Section 5  Polymer chain configuration and chain entropy

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5.1  The overall picture

Polymer Chain Configuration

The physical configuration of a polymer chain is important in relation to many process and end user properties.

Key Temperatures  \( T_d = \text{dissolution Temp.} \)

\( \text{often room temp} \rightarrow 150^\circ \text{C} \)

\( T_g = \text{Glass transition Temperature} \)

\( \approx -80^\circ \text{C} \rightarrow 300^\circ \text{C} \)

\( T_m = \text{melting temperature (if crystalline)} \)

\( \approx \text{RT} \rightarrow 350^\circ \text{C} \)
The polymer can be in a random coil configuration when the chain is in solution, in the melt or in the solid state.
5.2 The random walk of a single polymer chain

We wish to establish the chain configuration of polymer chains.

Reading. Treloar, Tanford, Flory.

Assume a chain consists of \( r \) links each of length \( a \). Let each link take a random configuration wrt adjacent link.

We are interested in determining the characteristic dimensions of the chain and we will show, route mean square end to end distance is given by,

\[
\langle r^2 \rangle^{1/2} = l_o = ar^{1/2}
\]

Typical example

- \( a = 1 \text{ nm} \quad \left(10 \text{ Å}\right)\)
- \( r = 10^4 \)

RMS end-to-end dist \( l_o = 10^2 \text{ nm} \quad \left(1,000 \text{ Å}\right)\)

Extended length \( ar = 10^4 \text{ nm} \text{, } 10 \mu\text{m} \text{, } 10^5 \text{ Å}\)

Polymer random coils occupy dimensions typically

\( l_o \sim 10 \text{ nm} 100 \text{ Å} \text{ - } 100 \text{ nm, } 1000 \text{ Å} \)

Note:-- very much less than extended length.
The one dimensional random walk

Lord Rayleigh (1919) Sci Papers Vol VI, 604 - 627

$r$ steps at random each of length $a$

$P(x)$ is probability that after $r$ random steps each of length $a$ that end of chain is at a position $x$ from origin.

Start at origin, $r$ steps each of length $a$.
Forward and backward steps equally likely.

In order to get to $x$ we make

$r_f = \text{number of forward steps}$
$r_b = \text{number of backward steps}$
total $r = r_f + r_b$

$x = ar_f + (-a)r_b$

So

$r_f = \frac{1}{2}(r + \frac{x}{a})$
$r_b = \frac{1}{2}(r - \frac{x}{a})$

A displacement $+x$ results from $r_f$ forward steps and $r_b$ backward steps in any order.

Number of ways displacement can be made

\[ \binom{n}{m} = \frac{n!}{m!(n - m)!} \]

number of ways $m$ can be selected from $n$ things.
\[W_x = \text{Nos ways displacement } x \text{ can be made.}\]

\[
\frac{r!}{r! \cdot r_b!} = \frac{r!}{\left( \frac{1}{2} \left( r + \frac{x}{a} \right) \right)! \left( \frac{1}{2} \left( r - \frac{x}{a} \right) \right)!}
\]

note \( r \) typically \( 10^2 - 10^4 \) i.e., large

Use Stirlings Approx \( \ln r! = r \ln r - r \)

\[\ln W_x = r \ln r - \frac{1}{2} \left( r + \frac{x}{a} \right) \ln \frac{1}{2} \left( r + \frac{x}{a} \right) - \frac{1}{2} \left( r - \frac{x}{a} \right) \ln \frac{1}{2} \left( r - \frac{x}{a} \right)
\]

(other terms cancel out) Now, \( \ln \frac{1}{2} \left( r + \frac{x}{a} \right) = \ln \frac{r}{2} \left( 1 + \frac{x}{ra} \right) \)

rearrange

\[\ln W_x = r \ln 2 - \frac{1}{2} \left( r + \frac{x}{a} \right) \ln \frac{r}{2} - \frac{1}{2} \left( r - \frac{x}{a} \right) \ln \frac{r}{2}
\]

\[-\frac{1}{2} \left( r + \frac{x}{a} \right) \ln \left( 1 + \frac{x}{ra} \right) - \frac{1}{2} \left( r - \frac{x}{a} \right) \ln \left( 1 - \frac{x}{ra} \right)
\]

if \( x \ll ra \) then \( \ln \left( 1 + \frac{x}{ra} \right) = \frac{x}{ra} - \frac{x^2}{2r^2 a^2} \) ...........

\[\ln W_x = r \ln 2 - \frac{1}{2} \left( r + \frac{x}{a} \right) \left( \frac{x}{ra} - \frac{x^2}{2r^2 a^2} \right) \]

\[-\frac{1}{2} \left( r - \frac{x}{a} \right) \left( -\frac{x}{ra} - \frac{x^2}{2r^2 a^2} \right) \]

assume \( x/ra \ll 1 \), 1st terms only

\[\ln W_x = r \ln 2 - \frac{r}{2} \left[ \frac{x}{ra} + \frac{x^2}{r^2 a^2} - \frac{x^2}{2r^2 a^2} - \frac{x}{ra} + \frac{x^2}{r^2 a^2} - \frac{x^2}{2r^2 a^2} \right]
\]

\[\ln W_x = r \ln 2 - \frac{x^2}{2ra^2}
\]

\[W_x = e^{r \ln 2} e^{-x^2/2ra^2}
\]

Now Probability of displ x is proportional to the number of ways displ can be made

\[P_x \propto W_x\]

\[P_x = A e^{-\frac{x^2}{2ra^2}}\]

where \( A \) is a constant for a given \( r \)
Determine \( A \) from BC

\[
\sum_{-r_a}^{r_a} P_x = 1 \approx \int_{-\infty}^{\infty} Ae^{-x^2/2r_a^2} \, dx = 1
\]

Discrete \hspace{1cm} Continuous

\[
\int_{-\infty}^{\infty} e^{-bx^2} \, dx = \left[ \frac{\Pi}{b} \right]^{1/2}
\]

Yields \( A = \frac{1}{a(2\Pi r)^{1/2}} \)

Then \( P_x = \frac{\beta^@}{\pi^{1/2}} e^{-\beta^@x^2} \, dx \) ........ (1)

\( P_x \) prob of finding and end between \( x \) and \( x + dx \).

where \( \beta^@ = \frac{1}{2ra^2} \)

Gaussian Probability

Magnitude and width of probability distribution controlled by number of repeat units (steps) and length of step (\( ra^2 \)) term.
5.2. 3 Dimensional random flight

Fix one end at origin, Probability \( P(x) \) with be less than 1D problem as total path will involve movements in \( x \) and \( y \).

\[
\begin{align*}
\beta^2 &= \frac{3}{2ra^2} \\
\end{align*}
\]

Given without proof.

Mean square projection of \( \mathbf{a} \) on \( x \) given by

\[
\frac{\mathbf{a}_x}{\mathbf{a}^2} = \frac{a^2}{3}
\]

For 3D (given without proof)

\[
\begin{align*}
P_x &= \frac{\beta}{\sqrt{\Pi}} e^{-\beta^2 x^2} dx \\
\end{align*}
\]

where \( \beta^2 = \frac{3}{2ra^2} \)

Probability of finding end with coordinate \((x, y, z)\) in element \( dx dy dz \).

\[
P_{xyz} = P_x P_y P_z dx dy dz
\]

\[
= \frac{\beta^3}{\sqrt{\Pi}} e^{-\beta^2 (x^2 + y^2 + z^2)} dx dy dz \quad (1)
\]

where \( \beta^2 = \frac{3}{2ra^2} \)
**Eliminate direction**

What is probability of finding chain with an end-to-end distance between $l$ and $l + dl$. 

![Diagram showing a chain with end points](image)

End could be anywhere on shell dist $l$ form origin

$$P_{xyz} = \frac{\beta^3}{\Pi^{3/2}} e^{-\beta^2(x^2 + y^2 + z^2)} dx dy dz$$

---

Prob end in a shell of inner radius $l$ and outer radius $l + dl$. 

$$P_1 = \frac{\beta^3}{\Pi^{3/2}} e^{-\beta^2 l^2} 4\Pi l^2 dl$$

$$P_1 = \frac{4\beta^3}{\Pi^{1/2}} l^2 e^{-\beta^2 l^2} dl$$

**$P_x$ plot**

Max at origin
We have a prob distribution and need "average" or representative length scales of that distribution. We could take moments (as with the MW distribution), however it is traditional to take one of the following.

5.3 Average Properties

a) Radius of maximum probability $l_{\text{max, prob}}$.

$$\frac{dP_l}{dl} = \frac{8\beta^3}{\Pi^{1/2}} e^{-\beta^2 l^2} \left(1 - \beta^2 l^2\right) = 0$$

Yields $l_{\text{max prob}} = \frac{1}{\beta} = \left(\frac{2}{3}\right)^{1/2} \text{ar}^{1/2}$

b) Average radius $\bar{l}$ (which is in fact the first moment)

$$\bar{l} = \frac{\int_0^\infty P_l dl}{\int_0^\infty P_l dl} = \frac{2}{\Pi^{1/2}} \frac{1}{\beta}$$

Yields $\bar{l} = 2\left(\frac{2}{3\Pi}\right)^{1/2} \text{ar}^{1/2}$
c) **Root mean square end-to-end distance** $l_0$

$$l_0 = \left( \frac{\bar{l}^2}{l} \right)^{1/2} = \left[ \frac{\int P l^2 dl}{\int P dl} \right]^{1/2} = \left( \frac{3}{2} \right)^{1/2} \frac{1}{\beta}$$

this is not the 2nd movement

Yields 

$$l_0 = ar^{1/2}$$

Ex. let $r = 5000$, $a = 0.2 \text{ Nm} \left( 2.0 \text{ Å} \right)$

$$l_{\text{max prob}} = 11.55 \text{ nm} \left( 115.5 \text{ Å} \right)$$

$$\bar{l} = 13.05 \text{ nm} \left( 130.5 \text{ Å} \right)$$

$$l_0 = 14.9 \text{ nm} \left( 149.0 \text{ Å} \right)$$

$$l_{\text{max prob}} < \bar{l} < l_0$$

Note extended length of chain $L = ra$

$$= 5 \times 10^3 \times 2 = 10^4 \text{ Å} = 1 \text{ µm}$$

(Justification for integration limits of $P_x$ distribution)
Extension ratio necessary to stretch chain from random coil to extended chain $\lambda_o$

$$\lambda_o = \frac{L}{l_o} = \frac{ra}{\sqrt{\frac{1}{2}a}} = r^{1/2}$$

say

For $r = 5 \times 10^3$, $\lambda_o = 70$ (a big number)

If chain exists in random configuration, the overall dimensions of chain is very much less than its extended length

$l_o$ typically 10 - 100 nm

**Random coils**

**The story so far**

$r =$ nos repeat units

$a =$ chain length

$l =$ end-to-end distance

RMS end-to-end distance $l_o = ar^{1/2}$

5.4 **The equivalent random chain**

Real polymer chains

Real chains may have finite bond angles between repeat units. This and other effects leads to the concept of the **equivalent random chain**.

We can (in principle) measure $l_o$ of real chain (light scattering) $l_o^R$

We can (with difficulty) measure extended length of real chain $L = L^R$

Match $l_o$ and $L$ for real and equiv random chain.

$l_o = ar^{1/2} = l_o^R$

$L = ar = L^R$

So
\[ a = \frac{[l_0 R]^2}{L^R} \]
\[ r = \left[ \frac{L^R}{l_0^R} \right]^2 \]

\[ [\text{CH}_2 - \text{CH}_2] \leftrightarrow 2.54\text{A} \]

Link length of equiv. random chain = 16.7 A

So simply replace equiv. random chain a and r and treat these as random coils.

### 5.5 Application of random coil concept - Entropy springs

#### 5.5.1 Individual polymer chains and entropy springs

One chain end at origin, other in vol \( d\tau \) dist \( l \) from origin

\[ P_1 = \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2 l^2} d\tau \]

where \( P_1 \) is prob of finding end is vol \( d\tau \)

\[ \beta^2 = \frac{3}{2ra^2} \]

\( r = \) equiv nos links

\( a = \) length of equiv repeat unit

Number of chain configurations available \( W \) for chain

\[ W = C P(1) d\tau \]
\[ = C^1 \exp\left(-\beta^2 l^2\right) d\tau \]

From Statistical Mechanics
\[ S = k \ln W \quad \text{k = Bolts Const.} \]
\[ k = 1.3806 \times 10^{-23} \text{JK}^{-1} \]

\[ S = k \ln \left( c^1 \exp\left(-\beta^2 l^2\right) \right) d\tau \]

\[ S = C'' - k\beta^2 l^2 \]

Entropy of chain is a max when \( l = 0 \)
"     " ' " min " 1 = ra
Chain stretches \( \rightarrow \) entropy decreases.

### 5.5.2 The tension, \( f \), in a single chain

Fix one end at origin. Determine force \( f \) on other end when held at dist \( l \) from origin.

Assume reversible process

\[ dW = dU - TdS \]

\[ dW = fdl \]

\[ f = \frac{dW}{dl} = \left[ \frac{\partial U}{\partial l} \right]_T - T \left[ \frac{\partial S}{\partial l} \right]_T \]

Assume \( \left[ \frac{\partial U}{\partial l} \right]_T = 0 \) (Justification comes from temp dependance of Elasticity for rubbers. See Treloar if worried about this).

but \( S = C'' - k\beta^2 l^2 \)
so $\frac{\partial S}{\partial l} = -2k\beta^2 l$
so $f = 2kT\beta^2 l$

$$f = \frac{3kT}{ra^2} l$$

- Single chain behaves as Hookian spring with zero unstrained length.
- Elastic response is entropic. Origin of elasticity in rubbers, polymers solns and melts (not polymer solids where elasticity can be entropic and or internal energy change).
- Note, $F$ increases with inc $T$ (surprise)?
  " " " " " $l$
  " decreases with inc nos repeat units (MM).

5.5.3 Modelling the behaviour of individual polymer chains

Points of hydrodynamic interaction
5.5.4 The Dumbell polymer chain and its associated "Rouse relaxation time"

The dumbell chain is a viscoelastic chain. It possesses Elasticity, from entropy and viscosity from hydrodynamic interaction.

Elasticity $\Rightarrow$ Entropy $f_E = -Kl$

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{dumbell_chain.png}
\end{figure}

**Entropic force** is always trying to bring ends together

$$K = \frac{3kT}{ra^2}$$

prop to end-to-end separation

**Viscosity** $\Rightarrow$ assume hydrodynamic interaction concentrated at ends

Stokes flow $f_v = 6\pi D \eta_0 U$

\begin{align*}
\text{Dia of sphere} \\
\text{Solvent viscosity} & \quad \text{Velocity of end}
\end{align*}

**Rouse relaxation time** $\lambda_R$

Stretch chain to end-to-end separation $l_0$. Follow relaxation behaviour. Fine balance on end (ignore inertia).

$$\sum F_i = m_\ddot{x} = 0$$

$$\sum F_i = 0$$
\(-f_E + f_v = 0\)

\[ \Pi D \eta_0 \frac{dl}{dt} = -\frac{3kT}{ra^2} x l \]

\[ \frac{dl}{l} = -\lambda_R dt \]

\[ l = l_0 e^{-t/\lambda_R} \]

where \(\lambda_R = \frac{\Pi D \eta_0}{3kT} \cdot ra^2\)

What is D? (Guess!) \(D = \frac{ar}{20}\) say

So \(\lambda_R = \frac{\Pi \eta_0 a^3 r^2}{10 kT}\)

Note \(M = M_0 r\)

\[ \lambda_R = \frac{\Pi}{10} \frac{\eta_0 a^3}{kT} \frac{(M)^2}{M_0^3} \]

So \(\lambda_R \propto M^2\)

Relaxation time increases with \((MM)^2\)

Ex. \(\eta_0 \sim 10^{-3}\) Pas

\(a \sim 1\) nm (say)

\(r \sim 10^{-3}\) (say)

\(\lambda_R \sim 10^{-3} 10^{-4}\) s

**Polymers in dilute solution** Relaxation times

\(\lambda \sim 10^{-1} \quad \rightarrow \quad 10^{-5} s^{-1}\)

high MM \quad low MM

**Polymers, conc soln and melt** (extra hydrodynamic interaction)

\(\lambda \sim 10^{3} \quad \rightarrow \quad 10^{-3} s^{-1}\)

high MM \quad low MM

Most polymers samples are polydisperse hence most polymer samples will possess a range/spectrum of relaxation times.