Polymers: The Size of a Coil

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Lecture 1/4
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Outline

We will have four lectures related to polymer physics:

• Introduction (this lecture) to polymers and basic models for determination of coil size.
• The influence from the solvent and attachment of polymers to surfaces.
• Polymer melts, mixtures, crystals and gels.
• Mechanical properties, rubbers and viscoelasticity of polymers.
**What is a Polymer?**

- Chain-like molecules where chemical groups are (at least to some extent) repeated.
- Covalent bonds between the units.

Jones: “physicists should note with due humility the tremendous intellectual and practical achievements of polymer chemists”

But now we focus on the physics!

We are interested in finding generic models that apply to all these molecules!

We are often interested in knowing how a property scales with the size of the polymer, which is what we can control!

**Natural and Synthetic Polymers**

- Plastics, simple organic compounds as monomers.
- Cellulose and starch, sugars as monomers.
- DNA.
- Rubber.
- Nylon, polyesters (clothes).
Plastics

Plastics are everywhere in our modern world. They usually consist of synthetic polymers originating from the petroleum industry.

But oil is a finite resource and plastic recycling is not so simple…

Possible solution: Plastics made of polymers produced biologically and that are biodegradable (e.g. corn starch).

The polymer physics will still be valid!

Video: Plant Bottle

30% sustainable production of polyethylene terephthalate (PET) from plants, but not necessarily biodegradable.
Synthesis

Polymers are generally synthesized by letting a solution of monomers attach to each other and form chains.

- The most common mechanism is free radical polymerization, where highly reactive unpaired electrons form covalent bonds.
- The reactions may require a catalyst to run efficiently.
- Some sort of initiation is done to start the reaction.
- There is also a termination step, or one waits until all monomers are gone.

Branching

Can occur for instance in starch and cellulose.

Drastically changes the properties of the polymer!
Copolymers

Different monomers!

The same monomer can appear in blocks or alternate regularly. Alternatively, the sequence is random.

- Blocks
- Regular
- Random

Stereochemistry

Different directions (usually two) are possible for the sidegroups sticking out from the main chain. They can be facing the same direction (isotactic), alternating (syndiotactic) or random (atactic).

- Isotactic polypropylene
- Syndiotactic polypropylene

Wikipedia: Tacticity
Components like light-emitting diodes and transistors can now be made of polymers!

Polymers containing aromatic rings with delocalized (π-conjugated) electrons are central because they can conduct electricity.

Since the polymers are soft they are excellent for flexible electronic devices.

- **Video: Acreo Display**

Display made of polymers (no metals or semiconductors).
Polydispersity

There is almost always a distribution in molecular weight $M$ because the degree of polymerization $N$, the number of monomers, is a random variable.

Number average $M_n$ based on number of molecules $n$:

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

Weight average $M_w$ based on weight fraction $w$:

$$M_w = \sum_i w_i M_i = \frac{\sum_i n_i M_i}{\sum_i n_i M_i}$$

The polydispersity index (PDI) is given by $M_w/M_n$.

Guidelines: PDI < 1.1 good, PDI < 1.5 OK, PDI > 2 bad.

Exercise 1.1

What is the polydispersity of poly(ethylene oxide) if
15% of the molecules have $N = 98$,
30% of the molecules have $N = 99$,
25% of the molecules have $N = 100$,
15% of the molecules have $N = 101$,
10% of the molecules have $N = 102$,
5% of the molecules have $N = 103$.

Comment on the value!
Exercise 1.1

The monomer has a weight of \(2 \times 12 \text{ (carbon)} + 4 \times 1 \text{ (hydrogen)} + 1 \times 16 \text{ (oxygen)} = 44 \text{ gmol}^{-1}\). The average based on number of molecules is then:

\[
M_n = [0.15 \times 98 \times 44 + 0.3 \times 99 \times 44 + 0.25 \times 100 \times 44 + 0.15 \times 101 \times 44 + 0.1 \times 102 \times 44 + 0.05 \times 103 \times 44] = 4395.6 \text{ gmol}^{-1}
\]

Note that the sum of \(n_i\) is one, we use fractions. The weight fraction average is:

\[
M_w = [0.15 \times (98 \times 44)^2 + 0.3 \times (99 \times 44)^2 + 0.25 \times (100 \times 44)^2 + 0.15 \times (101 \times 44)^2 + 0.1 \times (102 \times 44)^2 + 0.05 \times (103 \times 44)^2] / [0.15 \times 98 \times 44 + 0.3 \times 99 \times 44 + 0.25 \times 100 \times 44 + 0.15 \times 101 \times 44 + 0.1 \times 102 \times 44 + 0.05 \times 103 \times 44] = 4394.43\ldots \text{ gmol}^{-1}
\]

\[
PDI = M_w / M_n = 1.0001\ldots
\]

This is very monodisperse, probably not possible to achieve in reality.

Experiment: Chain Configuration

End to end distance of cables!
Polymers normally form random coils because it is a more probable configuration. The number of configurations is much higher for a coil compared to a stretched chain.

What is the expected distance \( R \) between the end points if \( r \) is a random variable?

Freely jointed chain segment model: At each “connection point” a new direction is acquired by random! Each segment is equal to the chemical monomer in size:

\[
\bar{r} = \sum_{i=1}^{N} \bar{a}_i
\]

We can write the magnitude of the vector \( r \) as scalar products:

\[
|\bar{r}|^2 = \bar{r} \cdot \bar{r} = \sum_{i=1}^{N} \bar{a}_i \cdot \sum_{j=1}^{N} \bar{a}_j = \sum_{i=1}^{N} \sum_{j=1}^{N} \bar{a}_i \cdot \bar{a}_j = \sum_{i=1}^{N} \bar{a}_i \cdot \bar{a}_i + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \bar{a}_i \cdot \bar{a}_j
\]

Consider the average or expected value of these sums. When \( i \neq j \) the expected value of any of these scalar products must be zero. Only the self products are important:

\[
\langle |\bar{r}|^2 \rangle = \sum_{i=1}^{N} \bar{a}_i \cdot \bar{a}_i + 0 = N|\bar{a}|^2
\]

If we skip vector denotation from now on, we can write the “random walk” distance, following the same principle as for Brownian motion:

\[
\langle r \rangle = R = aN^{1/2}
\]

Note that \( R \) is the expected value of the random variable \( r \).
End to End Distance Distribution

The probability distribution for $r$ is approximately Gaussian for large $N$ (Jones appendix):

$$p(r, N) = \left[ \frac{3}{2\pi Na^2} \right]^{3/2} \times \exp\left(-\frac{3r^2}{2Na^2}\right)$$

Note that the dimension is inverse volume! The probability is obtained by integration in 3D:

$$dP = 4\pi r^2 p(r) \, dr$$

Plot shows $dP$ vs normalized extension for different $N$.

Not Gaussian!

Repetition: Entropy (Statistical Mechanics)

Entropy is about probabilities and the number of microstates associated with a certain macrostate. The microstates are not observable! Entropy is lack of information.

Two dice have 36 microstates with equal probability. Entropy can be observed in the sum macrostate.

Example: Probability of getting macrostate 7 with two dice is 1/6 (6 out of 36 microstates). The probabilities for getting 2 or 12 are only 1/36 each.
Repetition: Boltzmann’s Entropy Formula

Most general entropy formula:

\[ S = -k_B \sum_{i=1}^{n} p_i \log(p_i) \]

The probability of microstate \( i \) is \( p_i \). Boltzmann’s constant \( k_B = 1.3806 \times 10^{-23} \text{JK}^{-1} \) relates entropy to free energy via temperature.

If all \( W \) microstates are equally probable \( p = 1/W \) for all \( i \) and \( n = W \). We can get the famous formula:

\[ S = -k_B \sum_{i=1}^{W} \frac{1}{W} \log \left( \frac{1}{W} \right) = k_B \sum_{i=1}^{W} \frac{1}{W} \log(W) = k_B \log(W) \]

The logarithmic dependence essentially comes from combinatorics: If there are \( W_A \) states in system A and \( W_B \) states in system B the total number of states is \( W_A W_B \), but entropy becomes additive:

\[ S_A + S_B = k_B \log(W_A) + k_B \log(W_B) = k_B \log(W_A W_B) \]

Test: Entropy of Gender

Alice and Bob have two kids…

I: One is a boy.
   p(the other is also a boy)?

I: The older is a boy.
   p(the younger is also a boy)?

I: (nothing more)
   p(both are boys)?
Number of Configurations

We want the number of configurations $W$ for a given $r$. It must be true that:

$$p(r, N) = \frac{W(r, N)}{\int_0^\infty W(r, N) \, dr}$$

Now Boltzmann’s formula can be used:

$$S(r) = k_B \log(W(r, N)) = k_B \log(\int_0^\infty W(r, N) \, dr) =$$

$$k_B \log(\int_0^\infty W(r, N) \, dr) =$$

$$k_B \log\left(\frac{3}{2\pi N a^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2Na^2}\right) + k_B \log(\int_0^\infty W(r, N) \, dr) =$$

Conformational Entropy

Our expression is now:

$$k_B \log\left(\frac{3}{2\pi N a^2}\right)^{3/2} + 3k_Br^2/2Na^2 + k_B \log(\int_0^\infty W(r, N) \, dr)$$

does not contain $r$

contains $r$ but does not really depend on it

Thus with help of Boltzmann we can write:

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

Now there is just one problem: A real polymer does not consist of stiff segments that are fully free to rotate at joints. The chemistry is more complex than that!
Kuhn Length

Imagine a “walk” along a real polymer chain.

The correlation in direction when moving forward must disappear eventually since there is always some freedom to rotate! Eventually you can have any direction.

In other words there must be a certain distance \( b \), the Kuhn length, along the polymer that corresponds to a segment in a freely jointed chain model but it is not equal to the size of the monomer.

Important: We will let \( a \) denote the length of the real monomer and keep the definition of \( N \) as number of monomers in the chain.

Flory’s Characteristic Ratio

One can estimate Kuhn length by experiment or theory (the chemical nature of the covalent bonds such as rotational freedom).

In principle \( b \) could be either bigger or smaller than \( a \), but it is always bigger in reality.

Flory’s characteristic ratio \([b/a]^2\) is a (dimensionless) measure of flexibility.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>( C_m )</th>
<th>( b ) (( \AA ))</th>
<th>( \rho ) (g/cm(^{-3}))</th>
<th>( M_w ) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Polyisoprene (PI)</td>
<td>-(CH(_2)CH(_2)CH(_2)CH(_2))-</td>
<td>4.6</td>
<td>8.2</td>
<td>0.830</td>
<td>113</td>
</tr>
<tr>
<td>1,4-Polybutadiene (PB)</td>
<td>-(CH(_2)CH(_2)CH(_2)CH(_2))-</td>
<td>5.3</td>
<td>9.6</td>
<td>0.826</td>
<td>105</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>-(CH(_2))(_n)-</td>
<td>5.9</td>
<td>11</td>
<td>0.791</td>
<td>180</td>
</tr>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td>-(CH(_2))(_n)-</td>
<td>6.7</td>
<td>11</td>
<td>1.064</td>
<td>137</td>
</tr>
<tr>
<td>Poly(dimethyl siloxane) (PDMS)</td>
<td>-(OSi(CH(_3))(_2))-</td>
<td>6.8</td>
<td>13</td>
<td>0.893</td>
<td>381</td>
</tr>
<tr>
<td>Polyethylene (PE)</td>
<td>-(CH(_2))(_n)-</td>
<td>7.4</td>
<td>14</td>
<td>0.784</td>
<td>150</td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td>-(CH(_2))(_n)C(COOCH(_2))(_n)-</td>
<td>9.0</td>
<td>17</td>
<td>1.13</td>
<td>655</td>
</tr>
<tr>
<td>Acrylic polyamide (PS)</td>
<td>-(CH(_2))(_n)C(=O)(_n)-</td>
<td>9.5</td>
<td>18</td>
<td>0.969</td>
<td>720</td>
</tr>
</tbody>
</table>

Rubinstein & Colby
Polymer Physics Oxford 2003
Rescaling

If the freely jointed chain should be valid, it must be based on Kuhn steps instead of monomers. We exchange $a$ with $b$ and $N$ to number of Kuhn steps: $r_{max}/b = aN/b$ The correct entropy becomes:

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

The expected value for end to end distance becomes:

$$
(r) = R = b \times \left( \frac{aN}{b} \right)^{1/2} = [abN]^{1/2}
$$

Sanity check: If $a = b$ we recover the previous expression. Thus, to predict $R$ we need:

- Monomer size $a$.
- Number of monomers $N$.
- Kuhn-length $b$.

Polymers as Entropic Springs

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

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

The force required to stretch the chain is:

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

The "spring constant" is:

$$
\frac{\partial^2 G}{\partial r^2} = \frac{\partial F}{\partial r} = \frac{3k_BT}{abN};
$$

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

Here all is based on conformational entropy, no interaction energies accounted for!
Exercise 1.2

In water, poly(ethylene oxide) has a Kuhn length of 0.72 nm and a monomer length of 0.28 nm. What is the expected end to end distance of a 20 kgmol$^{-1}$ coil in a random walk configuration?

The monomer weight is 44 gmol$^{-1}$ (previous exercise). This gives $N = 20000/44$. Using the random walk model modified with Kuhn steps gives:

$$R = b \left[\frac{aN}{b}\right]^{1/2} = (abN)^{1/2} = \left[0.28 \times 0.72 \times \frac{20000}{44}\right]^{1/2} = 9.57 \ldots \text{ nm}$$
Worm-Like Chain Model

One commonly used alternate model is a continuously bending worm-like chain. The correlation in direction decays exponentially:

$$R_{\text{wlc}} = \left( 2l_p r_{\text{max}} \left[ 1 - \frac{l_p}{r_{\text{max}}} \left( 1 - \exp \left( - \frac{r_{\text{max}}}{l_p} \right) \right) \right] \right)^{1/2}$$

Here $l_p$ is the persistence length, which clearly contains the same information as the Kuhn length. For $r_{\text{max}} = aN >> l_p$ we recover the random walk:

$$R_{\text{wlc}} = \left( 2l_p r_{\text{max}} \right)^{1/2} = \left( 2l_p aN \right)^{1/2}$$

Random walk had $R = [a b N]^{1/2}$; so $b = 2l_p$.

The worm-like chain is a useful model for stiff polymers (e.g. Kevlar or double stranded DNA) that bend little and continuously over long distances.

However, we still have one big problem to deal with: The chain has to avoid itself!

Repetition: Volumes and Entropy

Consider volume expansion from the viewpoint of statistical mechanics.

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

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

Now imagine the particle is a monomer…
Self Avoiding Chains

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

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

The entropy loss per segment is then:

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

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

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

Excluded Volume Entropy

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

$$\Delta S_{\text{seg}} = \frac{k_B Nv}{r^3}$$

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

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

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

$$G(r) = \frac{3k_B T r^2}{2a b N} + \frac{k_B T v N^2}{r^3} + \text{constant}$$
Sanity Check: Osmotic Pressure?

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

$$\Pi = k_BT \left( C + B C^2 \right)$$

"ideal" (dilute) behavior for $B = 0$

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

$$\Pi = k_BT \left( \frac{N}{V} + B \frac{N^2}{V} \right) \quad G = IV = k_BT \left[ N + \frac{N^2}{V} \right]$$

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

$$\Delta G = IV = k_BT \left( N + B \frac{N^2}{V} \right) - k_BT N = \frac{k_BTBN^2}{V}$$

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

We will look at interactions with the solvent later, including energetic ones.

Example of the Excluded Volume Effect

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

- $N = 1000$
- $a = 1$ nm
- $b = 1$ nm
- $v = 1$ nm$^3$

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

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

Minimum for some value of $r$!
The Flory Radius

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

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

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

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

This gives us:

$$R^5 = abvN^3$$

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

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

Validity?

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

“radius of gyration” of polystyrene chains in a “theta-solvent” (cyclohexane at 34.5°C) and in a good solvent (benzene at 25°C)
Who Cares About 1/2 or 3/5?

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

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

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

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Nobel Prize in Chemistry 1974

For predicting the "spatial configuration of macromolecular chains".

Paul Flory
The Size of a Coil

So after all this work, what is now the size of a polymer molecule?

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

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

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

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

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

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

Reflections and Questions
Exercise 1.3

What is the force required to maintain a coil following a random walk model at $r = 2R$, i.e. twice its expected distance between endpoints, as a function of $R$ and temperature?

$$F = \frac{6k_B T}{R}$$

Exercise 1.4

Consider a poly(ethylene oxide) coil with $N = 100$. Calculate its size by the random walk model, the worm-like chain model and the Flory radius (use monomer length 0.28 nm, Kuhn length 0.72 nm and $v = a^3$). Explain any differences in size estimates.

$R = 4.5$ nm by a random walk.

With two digits precision $R_{\text{wlc}}$ is the same (but would be smaller for lower $N$). The polymer is flexible since $r_{\text{max}}$ is much larger than the persistence length so the worm-like chain model is “not needed”.

$R_F$ is $5.4$ nm, i.e. significantly larger, because of the excluded volume effect.
Exercise 1.5

Repeat Exercise 1.3 with the excluded volume entropy taken into account! The force should now be a function of many things…

\[ F = \frac{93k_BT}{16(ab)^{9/5}N^{2/5}} \]

Exercise 1.6

Compare the end to end distance of 100 kgmol\(^{-1}\) polyethylene (monomer CH\(_2\)) by the random walk model and the Flory excluded volume model! The monomer is 0.18 nm, the Kuhn length 0.50 nm and \( v = a^3 \).

Random walk \( R = 25 \) nm, excluded volume \( R_F = 45 \) nm.