## Polymer Physics

10:10-11:05
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$\underline{\text { https://www.eng.uc.edu/~beaucag/Classes/Properties.html }}$
Zoom Meeting:
https://us02web.zoom.us/j/87233679564?pwd=ak1Xbm prdFBUQnRZOWszWU91VHdyUT09

## 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

$$
\mathrm{R}_{\mathrm{g}}, \mathrm{R}_{\mathrm{h}}, \mathrm{R}_{\text {eted }}
$$

Small-angle neutron, $x$-ray scattering and static light scattering
Intrinsic viscosity
Dynamic light scattering
Polymer melt rheology
DSC/DMTA/TGA
Table 1.4 Selected chain polymer structures and nomenclature

| Structure | Name | Where Used |
| :---: | :---: | :---: |
| $\overbrace{\left(\mathrm{CH}_{2}-\mathrm{CH}\right)_{n}}$ | "Vinyl" class |  |
| R |  |  |
| $\mathrm{R}=-\mathrm{H}$ | Polyethylene | Plastic |
| $\mathrm{R}=-\mathrm{CH}_{3}$ | Polypropylene | Rope |
|  | Polystyrene | Drinking cups |
| $\mathrm{R}=-\mathrm{Cl}$ | Poly(vinyl chloride) | "Vinyl", water pipes |
| $\bigcirc$ |  |  |
| $\mathrm{R}=-\mathrm{O}-\mathrm{C}-\mathrm{CH}_{3}$ | Poly(vinyl acetate) | Latex paints |
| $\mathrm{R}=-\mathrm{OH}$ | Poly(vinyl alcohol) | Fiber |
| x | $\mathrm{X}=-\mathrm{H}$, acrylics |  |
| $\left(\mathrm{CH}_{2}-\mathrm{C}\right)_{n}$ | $\mathrm{X}=-\mathrm{CH}_{3}$, methacrylics |  |
| $\mathrm{O}=\mathrm{C}-\mathrm{O}-\mathrm{R}$ |  |  |
| $\mathrm{X}=-\mathrm{H}, \mathrm{R}=-\mathrm{C}_{2} \mathrm{H}_{5}$ | Poly(ethyl acrylate) | Latex paints |
| $\mathrm{X}=-\mathrm{CH}_{3}, \mathrm{R}=-\mathrm{CH}_{3}$ | Poly(methyl methacrylate) | Plexiglas ${ }^{\text {a }}$ |
| $\mathrm{X}=-\underset{\mathrm{H}}{\mathrm{CH}_{3}, \mathrm{R}}=\mathrm{C}_{2} \mathrm{H}_{5}$ | Poly(ethyl methacrylate) | Adhesives |
| $\mathrm{CH}_{2}-\mathrm{C}-{ }_{n}$ | Polyacrylonitrile ${ }^{a}$ | Orlon ${ }^{\text {* }}$ |
| $\mathrm{C} \equiv \mathrm{N}$ |  |  |
| $+\mathrm{CH}_{2}-\mathrm{C}=\mathrm{CH}-\mathrm{CH}_{2}+\mathrm{n}^{\text {a }}$ | "Diene" class |  |
| R |  |  |
| $\mathrm{R}=-\mathrm{H}$ | Polybutadiene |  |
| $\mathrm{R}=-\mathrm{CH}_{3}$ $\mathrm{R}=-\mathrm{Cl}$ | Polyisoprene <br> Polychloroprene | Natural rubber <br> Neoprene |
| $\left.+\mathrm{CX}_{2}-\mathrm{CR}_{2}\right)_{n}$ | Vinylidenes |  |
| $\mathrm{X}=-\mathrm{H}, \mathrm{R}=-\mathrm{F}$ | Poly(vinylidene fluoride) | Plastic |
| $\mathrm{X}=-\mathrm{F}, \mathrm{R}=-\mathrm{F}$ | Polyterafluoroethylene | Teflon ${ }^{\text {s }}$ |
| $\mathrm{X}=-\mathrm{H}, \mathrm{R}=-\mathrm{CH}_{3}$ | Polyisobutene ${ }^{\text {b }}$ | Elastomer |
|  | Common Copolymers |  |
| EPDM | Ethylene-propylene-diene-monomer | Elastomer |
| SBR | Styrene-butadiene-rubber Poly(styrene-stat-butadiene) ${ }^{\text {c }}$ | Tire rubber |
| NBR | Acrylonitrile-butadiene-rubber Poly(acrylonitrile-stat-butadiene) | Elastomer |
| ABS | Acrylonitrile-butadiene-styrene ${ }^{4}$ | Plastic |

## Polymers



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 he following identifying groups:


Polyethers - O


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



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

## Polymers

Paul Flory [I] 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?<br>http://www.eng.uc.edu/~beaucag/Classes/IntrotoPolySci/Pictur esDNA.html

http://www.eng.uc.edu/~beaucag/Classes/IntrotoPolySci/What Does Searching
Configurational Space Mean for Polymers.html
I) Principles of Polymer Chemistry, Flory PJ, (1953).
ww.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/WhatIsAPolymerPlastic.html

# Random Walk Generator (Manias Penn State) 

 http://zeus.plmsc.psu.edu/~manias/MatSE443/Study/7.htm|
-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.
6

## Polymers

1 Survey


Fig. 1-1 Dependence of melting temperatures, $T_{\mathrm{M}}$, and boiling temperatures, $T_{\mathrm{bp}}$, of alkanes and poly(methylene)s, $\mathrm{H}\left(\mathrm{CH}_{2}\right)_{N} \mathrm{H}$, on the number $N$ of methylene groups per molecule [1,2].

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

(a)

(b)

1 Survey


Fig. 5.6 A model of a
polyentylene chain fold using four gauche bonds.
as suggested by frank. as sugested dy Frank.
Upent, view norm the the
plane of of olding: iowert, Uper, view normal to the
Plane of folong, ower,
view alogs the plane of foud ing. Reperinten by
permission from John 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.)


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. (C) Cambridge University Press 1989.)

Fold surface energy ~ 2 e-5 J/cm2
Enthalpy of melting ~ $300 \mathrm{~J} / \mathrm{cm} 3$
$\mathrm{T}_{\infty} \sim 414 \mathrm{~K}\left(141^{\circ} \mathrm{C}\right)$
$\mathrm{T} \sim 110^{\circ} \mathrm{C}$
$\mathrm{t}=2 \sigma \mathrm{~T}_{\infty} /\left(\Delta \mathrm{H}_{\mathrm{m}}\left(\mathrm{T}_{\infty}-\mathrm{T}\right)\right)$ (Hoffman-Lauritzen)
~ $1.78 \mathrm{e}-6 \mathrm{~cm}$ or 17.8 nm thick crystals regardless of N


Viscosity versus Rate of Strain


FIGURE 3.6-5. Composite plot of dimensionless viscosity $\eta^{\prime \prime} \boldsymbol{H}_{0}$ versus dimersionaless shear ras : for several difierent concectrated polystyrene $n$-butyl benzene solutions. Molecalar weiphts ano from $1.6 \times 10^{-}$to $2.4 \times 10^{5}$, conoentratons from 0.255 to $0.55 \mathrm{gemm}^{3}$, and teraperatures from $2 x$. 333 K. [W. W. Gtaessley, Ad. Polym. Scl., 16, 1-179 (1974).]


Figure 11.17. Conceniration Jependence of tie spectioc viscosity of diluts

 concentated
tis case).

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

Polymers

Specific Viscosity versus Concentration for Solutions

Zero Shear Rate Viscosity versus


## 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 $J_{\mathrm{e}}^{0}$ :

$$
J^{\prime}(\omega \rightarrow 0)=J_{\mathrm{e}}^{0}
$$

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

$$
\begin{equation*}
J(\omega \rightarrow 0)=J_{\mathrm{e}}^{0}+\mathrm{i} \frac{1}{\eta_{0} \omega} . \tag{6.103}
\end{equation*}
$$

As we can see, $\eta_{0}$ and $J_{\mathrm{e}}^{0}$ show up directly and separately, in the limiting As we can see, $\eta_{0}$ and
behavior of $J^{\prime}$ and $J^{\prime \prime}$.

The dynamic shear modulus follows as

$$
\begin{align*}
G(\omega \rightarrow 0) & =\frac{1}{J(\omega \rightarrow 0)}=\frac{\eta_{0} \omega}{\eta_{0} \omega J_{\mathrm{e}}^{0}+\mathrm{i}} \\
& =\frac{\eta_{0}^{2} \omega^{2} J_{\mathrm{e}}^{0}-\mathrm{i} \eta_{0} \omega}{\left(\eta_{0} \omega J_{\mathrm{e}}^{0}\right)^{2}+1}, \tag{6.104}
\end{align*}
$$

giving

$$
\begin{equation*}
G^{\prime}(\omega \rightarrow 0)=J_{\mathrm{e}}^{0} \eta_{0}^{2} \omega^{2} \tag{6.105}
\end{equation*}
$$

in agreement with Fig. 6.16, and

$$
\begin{equation*}
G^{\prime \prime}(\omega \rightarrow 0)=\eta_{0} \omega . \tag{6.106}
\end{equation*}
$$

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


Small Angle Neutron Scattering


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



## 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, $1_{K}$

This is extremely easy to simulate
1)Begin at the origin, $(0,0,0)$
2) Take a step in a random direction to ( $\mathrm{i}, \mathrm{j}, \mathrm{k}$ )
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 $1_{\mathrm{K}}$, the breadth of the walk will change.
$1_{\mathrm{K}}$ just changes proportionally the scale of the walk so $<\mathrm{R}^{2>1 / 2} \sim 1_{\mathrm{K}}$
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 $1_{\mathrm{K}}$, the breadth of the walk will change.
$1_{\mathrm{K}}$ just changes proportionally the scale of the walk so $<\mathrm{R}^{2}>^{1 / 2} \sim 1_{\mathrm{K}}$

The chain is composed of a series of steps with no orientational relationship to each other. So $<\mathrm{R}>=0$
$<\mathrm{R}^{2}>$ 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 .

$$
\begin{gathered}
\left\langle R^{2}\right\rangle=N r^{2} \\
<\mathrm{R}^{2>1 / 2} \sim \mathrm{~N}^{1 / 2} l_{\mathrm{K}}
\end{gathered}
$$

https://www.doitpoms.ac.uk/tlplib/polymerbasics/HTML5/Kuhn randomwalk2.html

## Synthetic Polymer Chain Structure (A Statistical Hierarchy)

```
<R2>1/2~ N
```

This function has the same origin as the function describing the root mean square distance of a diffusion pathway
$<\mathrm{R}^{2}>1 / 2 \sim \mathrm{t}^{1 / 2}(2 \mathrm{D})^{1 / 2}$
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 $=n /\left(n^{3 / 2} l^{3}\right) \sim n^{-1 / 2}=c^{*}$ overlap concentration
Below $c^{*} \sim 1 \mathrm{mg} / \mathrm{ml}$ 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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Below c*, dilute scattering curve; above c*;
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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


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

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# The Primary Structure for Synthetic Polymers 

Worm-like Chain<br>Freely Jointed Chain<br>Freely Rotating Chain<br>Rotational Isomeric State Model Chain (RISM)<br>Persistent Chain<br>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
$l_{\mathrm{K}}=2 l_{\mathrm{P}}$

Small Angle Neutron Scattering


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


$d=\lambda /(2 \sin \theta)$
$q=4 \pi / \lambda \sin \theta$

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/IntrotoP olySci/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.)

$$
\begin{aligned}
& \rho(x, t)+\tau \frac{\partial \rho(x)}{\partial t}+\cdots \\
& =\rho(x, t) \int_{-\infty}^{+\infty} P_{G}(\Delta x) d(\Delta x)+\frac{\partial \rho}{\partial x} \int_{-\infty}^{+\infty} \Delta x P_{G}(\Delta x) d(\Delta x)+\frac{\partial^{2} \rho}{\partial x^{2}} \int_{-\infty}^{+\infty} \frac{(\Delta x)^{2}}{2} P_{G}(\Delta x) d(\Delta x)+\cdots
\end{aligned}
$$

$\mathrm{P}_{\mathrm{G}}(\Delta \mathrm{x})$ is a normalized, symmetric probability distribution where $\Delta \mathrm{x}$ is the change in x from 0 . The integral of $\mathrm{P}_{\mathrm{G}}(\Delta \mathrm{x})$ 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 $\mathrm{x}=0$ and time $=0$,

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

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

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

For polymer chain $\left\langle R^{2}\right\rangle=I_{k}{ }^{2} N$

## 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 $\mathrm{v}_{\mathrm{g}}=\mathrm{mg} /\left(6 \pi \eta R_{h}\right)$ following Stokes Law. For particles at $\mathrm{x}=0$ and $\mathrm{x}=\mathrm{h}$ height, the density difference is governed by a Boltzmann probability function,

$$
\rho(h)=\rho_{0} e^{-\frac{m g h}{k T}}
$$

Fick's law gives the flux of particles, $\mathrm{J}=-\mathrm{D} d \rho / \mathrm{dh}$, and $\mathrm{J}=\rho \mathrm{v}$, so $\mathrm{v}=-(\mathrm{D} / \rho) \mathrm{d} \rho / \mathrm{dh}$, and $\mathrm{d} \rho / \mathrm{dh}=-\rho_{0} \mathrm{mg} /(\mathrm{kT}) \mathrm{e}^{-\mathrm{mgh} / \mathrm{kT}}=-\rho \mathrm{mg} /(\mathrm{kT})$. Then, $\mathrm{v}=\mathrm{Dmg} /(\mathrm{kT})$. At equilibrium this speed equals the gravitational speed, $\mathrm{v}_{\mathrm{g}}=\mathrm{mg} /\left(6 \pi \eta \mathrm{R}_{\mathrm{h}}\right)$. 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.)

$$
\frac{\left\langle x^{2}\right\rangle}{2 t}=D=\frac{k T}{6 \pi \eta R_{h}}=\frac{R T}{6 \pi \eta R_{h} N_{A}}
$$

The latter expression was used to determine Avagadro's number from colloidal particles that could be counted. $\mathrm{N}_{\mathrm{A}}$ 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
$v_{\mathrm{g}}=m g / 6 \pi R_{\mathrm{h}} \eta=-D / \rho \mathrm{d} \rho / \mathrm{d} h=D m g / \mathrm{k} T$
This yields the Einstein-Stokes Equation $D=\mathrm{k} T / 6 \pi R_{\mathrm{h}} \eta$

## The Gaussian Chain

## Boltzman Probability

For a Thermally Equilibrated System

$$
P_{B}(R)=\exp \left(-\frac{E(R)}{k T}\right)
$$

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

$$
E=k T \frac{3 R^{2}}{2 n l_{K}^{2}}
$$

## The Gaussian Chain

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$$
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$$



$$
F=\frac{d E}{d R}=\frac{3 k T}{n l_{K}^{2}} R=k_{s p r} R
$$

Force


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

## The Gaussian Chain

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$$

Use of $\mathrm{P}(\mathrm{R})$ to Calculate Moments:

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

Mean is the 1'st Moment:

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

## The Gaussian Chain

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Mean is the 1'st Moment:

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

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

## The Gaussian Chain

Boltzman Probability
For a Thermally Equilibrated System

$$
P_{B}(R)=\exp \left(-\frac{E(R)}{k T}\right)
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Gaussian Probability
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$$

Use of $\mathrm{P}(\mathrm{R})$ to Calculate Moments:

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

Mean Square is the 2'ndMoment:

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

## The Gaussian Chain

## Gaussian Probability

For a Chain of End-to-End Distance R

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

Mean Square is the 2 'nd Moment:

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

There is a problem to solve this integral since we can solve an integral of the form $k \exp (\mathrm{kR}) \mathrm{dR}$
$\mathrm{R} \exp \left(\mathrm{kR}^{2}\right) \mathrm{dR}$ but not $\mathrm{R}^{2} \exp \left(\mathrm{kR}^{2}\right) \mathrm{dR}$
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.

$$
\begin{equation*}
\left\langle R^{2}\right\rangle=\frac{\int_{-\infty}^{\infty} R^{2} P_{G}(R) d R}{\int_{-\infty}^{\infty} P_{G}(R) d R}=\frac{\int_{-\infty}^{\infty} R^{2} \exp \left(\frac{R^{2}}{k^{2}}\right) d R}{\int_{-\infty}^{\infty} \exp \left(\frac{R^{2}}{k^{2}}\right) d R} \tag{3}
\end{equation*}
$$

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

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

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

Then Cartesian coordinates are replaced with circular coordinates, r and $\theta$,

$$
\begin{aligned}
& (G(\alpha))^{2}=\int_{0}^{\infty} r d r \int_{0}^{2 \pi} d \theta \exp \left(-\alpha r^{2}\right)=2 \pi \int_{0}^{\infty} r d r \exp \left(-\alpha r^{2}\right) \\
& =\frac{-2 \pi}{2 \alpha} \int_{0}^{\infty}-2 \alpha r d r \exp \left(-\alpha r^{2}\right)=\frac{-\pi}{\alpha}\left[\exp \left(-\alpha r^{2}\right)\right]_{0}^{\alpha}=\frac{\pi}{\alpha}
\end{aligned}
$$

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

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

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

$$
\begin{equation*}
\left\langle R^{2}\right\rangle=\frac{\int_{-\infty}^{\infty} R^{2} \exp \left(\frac{R^{2}}{k^{2}}\right) d R}{\int_{-\infty}^{\infty} \exp \left(\frac{R^{2}}{k^{2}}\right) d R}=\frac{H(\alpha)}{G(\alpha)}=\frac{k^{3} \pi^{1 / 2} / 2}{k \pi^{1 / 2}}=\frac{k^{2}}{2} \tag{4}
\end{equation*}
$$

## 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:

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

So, the Gaussian function for a polymer coil is:

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

## The Gaussian Chain

$$
\left\langle R^{2}\right\rangle=n l_{K}^{2}
$$

Means that the coil size scales with $\mathrm{n}^{1 / 2}$
Or
Mass $\sim \mathrm{n} \sim$ Size $^{2}$
Generally, we say that
Mass $\sim$ Size ${ }^{\text {df }}$
Where $\mathrm{d}_{\mathrm{f}}$ 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 $\mathrm{n}^{1 / 2}$ 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: $\mathrm{p}^{\mathrm{c}} \sim \mathrm{n}$
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, $\mathrm{d}_{\text {min }}$ so that, $\mathrm{p} \sim \mathrm{R}^{\mathrm{dmin}}$
For a Gaussian Chain $\mathrm{d}_{\text {min }}=2$ since p is the path n
For a disk $\mathrm{d}_{\text {min }}=1$ since the short circuit is a straight line.
We find that $\mathrm{d}_{\mathrm{f}}=\mathrm{cd}_{\text {min }}$
There are other scaling dimensions, but they can all be related to two independent structural scaling dimensions such as c and $\mathrm{d}_{\text {min }}$ or $\mathrm{d}_{\text {min }}$ and $\mathrm{d}_{\mathrm{f}}$

## Disk



$$
\begin{aligned}
& d_{f}=2 \\
& d_{\min }=1 \\
& c=2
\end{aligned}
$$

Extended $\beta$-sheet (misfolded protein)


Random Coil


$$
d_{f}=2
$$

$$
d_{\min }=2
$$

$$
c=1
$$

Unfolded Gaussian chain


How Complex Mass Fractal Structures
Can be Decomposed


$$
\begin{gathered}
z \sim\left(\frac{R}{d}\right)^{d_{f}} \sim p^{c} \sim s^{d_{\min }} \quad p \sim\left(\frac{R}{d}\right)^{d_{\min }} \\
d_{f}=d_{\min } c \quad \begin{array}{ll|l|l|l|l|l|l|} 
& \mathrm{Z} & \mathrm{df}_{\mathrm{f}} & \mathrm{p} & \mathrm{~d}_{\min } & \mathrm{s} & \mathrm{c} & \mathrm{R} / \mathrm{d} \\
\hline 27 & 1.36 & 12 & 1.03 & 22 & 1.28 & 11.2 \\
\hline
\end{array}
\end{gathered}
$$


(a)

(b)

Figure 1. Micrographs of GMF sample showing micron-scale silica glass fibers in a polymer-ike mat. (a) SEM micrograph afer gold coating. This size scale corresponds to the persistence regime and the high-q end of the scaling regime. (b) Optical micrograph at 20x. 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 inci-
dent beam normal to the sample plane. Scaling regime dent beam normal to the sample plane. Scaling regime
at low-q follows good solvent sealing. High-q sealing at low-q follows good solvent sealing. High-q scalin
follows Porod's law. Fit uses the unified equation with follows Porods law. Fit uses the unifed equation with
four froe parameters and a model based on a polymer four free paran
like structure.


Figure 5. Orientation function and SALS data for and 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

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

$b_{k}$ 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

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

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

$$
\left\langle r_{i+1}\right\rangle_{\text {Random }}=\sum_{k=1}^{k=z} b_{k}=0=(z-1)\left\langle r_{i+1}\right\rangle_{\text {ShorrRangelneraccion }}-r_{i}
$$

so

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

# The Primary Structure for Synthetic Polymers <br> <br> Short-Range Interactions 

 <br> <br> Short-Range Interactions}

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

For Gaussian Chain
See slide 68

$$
\left\langle R^{2}\right\rangle=\sum_{i} \sum_{j} r_{i} \cdot r_{j}=\sum_{i} r_{i} \cdot r_{i}+\sum_{i} \sum_{j \neq i} r_{i} r_{j} \quad \text { yields } \quad\left\langle R^{2}\right\rangle=N r^{2}
$$

For SRI Chain the first term is not 0 .

$$
\left\langle r_{i} \bullet r_{j}\right\rangle=\frac{b^{2}}{(z-1)^{i-j \mid}} \quad \text { and } \quad\left\langle R^{2}\right\rangle=\sum_{i=1}^{n} \sum_{j=1}^{n}\left\langle r_{i} \bullet r_{j}\right\rangle \cong \sum_{i=1}^{n} \sum_{k=-\infty}^{\infty} \frac{b^{2}}{(z-1)^{|k|}}=n b^{2} \frac{z}{z-2}=n b_{e f f e c t i v e}^{2}
$$

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

For Cartesian simulation $\mathrm{z}=6$ and $\mathrm{b}_{\text {eff }}$ is 1.22 b so about a $25 \%$ increase for one step selfavoidance.

# The Primary Structure for Synthetic Polymers Short-Range Interactions 

Short-Range Interactions<br>Increase the persistence length<br>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
-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, $\mathbf{C}_{\infty}$

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

| Polymer | $C(M=\infty)^{2}$ |
| :--- | :---: |
| Polyethylene | 6.7 |
| Polyethyleneoxide | 4.0 |
| Polystyrene, atactic | 10.0 |

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

$$
\begin{aligned}
& \left\langle R^{2}\right\rangle=n_{\text {Kuhn }} l_{\text {Kuhn }}^{2}=L l_{\text {Kuhn }}=C_{\infty} n_{\text {Bond }} l_{\text {Bond }}^{2}=C_{\infty} L l_{\text {Bond }} \\
& l_{\text {Kuhn }} \sim b_{\text {Effective }} \\
& C_{\infty}=\frac{l_{\text {Kuhn }}}{l_{\text {Bond }}}
\end{aligned}
$$

Polymer physics
By Ulf W. Gedde

## The Primary Structure for Synthetic Polymers Short-Range Interactions

What kinds of short-range interactions can we expect
-Bond angle restriction
-Bond rotation restriction


Figure 7. The persistence length plots, $\left\langle l_{p}^{p}\right\rangle$, obtained via eq 10 , versus segment number, $k$, for various semiflexible, linea polymers, each of length 48. The strength of the intrinsic stiffness is varied between polymers by increasing the strengt
of the bending penalty,

Macromolecules 2005, 38, 5288-5299
"Intrinsic" and "Topological" Stiffness in Branched Polymers


$$
C_{\infty}=\frac{l_{K u h n}}{l_{B o n d}}
$$

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.

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

$$
\mathrm{n}_{\mathrm{b}}=\text { backbone length }
$$



Interestingly, for the linear chain, $l_{\text {pers }}$ has a power-law dependence on $n_{b}$,

$$
\begin{equation*}
l_{\mathrm{pers}}=a \cdot n_{b}^{\xi} \tag{16}
\end{equation*}
$$

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

$$
\begin{equation*}
l_{\text {pers }}^{\text {brust }} / l_{\text {pers }}^{\text {lin }}=A+B\left[1-\exp \left(-n_{b} / C\right)\right] \tag{17}
\end{equation*}
$$

for both bottle-brushes. The very existence of a plateau for
LD = Low branch density
$\mathrm{HD}=$ 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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$$
\begin{align*}
& \text { Interestingly, for the linear chain, } l_{\text {pers }} \text { has a power-law } \\
& \text { dependence on } n_{b} \text {, } \\
& \quad l_{\text {pers }}=a \cdot n_{b}^{\xi} \text {, }  \tag{16}\\
& \text { where } a=1.61(8) \text { and } \xi=0.18(1) \text {, confirming that it is in- } \\
& \text { ior (see Fig. 10). This ratio is larger than unity, indicating an } \\
& \text { increased stiffness due to the interarm repulsion, and is well } \\
& \text { reproduced by the functional form } \\
& l_{\text {pers }}^{\text {brust }} / l_{\text {pers }}^{\text {lin }}=A+B\left[1-\exp \left(-n_{b} / C\right)\right] \tag{17}
\end{align*}
$$

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

This is a 5 -parameter model for persistence length! (used to model 5 or 6 data points!!!)
(Also, this model fails to predict an infinite molecular weight persistence length.)

Molecular weight dependence of persistence length

Size and persistence length of molecular bottle-brushes by Monte Cario simulations
Stefano Elli, Fabio Ganazzoli, Edward G. Timoshenko, Yuri A. Kuznetsov, and Ronan Connolly
Ctataon: J. Chem. Phys. 120, 6257 (2004); doi: 10.1063/1.1651052

$\mathrm{LD}=$ Low branch density
$\mathrm{HD}=$ High branch density

Proposed End Group Functionality
$l_{p}=l_{p, \infty}-\left(\frac{2 K}{M}\right)$

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

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 $\left(N_{s}\right)$ and the number of beads between branch points $\left(N_{8}\right)$ and for $\varepsilon_{S}=\varepsilon_{B}=0$. The lines are meant to guide the eye.


Persistence Length ~ Bending Modulus/(Thermal Energy)
$1_{\mathrm{p}}=\mathrm{l}_{\mathrm{K}} / 2 \sim \mathrm{E}_{\text {bending }} / \mathrm{kT}$
(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 $l_{p}$

## Alternative Functionality

 based on increase in chain flexibility
## A Monte Carlo simulation study of branched polymers Arun Yethiraj <br> $$
\left(\frac{1}{l_{p}}\right)=\left(\frac{1}{l_{p, \infty}}\right)+\left(\frac{2 K}{M}\right)
$$ <br> Citation: J. Chem. Phys. 125, 204901 (2006); doi: 10.1063/1.2374884


G. 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 guide the eye.


Alternative Functionality based on increase in chain flexibility

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$$ <br> Citation: J. Chem. Phys. 125, 204901 (2006); doi: 10.1063/1.2374884



Alternative Functionality based on increase in chain flexibility

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

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

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$\mathrm{LD}=$ Low branch density
$\mathrm{HD}=$ High branch density


Alternative Functionality based on increase in chain flexibility

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

Size and persistence length of molecular bottle-brushes by Monte Carlo simulations
Stefano Elli, Fabio Ganazzoli, Edward G. Timoshenko, Yuri A. Kuznetsov, and Ronan Connolly
Citation: J. Chem. Phys. 120, 6257 (2004); doi: 10.1063/1.1651052

$\mathrm{LD}=$ Low branch density ( 0.5 branch per chain unit)
$\mathrm{HD}=$ High branch density (1 branch per chain unit)


Equation fails at low $n_{b}$ since it predicts $l_{p}=>0$ when $n_{b}=>0$

Fit Parameters versus branch density


Alternative Functionality based on increase in chain flexibility

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

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

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



FIG. 8. The persistence length $l^{(k)}$, 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 $1_{p} \Rightarrow 0$ when $n_{b}=>0$

Alternative Functionality based on increase in chain flexibility

## Size and persistence length of molecular bottle-brushes by Monte Cario

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

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



Equation fails at low $\mathrm{n}_{\mathrm{b}}$ since it predicts $\mathrm{l}_{\mathrm{p}}=>$ when $\mathrm{n}_{\mathrm{b}}=>0$

Alternative Functionality based on increase in chain flexibility

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

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

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


The $\mathbf{2 K}$ values imply that end groups become less important for more rigid chains

# The Primary Structure for Synthetic Polymers Short-Range Interactions 

What kinds of short-range interactions can we expect
-Bond angle restriction
-Bond rotation restriction
-Steric interactions
-Tacticity
-Charge (poly electrolytes)
-Hydrogen bonds
-Helicity

## The Primary Structure for Synthetic Polymers Short-Range Interactions

What kinds of short-range interactions can we expect
-Bond angle restriction
-Bond rotation restriction

Figure 1.1: A simple polymer in the trans conformation.

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

Figure 1.2: Dihedral angle energy of n-butane.


Polyethylene

## The Primary Structure for Synthetic Polymers Short-Range Interactions

What kinds of short-range interactions can we expect
-Bond angle restriction
-Bond rotation restriction


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


Ethane


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


Butane

## 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, $\mathbf{C}_{\infty}$
Table $2.1 C$ values for some polymers under
theta conditions theta conditions

| Polymer | $C(M=\infty)^{2}$ |
| :--- | :---: |
| Polyethylene | 6.7 |
| Polyethyleneoxide | 4.0 |
| Polystyrene, atactic | 10.0 |

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

$$
\begin{aligned}
& \left\langle R^{2}\right\rangle=n_{\text {Kulum }}{ }_{\text {Kulun }}^{2}=L_{\text {Kulun }}=C_{\infty} n_{\text {Boond }} l_{\text {Bood }}^{2}=C_{\infty} L L_{\text {Bond }} \\
& l_{\text {Kulun }} \sim b_{\text {Efjective }} \\
& C_{\infty}=\frac{l_{\text {Kuhn }}}{l_{\text {Bond }}}
\end{aligned}
$$

Polymer physics
By Ulf W. Gedde

## The Primary Structure for Synthetic Polymers Short-Range Interactions

What kinds of short-range interactions can we expect
-Bond angle restriction
-Bond rotation restriction
$C_{\infty}=\frac{l_{\text {Kuhn }}}{l_{\text {Bond }}}$
Consider a freely rotating chain that has a bond angle restriction of $109.5^{\circ}$
The scalar product of the arbitrary segment vectors $\overline{\mathbf{r}}_{i}$ and $\overline{\mathbf{r}}_{j}$ is:

$$
\left\langle\overline{\mathbf{r}}_{i} \overline{\mathbf{r}}_{j}\right\rangle=l^{2}\left\langle\cos \theta_{i j}\right\rangle
$$

where $\theta_{i j}$ is the angle between the two bond vectors. The following relationship is obtained by combining eqs (2.13) and (2.14);

Ising Chain Model


Colby/Rubenstein,

Polymer physics By UIf W. Gedde

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

## The Primary Structure for Synthetic Polymers Short-Range Interactions

Consider a freely rotating chain that has a bond
angle restriction of $109.5^{\circ}=\tau$

$$
\begin{aligned}
\left\langle\overline{\mathbf{r}}_{i} \overline{\mathbf{r}}_{i+1}\right\rangle & =l^{2} \cos (180-\tau) \\
\left\langle\overline{\mathbf{r}}_{i} \overline{\mathbf{r}}_{i+2}\right\rangle & =l^{2} \cos ^{2}(180-\tau) \\
\left\langle\overline{\mathbf{r}}_{i} \overline{\mathbf{r}}_{j}\right\rangle & =l^{2}[\cos (180-\tau)]^{j-i}
\end{aligned}
$$



See slide 46

$$
\begin{aligned}
&\left\langle r^{\prime}\right\rangle=n l^{2}+2 l^{2} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n}\left[\cos (180-\tau) l^{i-i}\right. \\
&=\left[\begin{array}{cccc}
l^{2} & \left.+l^{2} \cos (180-\tau)+\cdots+l^{2} \cos (180-\tau)\right)^{n-1}+ \\
l^{2} \cos (180-\tau)+ & l^{2} & +\cdots+l^{2} \cos \left(180-\left.\tau\right|^{-2}\right. & + \\
\cdots & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots \\
\left.l^{2} \cos (180-\tau)\right)^{n-1}+ & \cdots & \cdots & l^{2}
\end{array}\right](2.17) \\
& \text { Ising Model }
\end{aligned}
$$

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

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

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

Polymer physics By Ulf W. Gedde

Equation (2.18) can be simplified as follows:
$\left\langle r^{2}\right\rangle=n l^{2}\left[1+\frac{2}{n} \sum_{k=1}^{n-1}(n-k) x^{k}\right]$
$=n l^{2}\left[1+2 \sum_{k=1}^{n-1} \alpha^{k}-\frac{2}{n} \sum_{k=1}^{n-1} k \alpha^{k}\right]$
$=n l^{2}\left[1+\frac{2\left(\alpha-\alpha^{n}\right)}{1-\alpha}-\frac{2}{n}\left(\frac{\alpha(1-\alpha)^{n}}{(1-\alpha)^{2}}-\frac{n \alpha^{n}}{1-\alpha}\right)\right]$
$=n 1^{2}\left[1+\frac{2 \alpha}{1-\alpha}-\frac{2 \alpha}{n} \frac{(1-\alpha)^{n}}{(1-\alpha)^{2}}\right]$

## The Primary Structure for Synthetic Polymers Short-Range Interactions

> Consider a freely rotating chain that has a bond angle restriction of $109.5^{\circ}=\tau$

Equation (2,18) can be simplified as follows:

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

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

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

$$
\left\langle r^{2}\right\rangle \approx 2 n l^{2}
$$

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

| Polymer | $C(M=\infty)^{2}$ |
| :--- | ---: |
| Polyethylene | 6.7 |
| Polyethyleneoxide | 4.0 |
| Polystyrene, atactic | 10.0 |
| Bource: Flory (1989) |  |
| Sere (2.7). |  |

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

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

For a Freely Rotating Polyethylene Chain
http://books.google.com/books?id=lem3fC7XdnkC\&pg=PA23\&|pg=PA23\&dq=coil+expansion+facto \&source=bl\&ots=BGjRfhZYaU\&sig=10OPb2VRuf8Dm8qnrmrhyjXyEC8\&hl=en\&sa=X\&ei=fSVOT. \&source=bisots
XqMMHW0QHil-T_Ag\&ved=0CFOQ6AEwBw\#v=onepage\&q=coil\%20expansion\%20factor\&f=false

## The Primary Structure for Synthetic Polymers Short-Range Interactions

Consider a freely rotating chain that has a bond angle restriction of $109.5^{\circ}=\tau$

| Table 2.1 $C$ values for some polymers under <br> theta conditions |  |
| :--- | :---: |
| Polymer | $C(M=\infty)^{2}$ |
| Polyethylene | 6.7 |
| Polyethyleneoxide | 4.0 |
| Polystyrene, atactic | 10.0 |

$$
\begin{gathered}
\left\langle r^{2}\right\rangle \approx 2 n l^{2} \\
C_{\infty}=\frac{l_{\text {Kuhn }}}{l_{\text {Bond }}}
\end{gathered}
$$

If we consider restrictions to bond rotation for first order interactions

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

which is lower than the experimentally obtained $(6.7 \pm 0.1) n \|^{2}$ (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.

## The Primary Structure for Synthetic Polymers <br> Short-Range Interactions

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

| Polymer | $C(M=\infty)^{2}$ |
| :--- | :---: |
| Polyethylene | 6.7 |
| Polyethyleneoxide | 4.0 |
| Polystyrene, atactic | 10.0 |

Source Flory (1989)

- See eq (2.7).

Polymer physics
By Ulf W. Gedde



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 $\mathbf{r}(\mathbf{s})$. The unit tangent vector to the walk, $\mathbf{t}(\mathbf{s})$, is defined by,

$$
\begin{equation*}
\bar{t}(s)=\frac{\partial \bar{r}(s)}{\partial s} \tag{1}
\end{equation*}
$$



Figure 1. Brownian Path.
The end-to-end distance for the Brownian path is given by,

$$
\bar{R}=\int_{0}^{L} \bar{t}(s) d s
$$

(2)

Linear absorption
$d I=-I \alpha d x$ change is linear in intensity
$d I / I=-\alpha d x$ integrate
$\ln \left(1 / I_{0}\right)=-\alpha x$ or
$I=I_{0} \exp (-\alpha x)$

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

$$
\begin{equation*}
\langle t(s) \cdot t(0)\rangle=e^{-s / l_{p}} \tag{3}
\end{equation*}
$$

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

$$
\begin{equation*}
d(\langle t(s) \bullet t(0)\rangle)=-\langle t(s) \bullet t(0)\rangle\left(\frac{1}{l_{p}}\right) d s \tag{4}
\end{equation*}
$$

The persistence length is then similar to the linear absorption coefficient for radiation.
(2) and (3) can be used to calculate the mean square end-to-end distance $\underline{R}^{2}$,

$$
\begin{aligned}
\left\langle R^{2}\right\rangle=\langle\bar{R} \bullet \bar{R}\rangle & =\left\langle\int_{0}^{L} \bar{t}(s) d s^{\bullet} \int_{0}^{L} \bar{t}\left(s^{\prime}\right) d s^{\prime}\right\rangle=\int_{0}^{L}\left(d s \int_{0}^{L}\left\langle\bar{t}(s) \bullet \bar{t}\left(s^{\prime}\right)\right\rangle d s^{\prime}\right)=\int_{0}^{L}\left(d s \int_{0}^{L} \exp \left(\frac{-\left|s-s^{\prime}\right|}{l_{p}}\right) d s^{\prime}\right) \\
& =21_{\mathrm{p}} L\left(1-\frac{l_{p}}{L}\left(1-e^{-L / l_{p}}\right)\right) \cong 21_{\mathrm{p}} L
\end{aligned}
$$

We also can consider that for a freely jointed chain composed of $n_{K}$ Kuhn steps of length $1_{K}$,

$$
\left\langle R^{2}\right\rangle=n_{K} l_{K}^{2}=l_{K} L=2 l_{p} L
$$

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

# The Primary Structure for Synthetic Polymers 

## Short-Range Interactions

## Persistence Length, Ip

(Arun Yethiraj J. Chem. Phys. I25, 20490I (2006))

## Several Definitions

definitions are in terms of the projection of the end-to-end vector, $\mathbf{R}$, on a bond vector, averaged over all conformations, i.e.,

$$
\begin{equation*}
l_{k}=\left\langle\mathbf{R} \cdot \mathbf{u}_{k}\right\rangle, \tag{2}
\end{equation*}
$$

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 $\mathbf{R}$ on an interior bond vector $\mathbf{u}_{\text {in }}$ far from any chain ends, while Yamakawa ${ }^{22}$ defined the persistence length as $l_{1}$, i.e., the projection of $\mathbf{R}$ 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 $\theta$ is the angle between bond vectors separated by $s$ segments along the backbone. For an ideal semiflexible chain $\langle\cos \theta(s)\rangle \sim \exp \left(-s / \lambda_{C}\right)$, where $\lambda_{C}$ 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, $\left\langle R^{2}\right\rangle$, is given by

$$
\begin{equation*}
\left\langle R^{2}\right\rangle=\frac{L}{\lambda}-\frac{1}{2 \lambda^{2}}\left(1-e^{-2 \lambda L}\right), \tag{3}
\end{equation*}
$$

where $L$ is the contour length and $\lambda$ is a parameter that characterizes the stiffness. We define the persistence length as twice the value of $l_{1}$ for this model, i.e.,

$$
\begin{equation*}
l_{p} \equiv \frac{1}{\lambda}\left(1-e^{-2 \lambda L}\right) \tag{4}
\end{equation*}
$$

${ }^{21}$ P. J. Flory, Statistical Mechanics of Chain Molecules (Wiley-Interscience, New York, 1969).
${ }^{22} \mathrm{H}$. Yamakawa, Modern Theory of Polymer Solutions (Harper \& Row, ${ }_{23}$ 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, II.
-Bond Angle Correlation, $\lambda \mathrm{C}$.
-Kratky-Porod Worm-like Chain Model, Ip.

The evaluation of the integral is straightforward and yields

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

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

$$
\begin{equation*}
\left\langle R^{2}\right\rangle=2 l_{\mathrm{ps}} l_{\mathrm{ct}} . \tag{2.126}
\end{equation*}
$$

## From Strobl p. 57

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

$$
\begin{equation*}
\left\langle R^{2}\right\rangle=a_{\mathrm{K}} l_{\mathrm{ct}} \tag{2.127}
\end{equation*}
$$

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

$$
\begin{equation*}
2 l_{\mathrm{ps}}=a_{\mathrm{K}} \tag{2.128}
\end{equation*}
$$

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

$$
\begin{equation*}
\left\langle R^{2}\right\rangle=l_{\mathrm{ct}}^{2} . \tag{2.129}
\end{equation*}
$$

Equation (2.125) thus describes the transition from rod-like properties to a coil structure. Here the equation refers to chains with varying length $l_{\mathrm{ct}}$, but, when replacing $l_{c t}$ by $\Delta l$ and $\left\langle R^{2}\right\rangle$ by $\left\langle r_{i j}^{2}\right\rangle$, 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 $h-P H B$. 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].

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

The Primary Structure for Synthetic Polymers
Scattering Observation of the Persistence Length


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.

Zeta ( $\zeta$ ) Potential (Electric potential at the slipping (shear) plane)


Dale Schaefer Slides 2010

$$
\Phi=\text { electrostatic potential (Volt = J/coulomb) }
$$



## Debye-Hückel approximation for $\Phi(x)$

$\frac{z e \Phi_{o}}{k T} \ll 1 \quad \begin{aligned} & \text { Debye }- \text { Hückel Approximation } \\ & \text { Potential is stronger than } \mathbf{k T}\end{aligned}$
$\Phi(x)=\Phi_{0} \exp (-\kappa x)$
$\kappa=\left(\frac{2 e^{2} n_{0} z^{2}}{\varepsilon_{r} \varepsilon_{o} k T}\right)^{1 / 2} \quad \kappa^{-1}=$ Debye screening length

Counter ions $\left(\mathrm{n}_{0}\right)$ screen the charge


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,

$$
U(r)=\frac{e^{2}}{\varepsilon r} \exp \left(-\frac{r}{r_{D}}\right) \quad \mathrm{r}_{D}=\left(\frac{\varepsilon k T}{4 \pi n e^{2}}\right)^{1 / 2}
$$

$r_{D}$ is the Debye screening length, $n$ is the counter ion (salt) concentration, $r_{D}$ determines how quickly the electrostatic potential decays

## 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 $\underline{\text { Bjerrum length, }} 1_{\mathrm{B}}$.

$$
\frac{e^{2}}{4 \pi \varepsilon l_{B}}=k_{B} T \Rightarrow l_{B}=\frac{e^{2}}{4 \pi \varepsilon k_{B} T}
$$

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 $1_{B} \sim 7 \AA$
Below the Bjerrum length charges will feel specific interactions and will form ordered structures. Above $1_{B}$, 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.


FIG. 1 Typical $g(r)$ for a liquid. The first neighbor distance is $r_{1}$, the second is $r_{2}$, etc.


FIG. 2 Total correlation functions for a monovalent binary electrolyte with diameter of the ion $=5 \AA . g_{++}(r)$ 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

## 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

$$
U(r)=\frac{e^{2}}{\varepsilon r} \exp \left(-\frac{r}{r_{D}}\right) \quad \mathrm{r}_{D}=\left(\frac{\varepsilon k T}{4 \pi n e^{2}}\right)^{1 / 2}
$$

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

$$
r_{D}^{2}=\frac{V_{\text {per charge }} k T}{4 \pi r U(r)_{\text {with } r_{D}=\infty}}
$$

Below the Debye screening length charges will feel interactions, either specific if $r<1_{B}$ 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:

Charge spacing, $a$
Counterion concentration, $n$

Counterion
condensation

Polymeric contribution to screening

Micelles, liquid-
crystalline phases

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.

## 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, $1_{\text {e }}$
-Electrostatic Persistence Length
Persistence is increased by electrostatic charge. $1_{\text {per }}=1_{o}+1_{e}$
For a $\ll 1_{\text {per }} \ll \mathrm{r}_{\mathrm{D}}$
Interaction between charges separated by distance less than $\mathrm{r}_{\mathrm{D}}$, short range repulsion increases persistence length (short-range interactions)

Interaction between charges separated by a distance $>1_{\text {per }}$ effect chain scaling (long-range interactions)

$$
U(r)=\frac{e^{2}}{\varepsilon r} \exp \left(-\frac{r}{r_{D}}\right) \quad \mathrm{r}_{D}=\left(\frac{\varepsilon k T}{4 \pi n e^{2}}\right)^{1 / 2}
$$

Alexei Khoknov


## -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) }\quad\mp@subsup{V}{2}{}\mathrm{ and }\mp@subsup{V}{1}{}\mathrm{ are the initial and final cylinders
dU = -RT(dV/V)
U = -RTln(V2/V ( )
```

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

$$
\begin{array}{lr}
\begin{array}{lr}
\text { D-H Potential } \\
\mathrm{dU}=-\mathrm{e}^{2} / \varepsilon \mathrm{adr} / \mathrm{r} \\
\mathrm{U}=-\mathrm{e} / \varepsilon\left(\ln \left(\mathrm{r}_{2} / \mathrm{r}_{1}\right)\right) & \rho=\frac{e}{a} \\
\mathrm{U}=-\mathrm{e} \rho / 2 \varepsilon\left(\ln \left(\mathrm{~V}_{2} / \mathrm{V}_{1}\right)\right) & \\
\text { parameter } u, & u \equiv \frac{e^{2}}{\varepsilon a k T}
\end{array}, \begin{array}{l} 
\\
\hline
\end{array} &
\end{array}
$$

Balancing these two we have the parameter $u$,
$u<1$ 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

$$
u_{e f f}=\frac{\rho_{e f f} e}{\varepsilon k T}=1
$$

$\rho_{\text {eff }}$ is the final chain charge and condensed counter ion charge

Condensing counterions to neutralize charge on the chain


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.)

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

-Electrostatic Persistence Length
Figure 13. Illustration of the phenomenon of counterion condensation

Persistence is increased by electrostatic charge. $1_{\text {per }}=1_{o}+1_{e}$
For $\mathrm{a} \ll 1_{\text {per }} \ll \mathrm{r}_{\mathrm{D}}$
Interaction between charges separated by distance less than $r_{D}$, short range repulsion increases persistence length

Interaction between charges separated by a distance $>1_{\text {per }}$ effect chain scaling

When $u_{e f f}=\frac{\rho_{e f f} e}{\varepsilon k T}=1$ charge condensation stops since all charge on the chain is
neutralized neutralized $\quad \varepsilon k T$ a maximum effective linear charge density is reached $\rho_{e f f, \text { max }}=\frac{\varepsilon k T}{e}$
s

Alexei Khokniov


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 $\kappa^{-1}$ Debye Screening length
$1_{p, 0}$ bare persistence length with no charge
" $a$ " must be smaller than $r_{D}$ for there to be a change in persistence, this is so that neighboring charges can interact
$r_{D}$ must be smaller than $l_{p, 0}$ for there to be a change in persistence
The parameter "u" enthalpy of attraction divided by T*entropy of dispersion of charge governs $u>1$ charge condense; $u<1$ charges disperse
and as a consequence the persistence length is increased, too. The expression for the electrostatic persistence length $l_{e}$ has the form (Odijk 1977)

$$
l_{e}=\left\{\begin{array}{lll}
u r_{D}^{2} /(4 a), & \text { at } \quad u<1 & \text { (no condensation) }  \tag{30}\\
r_{D}^{2} /(4 u a), & \text { at } \quad u>1 & \text { (condensation takes place) } .
\end{array}\right.
$$

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 $\kappa^{-1}$ can be written as a sum of the bare persistence length $l_{0}$ and the electrostatic persistence length $l_{\mathrm{p}}^{\text {OSF }}$

$$
l_{\mathrm{p}} \approx l_{0}+l_{\mathrm{p}}^{\mathrm{OSF}} \approx l_{0}+\frac{l_{\mathrm{B}} f^{2}}{4(\kappa b)^{2}}
$$

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

# 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 $d_{\mathrm{T}}$
Kuhn Length $l \mathrm{k}$
Packing Length $p$


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 $\tau_{e}$ | $F$ definitions (Ferry) <br> Based on Eq. (22) for $M_{e}$ and Eq. (19) for $\tau_{e}$ | MM definitions <br> (Milner-McLeish) <br> Based on Eq. (22) <br> for $M_{c}$ and Eq. (14) <br> for $\tau_{e}$ |
| :---: | :---: | :---: | :---: |
| $M_{e}$ entanglement molecular weight | $M_{e}^{G}=\frac{4}{5} \frac{\rho R T}{G_{N}^{0}}$ | $M_{e}^{F}=\frac{\rho R T}{G_{N}^{0}}$ | $M_{e}^{F}=\frac{\rho R T}{G_{N}^{0}}$ |
| Z <br> number of tube segments | $Z=\frac{M}{M_{e}^{G}}$ | $Z=\frac{5}{4} \frac{M}{M_{e}^{F}}$ | $Z=\frac{5}{4} \frac{M}{M_{e}^{F}}$ |
| $\tau_{e}$ equilibration time | $\tau_{e}=\left(\frac{M_{e}^{G}}{M_{0}}\right)^{2} \frac{\zeta b^{2}}{3 \pi^{2} k_{B} T}$ | $\tau_{e}=\left(\frac{4}{5}\right)^{2}\left(\frac{M_{e}^{F}}{M_{0}}\right)^{2} \frac{\zeta b^{2}}{3 \pi^{2} k_{B} T}$ | $\tau_{e}^{\mathrm{MM}}=\left(\frac{M_{e}^{F}}{M_{0}}\right)^{2} \frac{\zeta b^{2}}{3 \pi^{2} k_{B} T}$ |
| $\tau_{R}$ <br> Rouse <br> rotational <br> time | $\tau_{R}=Z^{2} \tau_{e}$ | $\tau_{R}=Z^{2} \tau_{e}$ | $\tau_{R}=\left(\frac{4}{5}\right)^{2} Z^{2} \tau_{e}^{\mathrm{MM}}$ |
| reptation time | $\tau_{d}=3 Z^{3} \tau_{e}$ | $\tau_{d}=3 Z^{3} \tau_{e}$ | $\tau_{d}=3\left(\frac{4}{5}\right)^{2} Z^{3} \tau_{e} \mathrm{MM}$ |
| $\tau_{\text {early }}(s)$ early-time arm | $\tau_{\text {early }}(s)=\frac{9 \pi^{3}}{16}$ | $\tau_{\text {early }}(s)=\frac{5625 \pi^{3}}{4096}$ | $\tau_{\text {early }}(s)=\frac{225 \pi^{3}}{256}$ |
| fluctuation time | $\times\left(\frac{M}{M_{e}^{G}}\right)^{4} \tau_{e} s^{4}$ | $\times\left(\frac{M}{M_{e}^{F}}\right)^{4} \tau_{e} s^{4}$ | $\times\left(\frac{M}{M_{e}^{F}}\right)^{4} \tau_{e}^{\mathrm{MM}} s^{4}$ |

## Strobel Chapter 8

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

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



Fig. 6.8. Results of a quasiclastic neutron seattering experiment on a melt of
poly(ethy) poly(thyylena- co-propylene) at $199^{\circ} \mathrm{C}(10 \%$ protonated chains disoolvod in a deuter-
ahd masrix; $M=8.6 .10^{\circ}$.




Pig. 6.10. Modelling the latcral constraints on the chain motion imposed by the
entanglements hy a 'tabe' The averove over the tube defines the 'privitive. The average over the rapid wriggling motion within the tube defines the 'primitive path' (oontinuoss dark line)

Unconstrained motion $=>S(q)$ goes to 0 at very long times
Each curve is for a different $\mathrm{q}=1$ /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 dT


Figure 2
Quasi-clastic 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.
6.3 Entanglement Bifects


Fig. 6.9. Size of of the confincment range, as derived from the leng term limits of
the curven shown in Fiv. $6.8[67]$.
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 $\mathrm{N}^{3}$ (observed is $\mathrm{N}^{3.4}$ )


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

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


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

## Fick's Second Law

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

$$
n(x, t)=n_{0} \operatorname{erfc}\left(\frac{x}{2 \sqrt{D t}}\right)
$$

$$
n(x, t)=n_{0}\left[1-2\left(\frac{x}{2 \sqrt{D t \pi}}\right)\right]
$$

Reptation predicts that the diffusion coefficient will follow $\mathrm{N}^{2}$ (Experimentally it follows $\mathrm{N}^{2}$ )
Reptation has some experimental verification
Where it is not verified, we understand that tube renewal is the main issue.
(Rouse Model predicts D ~1/N)

## Reptation of DNA in a concentrated solution

6.4 Hydrodynamic Interaction in Solutions


Fig. 6.13. Series of images of a fluoreacently stained DNA chain embedded in a concentrated solution of unstained chains: Initial conformation (lefl); partial stretching by a rapid move of the bead at one end (sccond from the leff); chain recoil by a reptative motion in the tube (subsoquent pictures to the right). Reprinted with parmission 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. <br> 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)





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 $\left(f_{\mathrm{A}}\right)$ of the A block (black) increases to $\sim 0.5$. 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; $\chi$ is the average energy per kT per mer unit in a mixture of A and B )
One Chain Interfacial Energy $=\chi \mathrm{kT}\left(\mathrm{Ad}_{\mathrm{t}}\right) / \mathrm{V}_{\mathrm{c}}$
$d_{t}$ is the thickness of the interfacial layer where the A-B junction is located
A is the cross-sectional area of a polymer chain
$\mathrm{V}_{\mathrm{c}}$ is the occupied volume of a unit segment of a polymer chain
The total occupied volume of a block copolymer chain is $V_{\text {occupied }}=N_{A B} V_{c}$;


This occupied volume is also given by $V_{\text {occupied }}=d_{A B} A$ where $d_{A B}$ is the length of the block copolymer chain assuming it forms a cylindrical shaped object and the block copolymer domain spacing. So, $\mathbf{d}_{\mathrm{AB}}=\mathbf{N}_{\mathrm{AB}} \mathbf{V}_{\mathrm{c}} / \mathbf{A}$.

## Energy of Elongation of Polymer Chains, Elastic Energy

(makes domains smaller, $3 \mathrm{kTR}^{2} /\left(2 \mathrm{nl}^{2}\right)$ )
Assumes that one end is at the interface and the other end must fill the space.
Chain Energy of Elongation $=-3 \mathrm{kT} \mathrm{d}_{\mathrm{AB}}{ }^{2} /\left(2<\mathrm{R}^{2}>\right)=-3 \mathrm{kT} \mathrm{N}_{\mathrm{AB}} \mathrm{V}_{\mathrm{c}}{ }^{2} /\left(\mathrm{l}_{\mathrm{K}}{ }^{2} \mathrm{~A}^{2}\right)$
$\mathrm{d}_{\mathrm{AB}}=\mathrm{N}_{\mathrm{AB}} \mathrm{V}_{\mathrm{c}} / \mathrm{A}$ from above and $\left\langle\mathrm{R}^{2}\right\rangle=\mathrm{N}_{\mathrm{AB}} \mathrm{l}_{\mathrm{K}}{ }^{2}$
The free energy will be minimized in A to obtain the optimum phase size $d_{A B}$. So, it is the packing of the chains at the interface that governs the phase behavior of BCP's.

```
\DeltaG/kT = \chi Ad d
d}(\Delta\textrm{G}/\textrm{kT})/\textrm{dA}=\chi\mp@subsup{\textrm{d}}{\textrm{t}}{}/\mp@subsup{\textrm{V}}{\textrm{c}}{}+3\mp@subsup{\textrm{N}}{\textrm{AB}}{}\mp@subsup{V}{\textrm{c}}{2}/(\mp@subsup{1}{\textrm{K}}{2}\mp@subsup{\textrm{A}}{}{3})=
```



```
d
```


## Three terms arise from the consideration of microphase separation

A is the cross-sectional area of a polymer chain
$\mathrm{V}_{\mathrm{c}}$ is the occupied volume of a unit segment of a polymer chain
$V_{\text {occupied }}=N_{A B} V_{c}$ 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) $=a<\mathrm{R}^{2}>/\left(2 \mathrm{~V}_{\text {occupied }}\right)$ where $a=\mathrm{V}_{\text {occupied }} /<\mathrm{R}_{0}{ }^{2}>=\mathrm{V}_{\text {occupied }} /\left(\mathrm{N}_{\mathrm{K}} 1_{\mathrm{K}}^{2}\right)$
(Previously we had the spring constant $\mathrm{k}_{\text {spr }} / \mathrm{kT}=3 /<\mathrm{R}_{0}^{2}>=3 a / \mathrm{V}_{\text {occupied }} ; a=\mathrm{k}_{\text {spr }} \mathrm{V}_{\text {occupied }} / 3$ )
" $a$ " 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, $\mathrm{V}_{\text {occupied. " }} a$ " is a ratio between the packing volume and the molar mass as measured by $\left\langle\mathrm{R}_{0}{ }^{2}\right\rangle$.

Since $\mathrm{V}_{\text {occupied }}=\mathrm{N}_{\mathrm{K}} \mathrm{V}_{\mathrm{c}}$, and $<\mathrm{R}_{0}{ }^{2}>=\mathrm{N}_{\mathrm{K}} 1_{\mathrm{K}}{ }^{2}$, then $a=\mathrm{V}_{\mathrm{c}} / \mathrm{l}_{\mathrm{K}}{ }^{2}$, 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 " $a$ ", $\mathrm{A}=\pi \mathrm{a}^{2}$, and $\mathrm{V}_{\mathrm{c}}=a 1_{\mathrm{K}}{ }^{2}$, so the BCP phase size problem can be solved using only the parameter " $a$ ".

## 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 $\mathrm{G}_{0} \sim 0.39 \mathrm{kT} / a^{3}$

Structural Control of "a"
$a=m_{0} /\left(\rho 1_{\mathrm{K}} \mathrm{l}_{0}\right)$
Vary mass per chain length, $\mathrm{m}_{0} / \mathrm{l}_{0}$

$\log t$
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

$$
J^{*}(\omega \rightarrow 0)=J_{\mathrm{e}}^{0}-\mathrm{i} \frac{1}{\eta_{0} \omega}
$$

As we see, $\eta_{0}$ and $J_{\mathrm{e}}^{0}$ show up directly and separately, in the limiting behavior of $J^{\prime}$ and $J^{\prime \prime}$.

The dynamic shear modulus follows as

$$
\begin{aligned}
& \qquad \begin{aligned}
G^{*}(\omega \rightarrow 0) & =\frac{1}{J^{*}(\omega \rightarrow 0)}=\frac{\eta_{0} \omega}{\eta_{0} \omega J_{\mathrm{e}}^{0}-\mathrm{i}} \\
& =\frac{\eta_{0}^{2} \omega^{2} J_{\mathrm{e}}^{0}+\mathrm{i} \eta_{0} \omega}{\left(\eta_{0} \omega J_{\mathrm{e}}^{0}\right)^{2}+1}
\end{aligned} \\
& \text { giving } \\
& \text { in agreement with Fig. 5.15, and } \\
& G^{\prime}(\omega \rightarrow 0)=J_{\mathrm{e}}^{0} \eta_{0}^{2} \omega^{2}
\end{aligned} G^{\prime \prime}(\omega \rightarrow 0)=\eta_{0} \omega \text { (5.104) }
$$

We thus find characteristic power laws also for the storage and the loss modulus which again include $J_{e}^{0}$ and $\eta_{0}$ in a well-defined way

One may wonder if $\eta_{0}$ and $J_{\text {e }}^{0}$ can also be deduced from the time dependent response functions, as for example from $G(t)$. Indeed, direct relationship exist, expressed by the two equations

Low Frequency G' $\sim \omega^{2}$
From definition of viscoelastic
High Frequency G ${ }^{\prime} \sim \omega^{1 / 2}$
From Rouse Theory for $\mathrm{T}_{\mathrm{g}}$
Plateau follows rubber elasticity
$\mathrm{G}^{\prime} \sim 3 \mathrm{kT} /\left(\mathrm{N}_{\mathrm{K}, \mathrm{e}} \mathrm{l}_{\mathrm{K}}{ }^{2}\right)$

## Plateau Modulus

Not Dependent on N, Depends on T and concentration
2
40
160
0


$$
G_{0}=\frac{4 \rho R T}{5 M_{e}}=\frac{4 R T}{5 p^{3}}
$$

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]

Fig. 2. Dimensionless plateau moduli $\mathrm{Cl}_{\mathrm{K}}^{3} / k_{\mathrm{B}} T$ as a function of the dimensionless ratio $I_{K} / P$ 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) ( $\times$ ); (ii) plateau moduli inferred from the normal tensions measured in computer simulation of bead-spring melts $(35,36)$ ( $\square$ ) and a semi-
 $(35,36)$ atomistic polycarbonate melt (37) ( $\diamond$ ) 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 ( $\square$ ), bead-spring semidilute solutions ( $\bullet$ ), and the semi-atomistic polycarbonate melt ( $\leqslant$ ). 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 $d \mathrm{p} \sim \mathrm{p}$

Kuhn Length- conformations of chains $<\mathrm{R}^{2}>=1_{k} \mathrm{~L}$

Packing Length- length where polymers interpenetrate $\mathrm{p}=1 /\left(\rho_{\text {chain }}<\mathrm{R}^{2}>\right)$ where $\rho_{\text {chain }}$ is the number density of monomers
"Packing Length" Anywhere Web of Science

## Times Cited and Publications Over Time

DOWNLOAD

"Packing Length" Anywhere Web of Science


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

dilute polyelectrolyte with no salt


Fig. 1 Conformations of polymers in dilute solution. Neutral polymers in poor solvent collapse into dense coils with size $\approx b N^{1 / 3}$ (purple). Neutral polymers in $\theta$-solvent are random walks with ideal end-to-end distance $R_{0}=b N^{1 / 2}$ (black). Neutral polymers in good solvent are self-avoiding walks with Flory end-toend distance $R_{\mathrm{F}}=b N^{0.588}(\mathrm{red})$. Polyelectrolytes with no salt adopt the highly extended directed random walk conformation (blue) with length $L$ proportional to $N$

