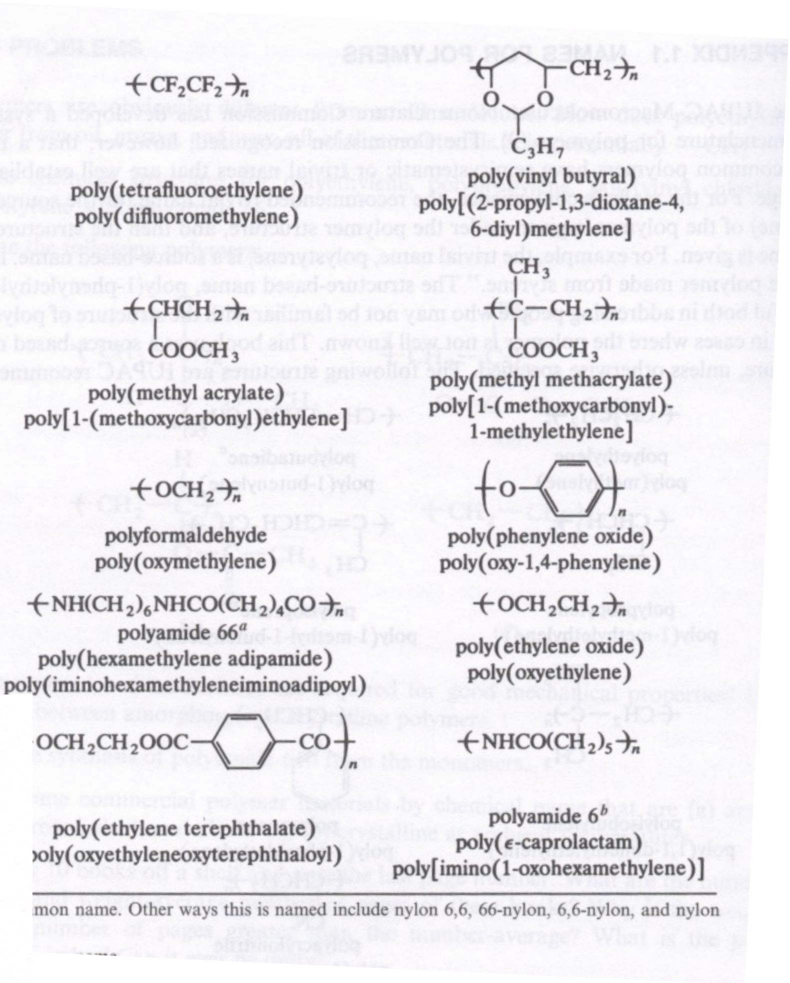
1.4 POLYMER SYNTHESIS AND STRUCTURE 13

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



$(CF_2CF_2)_n$ 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), oly(oxyethyleneoxyterephthaloyl)

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

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mon name. Other ways this is named include nylon 6,6, 66-nylon, 6,6-nylon, and nylon

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

Polymers

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

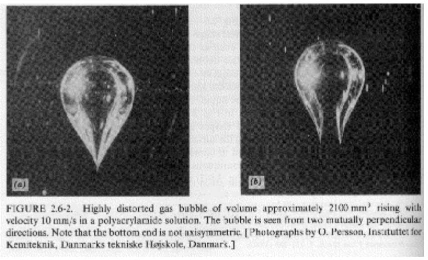
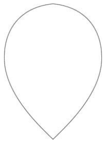
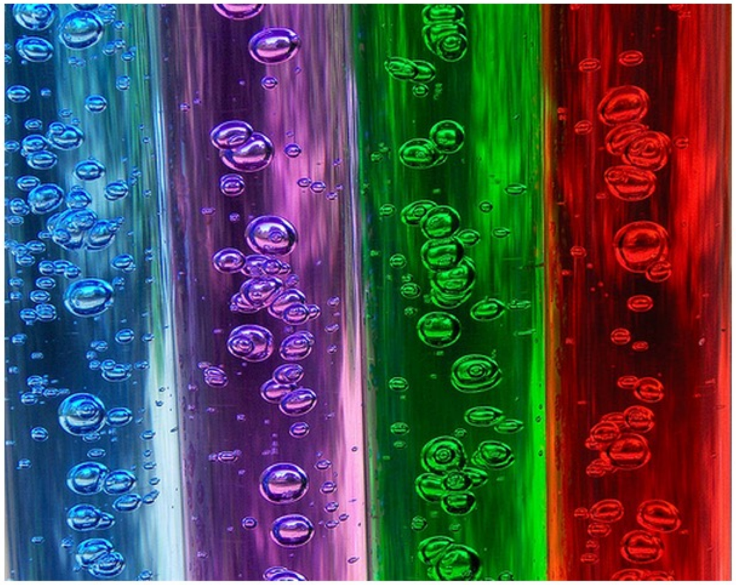
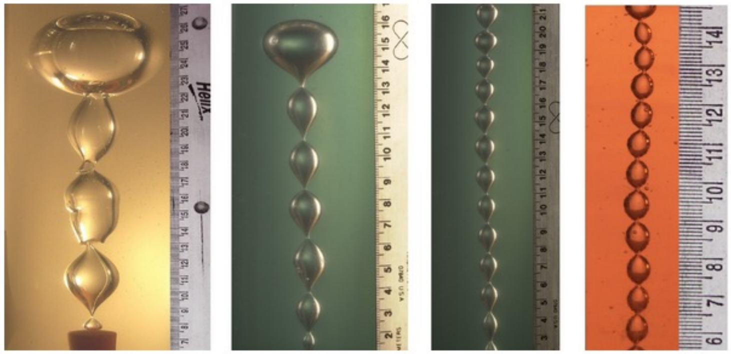


FIGURE 2.6-2. Highly distorted gas bubble of volume approximately 2100 mm^3 rising with velocity 10 mm/s in a polyacrylamide solution. The bubble is seen from two mutually perpendicular directions. Note that the bottom end is not axisymmetric. [Photographs by O. Persson, Instituttet for Kemiteknik, Danmarks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





Newtonian Fluid Bubbles

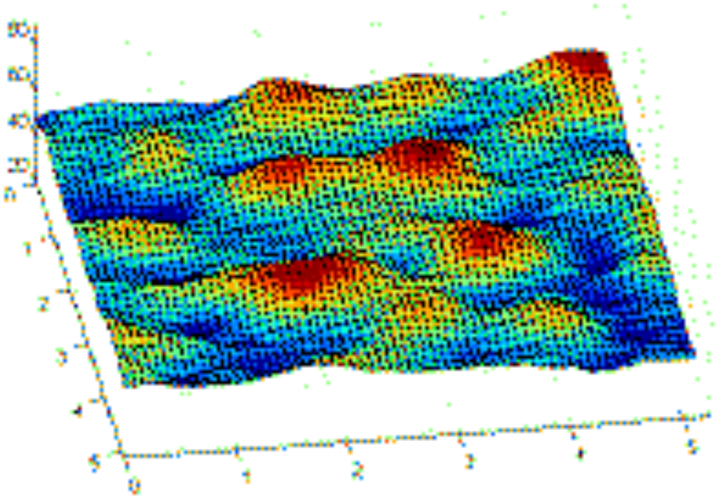


Bubbles in Polymer Solution

Polymer Rheology

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/~beaucag/Classes/IntrotoPolySci/PicturesDNA.html

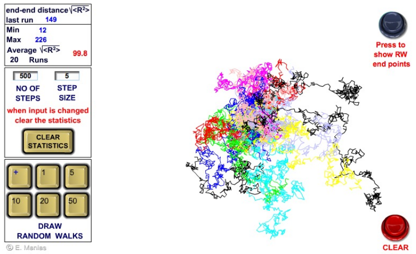
http://www.eng.uc.edu/~beaucag/Classes/IntrotoPolySci/What Does Searching Configurational Space Mean for Polymers.html

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
NO OF STEPS 500
STEP SIZE 5

http://e.sci.osaka-cu.ac.jp/yoshino/download/rw/

-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.

-Rheology is a major property of interest for processing and properties

-Simulation is useful to observe single chain behavior in a crowded environment etc.

Polymers

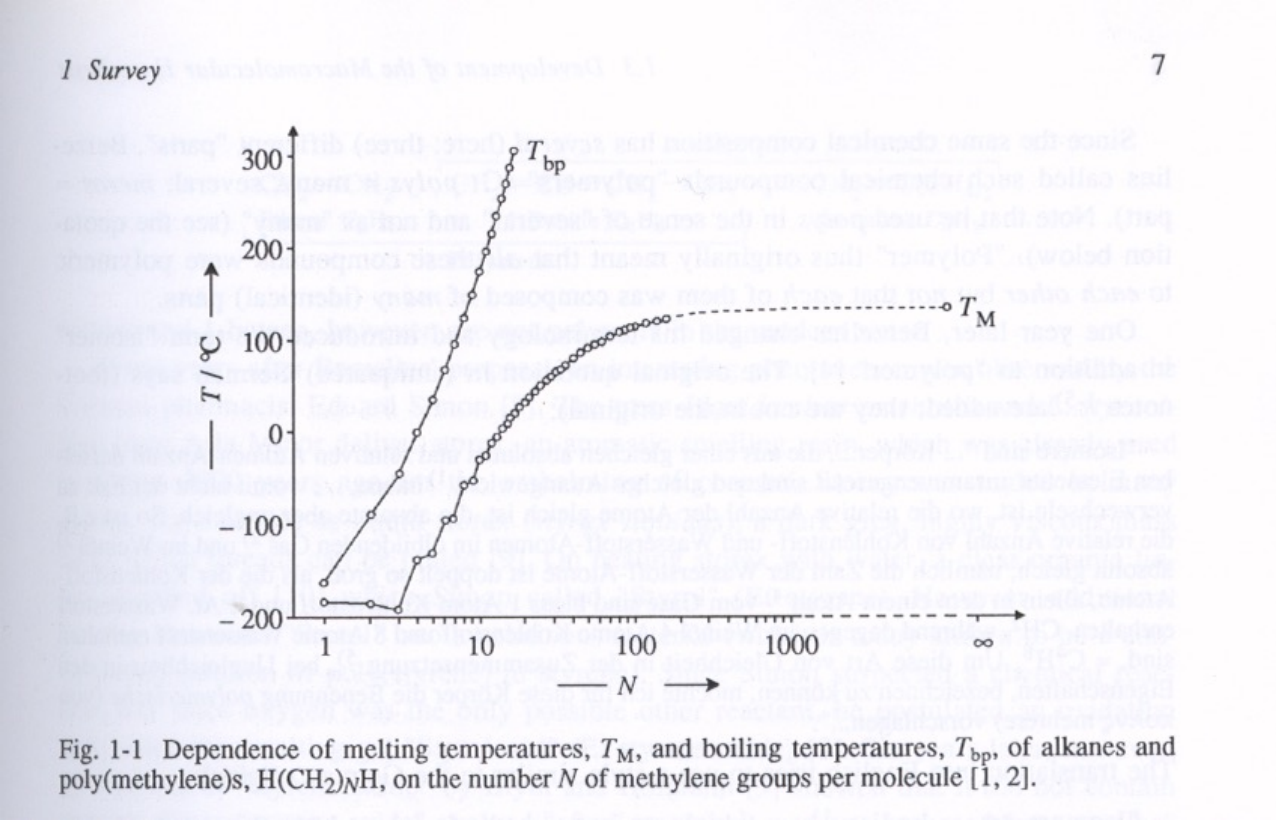
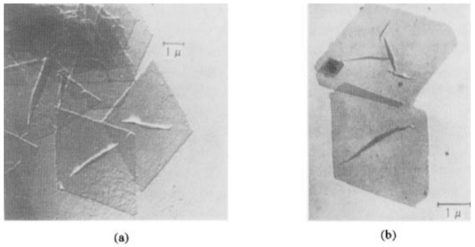


Fig. 1-1 Dependence of melting temperatures, T_M, and boiling temperatures, T_{bp}, of alkanes and poly(methylene)s, $H(CH_2)_NH$, on the number N of methylene groups per molecule [1, 2].

Fig. 5.3 Electron micrographs of single crystals of polyethylene crystallised from dilute solution in xylene: (a) diamond-shaped crystals and (b) truncated crystals. (Reprinted by permission of John Wiley & Sons, Inc.)



(a) (b)

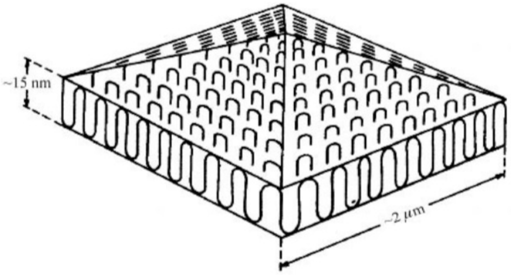
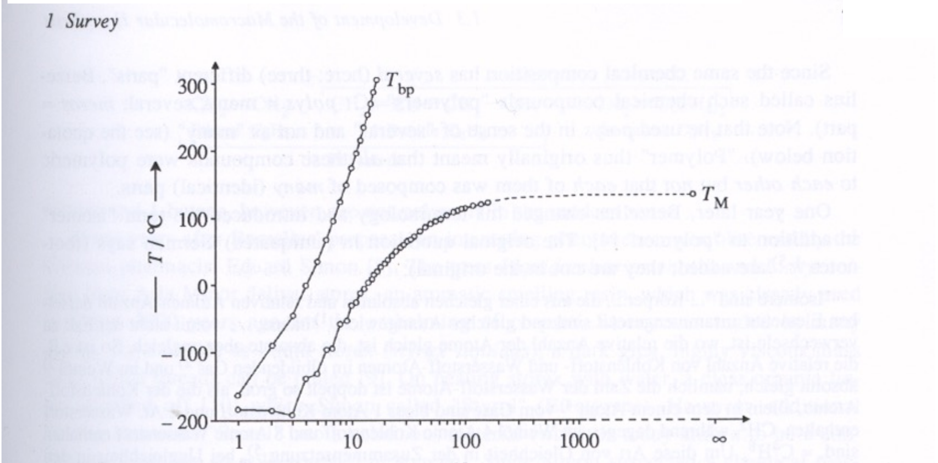


Fig. 5.8 A schematic diagram of chain folding in a solution-grown single crystal of polyethylene. (Reproduced from *The Vibrational Spectroscopy of Polymers* by D. I. Bower and W. F. Maddams. © Cambridge University Press 1989.)



Fold surface energy ~ 2 e-5 J/cm2

Enthalpy of melting ~ 300 J/cm3

T_∞ ~ 414K (141°C)

T ~ 110°C

$t = 2\sigma T_\infty/(\Delta H_m (T_\infty - T))$ (Hoffman-Lauritzen)

~ 1.78e-6 cm or 17.8 nm thick crystals regardless of N

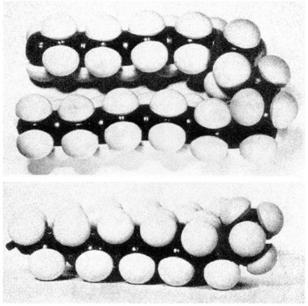
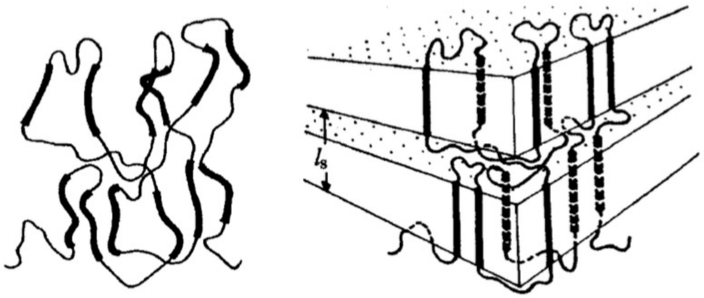


Fig. 5.6 A model of a polyethylene chain folded using four *gauche* bonds, as suggested by Frank. Upper, view normal to the plane of folding; lower, view along the plane of folding. (Reprinted by permission from John Wiley & Sons Limited.)

Fig. 5.7 The 'solidification model' of the crystallisation process, showing how a chain can be incorporated into a lamellar structure without significant change of overall shape. (Reproduced by permission of IUPAC.)



Polymers

Viscosity versus Rate of Strain

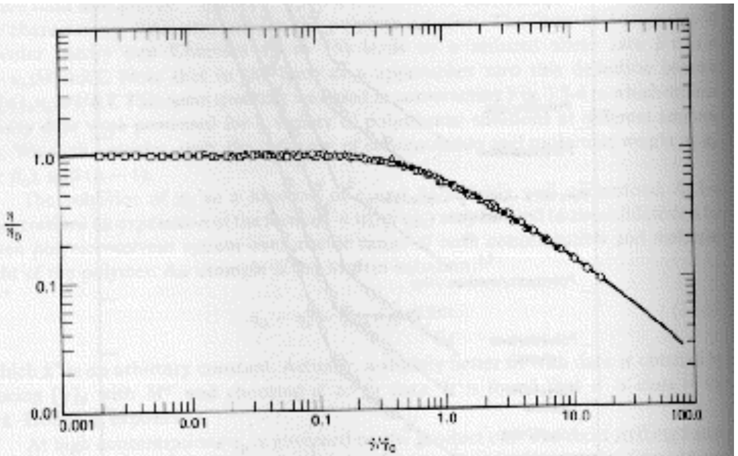


FIGURE 3.6-5. Composite plot of dimensionless viscosity η/η_0 versus dimensionless shear rate $\dot\gamma/\dot\gamma_0$ for several different concentrated polystyrene-*n*-butyl benzene solutions. Molecular weights varied from 1.6×10^5 to 2.4×10^6, concentrations from 0.255 to 0.55 g/cm³, and temperatures from 303 to 333 K. [W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1–179 (1974).]

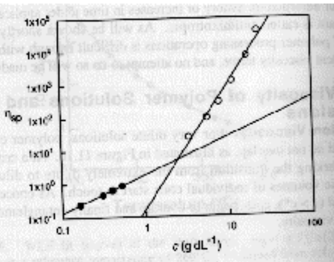


Figure 11.17. Concentration dependence of the specific viscosity of dilute and moderately concentrated solutions of cellulose acetate in dimethyl sulfoxide.³ The intersection of straight lines that are drawn through the dilute-solution (●) and concentrated-solution (○) data marks the critical concentration,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

Specific Viscosity versus Concentration for Solutions

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

Zero Shear Rate Viscosity versus Molecular Weight

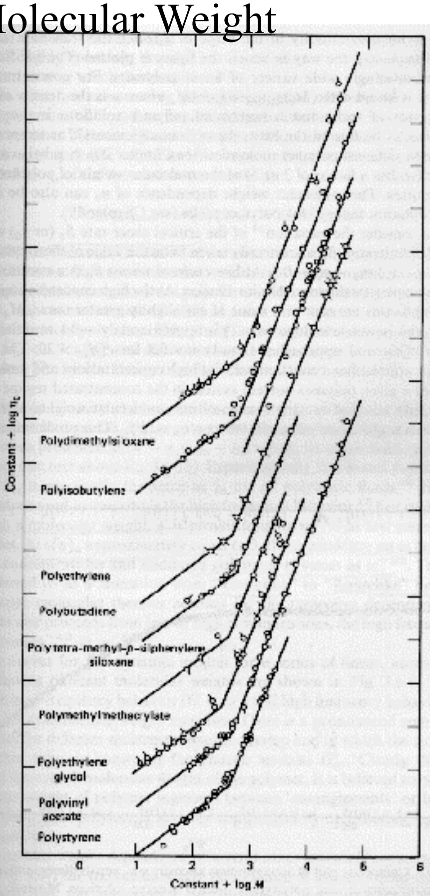


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of 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 Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids Vol. 1"

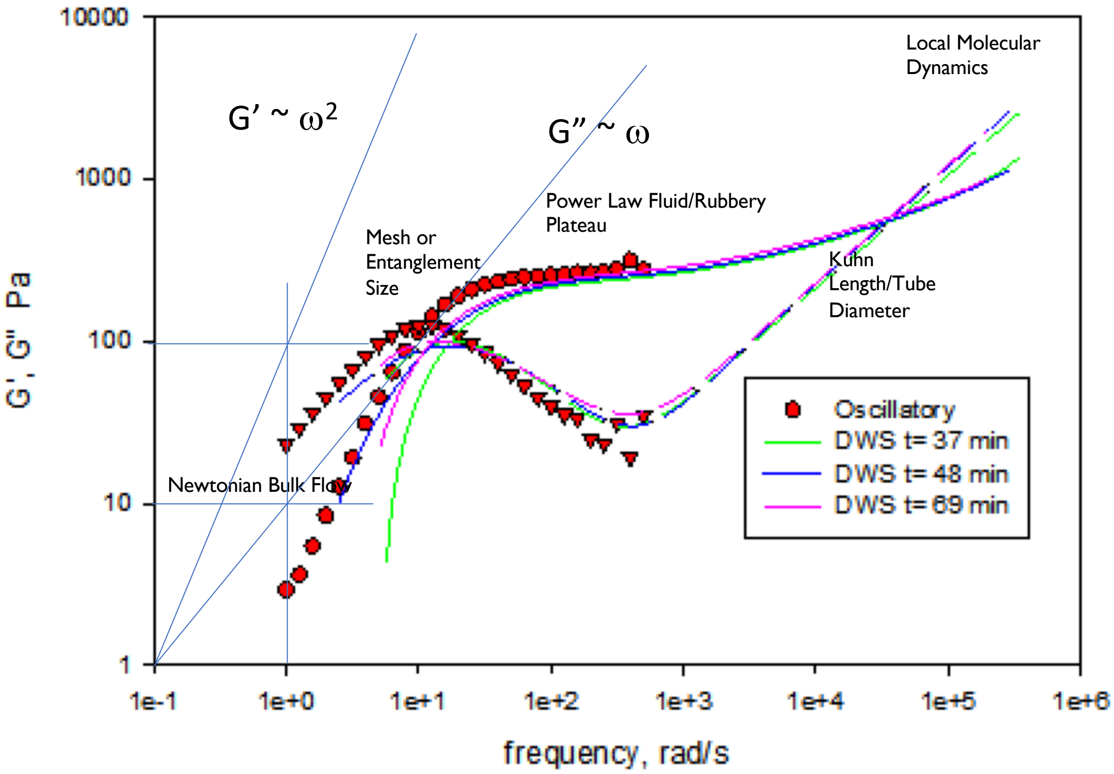
Polymers

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



Polymers

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

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

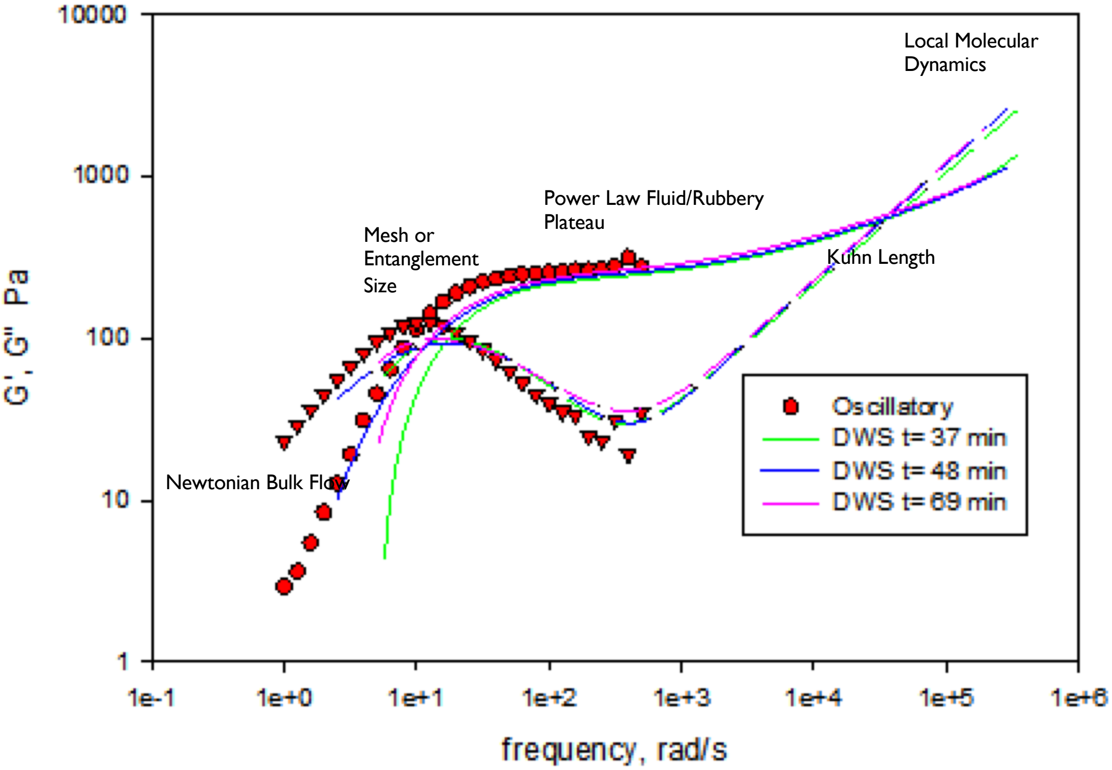
giving

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

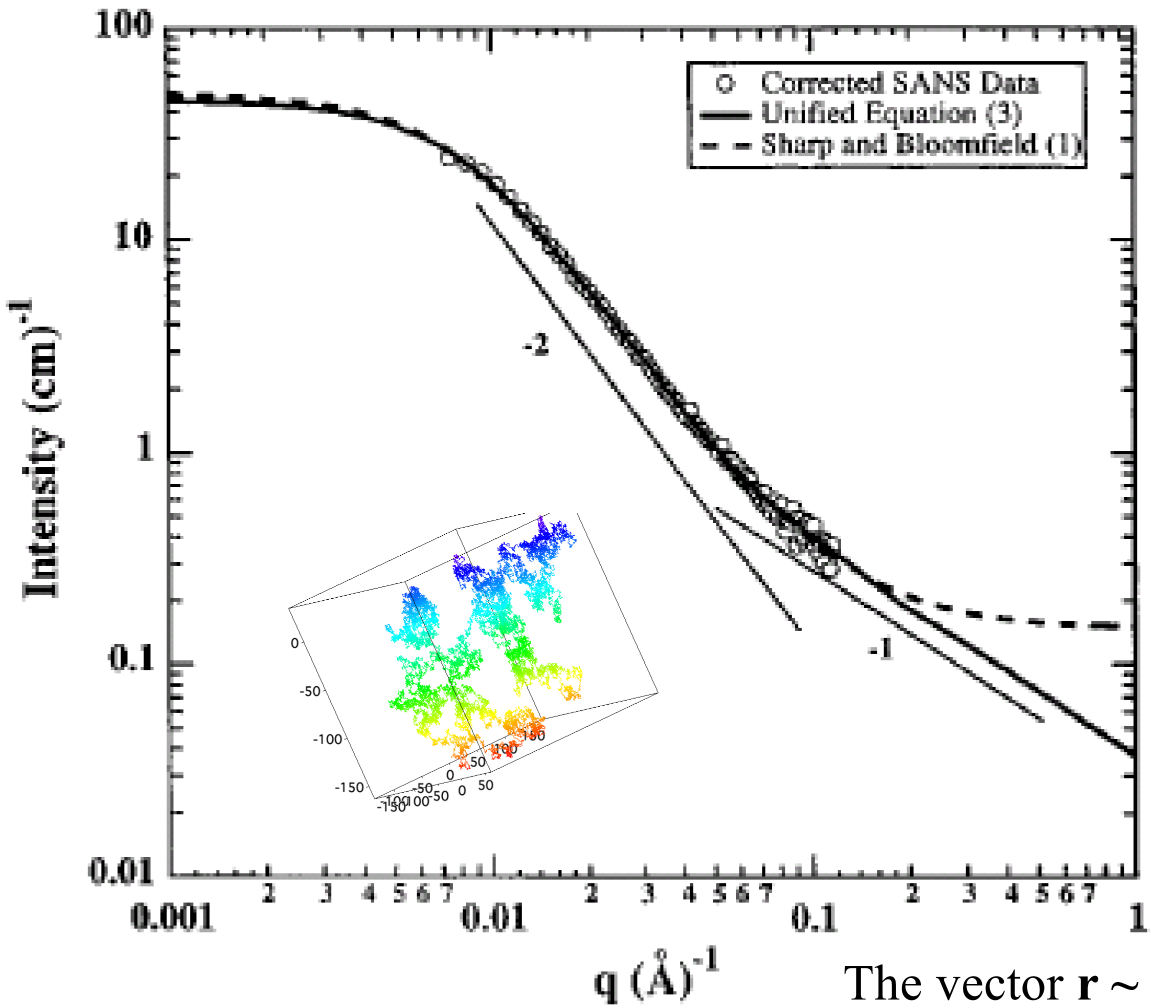
in agreement with Fig. 6.16, and

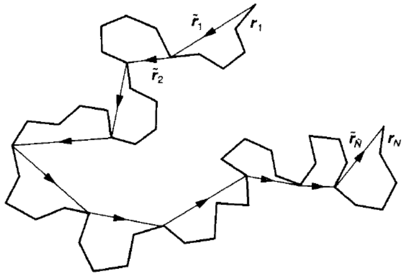
$$G''(\omega \to 0) = \eta_0 \omega \; . \tag{6.106}$$

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.



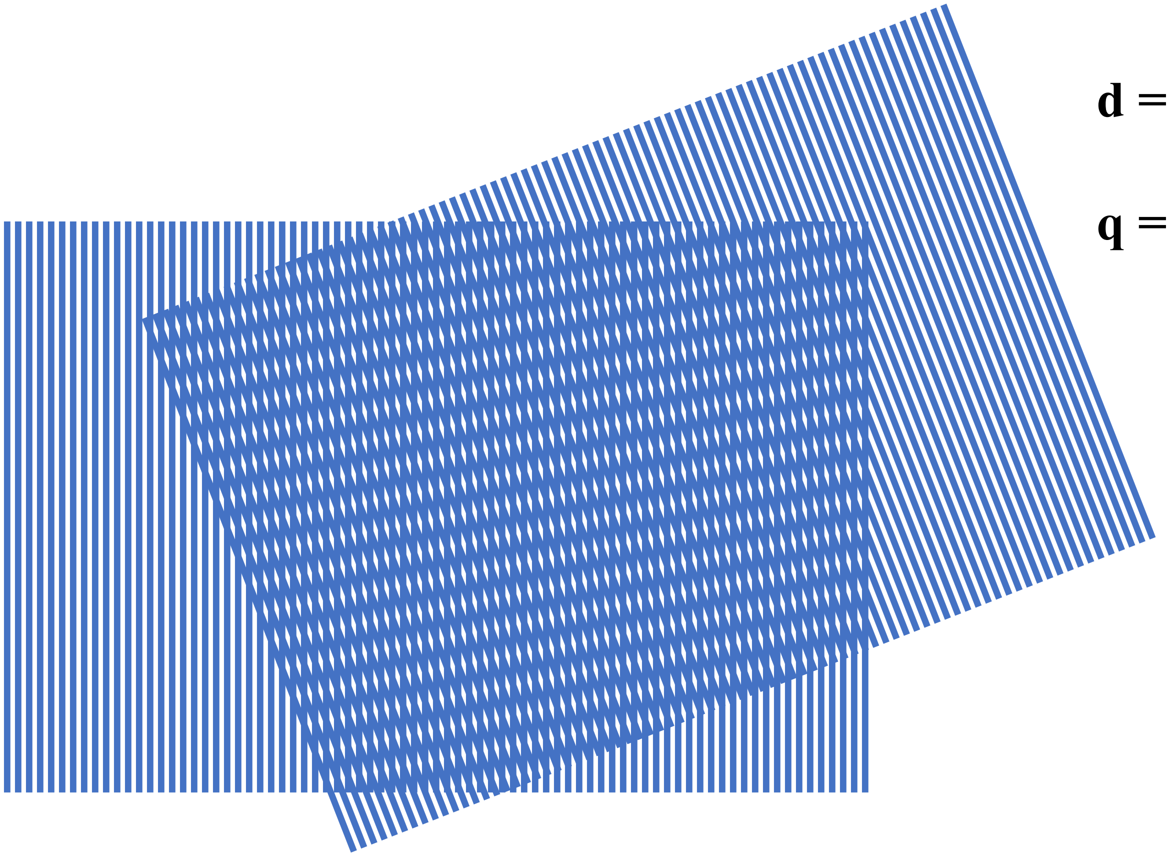
Small Angle Neutron Scattering





The vector **r ~ 2π/q**

The vector $\mathbf{d} \sim 2\pi/\mathbf{q}$



$$\mathbf{d} = \lambda/(2 \sin \theta)$$

$$\mathbf{q} = 4\pi/\lambda \sin \theta$$

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)

The walk does have a breadth, 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
$\langle R^2\rangle^{1/2} \sim l_K$

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

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

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

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

$$\langle R^2\rangle^{1/2} \sim N^{1/2}\, l_K$$

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

Synthetic Polymer Chain Structure
(A Statistical Hierarchy)

$$\langle R^2\rangle^{1/2} \sim N^{1/2}\, l_K$$

This function has the same origin as the function describing the root mean square distance of a diffusion pathway
$\langle R^2\rangle^{1/2} \sim t^{1/2}(2D)^{1/2}$
So, the Kuhn length bears some resemblance to the diffusion coefficient

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

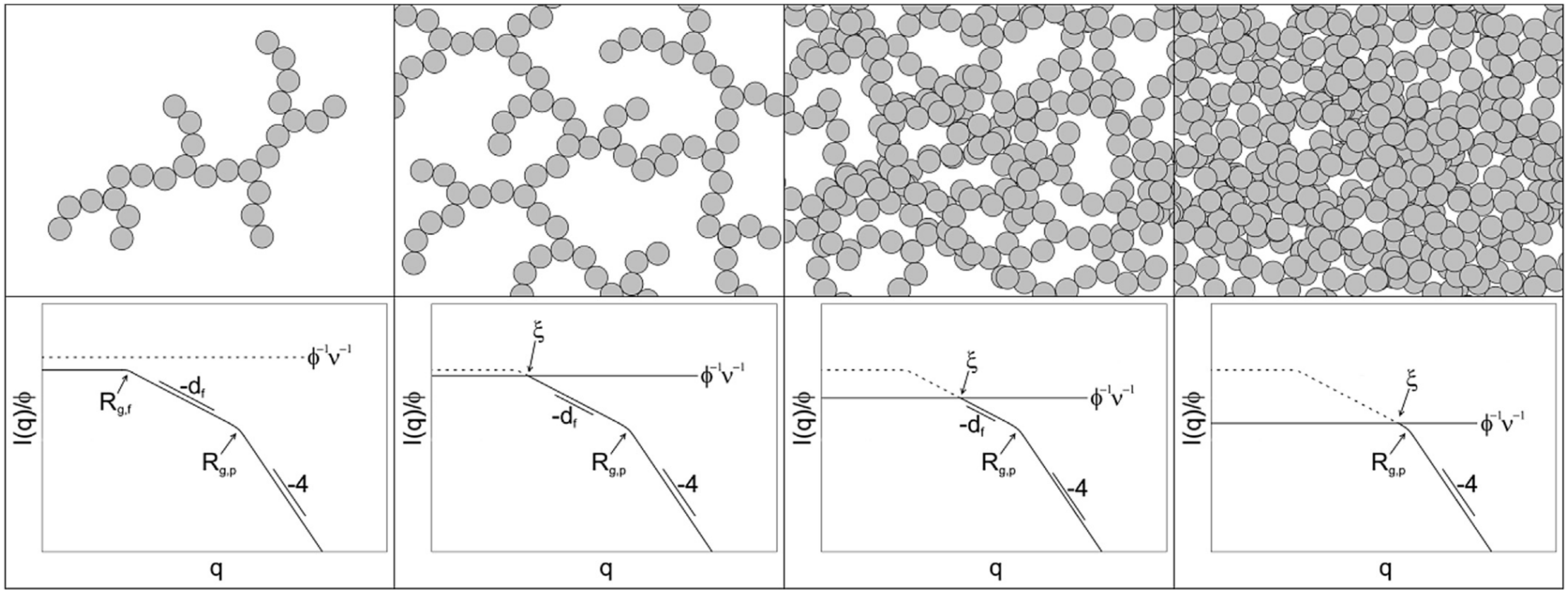
The random chain is sometimes called a “Brownian Chain”, a drunken walk, a random walk, a Gaussian Coil or Gaussian Chain among other names.

$<R^2>^{1/2} = n^{1/2}\, l$

Concentration within a coil = $n/(n^{3/2}\, l^3) \sim n^{-1/2} = c^*$ overlap concentration

Below c* ~ 1 mg/ml dilute conditions (most analytic measurements), Above c* “semi-dilute”

Below c*, dilute scattering curve; above c*;
the scattering is screened in the semi-dilute regime;
when screening/mesh size matches the persistence length we reach the concentrated regime or the melt



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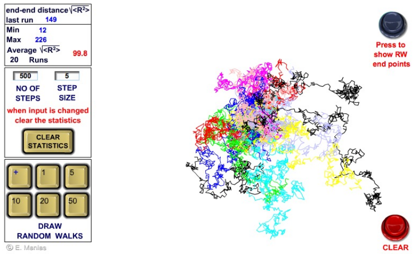
the scattering is screened in the semi-dilute regime;
when screening/mesh size matches the persistence length we reach the concentrated regime or the melt

Rheology view linear below c*, c* and entanglement concentration might be similar

Random Walk Generator (Manias Penn State)

http://zeus.plmsc. http://e.sci.osaka-cu.ac.jp/yoshino/download/rw/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

http://e.sci.osaka-cu.ac.jp/yoshino/download/rw/

-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.

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

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.

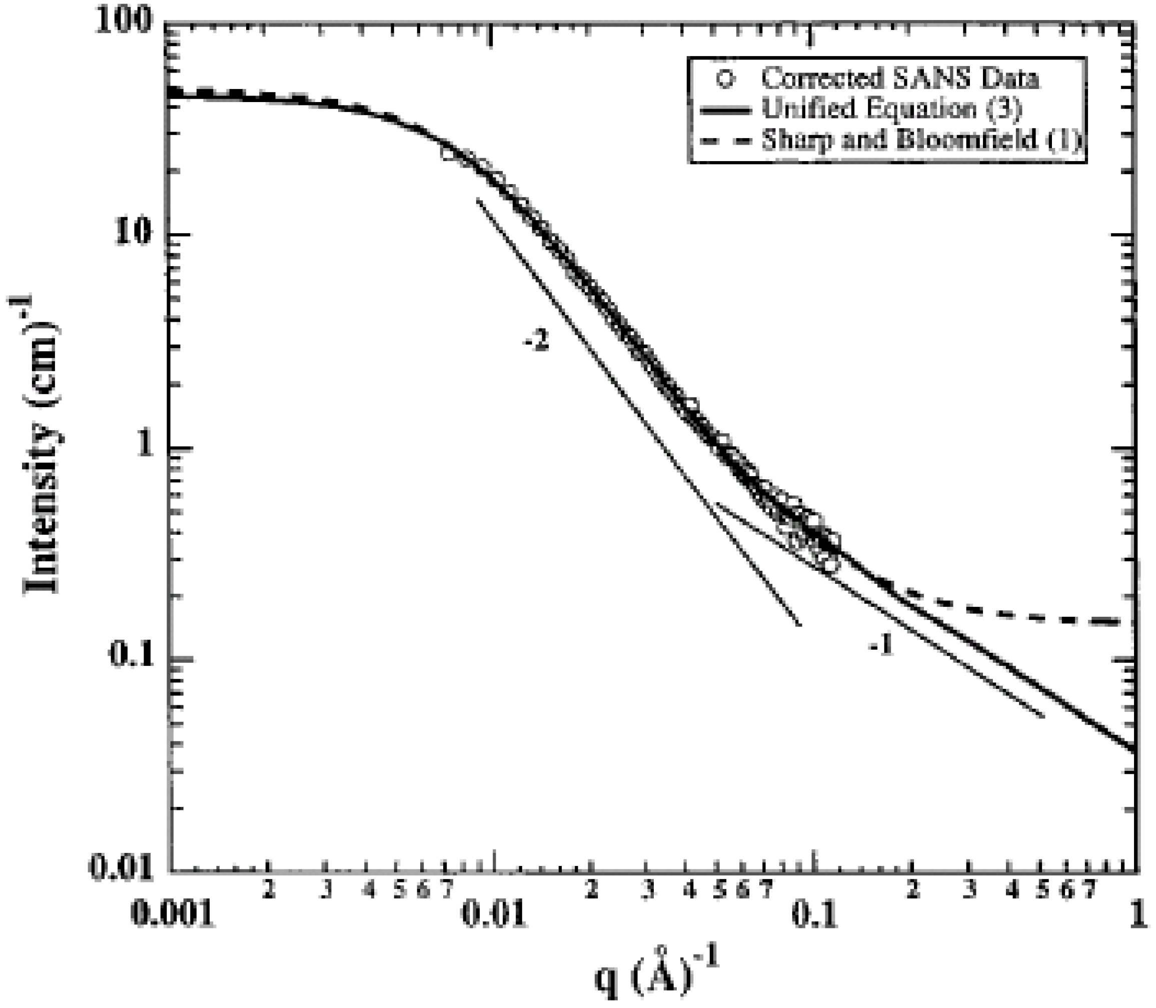
Generally, the chain is composed of chemical bonds
that are directional, that is they are rods connected at their ends.

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).

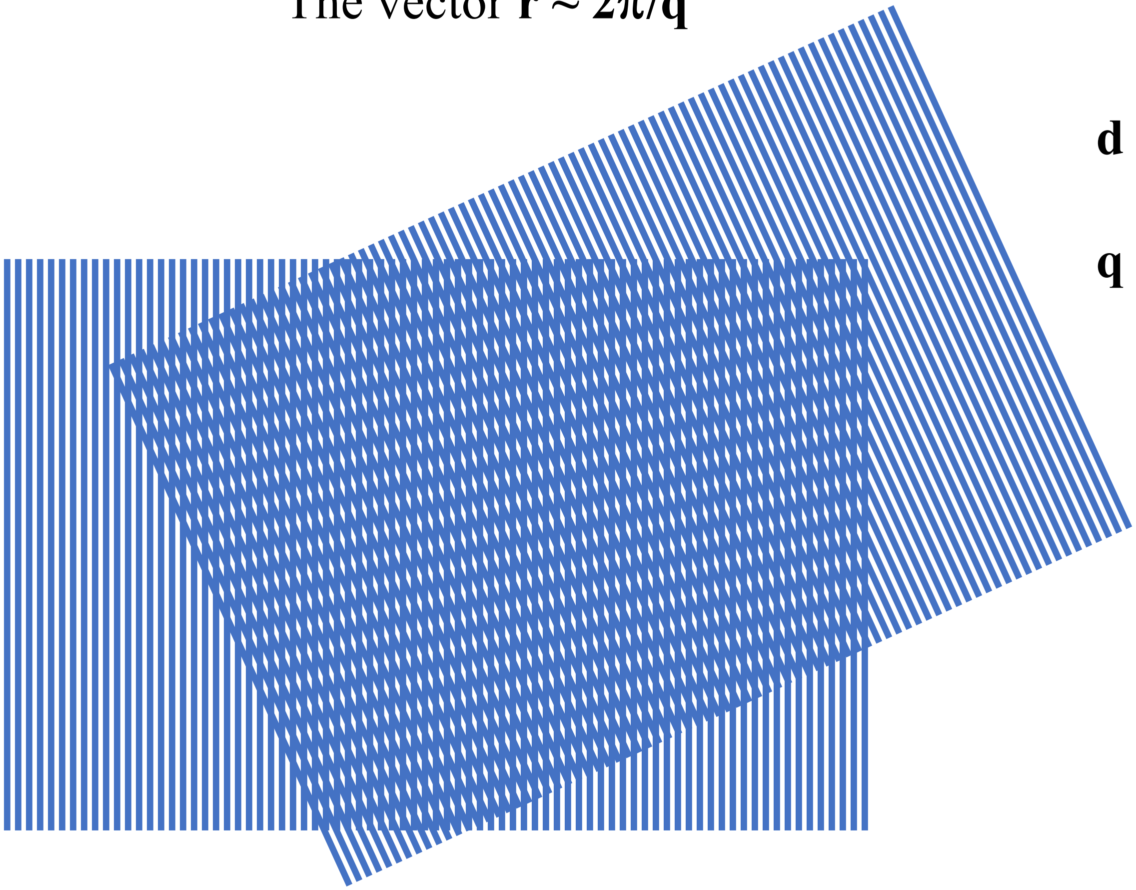
The persistence length can be measured in scattering
or can be inferred from rheology through the Kuhn length

$l_K = 2\ l_P$

Small Angle Neutron Scattering



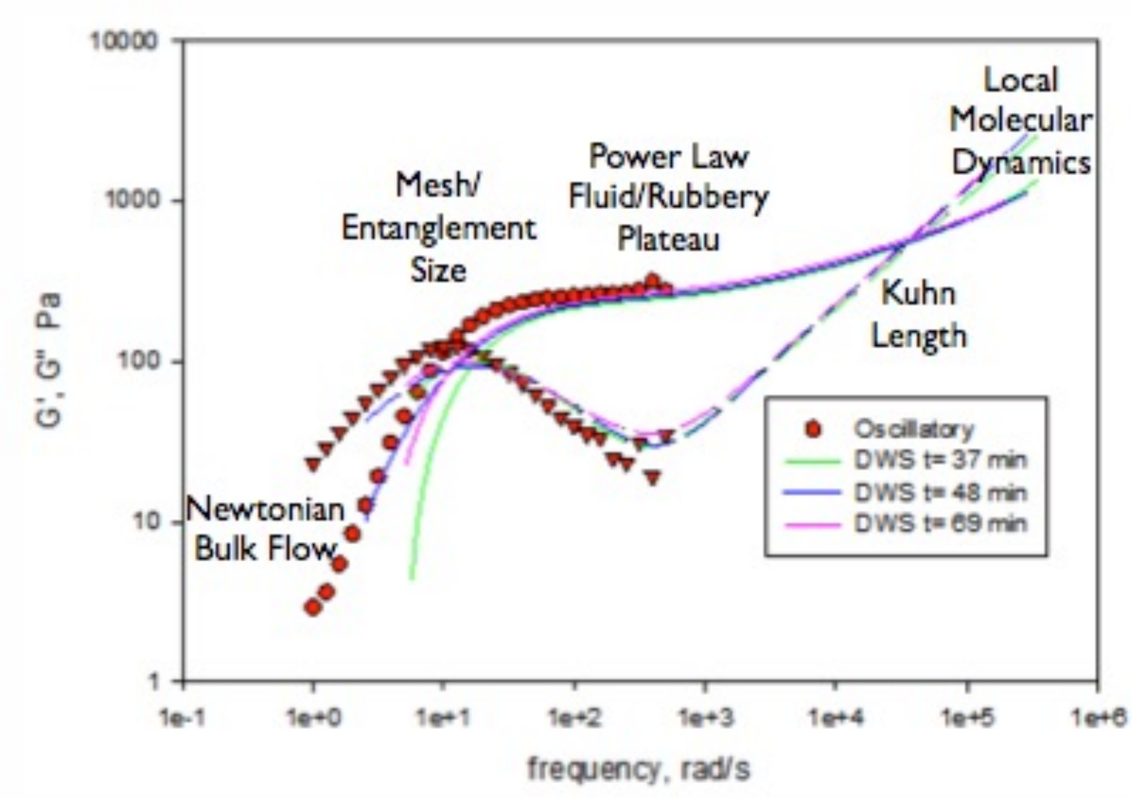
The vector **r** ~ **2π/q**



$$\mathbf{d = \lambda/(2\ \sin\ \theta)}$$

$$\mathbf{q = 4\pi/\lambda\ \sin\ \theta}$$

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.

https://www.eng.uc.edu/~beaucag/Classes/IntrotoPolySci/PicturesDNA.html

The Gaussian Chain

Gaussian chain is based on Brownian walk or Brownian motion that was described mathematically by Einstein in a 1905 paper

For particles (or a particle) subject to thermal, diffusive motion initially at a fixed position, the density of the particles is a function of time and space. These dependencies can be expressed as Taylor series expansions. For simplicity consider a one-dimensional space (though this can be worked out in any dimensional space). Particles have an equal probability of moving to the left or to the right. The motion is symmetric about the zero point. The dependence with time, in contrast, is in only one direction. (*This, it turns out, is the essence of Brownian motion as compared to ballistic motion where both space and time move in only one direction.*)

$$\rho(x,t) + \tau\frac{\partial\rho(x)}{\partial t} + \cdots$$
$$= \rho(x,t)\int_{-\infty}^{+\infty} P_G(\Delta x)d(\Delta x) + \frac{\partial\rho}{\partial x}\int_{-\infty}^{+\infty} \Delta x\, P_G(\Delta x)d(\Delta x) + \frac{\partial^2\rho}{\partial x^2}\int_{-\infty}^{+\infty}\frac{(\Delta x)^2}{2}P_G(\Delta x)d(\Delta x) + \cdots$$

$P_G(\Delta x)$ is a normalized, symmetric probability distribution where Δx is the change in x from 0. The integral of $P_G(\Delta x)$ is 1 since it is normalized. The integral of $\Delta x\, P_G(\Delta x)$ is zero since it it symmetric.

$$\frac{\partial\rho(x,t)}{\partial t} = D\frac{\partial^2\rho(x,t)}{\partial x^2} \quad \text{with} \quad D = \int_{-\infty}^{+\infty}\frac{(\Delta x)^2}{2\tau}P_G(\Delta x)d(\Delta x)$$

The Gaussian Chain

$$\frac{\partial\rho(x,t)}{\partial t} = D\,\frac{\partial^2\rho(x,t)}{\partial x^2}$$

For N particles starting at x = 0 and time = 0,

$$\rho(x,t) = \frac{N}{\sqrt{4\pi Dt}}e^{-\frac{x^2}{4Dt}}$$

First moment in space is 0, second moment (variance of Gaussian) is:

$$\langle x^2\rangle = 2\mathrm{Dt}$$

For polymer chain $<R^2> = l_K^2\ N$

The Einstein-Stokes Equation/Fluctuation Dissipation Theorem

Consider a particle in a field which sets up a gradient mitigated by thermal diffusion such as sedimentation of particles in the gravitational field.
The velocity of the particles due to gravity is $v_g = mg/(6\pi\eta R_h)$ following Stokes Law. For particles at $x = 0$ and $x=h$ height, the density difference is governed by a Boltzmann probability function,

$$\rho(h) = \rho_0 e^{-\frac{mgh}{kT}}$$

Fick's law gives the flux of particles, $J = -D\, d\rho/dh$, and $J = \rho v$, so $v = -(D/\rho)\, d\rho/dh$, and
$d\rho/dh = -\rho_0 mg/(kT)\, e^{-mgh/kT} = -\rho mg/(kT)$. Then, $v = Dmg/(kT)$. At equilibrium this speed equals the gravitational speed, $v_g = mg/(6\pi\eta R_h)$. Equating the two removes the details of the field, making a universal expression for any particle in any field, the Stokes-Einstein equation based on the Fluctuation Dissipation Theorem. (This was done in 1-d, the same applies in 3d.)

$$\frac{\langle x^2 \rangle}{2t} = D = \frac{kT}{6\pi\eta R_h} = \frac{RT}{6\pi\eta R_h N_A}$$

The latter expression was used to determine Avagadro's number from colloidal particles that could be counted. N_A was then applied to molecular species to determine, for the first time, the molecular weight.

The Einstein-Stokes Equation/Fluctuation Dissipation Theorem

For a particle in a field the velocity can be calculated from Fick's First Law or from a balance of acceleration and drag forces

$v_g = mg/6\pi R_h \eta = -D/\rho \, \mathrm{d}\rho/\mathrm{d}h = Dmg/\mathrm{k}T$

This yields the Einstein-Stokes Equation $D = \mathrm{k}T/6\pi R_h \eta$

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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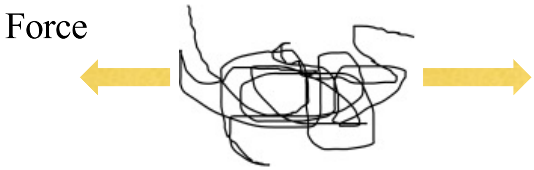

$$F = \frac{dE}{dR} = \frac{3kT}{nl_K^2}R = k_{spr}R$$

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

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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:

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

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:

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

Mean is the 1'st Moment:

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

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

The Gaussian Chain

Boltzman Probability For a Thermally Equilibrated System	Gaussian Probability For a Chain of End-to-End Distance R
$P_B(R) = \exp\left(-\frac{E(R)}{kT}\right)$	$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$

Use of P(R) to Calculate Moments:

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

Mean Square is the 2’ndMoment:

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

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'nd Moment:

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

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

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,

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

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

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(α) = $(\pi/\alpha)^{1/2}$, then $H(\alpha) = \frac{\pi^{1/2}}{2\alpha^{3/2}}$ so, with α = $1/k^2$ 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:

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

So, the Gaussian function for a polymer coil is:

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

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,
$p \sim R^{dmin}$
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

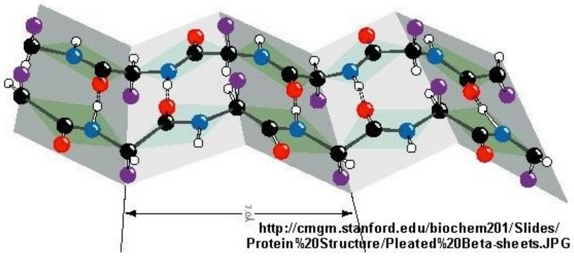
Disk

$d_f = 2$

$d_{\min} = 1$

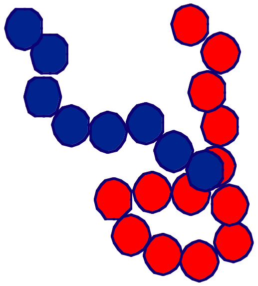
$c = 2$

Extended β-sheet
(misfolded protein)



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

Random Coil

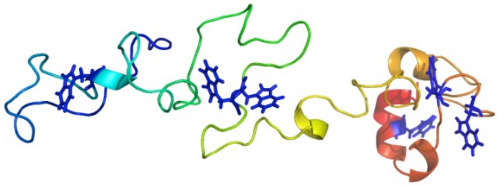


$d_f = 2$

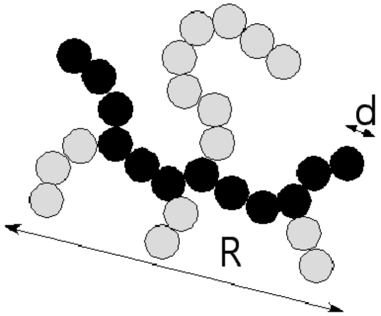
$d_{\min} = 2$

$c = 1$

Unfolded Gaussian chain

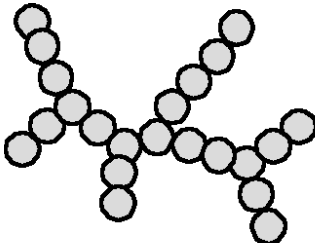


How Complex Mass Fractal Structures Can be Decomposed



Tortuosity

Connectivity



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

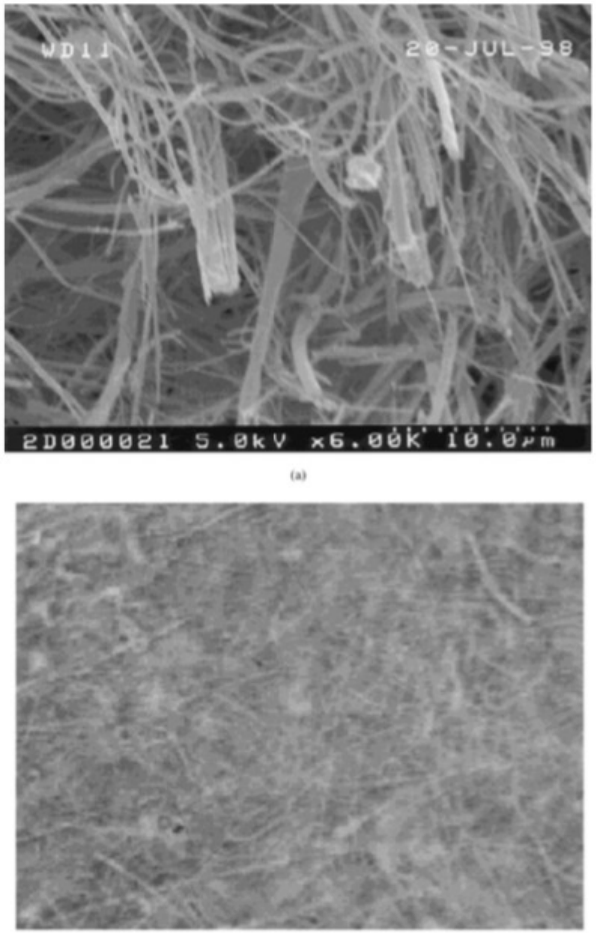
$$p \sim \left(\frac{R}{d}\right)^{d_{\min}}$$

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

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

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)



(a)

(b)

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

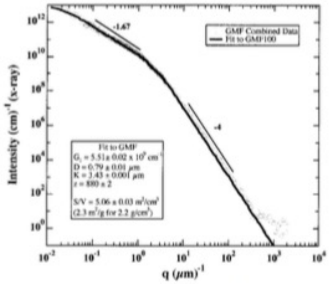


Figure 2. Log I vs. log q plot for GMF with an incident beam normal to the sample plane. Scaling regime at low-q follows good solvent scaling. High-q scaling follows Porod's law. Fit uses the unified equation with four free parameters and a model based on a polymer-like structure.

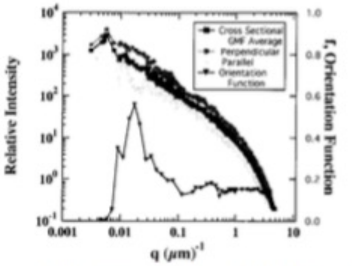


Figure 5. Orientation function and SALS data for GMF in cross-section as a function of q. Perpendicular and parallel are with respect to the plane of the mat.

Orientation partly governs separation

Pore size and fractal structure govern wicking

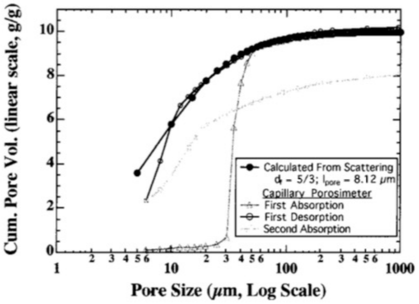


Figure 6. Cumulative pore volume vs. pore size from SALS and from capillary porosimetry.

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 have an effect on 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

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

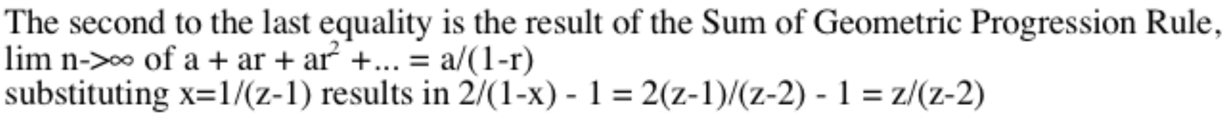
For Gaussian Chain

See slide 68

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

For SRI Chain the first term is not 0.

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



The second to the last equality is the result of the Sum of Geometric Progression Rule,
lim n->∞ of a + ar + ar^2 +... = 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

$$\langle R^2\rangle_{SAI} = n_{SAI}\, b_{SAI}^2 = n b^2 \frac{z}{z-2}$$

$$L_{SAI} = L = n b = n_{SAI}\, b_{SAI}$$

$$n_{SAI} = \frac{n b}{b_{SAI}}$$

$$n \frac{\cancel{b}}{\cancel{b_{SAI}}}\, b_{SAI}^{\cancel{2}} = \cancel{n} b^{\cancel{2}} \frac{z}{z-2}$$

$$\boxed{b_{SAI} = b \frac{z}{z-2}} = 1.5\, b$$

$$\boxed{n_{SAI} = n\left(\frac{z-2}{z}\right)} = 0.67\, n$$

$$\rho = \frac{n}{(n b^2)^{3/2}} \qquad \rho_{SAI} = \frac{n\left(\frac{z-2}{z}\right)}{n^{3/2}\left(\frac{z-2}{z}\right)^{3/2} b^3 \left(\frac{z}{z-2}\right)^3}$$

$$= \rho \left(\frac{z-2}{z}\right)^{2.5} = 0.36\, \rho$$

for $z = 6$

$$\boxed{\begin{aligned} b_{SAI} &= b(1.5) \\ n_{SAI} &= (0.67)\, n \\ \rho_{SAI} &= (0.36)\, \rho \end{aligned}}$$

Largest Impact is Density

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.

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
-Conjugation
-Main chain aromatics/cyclics
-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_∞

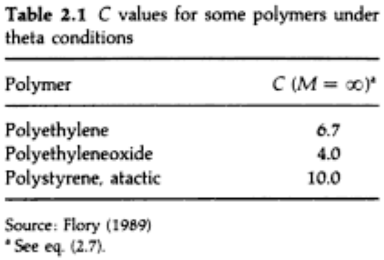


Table 2.1 *C* values for some polymers under theta conditions

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

Source: Flory (1989)
[a] See eq. (2.7).

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

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

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

Polymer physics
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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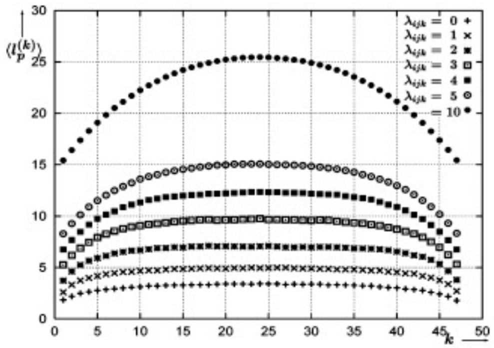


Figure 7. The persistence length plots, $\langle l_p^{(k)} \rangle$, obtained via eq 10, versus segment number, k, for various semiflexible, linear polymers, each of length 48. The strength of the intrinsic stiffness is varied between polymers by increasing the strength of the bending penalty, λ_{ijk}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

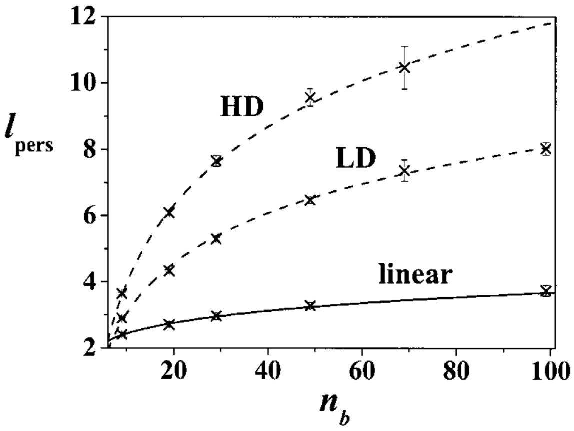
Molecular weight dependence of persistence length

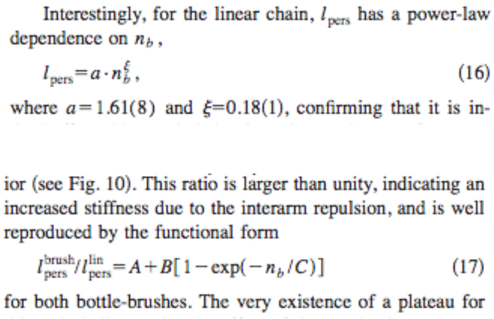
Size and persistence length of molecular bottle-brushes by Monte Carlo simulations

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

n_b = backbone length





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

$$l_{pers} = a \cdot n_b^{\xi}, \tag{16}$$

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

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

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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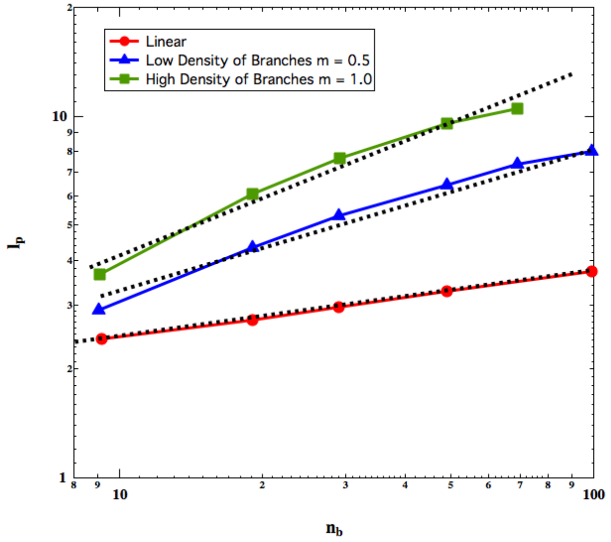

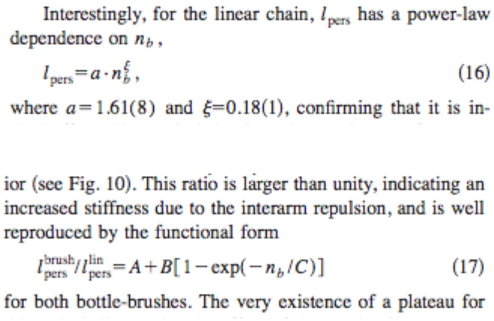

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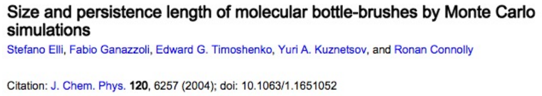
This is a 5-parameter model for persistence length!
(used to model 5 or 6 data points!!!)

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

Molecular weight dependence of persistence length



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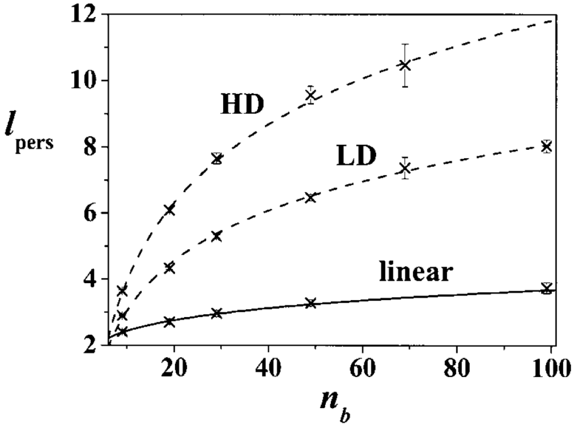
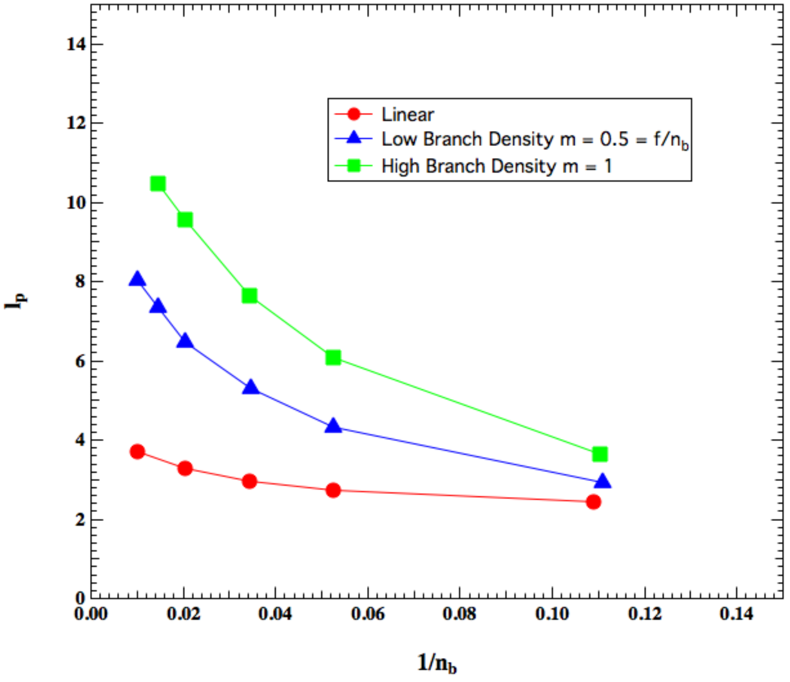


LD = Low branch density
HD = High branch density

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

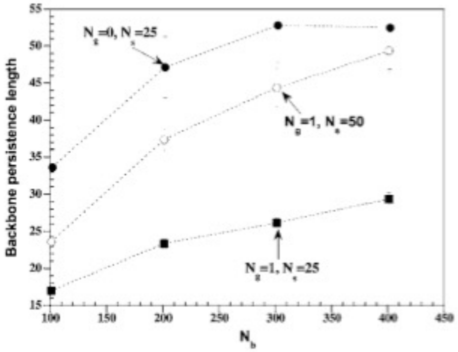
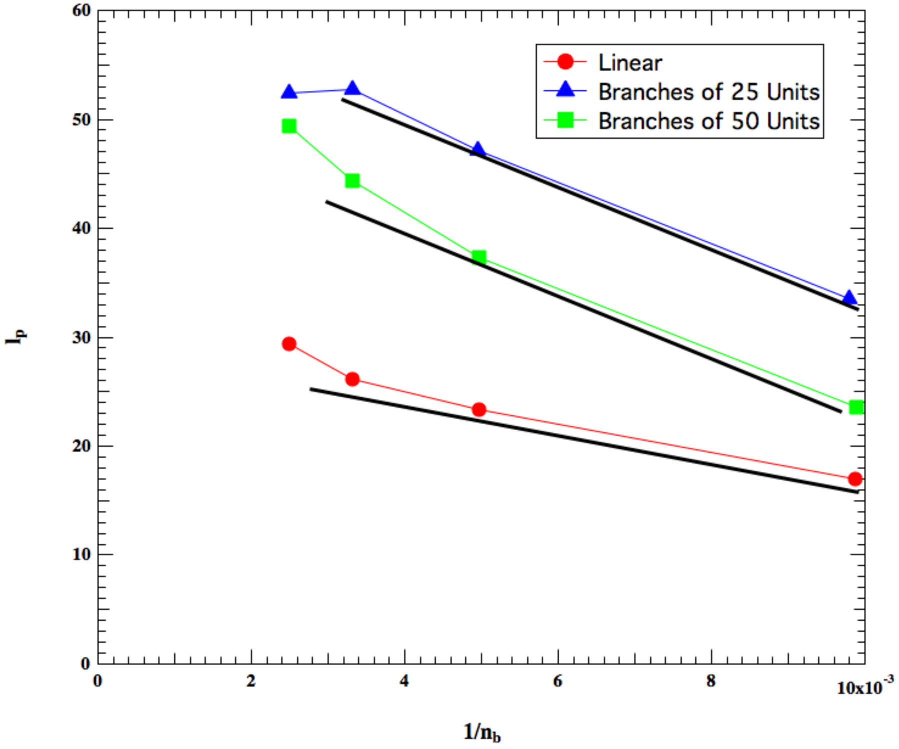


FIG. 2. Persistence length of the backbone as a function of number of backbone beads for various values of the branch length (N_s) and the number of beads between branch points (N_g) and for $\varepsilon_S = \varepsilon_B = 0$. The lines are meant to guide the eye.



Persistence Length ~ Bending Modulus/(Thermal Energy)
$l_p = l_K/2 \sim E_{bending}/kT$
(We will derive this later with respect to the persistent chain Colby/Rubenstein pp. 58)

Motion of the end-groups is proportional to thermal energy and reduces the persistence length

The energy is related to the flexibility of the chain not the stiffness, $1/l_p$, so we should consider $1/l_p$ as the parameter of interest in terms of an end group effect not l_p

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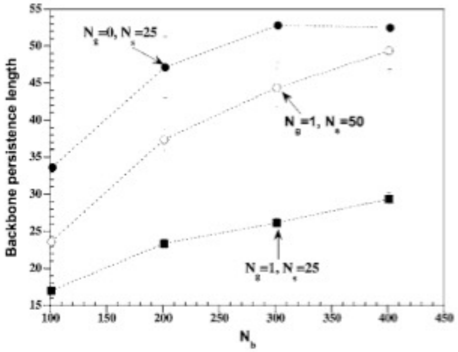

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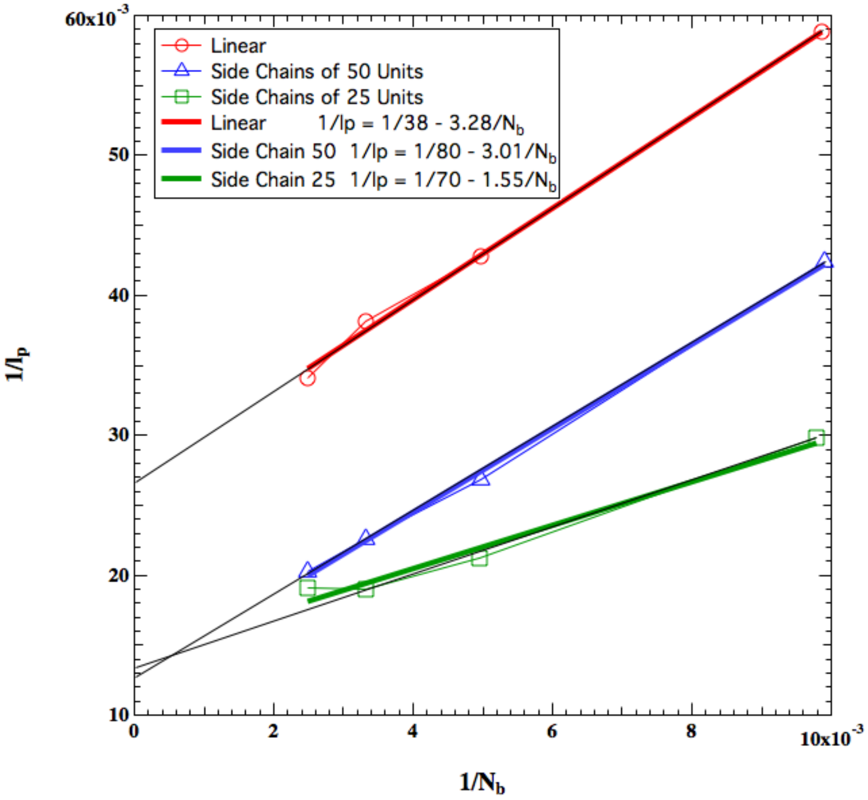
Alternative Functionality based on increase in chain flexibility

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



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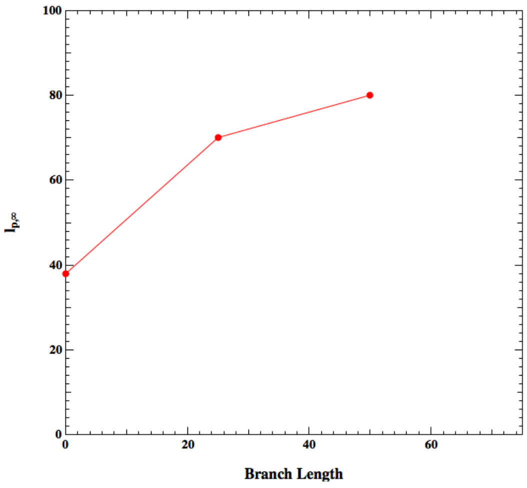

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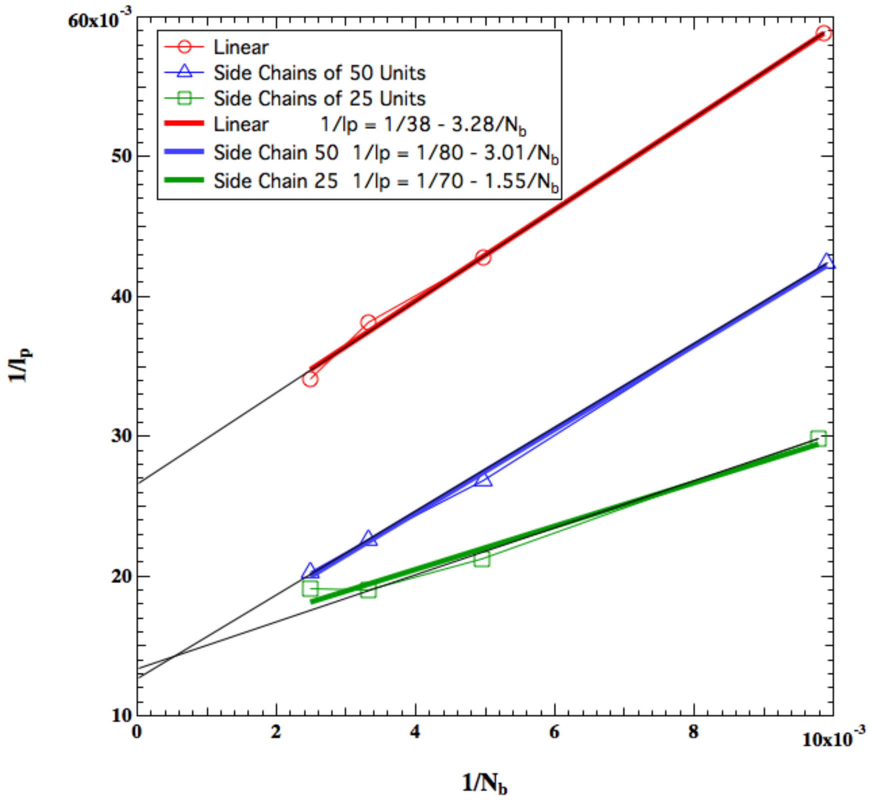

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Size and persistence length of molecular bottle-brushes by Monte Carlo simulations

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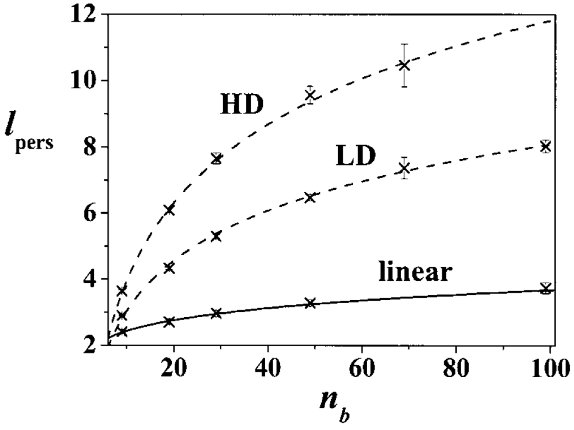
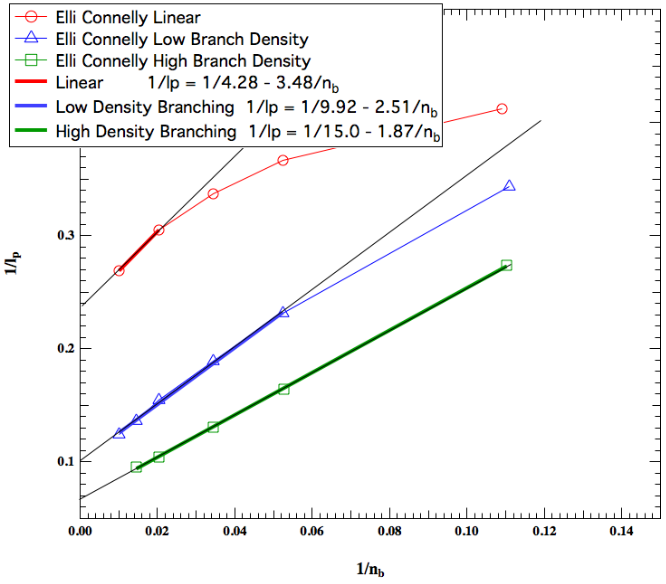


LD = Low branch density
HD = High branch density



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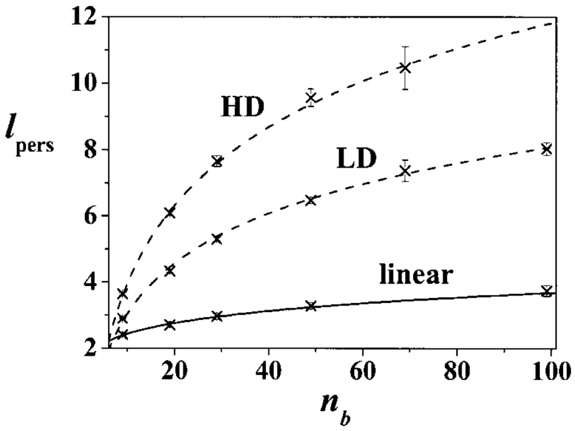
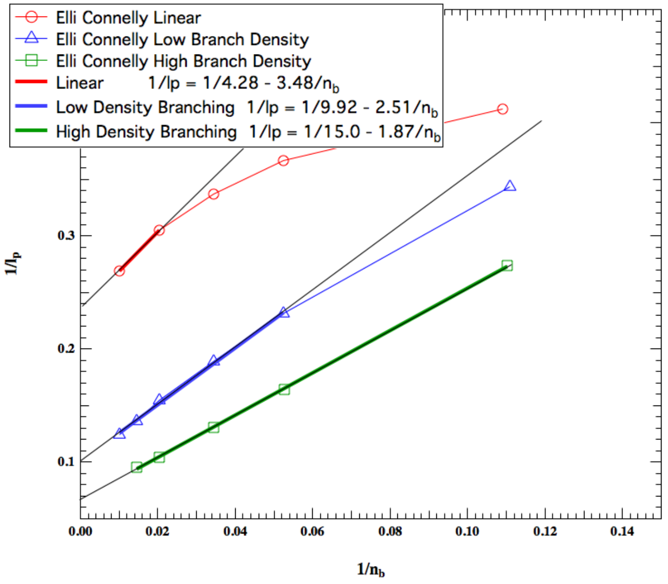
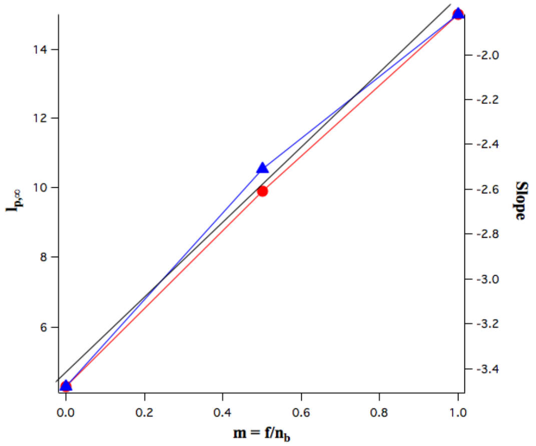




LD = Low branch density (0.5 branch per chain unit)
HD = High branch density (1 branch per chain unit)

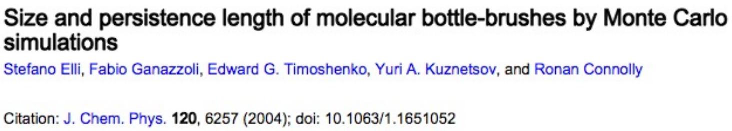
Fit Parameters versus branch density



Equation fails at low n_b since it predicts $l_p \Rightarrow 0$ when $n_b \Rightarrow 0$

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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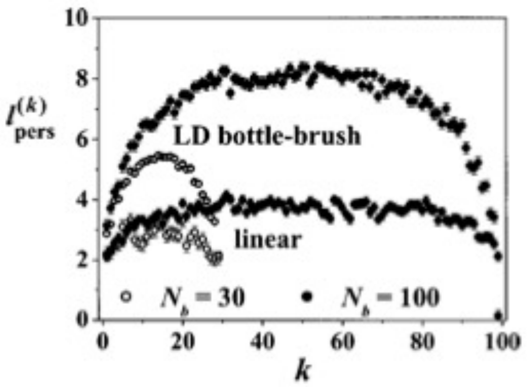
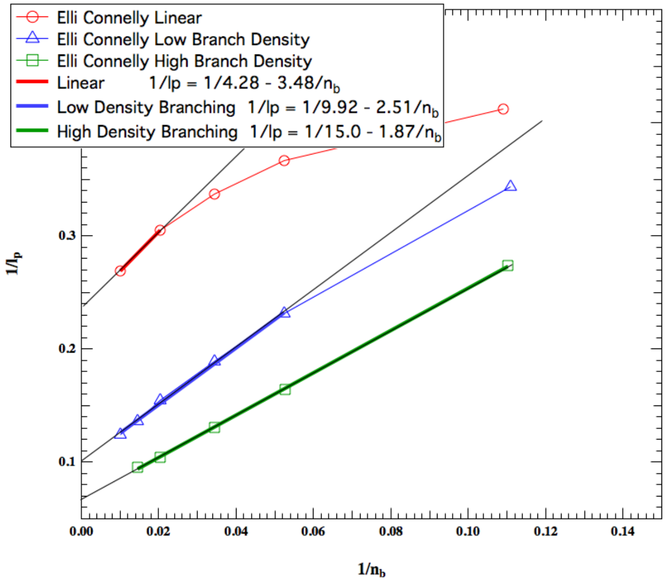


FIG. 8. The persistence length $l^{(k)}_{\text{pers}}$ obtained through Eq. (5) for the linear chain (lower data points) and the LD bottle-brushes with $N_a = 5$ beads per arm (upper data points) as a function of the spring location k within the chain ($k = 1$ and $k = N_b - 1$ are the terminal spring)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



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

Alternative Functionality based on increase in chain flexibility

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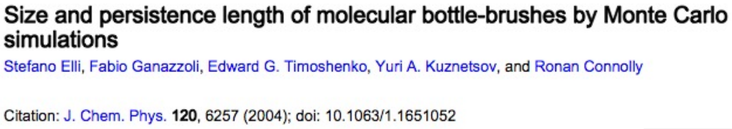

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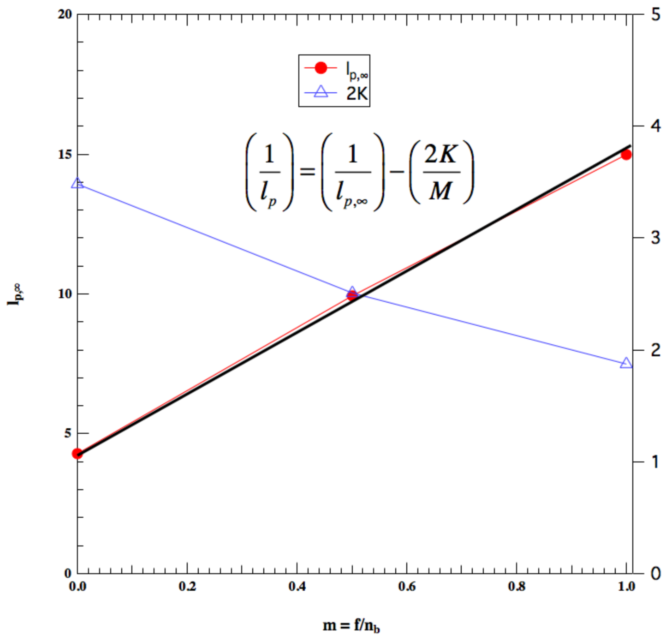

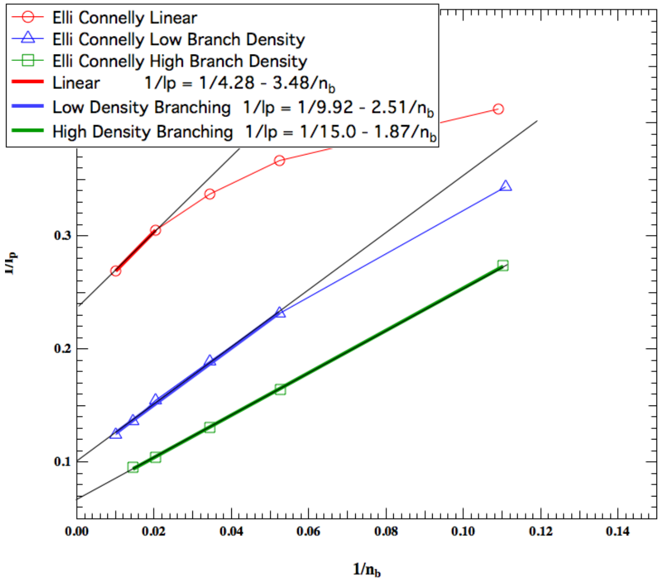

Equation fails at low n_b since it predicts l_p => 0 when n_b => 0

$$l_p=\frac{M\,l_{p\infty}}{M+2K\,l_{p\infty}}+l_{p0}$$

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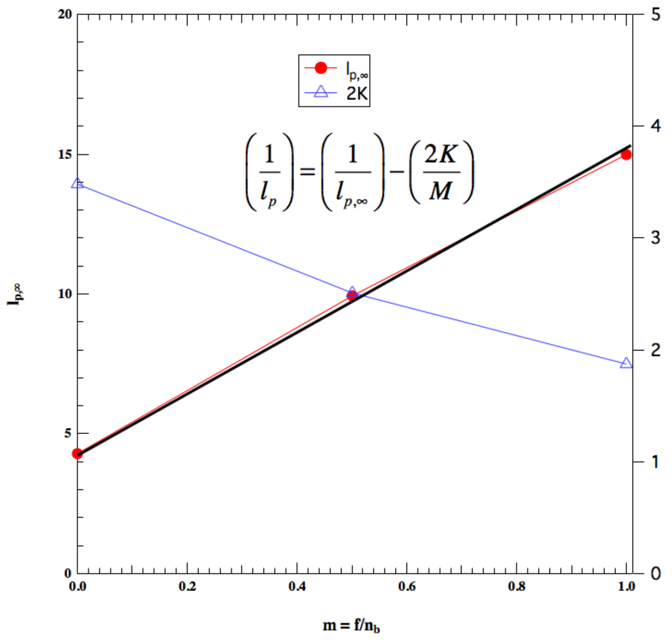

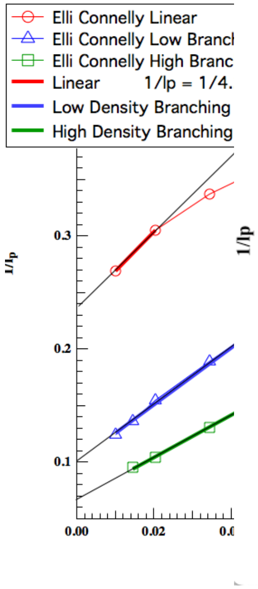

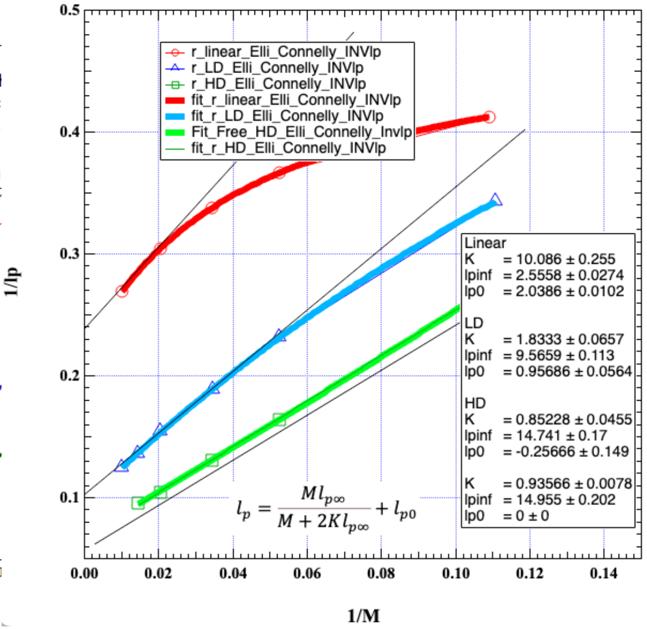

Linear
K = 10.086 ± 0.255
lpinf = 2.5558 ± 0.0274
lp0 = 2.0386 ± 0.0102

LD
K = 1.8333 ± 0.0657
lpinf = 9.5659 ± 0.113
lp0 = 0.95686 ± 0.0564

HD
K = 0.85228 ± 0.0455
lpinf = 14.741 ± 0.17
lp0 = -0.25666 ± 0.149

K = 0.93566 ± 0.0078
lpinf = 14.955 ± 0.202
lp0 = 0 ± 0

$$l_p = \frac{M l_{p\infty}}{M + 2K l_{p\infty}} + l_{p0}$$

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

Alternative Functionality
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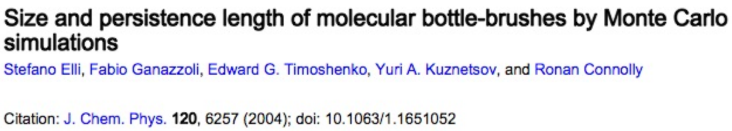

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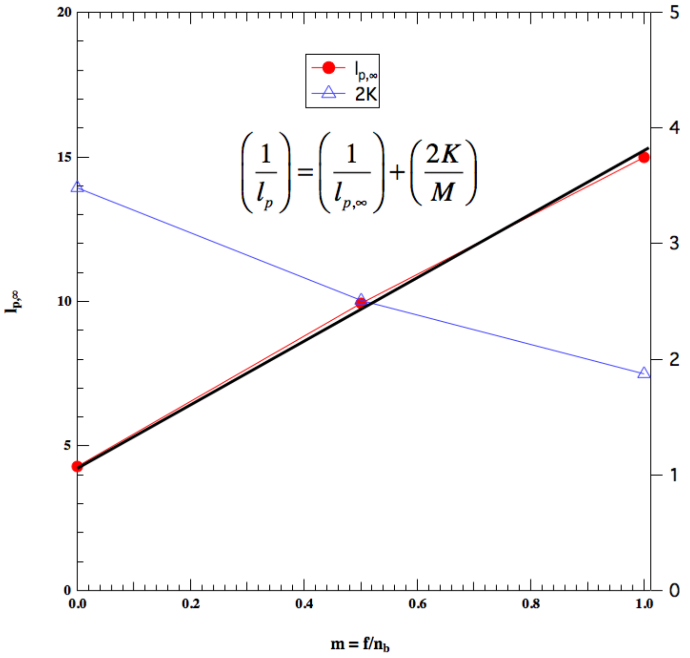

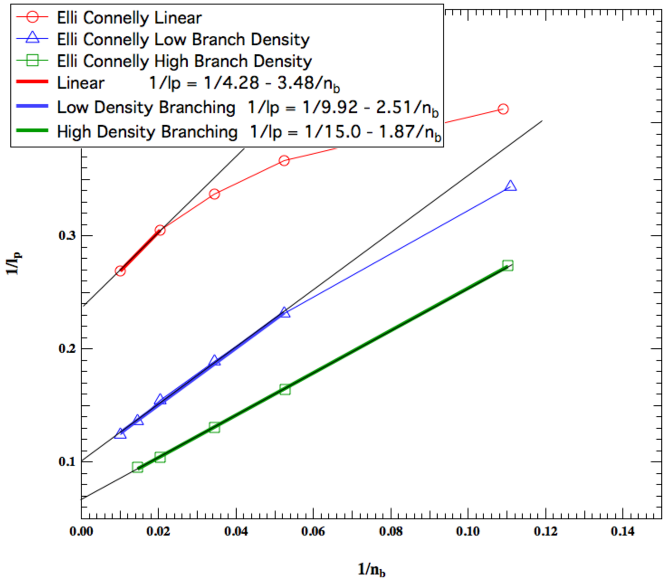

The 2K values imply that end groups become less important for more rigid chains

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
-Conjugation
-Main chain aromatics/cyclics
-Charge (poly electrolytes)
-Hydrogen bonds
-Helicity

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-Bond rotation restriction

Figure 1.1: A simple polymer in the trans conformation.

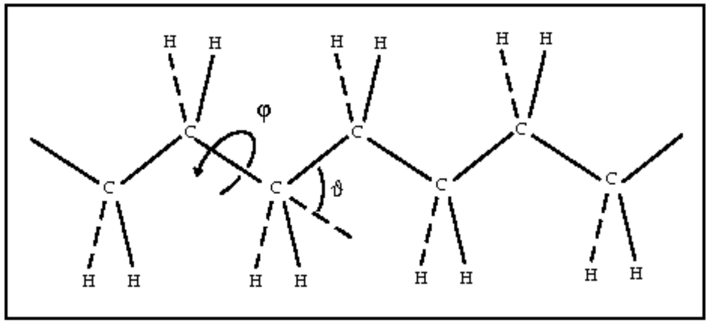
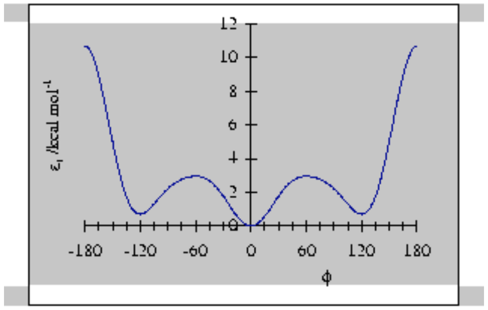
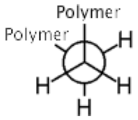


Figure 1.2: Dihedral angle energy of n-butane.



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

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-Bond rotation restriction

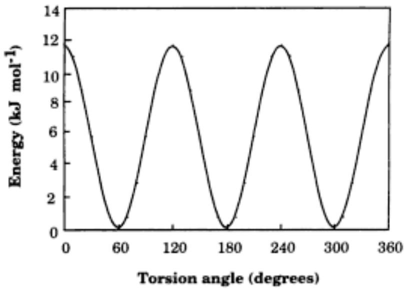


Figure 2.2 Conformational energy of ethane as a function of torsion angle.

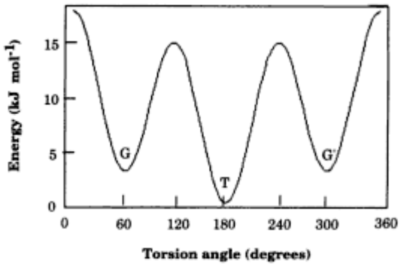
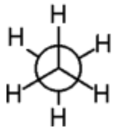
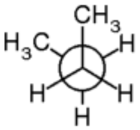


Figure 2.4 Conformational energy of *n*-butane as a function of torsion angle of the central carbon–carbon bond. The outer carbon–carbon bonds are assumed to be in their minimum energy states (staggered positions).



Ethane



Butane

Polymer physics
By Ulf W. Gedde

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-Bond angle restriction
-Bond rotation restriction

Characteristic Ratio, C_∞

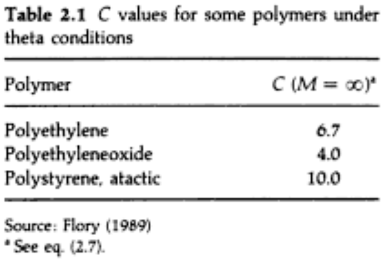


Table 2.1 *C* values for some polymers under theta conditions

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
By Ulf W. Gedde

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

The Primary Structure for Synthetic Polymers

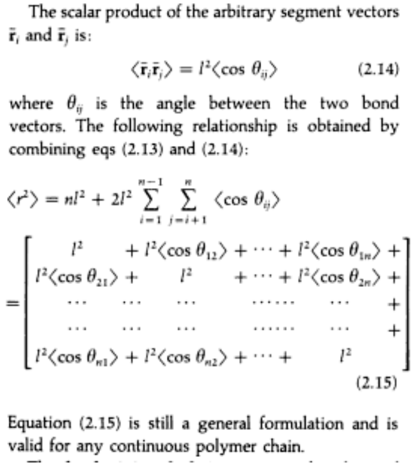
Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction

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

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

Ising Chain Model in Colby/Rubenstein, pp. 59

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

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

See slide 68

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

For SRI Chain the first term is not 0.

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

The second to the last equality is the result of the Sum of Geometric Progression Rule,
lim n->∞ of a + ar + ar^2 +... = 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

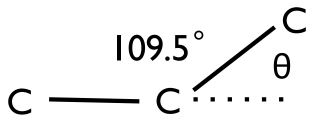
Volkenstein on Flory II

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

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

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

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



See slide 46

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

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

Ising Model

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

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

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

Equation (2.18) can be simplified as follows:

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

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

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

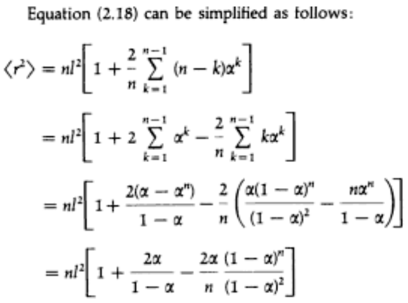
$$= n l^2 \left[1 + \frac{2\alpha}{1 - \alpha} - \frac{2\alpha}{n} \frac{(1 - \alpha)^n}{(1 - \alpha)^2} \right]$$

Polymer physics
By Ulf W. Gedde

The Primary Structure for Synthetic Polymers

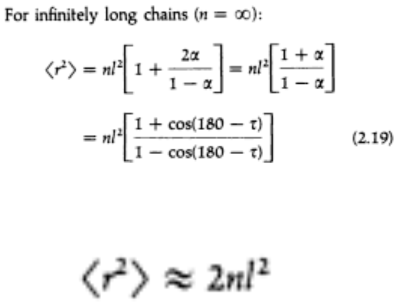
Short-Range Interactions

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



Equation (2.18) can be simplified as follows:

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



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

$$\begin{aligned}\langle r^2\rangle &= nl^2\left[1+\frac{2\alpha}{1-\alpha}\right]=nl^2\left[\frac{1+\alpha}{1-\alpha}\right]\\ &= nl^2\left[\frac{1+\cos(180-\tau)}{1-\cos(180-\tau)}\right] \qquad (2.19)\end{aligned}$$

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

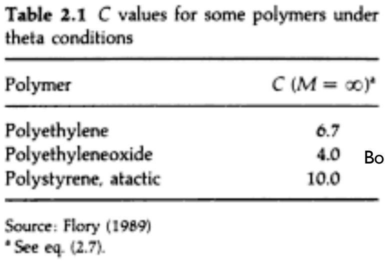


Table 2.1 *C* values for some polymers under theta conditions

Moderate Flexibility
High Rotational Flexibility
Lower Rot. Flexibility

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

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

Bond angles 109.5° : 104.5°

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

For a Freely Rotating Polyethylene Chain

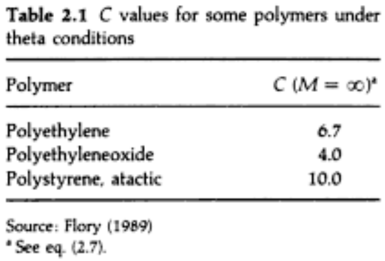
http://books.google.com/books?id=Iem3fC7XdnkC&pg=PA23&lpg=PA23&dq=coil+expansion+factor&source=bl&ots=BGjRfhZYaU&sig=I0OPb2VRuf8Dm8qnrmrhyjXyEC8&hl=en&sa=X&ei=fSV0T-XqMMHW0QHi1-T_Ag&ved=0CF0Q6AEwBw#v=onepage&q=coil%20expansion%20factor&f=false

Polymer physics
By Ulf W. Gedde

The Primary Structure for Synthetic Polymers

Short-Range Interactions

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



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Polyethylene	6.7
Polyethyleneoxide	4.0
Polystyrene, atactic	10.0

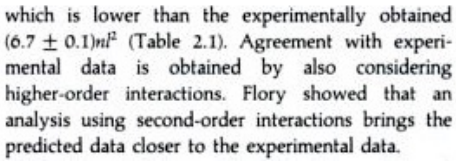
Source: Flory (1989)
[a] See eq. (2.7).

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

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

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.

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

Polymer physics
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The Primary Structure for Synthetic Polymers

Short-Range Interactions

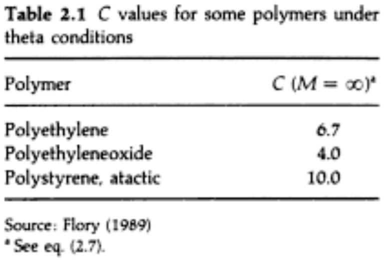

Table 2.1 *C* values for some polymers under theta conditions

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Polymer physics
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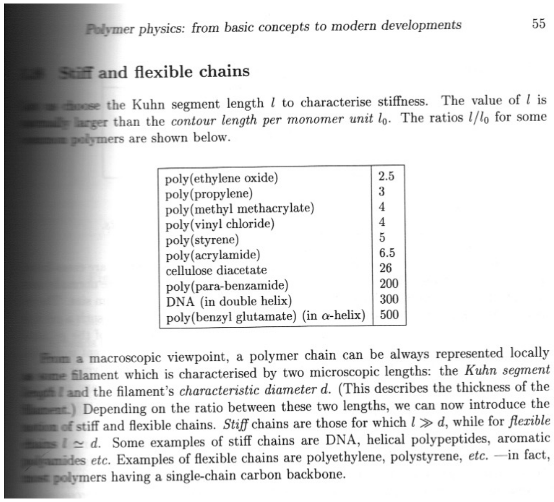


Polymer physics: from basic concepts to modern developments 55

Stiff and flexible chains

choose the Kuhn segment length l to characterise stiffness. The value of l is usually 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.

Alexei Khokhlov in Soft and Fragile Matter (2000)

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

Contour length per monomer is 2 * bond length

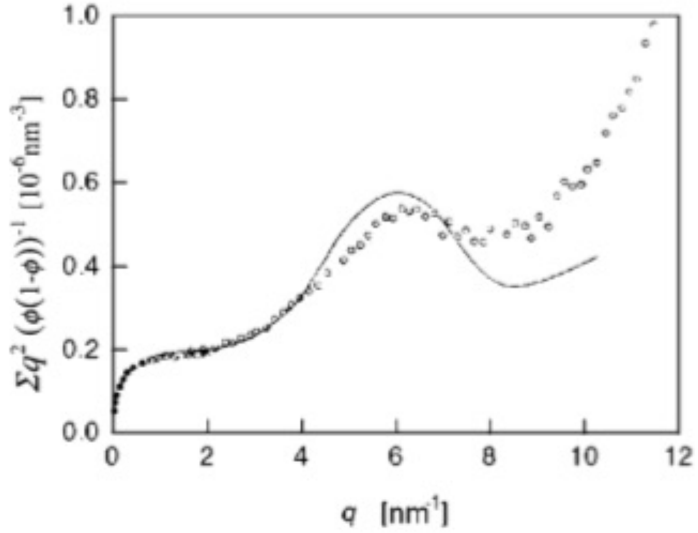


Fig. 2.23. Neutron scattering experiment on mixtures of PC and d-PC. The *continuous curve* has been calculated on the basis of the RIS model. Data from Gawrisch et al. [8]

From Colby/Rubeinstein pp. 66

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,

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

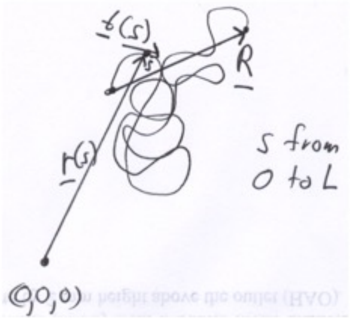


Figure 1. Brownian Path.

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

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

Linear absorption

$dI = -I\ \alpha\ dx$ change is linear in intensity

$dI/I = -\ \alpha\ dx$ integrate

$\ln(I/I_0) = -\ \alpha x$ or

$I = I_0 \exp(-\alpha x)$

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

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

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

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

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

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

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 $\underline{\mathbf{R}}^2$,

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

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

We also can consider that for a freely jointed chain composed of $\mathrm{n_K}$ Kuhn steps of length $\mathrm{l_K}$,

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

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

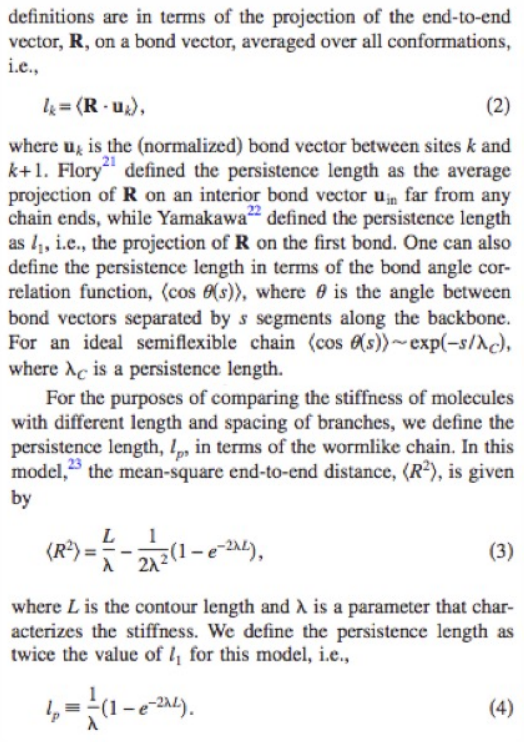
The Primary Structure for Synthetic Polymers

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.,

$$l_k = \langle \mathbf{R} \cdot \mathbf{u}_k \rangle, \tag{2}$$

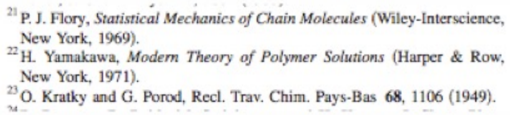
where $\mathbf{u}_k$ is the (normalized) bond vector between sites k and $k+1$. Flory[21] defined the persistence length as the average projection of **R** on an interior bond vector $\mathbf{u}_{\rm in}$ far from any chain ends, while Yamakawa[22] defined the persistence length as l_1, i.e., the projection 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

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

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.,

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

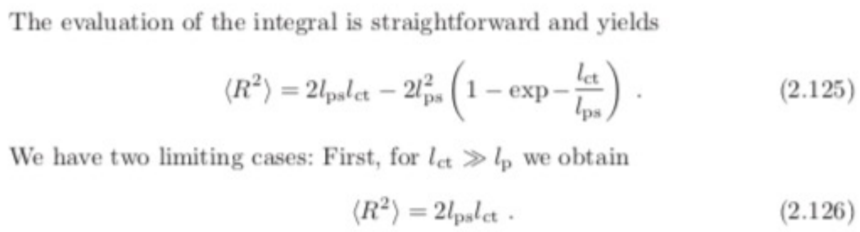


[21] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley-Interscience, New York, 1969).

[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**.



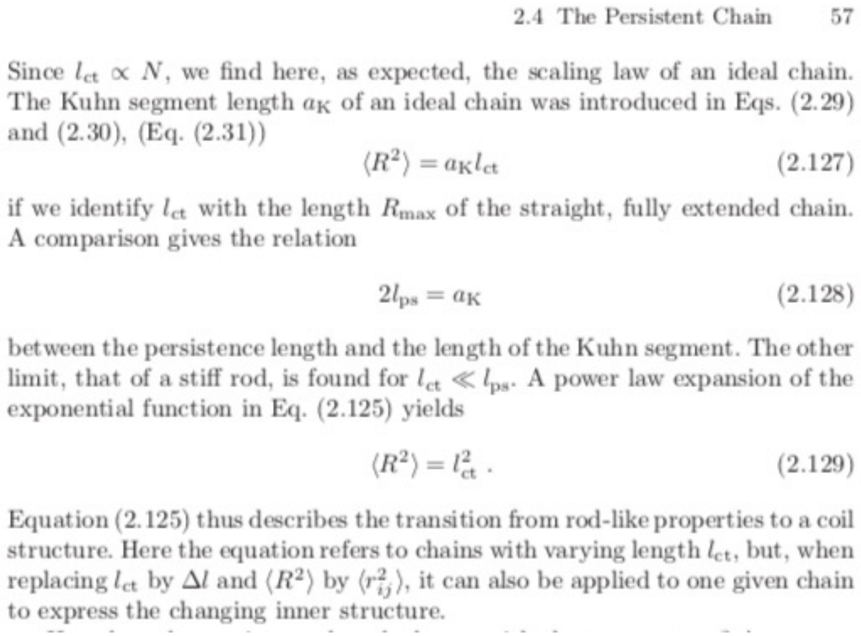
The evaluation of the integral is straightforward and yields

$$\langle R^2 \rangle = 2l_{\mathrm{ps}}l_{\mathrm{ct}} - 2l_{\mathrm{ps}}^2\left(1 - \exp - \frac{l_{\mathrm{ct}}}{l_{\mathrm{ps}}}\right) . \qquad (2.125)$$

We have two limiting cases: First, for $l_{\mathrm{ct}} \gg l_{\mathrm{p}}$ we obtain

$$\langle R^2 \rangle = 2l_{\mathrm{ps}}l_{\mathrm{ct}} . \qquad (2.126)$$

From Strobl p. 57



Since $l_{\mathrm{ct}} \propto N$, we find here, as expected, the scaling law of an ideal chain. The Kuhn segment length a_{K} of an ideal chain was introduced in Eqs. (2.29) and (2.30), (Eq. (2.31))

$$\langle R^2 \rangle = a_{\mathrm{K}}l_{\mathrm{ct}} \qquad (2.127)$$

if we identify l_{ct} with the length R_{max} of the straight, fully extended chain. A comparison gives the relation

$$2l_{\mathrm{ps}} = a_{\mathrm{K}} \qquad (2.128)$$

between the persistence length and the length of the Kuhn segment. The other limit, that of a stiff rod, is found for $l_{\mathrm{ct}} \ll l_{\mathrm{ps}}$. A power law expansion of the exponential function in Eq. (2.125) yields

$$\langle R^2 \rangle = l_{\mathrm{ct}}^2 . \qquad (2.129)$$

Equation (2.125) thus describes the transition from rod-like properties to a coil structure. Here the equation refers to chains with varying length l_{ct}, but, when replacing l_{ct} by Δl and $\langle R^2 \rangle$ by $\langle r_{ij}^2 \rangle$, it can also be applied to one given chain to express the changing inner structure.

The Primary Structure for Synthetic Polymers

Scattering Observation of the Persistence Length

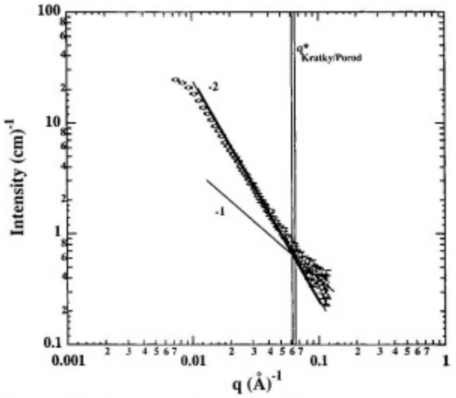
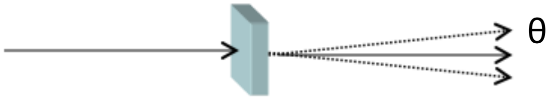


Figure 2. *Kratky/Porod graphical analysis in a log-log plot of corrected SANS data from a 5% by volume d-PHB sample in h-PHB. The lower power -2 line is the best visual estimate; the upper line is shifted to match a global unified fit. Key: left, q* corresponds to best visual estimate; right, plot to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

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

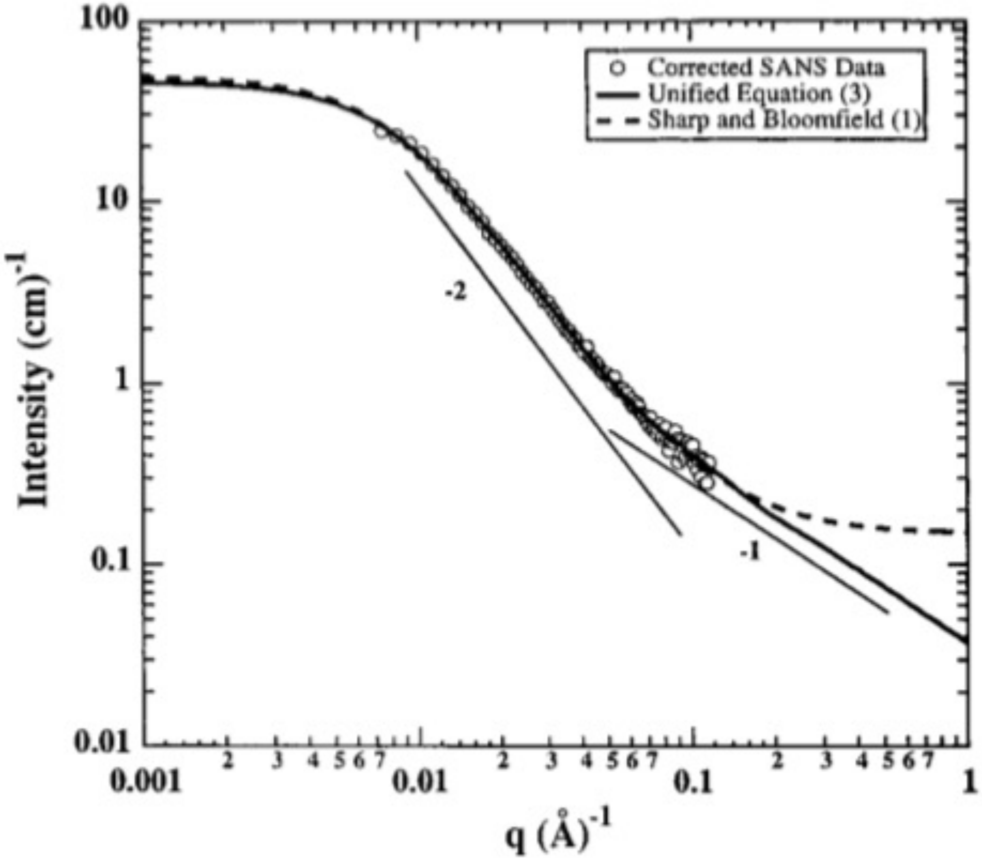
$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) \qquad d = \frac{2\pi}{q}$$



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

The Primary Structure for Synthetic Polymers

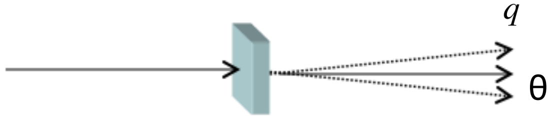
Scattering Observation of the Persistence Length



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

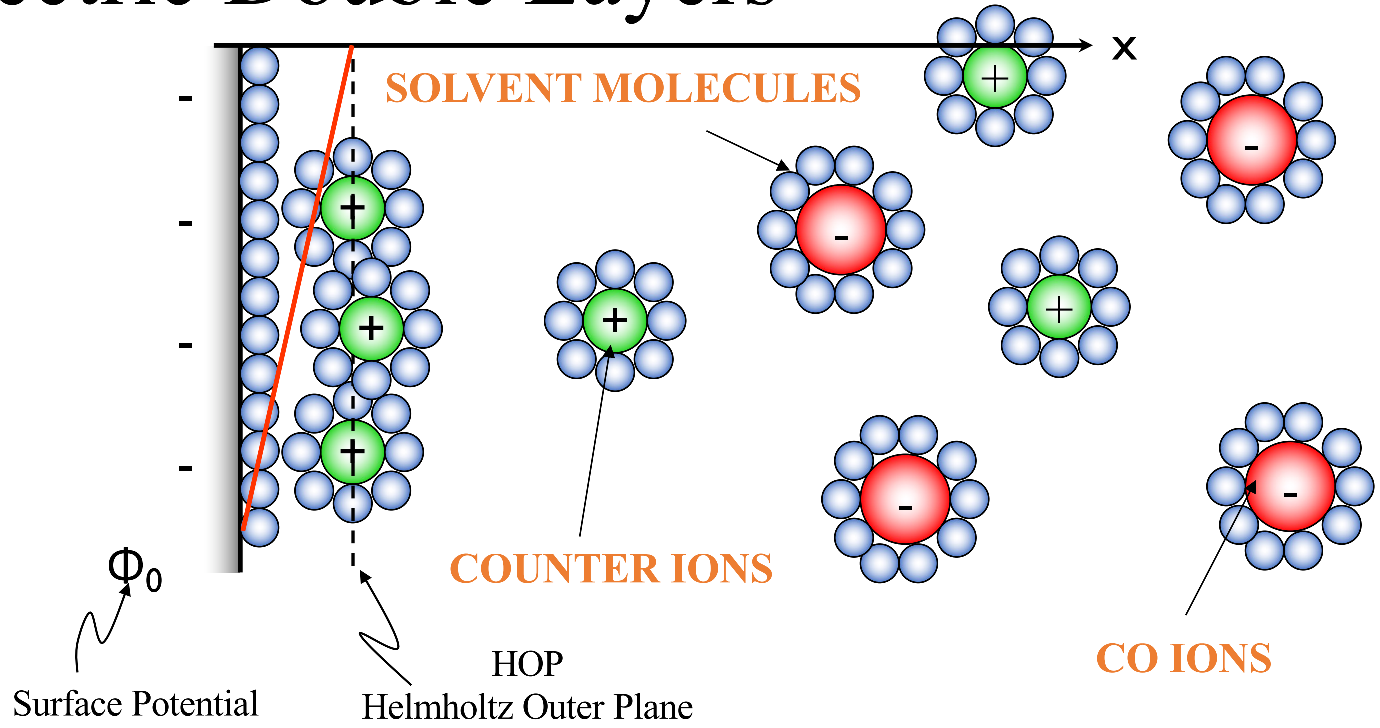
$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

$$d = \frac{2\pi}{q}$$



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

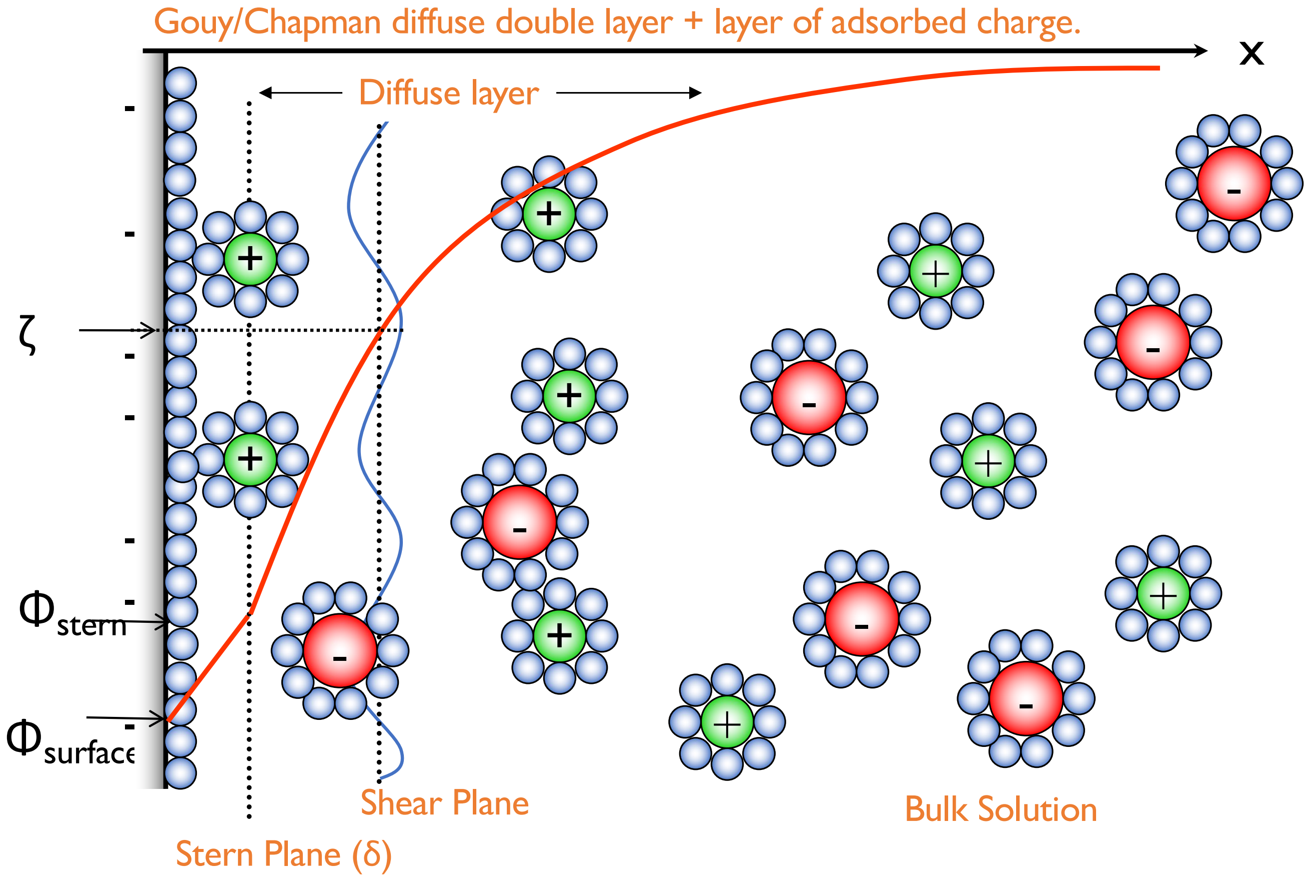
Electric Double Layers



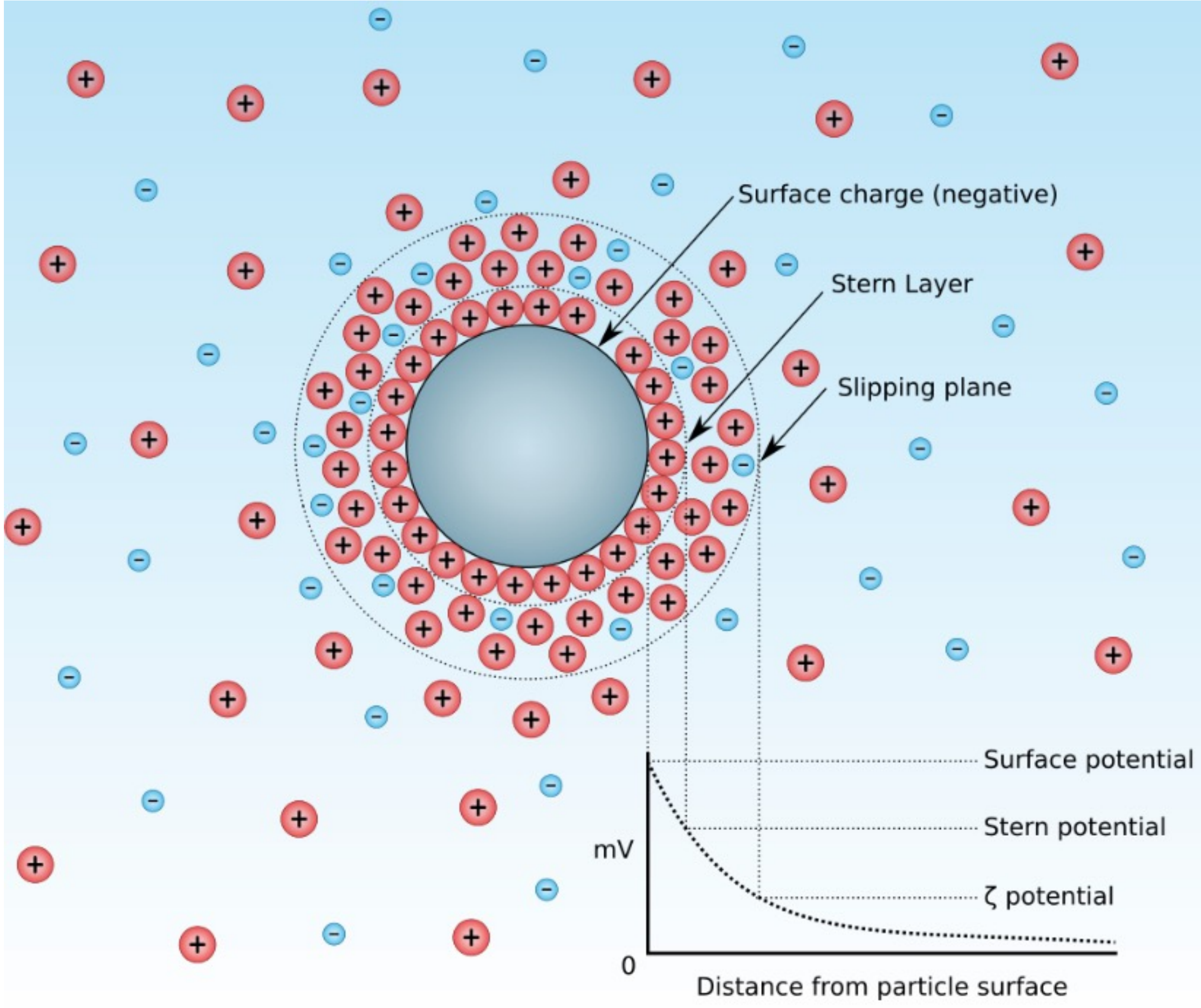
Helmholtz (100+ years ago) proposed that surface charge is balanced by a layer of oppositely charged ions.

All colloids should flocculate.

Zeta (ζ) Potential (Electric potential at the slipping (shear) plane)



Φ = electrostatic potential (Volt = J/coulomb)


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

Debye-Hückel approximation for Φ(x)

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

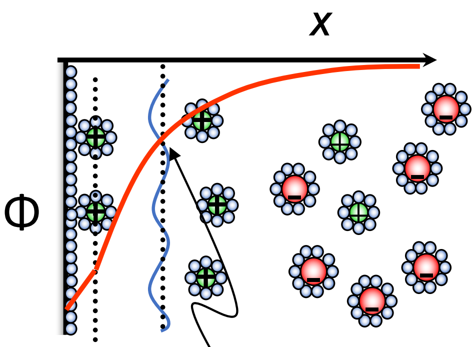
Potential is stronger than kT

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

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

Counter ions (n_0) screen the charge

Gouy-Chapman Model

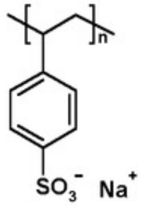


Exponential function

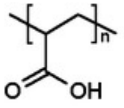
http://www.eng.uc.edu/~gbeaucag/Classes/MorphologyofComplexMaterials/Persistence/Persistence.html

Polyelectrolytes (proteins, charged polymers (sulfonated polystyrene), polyacrylic acid, polyethylene oxide, polypropylene oxide, poly nucleic acids, etc.)

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



SCPE



WCPE

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,

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

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

Distances where a mean field is felt.

Potential is similar to kT

Consider two isolated charges subject to thermal motion at kT

The energy associated with the charge attraction/repulsion
is equal to the thermal energy, kT, at the **Bjerrum length**, l_B.

$$\frac{e^2}{4\pi\varepsilon l_B} = k_B T \quad \Rightarrow \quad l_B = \frac{e^2}{4\pi\varepsilon k_B T}$$

Thermal diffusion/Brownian motion takes over

https://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2014/study-materials/MIT10_626S14_S11lec28.pdf

In water at room temperature $l_B \sim 7$ Å

Below the Bjerrum length charges will feel specific interactions and will form ordered structures. Above l_B, charges feel a "*mean field*" and do not form ordered structures but can still feel repulsive and attractive forces.

You hear the report of a gun but can't tell its location, so you take cover, you are beyond its Bjerrum length.
You hear the report of the gun and run in the opposite direction; you are within its Bjerrum length.

Distances where a mean field is felt.

Potential is similar to kT

Consider two isolated charges subject to thermal motion at kT

The energy associated with the charge attraction/repulsion
is equal to the thermal energy, kT, at the **Bjerrum length**, l_B.

Debye Screeening Length 1923
Bjerrum length 1926

$$\frac{e^2}{4\pi\varepsilon l_B} = k_B T \quad \Rightarrow \quad l_B = \frac{e^2}{4\pi\varepsilon k_B T}$$

Thermal diffusion/Brownian motion takes over

https://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2014/study-materials/MIT10_626S14_S11lec28.pdf

In water at room temperature $l_B \sim 7$ Å

Below the Bjerrum length charges will feel specific interactions and will form ordered structures. Above l_B, charges feel a "*mean field*" and do not form ordered structures but can still feel repulsive and attractive forces.

You hear the report of a gun but can't tell its location, so you take cover, you are beyond its Bjerrum length.
You hear the report of the gun and run in the opposite direction; you are within its Bjerrum length.

Distances where a mean field is felt.

Potential is similar to kT

Consider two isolated charges subject to thermal motion at kT

- ε is the ability to store charge per unit length, C/(Vm) or F/m

Energy is kT or CV so a length naturally emerges

The energy associated with the charge attraction/repulsion is equal to the thermal energy, kT, at the **Bjerrum length**, l_B.

$$\frac{e^2}{4\pi\varepsilon l_B} = k_B T \quad \Rightarrow \quad l_B = \frac{e^2}{4\pi\varepsilon k_B T}$$

Thermal diffusion/Brownian motion takes over

https://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2014/study-materials/MIT10_626S14_S11lec28.pdf

In water at room temperature $l_B \sim 7$ Å

Below the Bjerrum length charges will feel specific interactions and will form ordered structures. Above l_B, charges feel a "*mean field*" and do not form ordered structures but can still feel repulsive and attractive forces.

You hear the report of a gun but can't tell its location, so you take cover, you are beyond its Bjerrum length. You hear the report of the gun and run in the opposite direction; you are within its Bjerrum length.

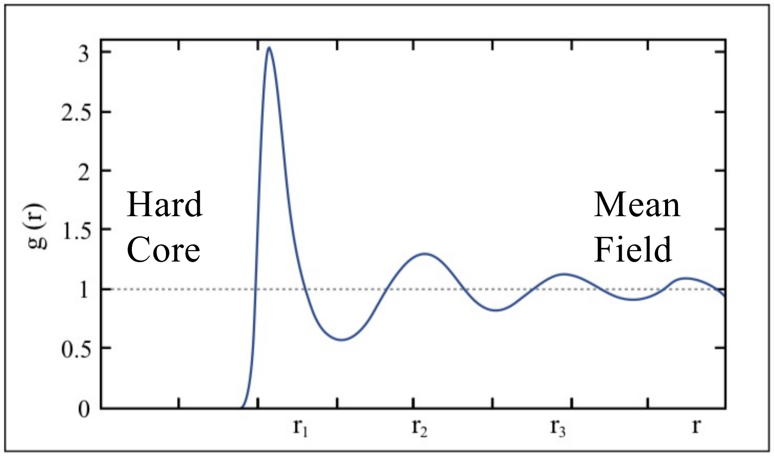


Image by MIT OpenCourseWare.

FIG. 1 Typical g(r) for a liquid. The first neighbor distance is r_1, the second is r_2, etc.

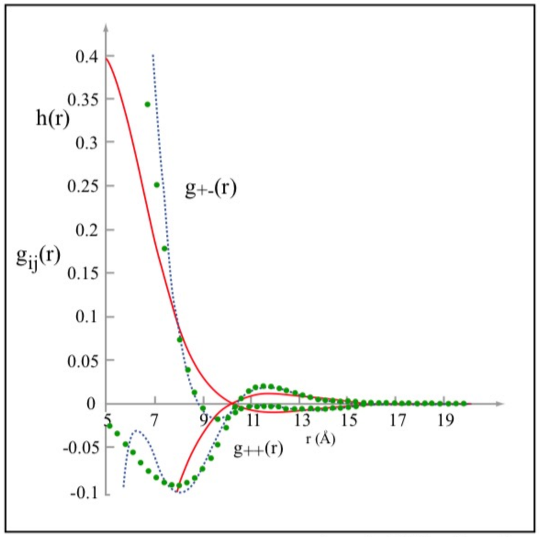


Image by MIT OpenCourseWare.

FIG. 2 Total correlation functions for a monovalent binary electrolyte with diameter of the ion = 5Å. $g_{++}(r)$ is the pair correlation function for a central atom and a neighboring co-ion and shows repulsion. $g_{+-}(r)$ is the counter-ion pair correlation function and shows attraction. The solid lines result from asymptotic analysis of the double layer and the dashed lines result from setting the mean force potential equal to the sum of the core and electrostatic asymptotes.

https://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2014/study-materials/MIT10_626S14_S11lec28.pdf

Distances where charges are not felt at all.

For Charges separated by distance r in the presence of n = number/volume counter ions or other charges

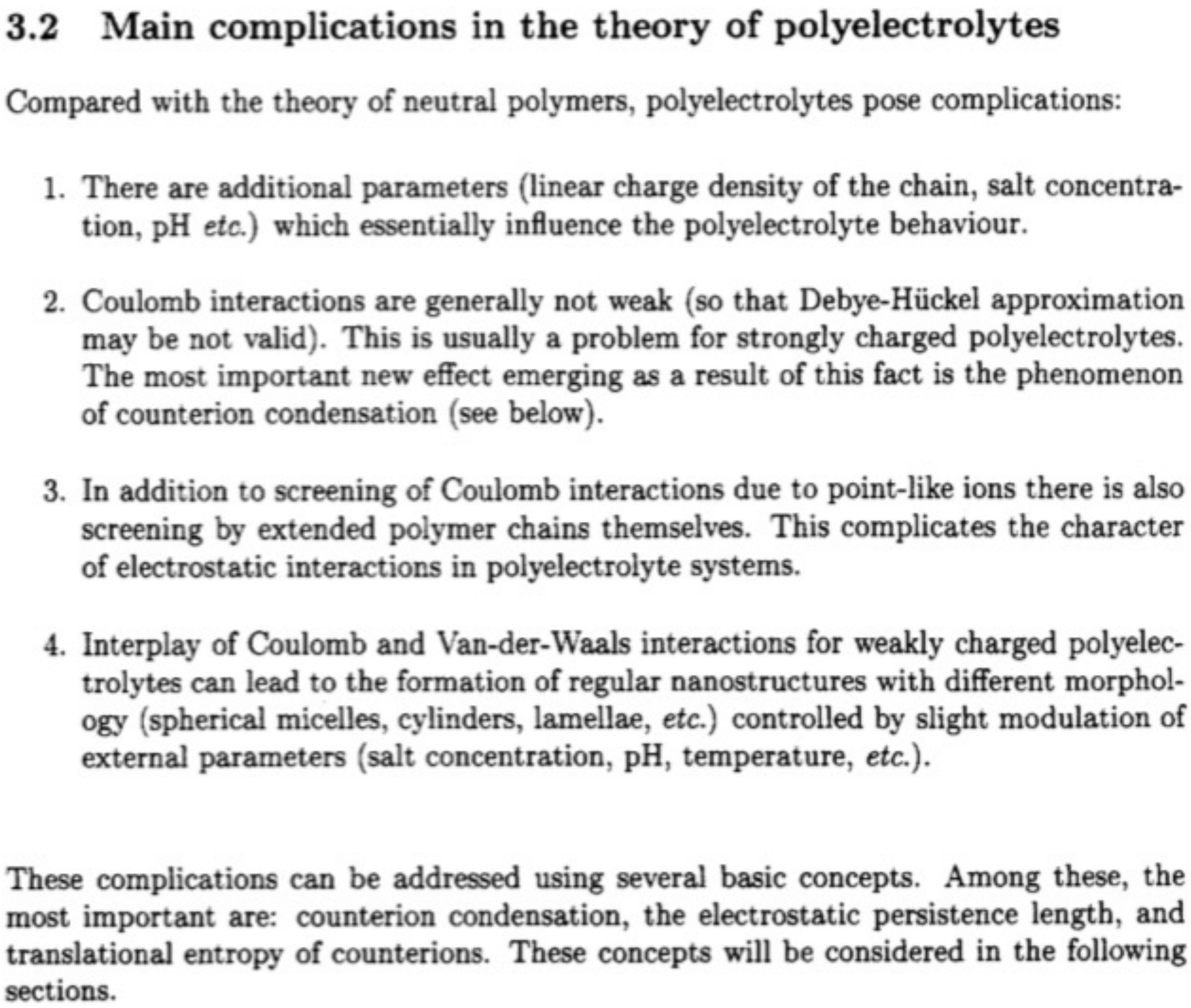
$$U(r) = \frac{e^2}{\varepsilon r} \exp\left(-\frac{r}{r_D}\right) \qquad \mathrm{r}_D = \left(\frac{\varepsilon kT}{4\pi n e^2}\right)^{1/2}$$

Debye length is the distance where kT random motion balances the U(r) potential in the presence of n counter ion density

$$r_D^2 = \frac{V_{per\ charge} kT}{4\pi r U(r)_{with\ r_D=\infty}}$$

Below the Debye screening length charges will feel interactions, either specific if r < l_B and or mean field if r > l_B . Above l_D, charges do not feel interactions at all, they act as uncharged species.

You hear the report of a gun but can’t tell its location so you take cover, you are beyond its Bjerrum length but within its Debye screening length. You can’t hear the gun due to too many other guns firing closer to you, you are beyond its Debye screening length.



3.2 Main complications in the theory of polyelectrolytes

Compared with the theory of neutral polymers, polyelectrolytes pose complications:

1. There are additional parameters (linear charge density of the chain, salt concentration, pH *etc.*) which essentially influence the polyelectrolyte behaviour.
2. Coulomb interactions are generally not weak (so that Debye-Hückel approximation may be not valid). This is usually a problem for strongly charged polyelectrolytes. The most important new effect emerging as a result of this fact is the phenomenon of counterion condensation (see below).
3. In addition to screening of Coulomb interactions due to point-like ions there is also screening by extended polymer chains themselves. This complicates the character of electrostatic interactions in polyelectrolyte systems.
4. Interplay of Coulomb and Van-der-Waals interactions for weakly charged polyelectrolytes can lead to the formation of regular nanostructures with different morphology (spherical micelles, cylinders, lamellae, *etc.*) controlled by slight modulation of external parameters (salt concentration, pH, temperature, *etc.*).

These complications can be addressed using several basic concepts. Among these, the most important are: counterion condensation, the electrostatic persistence length, and translational entropy of counterions. These concepts will be considered in the following sections.

Charge spacing, a
Counterion concentration, n

Counterion condensation

Polymeric contribution to screening

Micelles, liquid-crystalline phases

Increase in persistence length due to charges on chain

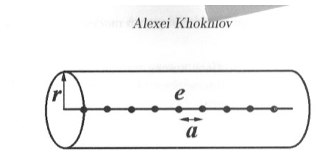


Figure 13. *Illustration of the phenomenon of counterion condensation.*

A new size scale is introduced:
Charge spacing “a” which contributes an electrostatic persistence length, l_e

-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 (short-range interactions)

Interaction between charges separated by a distance > l_{per} effect chain scaling (long-range interactions)

Increase in persistence length due to charges on chain

Manning length, ξ

$$\xi = \frac{l_b}{b} = \frac{e^2}{4\pi\varepsilon\varepsilon_o kTb}$$

- Ratio of Bjerrum length to the spacing of charges on the chain (a or here b)
- If $\xi = 1$ then the charges are at the point where $kT = e^2/\varepsilon$ and thermal energy equals charge energy
- If $\xi > 1$ we have specific interactions and the persistence can increase This is called a strongly charged polyelectrolyte
- If $\xi < 1$ we have mean-field interactions and the persistence doesn’t change but the chain still has charge interactions, that is if $a < \lambda_D$ This is called a weakly charged polyelectrolyte
- For water l_b is 7.1 Å

Increase in persistence length due to charges on chain

Odijk-Skolnick-Fixman (OSF) Model

$$l_p = l_{p,o} + l_{p,e}$$

$$l_{p,e} = \frac{l_b}{4}\left(\frac{1}{\kappa b}\right)^2$$

b (or a) is the charge spacing on the chain

$$\xi = \frac{l_b}{b} \qquad \text{so,} \qquad l_{p,e} = \xi \left(\frac{\lambda_D}{b}\right)\left(\frac{\lambda_D}{4}\right)$$

The Manning parameter is the mean-field cutoff to charge spacing (>1 for SCP) and λ_D/b is the charge cutoff to spacing (>>1) so $l_{p,e}$ depends on the Debye screening length by a factor near 1 and inverse to the counter ion concentration

Increase in persistence length due to charges on chain

Odijk-Skolnick-Fixman (OSF) Model

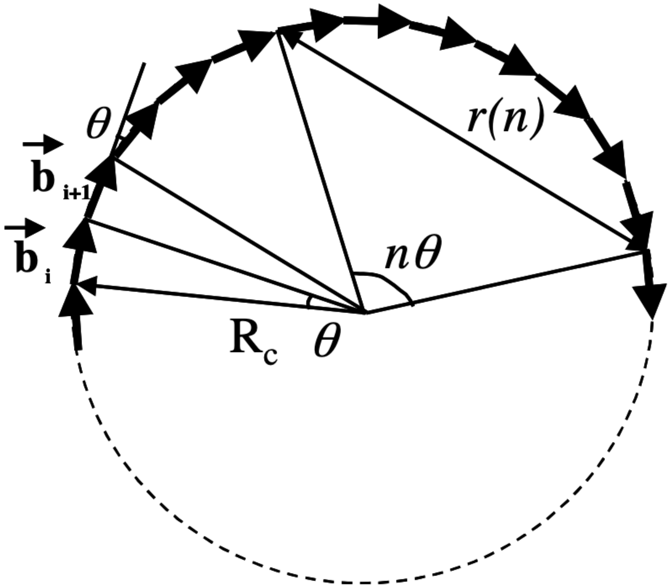


Fig. 17. Schematic representation of the conformation of a polyelectrolyte chain for calculation of the OSF electrostatic persistence length.

Andrey V. Dobrynin[a,*], Michael Rubinstein[b,*]
Prog. Polym. Sci. 30 (2005) 1049–1118

$$r(n) = 2R_c \sin(n\theta/2) = \frac{b\sin(n\theta/2)}{\sin(\theta/2)} \underset{\theta \ll 1}{\approx} bn(1 - n^2\theta^2/24) \qquad (2.73)$$

The difference between the electrostatic energy per monomer in the circular and rod-like conformations is

$$\frac{\Delta U_{\text{electr}}(\theta)}{k_B T} \approx l_B \sum_{n=1}^{\infty} \left(\frac{\exp(-\kappa r(n))}{r(n)} - \frac{\exp(-\kappa bn)}{bn} \right) \underset{\kappa b \ll 1}{\approx} \frac{l_B}{8\kappa^2 b^3} \theta^2 \qquad (2.74)$$

The expression (2.74) was obtained [22] by substituting expression for $r(n)$ (Eq. (2.73)) into the right-hand side of Eq. (2.74) and expanding it into the power series over θ. A chain in the circular configuration makes a complete turn after $n_p \propto \theta^{-1}$ steps leading to the persistence length $b\theta^{-1}$.

In the OSF derivation of the electrostatic persistence length [77,78] , it was assumed that such bending of a chain can be induced by thermal fluctuations if the change in the electrostatic energy per persistence length $n_p \Delta U_{\text{electr}}(\theta)$is on the order of the thermal energy $k_B T$. This leads to the typical values of the bending angle $\theta_{\text{OSF}} \approx \kappa^2 b^3 / l_B$ and the OSF electrostatic persistence length equal to

$$l_p^{\text{OSF}} \approx \frac{b}{\theta_{\text{OSF}}} \approx \frac{l_B r_D^2}{4b^2} \qquad (2.75a)$$

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

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

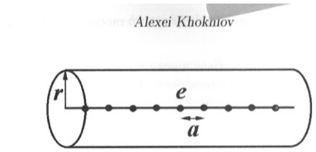


Figure 13. *Illustration of the phenomenon of counterion condensation.*

-Counterion Condensation

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

Ideal gas
dU = -pdV (for dQ = 0)
dU = -RT(dV/V)
U = -RTln(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* = distance of charge separation on chain)

D-H Potential
dU = -$e^2/\varepsilon a$ dr/r
U = -eρ/ε (ln(r_2/r_1))
U = -eρ/2ε (ln(V_2/V_1))

$$\rho=\frac{e}{a}$$

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 counter ions move in (condense on chain)

Counter ions condense until the chain charge is neutralized, when

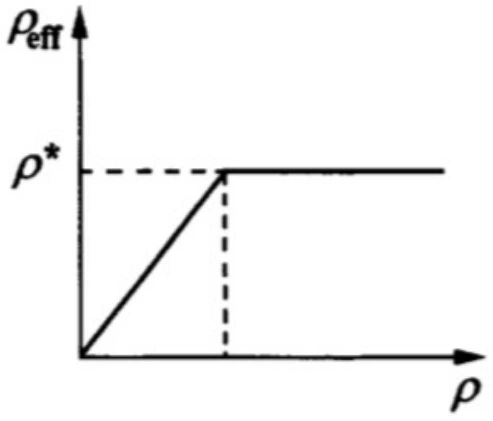
$$u_{eff}=\frac{\rho_{eff}e}{\varepsilon kT}=1$$

ρ_{eff} is the final 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

Condensing counterions to neutralize charge on the chain

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



$$\rho^* = \frac{\varepsilon k_B T}{e}$$

Figure 14. *The dependence of the effective charge on the line as a function of its initial charge.*

This removes counterions from the solution so that there is less Debye screening

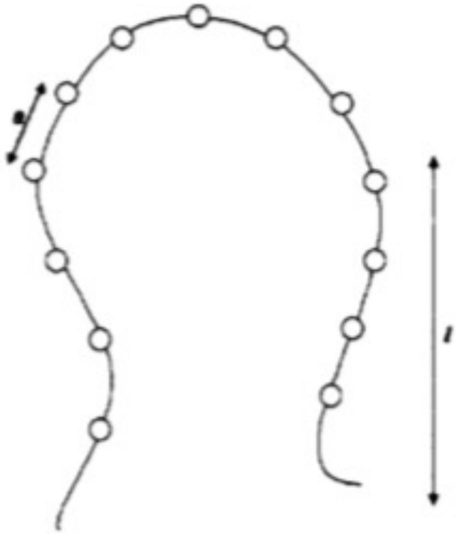


Figure 15. *Persistence length renormalisation in a polyelectrolyte chain.*

That the Coulomb interaction leads to an effective renormalisation of the persistence length can be illustrating using Figure 15, in which a chain is shown for the case $a \ll r_D \ll l$. (This corresponds to a strongly charged polyelectrolyte, with a moderate concentration of a low-molecular-weight salt in the solution.) In this case two types of Coulomb interaction are possible:

1. Interaction between the charges separated by a distance $< r_D$ along the chain. (This is a short range repulsion, tending to increase the persistence length.)
2. Interaction between the charges separated by a distance $> l$ along the chain. (Such charges approach one another closer than the distance r_D as a result of random bending of the chain; their interaction should naturally be classified with the volume interaction.)

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

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

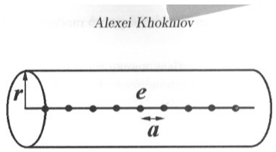


Figure 13. *Illustration of the phenomenon of counterion condensation.*

-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

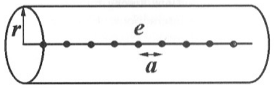


Figure 13. *Illustration of the phenomenon of counterion condensation.*

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
- (l_B Bjerrum length for mean field)

"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 and as a consequence the persistence length is increased, too. The expression for the electrostatic persistence length l_e has the form (Odijk 1977)

$$l_e = \begin{cases} ur_D^2/(4a), & \text{at} \quad u < 1 \quad \text{(no condensation)} \\ r_D^2/(4ua), & \text{at} \quad u > 1 \quad \text{(condensation takes place).} \end{cases} \tag{30}$$

Taking into account that for typical cases $u \sim 1$ and $r_D \gg a$ (if the salt concentration is not very high), we reach the conclusion that $l_e \gg r_D$, so that the stiffening of the polymer chain because of electrostatic interactions occurs on length scales much larger than the Debye radius r_D (despite the fact that this interaction only acts over a radius r_D). In many cases, provided that the corresponding uncharged chains are not too stiff, we obtain $l_e \gg l_0$ so that the electrostatic contribution to the persistence length prevails.

Note that in the regime of counterion condensation, the quantity l_e is independent of the linear charge density $\rho = e/a$ of the polymer chain, as it should be, because the charge density in excess of e/a is compensated by the counterions condensing onto the chain.

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 $k_B T$). 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

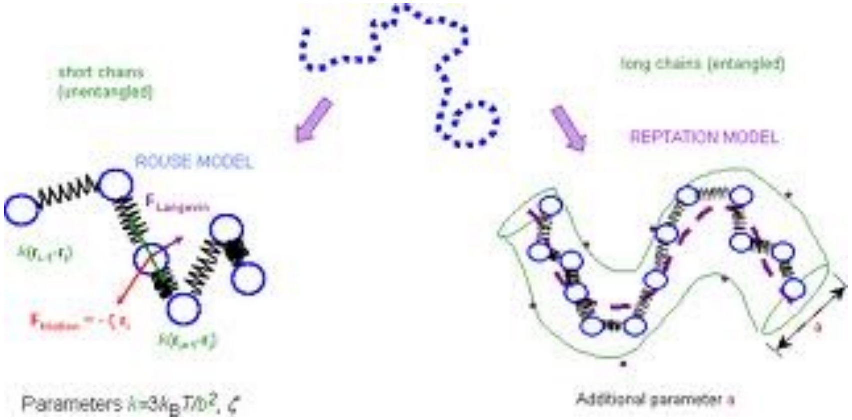
Tube Diameter: Dynamic measure of chain lateral size

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 parameters"

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

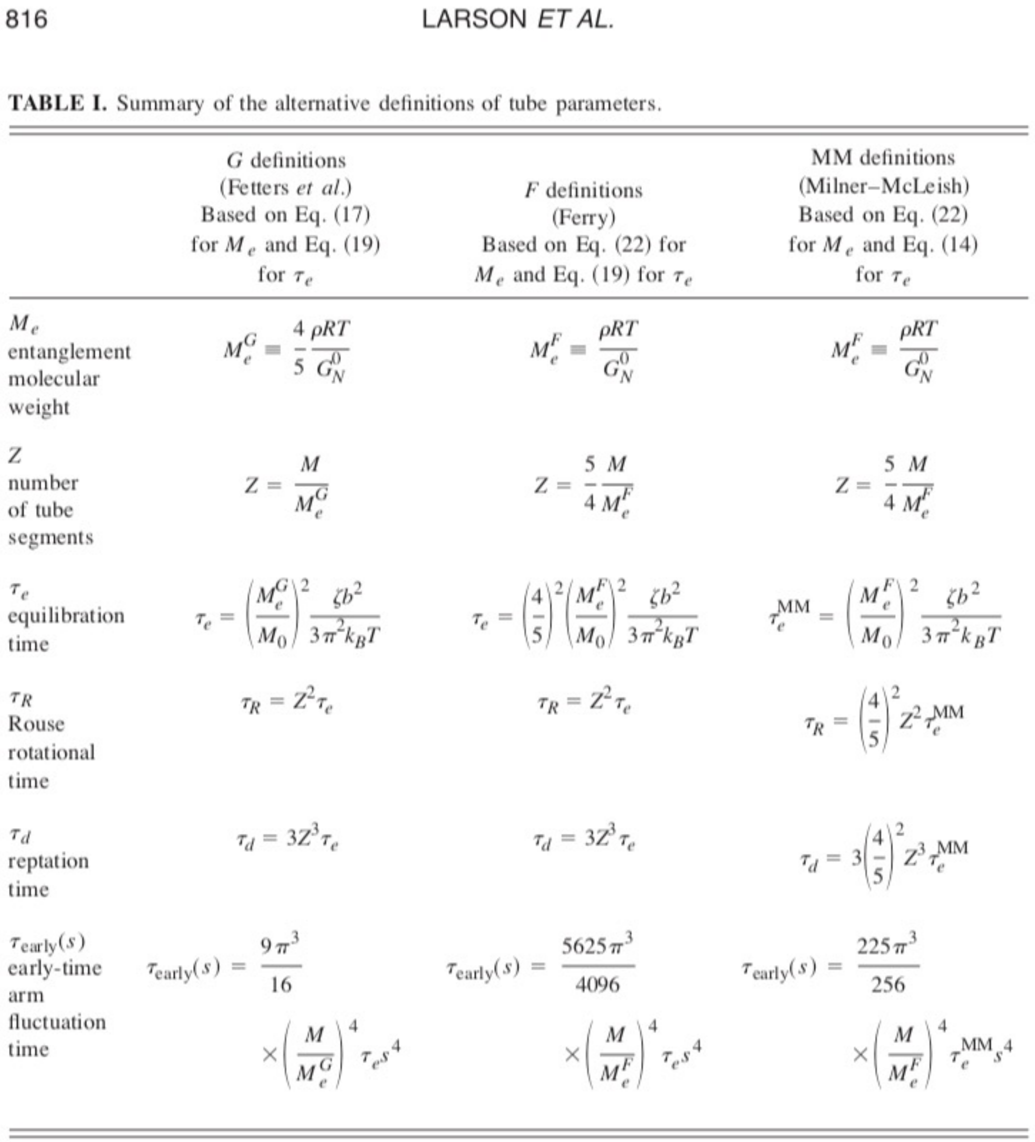


TABLE I. Summary of the alternative definitions of tube parameters.

	G definitions (Fetters *et al.*) Based on Eq. (17) for M_e and Eq. (19) for τ_e	F definitions (Ferry) Based on Eq. (22) for M_e and Eq. (19) for τ_e	MM definitions (Milner–McLeish) Based on Eq. (22) for M_e and Eq. (14) for τ_e
M_e entanglement molecular weight	$M_e^G \equiv \frac{4}{5}\frac{\rho RT}{G_N^0}$	$M_e^F \equiv \frac{\rho RT}{G_N^0}$	$M_e^F \equiv \frac{\rho RT}{G_N^0}$
Z number of tube segments	$Z = \frac{M}{M_e^G}$	$Z = \frac{5}{4}\frac{M}{M_e^F}$	$Z = \frac{5}{4}\frac{M}{M_e^F}$
τ_e equilibration time	$\tau_e = \left(\frac{M_e^G}{M_0}\right)^2 \frac{\zeta b^2}{3\pi^2 k_B T}$	$\tau_e = \left(\frac{4}{5}\right)^2 \left(\frac{M_e^F}{M_0}\right)^2 \frac{\zeta b^2}{3\pi^2 k_B T}$	$\tau_e^{\mathrm{MM}} = \left(\frac{M_e^F}{M_0}\right)^2 \frac{\zeta b^2}{3\pi^2 k_B T}$
τ_R Rouse rotational time	$\tau_R = Z^2 \tau_e$	$\tau_R = Z^2 \tau_e$	$\tau_R = \left(\frac{4}{5}\right)^2 Z^2 \tau_e^{\mathrm{MM}}$
τ_d reptation time	$\tau_d = 3Z^3 \tau_e$	$\tau_d = 3Z^3 \tau_e$	$\tau_d = 3\left(\frac{4}{5}\right)^2 Z^3 \tau_e^{\mathrm{MM}}$
$\tau_{\mathrm{early}}(s)$ early-time arm fluctuation time	$\tau_{\mathrm{early}}(s) = \frac{9\pi^3}{16} \times \left(\frac{M}{M_e^G}\right)^4 \tau_e s^4$	$\tau_{\mathrm{early}}(s) = \frac{5625\pi^3}{4096} \times \left(\frac{M}{M_e^F}\right)^4 \tau_e s^4$	$\tau_{\mathrm{early}}(s) = \frac{225\pi^3}{256} \times \left(\frac{M}{M_e^F}\right)^4 \tau_e^{\mathrm{MM}} s^4$

Larson Review of Tube Model for Rheology

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.

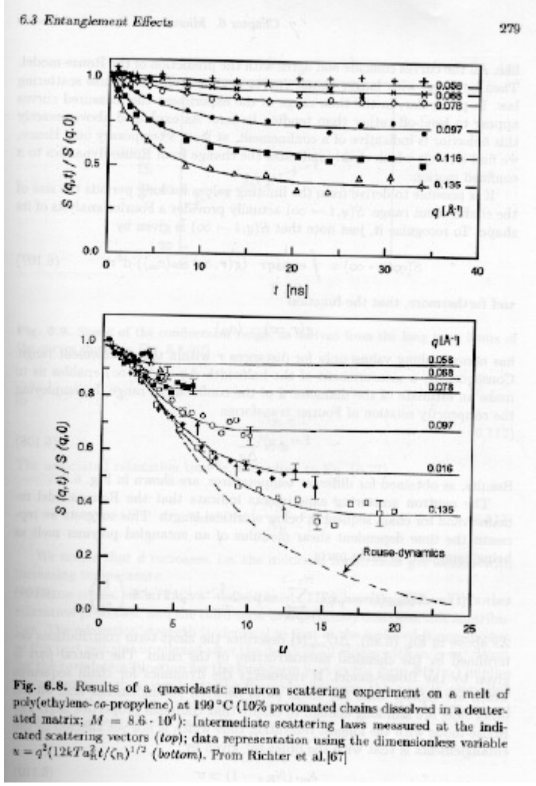


Fig. 6.8. Results of a quasielastic neutron scattering experiment on a melt of poly(ethylene-*co*-propylene) at 199 °C (10% protonated chains dissolved in a deuterated matrix; $M = 8.6 \cdot 10^4$): Intermediate scattering laws measured at the indicated scattering vectors (*top*); data representation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

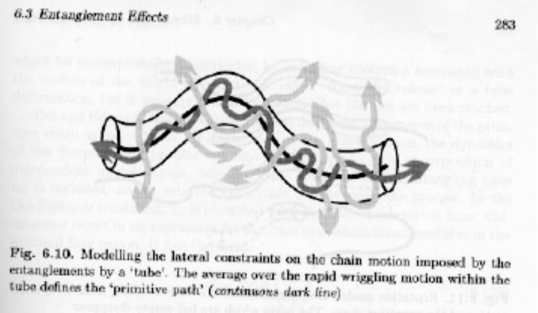


Fig. 6.10. Modelling the lateral constraints on the chain motion imposed by the entanglements by a 'tube'. The average over the rapid wriggling motion within the tube defines the 'primitive path' (*continuous dark line*)

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

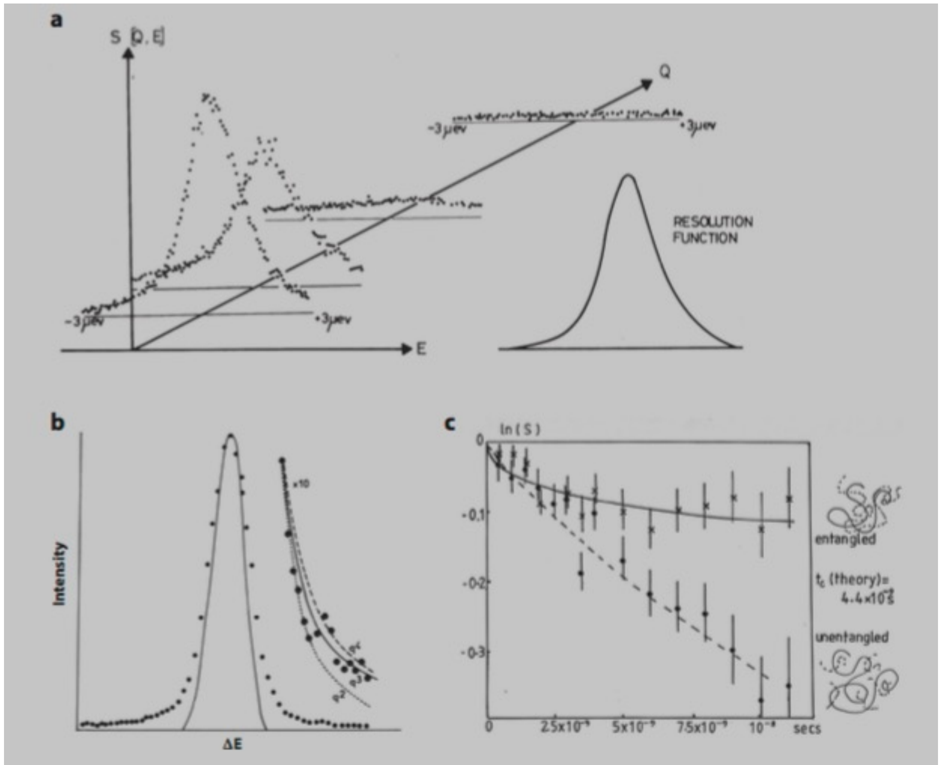


Figure 2

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)

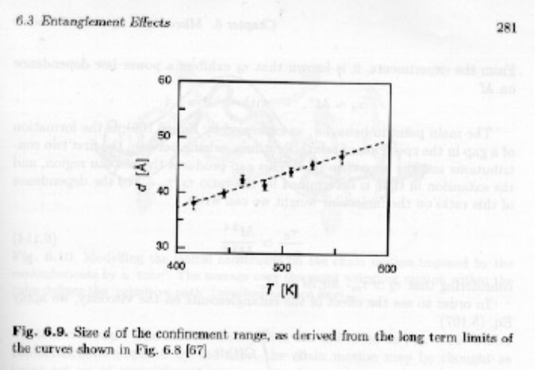


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Fig. 6.9. Size d of the confinement range, as derived from the long term limits of the curves shown in Fig. 6.8 [67]

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 $N^{3.4}$)

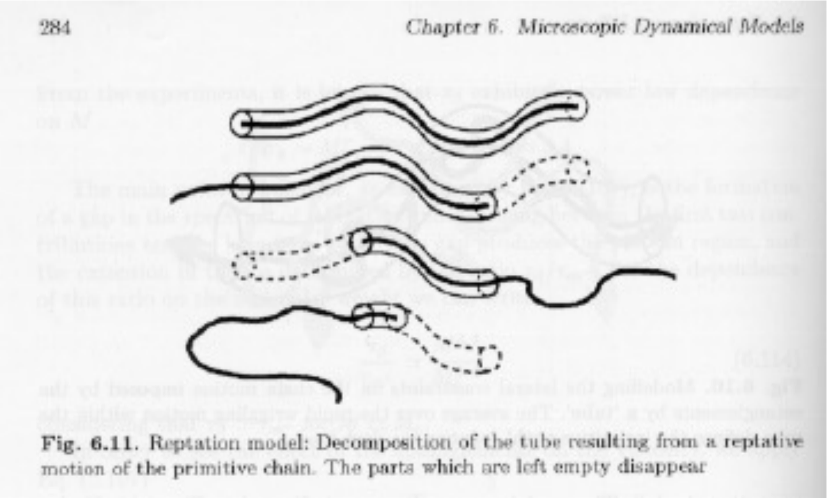

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Fig. 6.11. Reptation model: Decomposition of the tube resulting from a reptative motion of the primitive chain. The parts which are left empty disappear

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

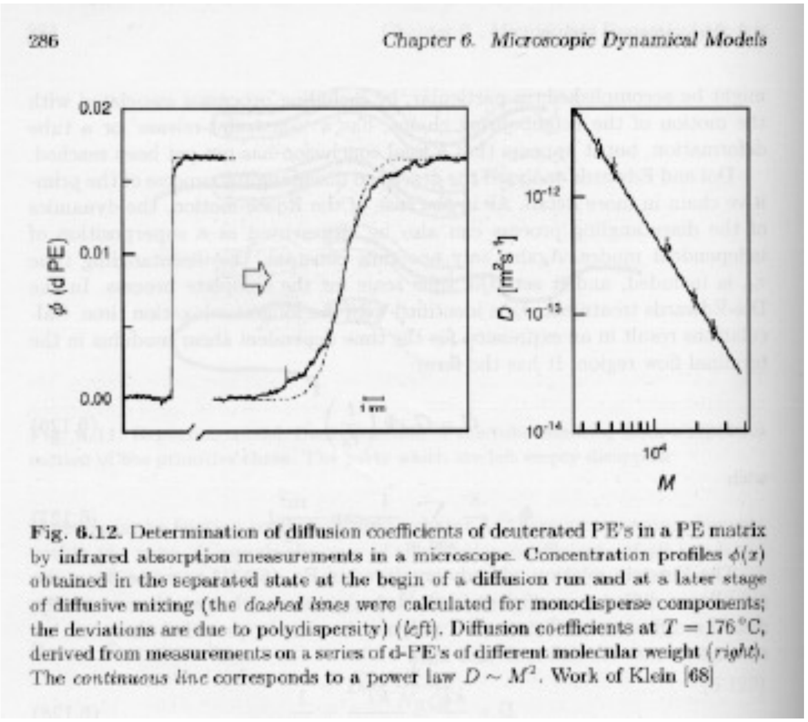

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Fig. 6.12. Determination of diffusion coefficients of deuterated PE's in a PE matrix by infrared absorption measurements in a microscope. Concentration profiles $\phi(x)$ obtained in the separated state at the begin of a diffusion run and at a later stage of diffusive mixing (the *dashed lines* were calculated for monodisperse components; the deviations are due to polydispersity) (*left*). Diffusion coefficients at $T = 176\,^{\circ}$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

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

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

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

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 $D \sim 1/N$)

Reptation of DNA in a concentrated solution

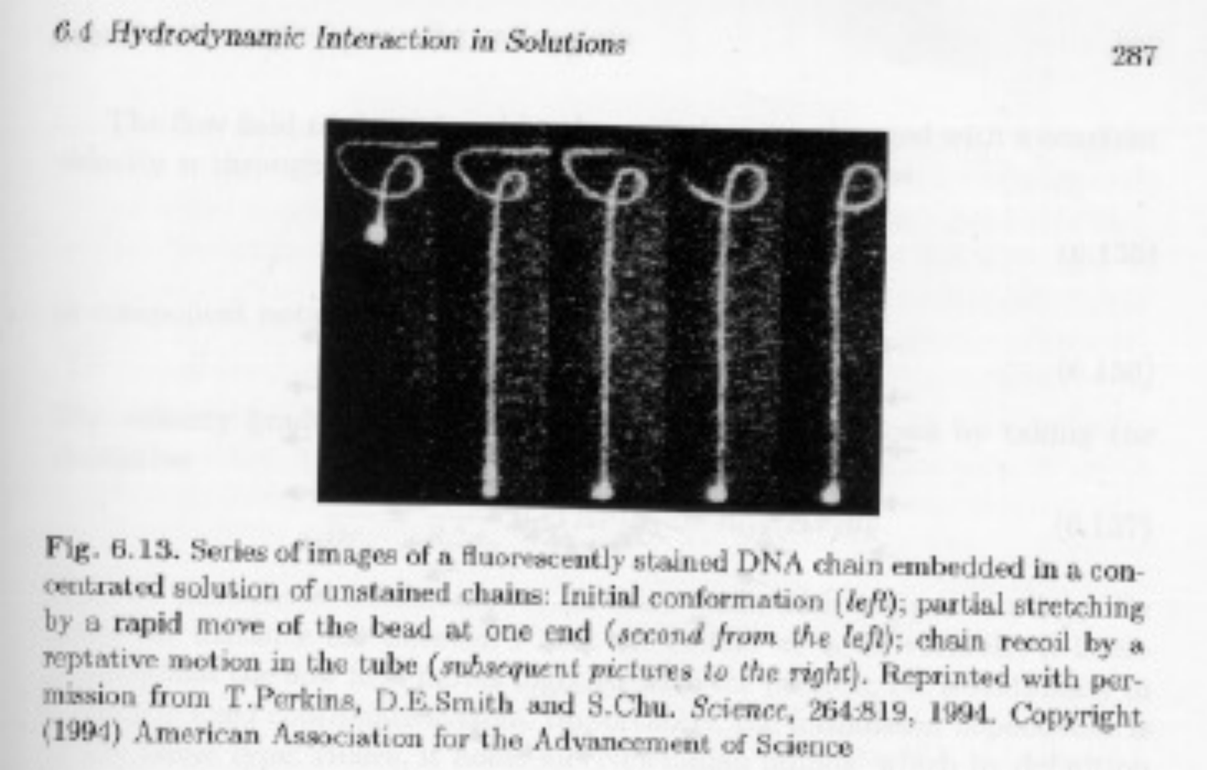


Fig. 6.13. Series of images of a fluorescently stained DNA chain embedded in a concentrated solution of unstained chains: Initial conformation (*left*); partial stretching by a rapid move of the bead at one end (*second from the left*); chain recoil by a reptative motion in the tube (*subsequent pictures 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

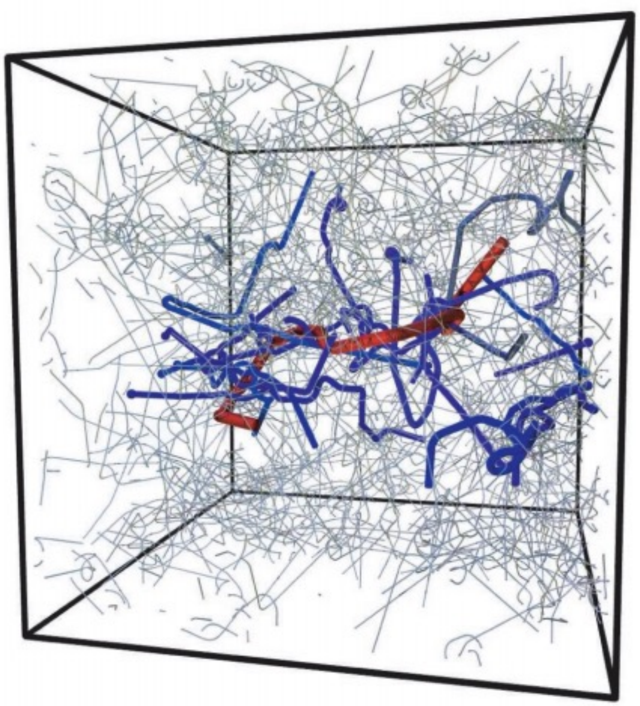


Fig. 3. Result of the primitive-path analysis of a melt of 200 chains of $N + 1 = 350$ beads. We show the primitive path of one chain (red) together with all of those it is entangled with (blue). The primitive paths of all other chains in the system are shown as thin lines.

Simulation of the tube

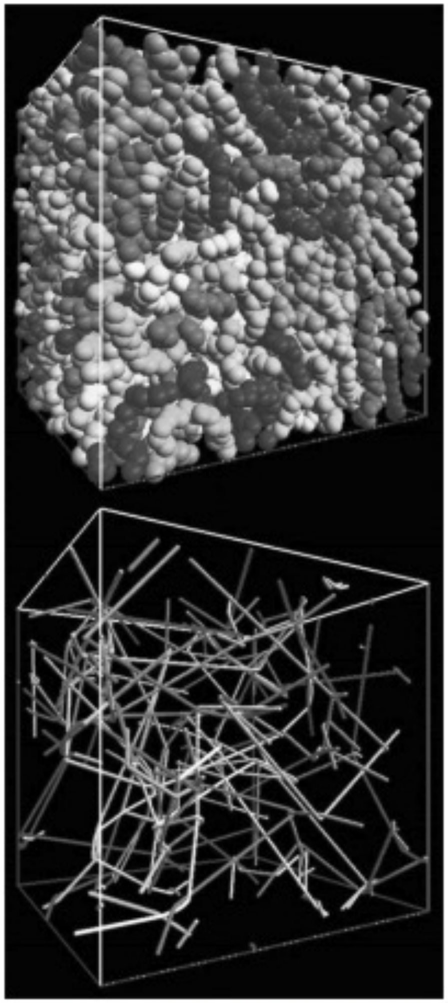


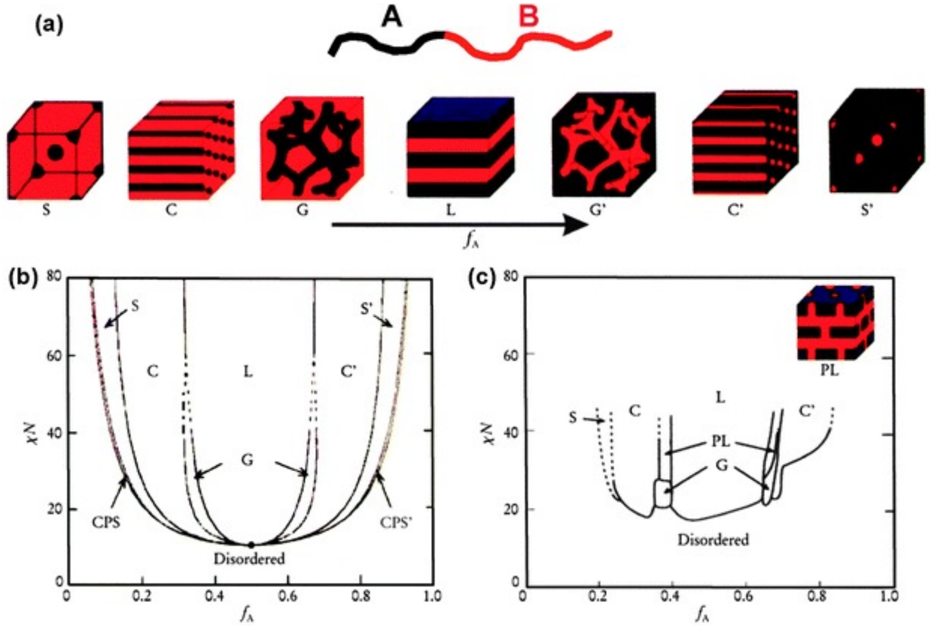
Fig. 3. A representative amorphous polymer sample and the corresponding network of primitive paths.

Packing Length

Origin of the Packing Length:

Contemporary Topics in Polym. Sci. Vol. 6 Multiphase Macromolecular Systems, Culbertson BM Ed.
Theory of Stress Distribution in Block Copolymer Microdomains, Witten TA, Milner ST, Wang Z-G p. 656

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



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

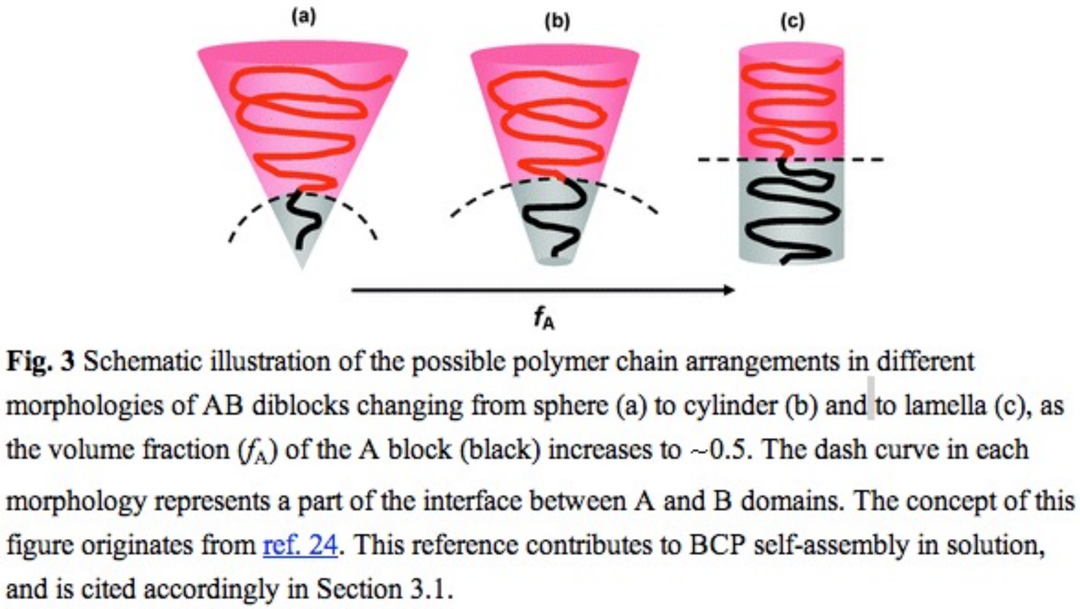


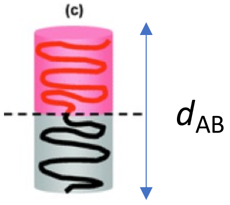
Fig. 3 Schematic illustration of the possible polymer chain arrangements in different morphologies of AB diblocks changing from sphere (a) to cylinder (b) and to lamella (c), as the volume fraction (f_A) of the A block (black) increases to ~0.5. The dash curve in each morphology represents a part of 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 larger** to reduce surface area; χ is the average energy per kT per mer unit in a mixture of A and B)



One Chain Interfacial Energy = $\chi kT(Ad_t)/V_c$

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. So, $\mathbf{d_{AB} = N_{AB}V_c/A}$.

Energy of Elongation of Polymer Chains, Elastic Energy

(**makes domains smaller**, $3kTR^2/(2nl^2)$)

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

Chain Energy of Elongation = $-3kT\ d_{AB}{}^2/(2<R^2>) = -3kT\ N_{AB}V_c{}^2/(2l_K{}^2A^2)$

Using $d_{AB} = N_{AB}\ V_c/A$ from above and $<R^2> = N_{AB}l_K{}^2$

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.

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

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

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

$d_{AB} = N_{AB}\ V_c/A = N_{AB}{}^{2/3}/(3l_K{}^2\chi d_t)^{1/3}$ 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 the term "*a*" that he calls the **intrinsic elasticity** of a polymer chain
Elastic Energy/(3kT) = $a \langle R^2 \rangle / (2V_{occupied})$ where $a = V_{occupied} / \langle R_0^2 \rangle = V_{occupied} / (N_K l_K^2)$
(Previously we had the spring constant $k_{spr}/kT = 3/\langle R_0^2 \rangle = 3a/V_{occupied}$; $a = k_{spr} V_{occupied}/3$)

"*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 $\langle R_0^2 \rangle$.

Since $V_{occupied} = N_K V_c$, and $\langle R_0^2 \rangle = N_K l_K^2$, 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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Theory of Stress Distribution in Block Copolymer Microdomains, Witten TA, Milner ST, Wang Z-G p. 656

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 $G_0 \sim 0.39\ kT/a^3$

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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Theory of Stress Distribution in Block Copolymer Microdomains, Witten TA, Milner ST, Wang Z-G p. 656

Lin, Y-H *Macro.* **20** 3080 (1987)

Lohse DT *J. Macromol. Sci. Part C Polym. Rev.* **45** 298 (2005).

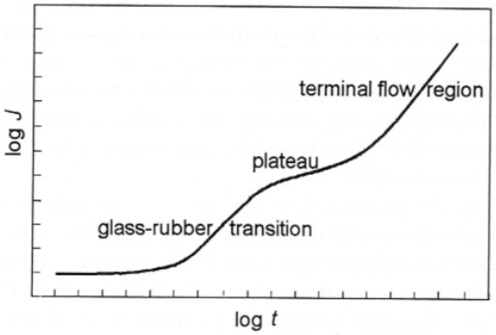


Fig. 5.12. General shape of the complete creep curve of PS, as suggested by the appearance of the different parts shown in Fig. 5.11

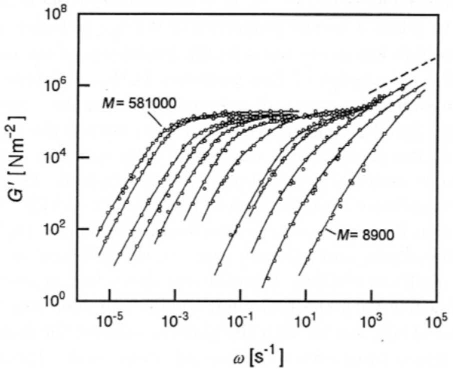
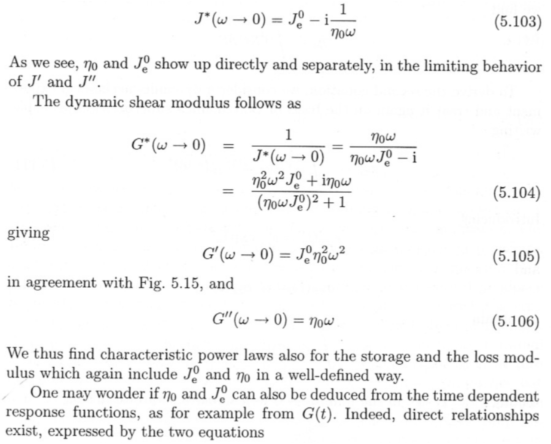


Fig. 5.15. Storage shear moduli measured for a series of fractions of PS with different molecular weights in the range $M = 8.9 \cdot 10^3$ to $M = 5.81 \cdot 10^5$. The *dashed line* in the upper right corner indicates the slope corresponding to the power law Eq. (6.81) derived for the Rouse-model of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

Strobl, Physics of Polymers



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

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

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

giving

$$G'(\omega \to 0) = J_e^0\eta_0^2\omega^2 \tag{5.105}$$

in agreement with Fig. 5.15, and

$$G''(\omega \to 0) = \eta_0\omega \tag{5.106}$$

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 $G' \sim \omega^2$
From definition of viscoelastic

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

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

Plateau Modulus

Not Dependent on N, Depends on T and concentration

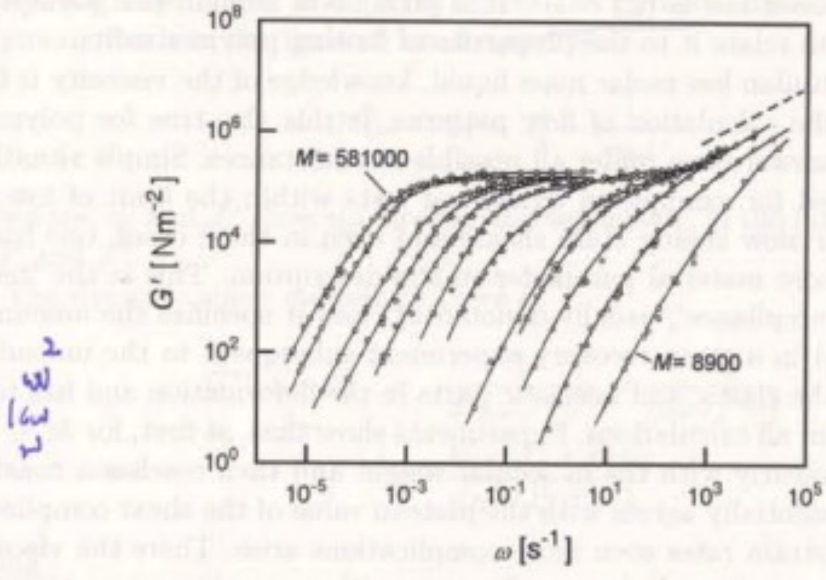


Fig. 5.15. Storage shear moduli measured for a series of fractions of PS with different molecular weights in the range $M = 8.9 \cdot 10^3$ to $M = 5.81 \cdot 10^5$. The *dashed line* in the upper right corner indicates the slope corresponding to the power law Eq. (6.81) derived for the Rouse-model of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

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

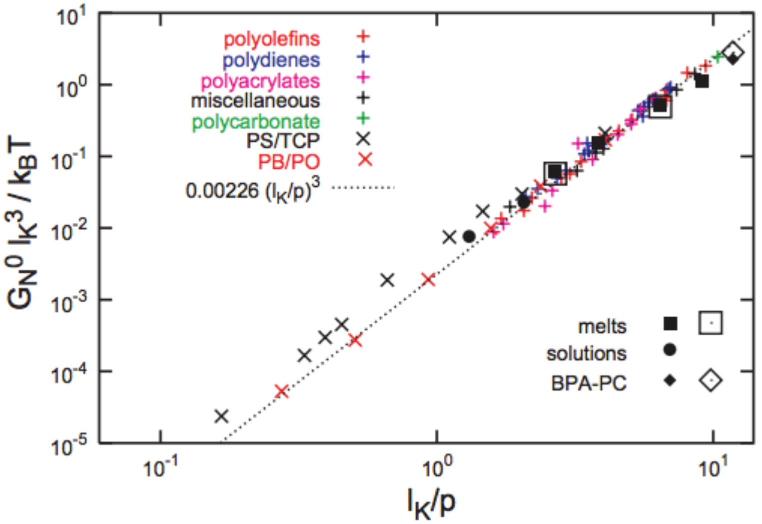


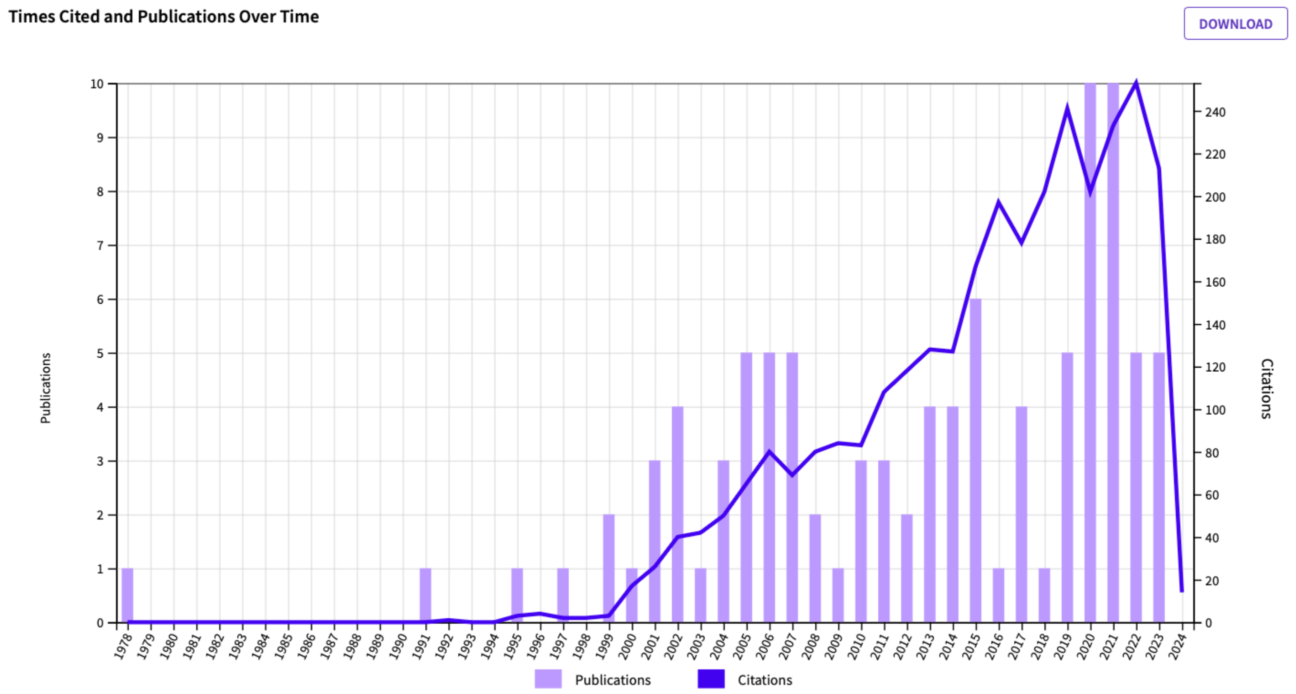
Fig. 2. Dimensionless plateau moduli Gl_K^3/k_BT as a function of the dimensionless ratio l_K/p of Kuhn length l_K and packing length p. The figure contains (i) experimentally measured plateau moduli for polymer melts (*25*) (+; colors mark different groups of polymers as indicated) and semidilute solutions (*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

“Packing Length” Anywhere Web of Science



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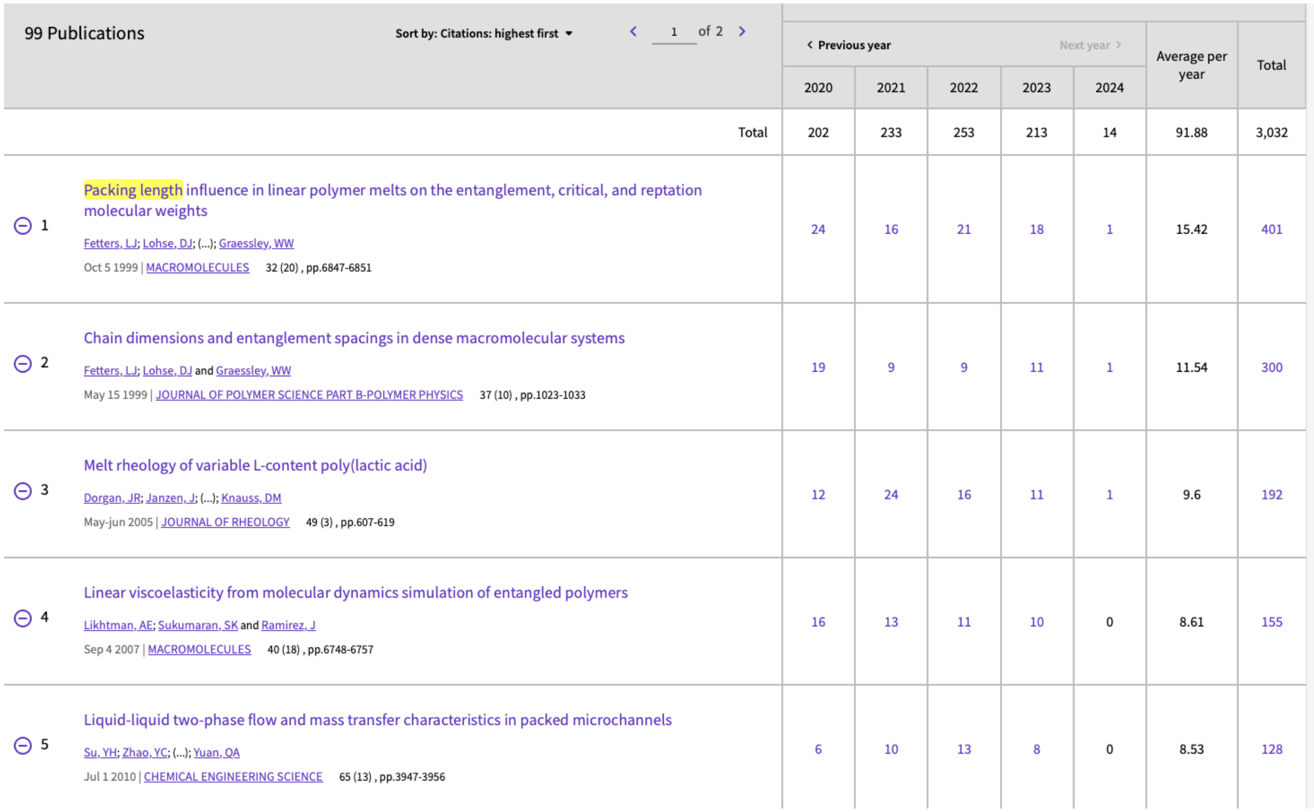

99 Publications

Sort by: Citations: highest first

1 of 2

		2020	2021	2022	2023	2024	Average per year	Total
	Total	202	233	253	213	14	91.88	3,032
1	Packing length influence in linear polymer melts on the entanglement, critical, and reptation molecular weights Fetters, LJ; Lohse, DJ; (...); Graessley, WW Oct 5 1999 | MACROMOLECULES 32 (20) , pp.6847-6851	24	16	21	18	1	15.42	401
2	Chain dimensions and entanglement spacings in dense macromolecular systems Fetters, LJ; Lohse, DJ and Graessley, WW May 15 1999 | JOURNAL OF POLYMER SCIENCE PART B-POLYMER PHYSICS 37 (10) , pp.1023-1033	19	9	9	11	1	11.54	300
3	Melt rheology of variable L-content poly(lactic acid) Dorgan, JR; Janzen, J; (...); Knauss, DM May-jun 2005 | JOURNAL OF RHEOLOGY 49 (3) , pp.607-619	12	24	16	11	1	9.6	192
4	Linear viscoelasticity from molecular dynamics simulation of entangled polymers Likhtman, AE; Sukumaran, SK and Ramirez, J Sep 4 2007 | MACROMOLECULES 40 (18) , pp.6748-6757	16	13	11	10	0	8.61	155
5	Liquid-liquid two-phase flow and mass transfer characteristics in packed microchannels Su, YH; Zhao, YC; (...); Yuan, QA Jul 1 2010 | CHEMICAL ENGINEERING SCIENCE 65 (13) , pp.3947-3956	6	10	13	8	0	8.53	128

Structure and linear viscoelasticity of flexible polymer solutions: comparison of polyelectrolyte and neutral polymer solutions R. Colby, Rheo. Acta **49** 425-442 (2010)

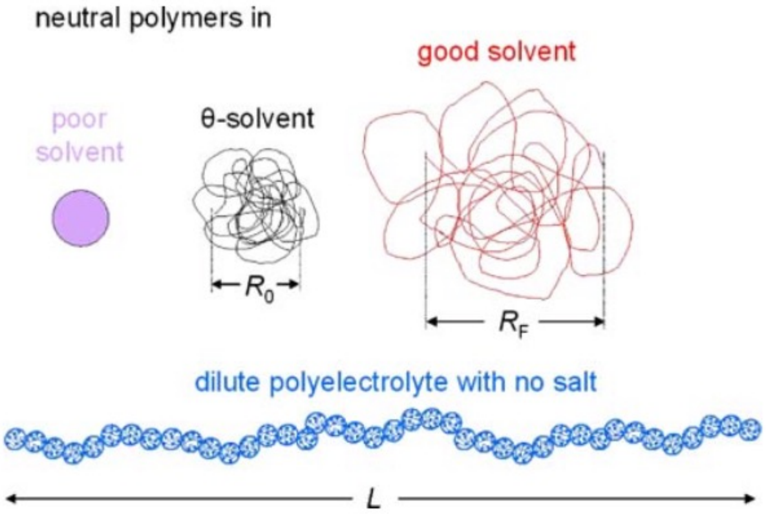

Fig. 1 Conformations of polymers in dilute solution. Neutral polymers in poor solvent collapse into dense coils with size $\approx bN^{1/3}$ (*purple*). Neutral polymers in θ-solvent are random walks with ideal end-to-end distance $R_0 = bN^{1/2}$ (*black*). Neutral polymers in good solvent are self-avoiding walks with Flory end-to-end distance $R_F = bN^{0.588}$ (*red*). Polyelectrolytes with no salt adopt the highly extended directed random walk conformation (*blue*) with length L proportional to N

Summary