Polymer Physics
10:10 – 11:45
Baldwin 645

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

Zoom Meeting:
https://us02web.zoom.us/j/87233679564?pwd=ak1XbmprdBUQnRZWszWU91VHdyUT09

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
\( R_g, R_h, R_{etd} \)
Small-angle neutron, x-ray scattering and static light scattering
Intrinsic viscosity
Dynamic light scattering
Polymer melt rheology
Polymers

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

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

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

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

- 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.
Fig. 1-1 Dependence of melting temperatures, $T_M$, and boiling temperatures, $T_{bp}$, of alkanes and poly(methylene)s, H(CH$_2$)$_n$H, on the number $N$ of methylene groups per molecule [1, 2].
Fold surface energy $\sim 2\times 10^{-5}$ J/cm$^2$

Enthalpy of melting $\sim 300$ J/cm$^3$

$T_{\infty} \sim 414$K ($141^\circ$C)

$T \sim 110^\circ$C

t $= \frac{2\sigma T_{\infty}}{(\Delta H_{m}(T_{\infty}-T))}$ (Hoffman-Lauritzen)

$\sim 1.78\times 10^{-6}$ cm or 17.8 nm thick crystals

regardless of $N$
Viscosity versus Rate of Strain

Specific Viscosity versus Concentration for Solutions

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

Polymers

Zero Shear Rate Viscosity versus Molecular Weight

From Bird, Armstrong, Hassager, "Dynamics of Polymeric Liquids Vol. I"
If polymers are defined by dynamics why should we consider first statics?

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

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

Polymers are a material defined by dynamics and described by statistical thermodynamics
In a polymer melt, the viscous properties of Newtonian liquids combine with elastic forces. The latter contribute a real part to the dynamic shear compliance, to be identified with \( J_0^p \):

\[
J'(\omega \to 0) = J_0^p \cdot \eta_0 \omega .
\]  

(6.102)

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

\[
J(\omega \to 0) = J_0^p + \frac{1}{\eta_0 \omega} .
\]  

(6.103)

As we can see, \( \eta_0 \) and \( J_0^p \) show up directly and separately, in the limiting behavior of \( J' \) and \( J'' \).

The dynamic shear modulus follows as

\[
G(\omega \to 0) = \frac{1}{J(\omega \to 0)} = \frac{\eta_0 \omega}{\eta_0 \omega J_0^p + 1} = \frac{\eta_0 \omega^2 J_0^p}{(\eta_0 \omega J_0^p)^2 + 1} .
\]  

(6.104)

giving

\[
G'(\omega \to 0) = J_0^p \eta_0 \omega^2
\]  

(6.105)

in agreement with Fig. 6.16, and

\[
G''(\omega \to 0) = \eta_0 \omega .
\]  

(6.106)

We thus find characteristic power laws also for the storage and the loss modulus that again include \( J_0^p \) and \( \eta_0 \) in a well-defined way.
Small Angle Neutron Scattering
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 $<R^2>^{1/2} \sim l_K$. 
**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.

\[ <R^2>^{1/2} \sim l_K \]

\(l_K\) just changes proportionally the scale of the walk so

The chain is composed of a series of steps with no orientational relationship to each other. So \(<R> = 0\)

\(<R^2>\) has a value:

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

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

\[ \langle R^2 \rangle = Nr^2 \]

\[ <R^2>^{1/2} \sim N^{1/2} l_K \]
Synthetic Polymer Chain Structure
(A Statistical Hierarchy)

\[ <R^2>^{1/2} \sim N^{1/2} |_{K} \]

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

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

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

![Graph showing Small Angle Neutron Scattering data. The graph plots intensity versus q (Å⁻¹). The data points are shown as circles, and the graphs are labeled as Corrected SANS Data, Unified Equation (3), and Sharp and Bloomfield (1).]
The Primary Structure for Synthetic Polymers
The synthetic polymer is composed of linear bonds, covalent or ionic bonds have a direction.

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

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

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

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

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.)

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

$P_G(\Delta x)$ is a normalized, symmetric probability distribution where $\Delta x$ 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 \( t = 0 \),

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

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

\[
\langle x^2 \rangle = 2Dt
\]

For polymer chain \( \langle R^2 \rangle = l k^2 N \)
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 \( v_g = \frac{mg}{(6\pi \eta R_h)} \) following Stokes Law. For particles at \( x = 0 \) and \( x = h \) height, the density difference is governed by a Boltzmann probability function,

\[
\rho(h) = \rho_0 e^{- \frac{mg h}{kT}}
\]

Fick’s law gives the flux of particles, \( J = -D \frac{d\rho}{dh} \), and \( J = \rho v \), so \( v = -(D/\rho) \frac{d\rho}{dh} \), and \( d\rho/dh = -\rho_0 m g/(kT) e^{-mg h/kT} = -\rho m g h/(kT) \). Then, \( v = D m g/(kT) \). 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 Gaussian Chain

Boltzmann Probability
For a Thermally Equilibrated System

\[ P_s(R) = \exp\left( -\frac{E(R)}{kT} \right) \]

Gaussian Probability
For a Chain of End to End Distance R

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

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

\[ E = kT \frac{3R^2}{2n \ell_k^2} \]
The Gaussian Chain

Boltzmann Probability
For a Thermally Equilibrated System

\[ P_s(R) = \exp \left( -\frac{E(R)}{kT} \right) \]

Gaussian Probability
For a Chain of End to End Distance R

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

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

\[ E = kT \frac{3R^2}{2n\ell_K^2} \]

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

Boltzman Probability
For a Thermally Equilibrated System

\[ P_s(R) = \exp\left( -\frac{E(R)}{kT} \right) \]

Gaussian Probability
For a Chain of End to End Distance \( R \)

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

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:

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

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

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

Boltzmann 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 \( R \)

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

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

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

Mean Square is the 2’nd Moment:

\[ \langle R^2 \rangle = \int_{-\infty}^{\infty} R^2 P(R) dR = \sum_{i=0}^{N} \sum_{j=0}^{N} r_i \cdot r_j = Nr^2 \]
The Gaussian Chain

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

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

Mean Square is the 2’nd Moment:

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

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.
\[ \langle R^2 \rangle = \frac{\int R^2 P_G(R) dR}{\int P_G(R) dR} = \frac{\int R^2 \exp \left( \frac{R^2}{k^2} \right) dR}{\int \exp \left( \frac{R^2}{k^2} \right) dR} \]  

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

\[ G(\alpha) = \int_{-\infty}^{\infty} \exp(-\alpha x^2) dx \]

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

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

\[ (G(\alpha))^2 = \int_0^\infty r dr \int_0^{2\pi} d\theta \exp(-\alpha r^2) = 2\pi \int_0^\infty r dr \exp(-\alpha r^2) \]

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

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

\[ H(\alpha) = \int_{-\infty}^{\infty} x^2 \exp(-\alpha x^2) dx = -\frac{dG(\alpha)}{d\alpha} \]

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

\[ \langle R^2 \rangle = \frac{\int R^2 \exp \left( \frac{R^2}{k^2} \right) dR}{\int \exp \left( \frac{R^2}{k^2} \right) dR} = \frac{H(\alpha)}{G(\alpha)} = \frac{k^3 \pi^{1/2}/2}{k \pi^{1/2}} = \frac{k^2}{2} \]  

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

Gaussian Probability
For a Chain of End to End Distance R

\[ p(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(R)^2}{2\sigma^2}\right) \]

Mean Square is the 2’nd Moment:

\[ \langle R^2 \rangle = \left(\frac{3}{2\pi\sigma^2}\right)^{\frac{3}{2}} \int R^2 \exp\left(-\frac{3R^2}{2\sigma^2}\right) dR = \sigma^2 \equiv nl_k^2 \]

So the Gaussian function for a polymer coil is:

\[ \langle R^2 \rangle = \left(\frac{3}{2\pi nl_k^2}\right)^{\frac{3}{2}} \int R^2 \exp\left(-\frac{3R^2}{2nl_k^2}\right) dR \]
The Gaussian Chain

\[ \langle R^2 \rangle = n l_k^2 \]

Means that the coil size scales with \( n^{1/2} \)
Or
Mass \( \sim n \sim \text{Size}^2 \)
Generally we say that
Mass \( \sim \text{Size}^{df} \)
Where \( df \) is the mass fractal dimension
A Gaussian Chain is a kind of 2-dimensional object like a disk.
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

\[ \langle R^2 \rangle = n l_k^2 \]

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, \( d_{\text{min}} \) so that,

\[ p \sim R^{d_{\text{min}}} \]

For a Gaussian Chain \( d_{\text{min}} = 2 \) since \( p \) is the path \( n \)

For a disk \( d_{\text{min}} = 1 \) since the short circuit is a straight line.

We find that \( d_f = c \ d_{\text{min}} \)

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

$\begin{align*}
    d_f &= 2 \\
    d_{\text{min}} &= 1 \\
    c &= 2
\end{align*}$

Extended $\beta$-sheet (misfolded protein)

Random Coil

$\begin{align*}
    d_f &= 2 \\
    d_{\text{min}} &= 2 \\
    c &= 1
\end{align*}$

Unfolded Gaussian chain
How Complex Mass Fractal Structures Can be Decomposed

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

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

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

\[ d_f = d_{\min} c \]

\[
\begin{array}{ccccccc}
| z | & | d_f | & | p | & | d_{\min} | & | s | & | c | & | R/d |
|---|---|---|---|---|---|---|---|
| 27 | 1.36 | 12 | 1.03 | 22 | 1.28 | 11.2 |
\end{array}
\]
Fibers follow either Gaussian or Self-avoiding structure depending on binding of fibers

Orientation partly governs separation

Pore size and fractal structure govern wicking
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

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

so

\[ \langle r_{i+1} \rangle_{\text{ShortRangeInteraction}} = \frac{r_i}{(z-1)} \]
The Primary Structure for Synthetic Polymers
Short-Range Interactions

\[ \langle r_{i+1} \rangle_{\text{Short Range Interaction}} = \frac{r_i}{(z-1)} \]

For Gaussian Chain

\[ \langle R^2 \rangle = \sum_i \sum_j r_i \cdot r_j = \sum_i r_i \cdot r_i + \sum_{i \neq j} r_i \cdot r_j \]

yields

\[ \langle R^2 \rangle = N r^2 \]

For SRI Chain the first term is not 0.

\[ \langle r_i \cdot r_j \rangle = \frac{b^2}{(z-1)^{|i-j|}} \]

and

\[ \langle R^2 \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle r_i \cdot r_j \rangle \equiv \sum_{i=1}^{n} \sum_{k=-\infty}^{\infty} \frac{b^2}{(z-1)^{|k|}} = nb^2 \frac{z}{z-2} = nb_{\text{effective}}^2 \]

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

For Cartesian simulation \( z = 6 \) and \( b_{\text{eff}} \) 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

Increase the persistence length

Chain scaling is not effected 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, $C_{\infty}$

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

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

$$C_{\infty} = \frac{l_{\text{Kuhn}}}{l_{\text{Bond}}}$$
The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

- Bond angle restriction
- Bond rotation restriction

\[ C_\infty = \frac{l_{Kuhn}}{l_{Bond}} \]

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

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!!!)
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

Proposed End Group Functionality

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

LD = Low branch density
HD = High branch density
This works better for Yethiraj’s data.
(Except that the infinite persistence length is not monotonic in branch length)

Proposed End Group Functionality

\[ l_p = l_{p,\infty} - \left( \frac{2K}{M} \right) \]
Persistence Length ~ Bending Modulus/(Thermal Energy)

\[ l_p = \frac{1}{k} \sim \frac{E_{\text{bending}}}{kT} \]

(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 \(l_p\).
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 \(N_b\) and the number of beads between branch points \(N_b\) for \(e = 0\). The lines are meant to guide the eye.

Alternative Functionality
based on increase in chain flexibility

\[
\left( \frac{1}{l_p} \right) = \left( \frac{1}{l_{p,\infty}} \right) + \left( \frac{2K}{M} \right)
\]
A Monte Carlo simulation study of branched polymers
Arun Yethiraj

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Alternative Functionality
based on increase in chain flexibility

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\frac{1}{l_p} = \left( \frac{1}{l_{p,\infty}} \right) + \left( \frac{2K}{M} \right)
\]
LD = Low branch density
HD = High branch density

Alternative Functionality
based on increase in chain flexibility

\[
\left( \frac{1}{l_p} \right) = \left( \frac{1}{l_{p,\infty}} \right) + \left( \frac{2K}{M} \right)
\]
LD = Low branch density (0.5 branch per chain unit)
HD = High branch density (1 branch per chain unit)

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

\[
\frac{1}{l_p} = \frac{1}{l_{p,\infty}} + \frac{2K}{M}
\]

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

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

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

\[
\frac{1}{l_p} = \frac{1}{l_{p,\infty}} + \frac{2K}{M}
\]

The 2K values imply that end groups become less important for more rigid chains.
The Primary Structure for Synthetic Polymers
Short-Range Interactions

What kinds of short-range interactions can we expect

-Bond angle restriction
-Bond rotation restriction
-Steric interactions
-Tacticity
-Charge (poly electrolytes)
-Hydrogen bonds
-Helicity
The Primary Structure for Synthetic Polymers
Short-Range Interactions

What kinds of short-range interactions can we expect

- Bond angle restriction
- Bond rotation restriction

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

Polyethylene

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf
The Primary Structure for Synthetic Polymers
Short-Range Interactions

What kinds of short-range interactions can we expect

- Bond angle restriction
- Bond rotation restriction

![Energy vs Torsion Angle Graphs for Ethane and Butane](http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf)
The Primary Structure for Synthetic Polymers

Short-Range Interactions

What kinds of short-range interactions can we expect

- Bond angle restriction
- Bond rotation restriction

**Characteristic Ratio, $C_\infty$**

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

\[
l_{Kuhn} \sim b_{Effective}
\]

\[
C_\infty = \frac{l_{Kuhn}}{l_{Bond}}
\]

---

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>C $(M = \infty)^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>0.7</td>
</tr>
<tr>
<td>Polystyrene oxide</td>
<td>4.0</td>
</tr>
<tr>
<td>Polystyrene, atactic</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Source: Flory (1969)

$^\dagger$ See eq. (2.7).
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°.

Ising Chain Model in Colby/Rubenstein, pp. 59

http://www.eng.uc.edu/~gbeaucag/Classes/Physics/Chapter1.pdf
Consider a freely rotating chain that has a bond angle restriction of $109.5^\circ = \tau$

\[
\begin{align*}
\langle \mathbf{r}_i \mathbf{r}_{i+1} \rangle &= l^2 \cos(180 - \tau) \\
\langle \mathbf{r}_i \mathbf{r}_{i+2} \rangle &= l^2 \cos^2(180 - \tau) \\
\langle \mathbf{r}_i \mathbf{r}_j \rangle &= l^2 [\cos(180 - \tau)]^{j-i}
\end{align*}
\]

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

\[
\begin{bmatrix}
I^2 \\
I^2 \cos(180 - \tau) + \cdots + l^2 \cos(180 - \tau)]^{n-1} + \\
\cdots \\
\cdots \\
I^2 [\cos(180 - \tau)]^{n-1} + \cdots + l^2
\end{bmatrix}
\]

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

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

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

For a Freely Rotating Polyethylene Chain

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

Table 2.1 C values for some polymers under theta conditions

<table>
<thead>
<tr>
<th>Polymer</th>
<th>C (M = \infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>6.7</td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>4.0</td>
</tr>
<tr>
<td>Polystyrene, amorphous</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Source: Flory (1999)

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

$$\langle \gamma^2 \rangle = 2n\ell^2$$
Consider a freely rotating chain that has a bond angle restriction of $109.5^\circ = \tau$

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

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

If we consider restrictions to bond rotation for first order interactions

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

which is lower than the experimentally obtained $(6.7 \pm 0.1)l^2$ (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
Short-Range Interactions

\[ C_\infty = \frac{l_{Kuhn}}{l_{Bond}} \]


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 position 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, \(\overline{t}(s)\), is defined by,

\[
\overline{t}(s) = \frac{\partial r(s)}{\partial s}
\]  

(1)

![Figure 1. Brownian Path.](image)

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

\[
\overline{R} = \int_{0}^{L} \overline{t}(s) ds
\]  

(2)
The auto-correlation function for the tangent vector can be written,

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

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

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

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

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

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

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

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

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

showing that the freely jointed Kuhn length is just twice the persistence length.
The Primary Structure for Synthetic Polymers

Short-Range Interactions

Persistence Length, $l_p$

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.,

$$l_{k} = \langle \mathbf{R} \cdot \mathbf{u}_k \rangle,$$

(2)

where $\mathbf{u}_k$ is the (normalized) bond vector between sites $k$ and $k+1$. Flory\textsuperscript{21} defined the persistence length as the average projection of $\mathbf{R}$ on an interior bond vector $\mathbf{u}_k$ far from any chain ends, while Yamakawa\textsuperscript{22} defined the persistence length as $l_{\perp}$, 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 $\langle \cos \theta(s) \rangle = \exp(-s/\lambda_c)$, 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,\textsuperscript{23} the mean-square end-to-end distance, $\langle \mathbf{R}^2 \rangle$, is given by

$$\langle \mathbf{R}^2 \rangle = \frac{L}{\lambda} - \frac{1}{2\lambda^2} \left(1 - e^{-2\lambda l_p}\right),$$

(3)

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 $l_p$ for this model, i.e.,

$$l_p = \frac{1}{\lambda} \left(1 - e^{-2\lambda l_p}\right).$$

(4)


-Yamakawa's book is online, II.
-Bond Angle Correlation, $\lambda_c$.
-Kratky-Porod Worm-like Chain Model, $l_p$. 
The evaluation of the integral is straightforward and yields

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

(2.125)

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

$$\langle R^2 \rangle = 2l_{ps}l_{ct}.$$

(2.126)

2.4 The Persistent Chain

Since $l_{ct} \propto N$, 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))

$$\langle R^2 \rangle = a_K l_{ct}$$

(2.127)

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

$$2l_{ps} = a_K$$

(2.128)

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

$$\langle R^2 \rangle = l_{ct}^2.$$

(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 $\Delta l$ 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

\[ I(q) = Bq^{-d_f} \]

\[ q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad d = \frac{2\pi}{q} \]

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].

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.
Helmholtz (100+ years ago) proposed that surface charge is balanced by a layer of oppositely charged ions. All colloids should flocculate.
Zeta (ζ) Potential

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

Φ = electrostatic potential (Volt = J/coulomb)
Debye-Hückel approximation for $\Phi(x)$

$$\frac{ze\Phi_0}{kT} \ll 1 \quad \text{Debye–Hückel Approximation}$$

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

$$\kappa = \left( \frac{2e^2 n_0 z^2}{\varepsilon_r \varepsilon_0 kT} \right)^{1/2} \quad \kappa^{-1} = \text{Debye screening length}$$

Dale Schaefer Slides 2010
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

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 $r$,

$$ U(r) = \frac{e^2}{\varepsilon r} \exp \left( -\frac{r}{r_D} \right) $$

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

$r_D$ is the Debye screening length, $n$ is the counter ion (salt) concentration, $r_D$ determines how quickly the electrostatic potential decays.
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 \textbf{Bjerrum length}, $l_B$.

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

In water at room temperature $l_B \approx 7 \text{ Å}$

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.
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 = 5Å. $g_{ss}(r)$ is the pair correlation function for a central atom and a neighboring co-ion and shows repulsion. $g_{cc}(r)$ 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.
For Charges separated by distance $r$ in the presence of $n = \text{number/volume counter ions or other charges}$

\[
U(r) = \frac{e^2}{\varepsilon r} \exp\left(-\frac{r}{r_D}\right) \quad r_D = \left(\frac{\varepsilon kT}{4\pi ne^2}\right)^{\frac{1}{2}}
\]

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

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

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.
Increase in persistence length due to charges on chain

Persistence is increased by electrostatic charge. $l_{\text{per}} = l_0 + l_e$

For $a \ll l_{\text{per}} \ll r_D$

Interaction between charges separated by a distance less than $r_D$, short range repulsion increases persistence length (short-range interactions)

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

A new size scale is introduced:
Charge spacing “a” which contributes an electrostatic persistence length, $l_e$
\[ U(r) = \frac{e^2}{\varepsilon r} \exp \left( -\frac{r}{r_D} \right) \quad r_D = \left( \frac{\varepsilon kT}{4\pi n e^2} \right)^{\frac{1}{2}} \]

**-Counterion Condensation**

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

\[
\begin{align*}
\text{Ideal gas} & \quad dU = -pdV \text{ (for } dQ = 0) \\
\text{dU} = -RT(dV/V) & \quad \text{U} = -RT \ln(V_2/V_1)
\end{align*}
\]

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

\[
\text{D-H Potential} \\
\begin{align*}
dU &= -e^2/ea \, dr/r \\
U &= -e^2/e \left( \ln(r_2/r_1) \right) \\
U &= -e^2/2e \left( \ln(V_2/V_1) \right)
\end{align*}
\]

Balancing these two we have the parameter \(u\),

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

\(\rho_{\text{eff}}\) is the chain charge and condensed counter ion charge

Counter ions condense until the chain charge is neutralized, when

\[
u_{\text{eff}} = \frac{\rho_{\text{eff}} e}{\varepsilon kT} = 1
\]
Condensing counterions to neutralize charge on the chain

\[ u_{\text{eff}} = \frac{\rho_{\text{eff}} e}{\varepsilon k T} = 1 \]

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

Persistence is increased by electrostatic charge. \( l_{\text{per}} = l_o + l_e \)

For a \( l_{\text{per}} << r_D \)

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

Interaction between charges separated by a distance > \( l_{\text{per}} \) effect chain scaling

When \( u_{\text{eff}} = \frac{\rho_{\text{eff}} e}{e k T} = 1 \) charge condensation stops since all charge on the chain is neutralized and a maximum effective linear charge density is reached

\[ \rho_{\text{eff}, \text{max}} = \frac{e k T}{e} \]

Soft and Fragile Matter, M. E. Cates, M. R. Evans Chapter 3 Alexei Khokhlov (2000); Chinese review of polyelectrolytes from web
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
- $l_{p,0}$ bare persistence length with no charge

“a” must be smaller than $r_D$ for there to be a change in persistence, this is so that neighboring charges can interact

$r_D$ must be smaller than $l_{p,0}$ for there to be a change in persistence

The parameter “$u$” enthalpy of attraction divided by T*entropy of dispersion of charge governs $u > 1$ charge condense; $u < 1$ charges disperse
and as a consequence the persistence length is increased, too. The expression for the electrostatic persistence length \( l_e \) has the form (Odijk 1977)

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

(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 \(\kappa^{-1}\) can be written as a sum of the bare persistence length \(I_0\) and the electrostatic persistence length \(I_p^\text{ele}\)

\[ I_p \approx I_0 + I_p^\text{ele} \approx I_0 + \frac{I_0 f^2}{4(\varepsilon b)^2} \]

where \(b\) is the bond length and \(I_0\) is the Bjerrum length \(I_0 = e^2/\varepsilon k_B T\) is the distance at which the Coulomb interaction between two elementary charges \(e\) in a dielectric medium with the dielectric constant \(\varepsilon\) is equal to the thermal energy \(k_B T\). 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 $d_T$
Kuhn Length $l_K$
Packing Length $p$
TABLE I. Summary of the alternative definitions of tube parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>G definitions (Fetters et al.)</th>
<th>F definitions (Ferry)</th>
<th>MM definitions (Milner–McLeish)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Based on Eq. (17) for $M_e$ and Eq. (19)</td>
<td>Based on Eq. (22) for $M_e$ and Eq. (19) for $\tau_e$</td>
<td>Based on Eq. (22) for $M_e$ and Eq. (14) for $\tau_e$</td>
</tr>
<tr>
<td>$M_e$ (entanglement molecular weight)</td>
<td>$M_e^G = \frac{4 \rho R T}{5 G_N}$</td>
<td>$M_e^F = \frac{\rho R T}{G_N}$</td>
<td>$M_e^\text{MM} = \frac{\rho R T}{G_N}$</td>
</tr>
<tr>
<td>$Z$ (number of tube segments)</td>
<td>$Z = \frac{M}{M_e^G}$</td>
<td>$Z = \frac{5 M}{4 M_e^F}$</td>
<td>$Z = \frac{5 M}{4 M_e^\text{MM}}$</td>
</tr>
<tr>
<td>$\tau_e$ (equilibration time)</td>
<td>$\tau_e = \left( \frac{M_e^G}{M_0} \right)^2 \frac{\eta^2}{3\pi k_B T}$</td>
<td>$\tau_e = \left( \frac{4}{5} \right) \left( \frac{M_e^F}{M_0} \right)^2 \frac{\eta^2}{3\pi k_B T}$</td>
<td>$\tau_e = \left( \frac{4}{5} \right) \left( \frac{M_e^\text{MM}}{M_0} \right)^2 \frac{\eta^2}{3\pi k_B T}$</td>
</tr>
<tr>
<td>$\tau_R$ (Rouse rotational time)</td>
<td>$\tau_R = Z^2 \tau_e$</td>
<td>$\tau_R = Z^2 \tau_e$</td>
<td>$\tau_R = \left( \frac{4}{5} \right) Z^2 \tau_e^\text{MM}$</td>
</tr>
<tr>
<td>$\tau_d$ (reptation time)</td>
<td>$\tau_d = 3Z^3 \tau_e$</td>
<td>$\tau_d = 3Z^3 \tau_e$</td>
<td>$\tau_d = \left( \frac{4}{5} \right) Z^3 \tau_e^\text{MM}$</td>
</tr>
<tr>
<td>$\tau_{\text{early}}(s)$ (early-time arm fluctuation time)</td>
<td>$\tau_{\text{early}}(s) = \frac{9 \pi^3}{16}$</td>
<td>$\tau_{\text{early}}(s) = \frac{5625 \pi^3}{4096}$</td>
<td>$\tau_{\text{early}}(s) = \frac{225 \pi^3}{256}$</td>
</tr>
<tr>
<td></td>
<td>$\times \left( \frac{M}{M_e^G} \right)^4 \tau_e s^4$</td>
<td>$\times \left( \frac{M}{M_e^F} \right)^4 \tau_e s^4$</td>
<td>$\times \left( \frac{M}{M_e^\text{MM}} \right)^4 \tau_e s^4$</td>
</tr>
</tbody>
</table>
Quasi-elastic neutron scattering data demonstrating the existence of the tube

Unconstrained motion $\Rightarrow S(q)$ goes to 0 at very long times

Each curve is for a different $q = 1/\text{size}$

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, IN11, 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) resolved 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.
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 $N^{3.4}$)
Without tube renewal the Reptation model predicts that viscosity follows $N^3$ (observed is $N^{3.4}$)
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.
Origin of the Packing Length:

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.
Free Energy Contributions:

*Interfacial Energy Proportional to the Total Surface Area*

(makes domains large to reduce surface area)

\[
\text{Sur} = \chi kT d_t/V_c
\]

\(d_t\) 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 \(V_{\text{occupied}} = N_{AB} V_c\);

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

*Energy of Elongation of Polymer Chains, Elastic Energy*

(makes domains small)

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

\[
\text{Chain} = -3kT \frac{d_{AB}^2}{(2<R^2>)} = -3kT \frac{N_{AB} V_c^2}{(l^2 A^2)}
\]

\(d_{AB} = N_{AB} V_c/A\) from above and \(<R^2> = N_{AB} l^2\)

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.

\[
\frac{\Delta G}{kT} = \chi kT d_t/V_c - 3kT N_{AB} V_c^2/(2(l^2 A^2))
\]

\[
d\left(\frac{\Delta G}{kT}\right)/dA = \chi d_t/V_c + 3 N_{AB} V_c^2/(l^2 A^3) = 0
\]

\(A = \left\{3 N_{AB} V_c^3/(l^2 \chi d_t)\right\}^{1/3}

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

$V_{\text{occupied}} = NABV_c$ The total occupied volume of a block copolymer chain

Witten defines a term “a” that he calls the intrinsic elasticity of a polymer chain

$\text{Elastic Energy/(3kT)} = \frac{<R^2>}{(2V_{\text{occupied}})}$ where $a = \frac{V_{\text{occupied}}}{<R_0^2>} = \frac{V_{\text{occupied}}}{(N\kappa l_k^2)}$

(Previously we had the spring constant $k_{\text{spr}}/kT = \frac{3}{<R_0^2>} = \frac{3a}{V_{\text{occupied}}}$; $a = k_{\text{spr}}V_{\text{occupied}}/3$)

“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, $V_{\text{occupied}}$. “a” is a ratio between the packing volume and the molar mass as measured by $<R_0^2>$.

Since $V_{\text{occupied}} = N\kappa V_c$, and $<R_0^2> = N\kappa l_k^2$, 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”.

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 $G \sim 0.39 \, kT/a^3$

Structural Control of “a”

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

Vary mass per chain length, $m_0/l_0$

Theory of Stress Distribution in Block Copolymer Microdomains, Witten TA, Milner ST, Wang Z-G p. 656
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
$G' \sim 3kT/(Nk_e k^2)$
Plateau Modulus

Not Dependent on N, Depends on T and concentration

\[ G_0 = \frac{4\rho RT}{5M_c} = \frac{4RT}{5p^3} \]

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]
this implies that $d r \sim p$
Kuhn Length - conformations of chains $<R^2> = \kappa L$

Packing Length - length were polymers interpenetrate $p = 1/(\rho_{\text{chain}} <R^2>)$
where $\rho_{\text{chain}}$ is the number density of monomers
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 $\theta$-solvent are random walks with ideal end-to-end distance $R_\theta = bN^{1/2}$ (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