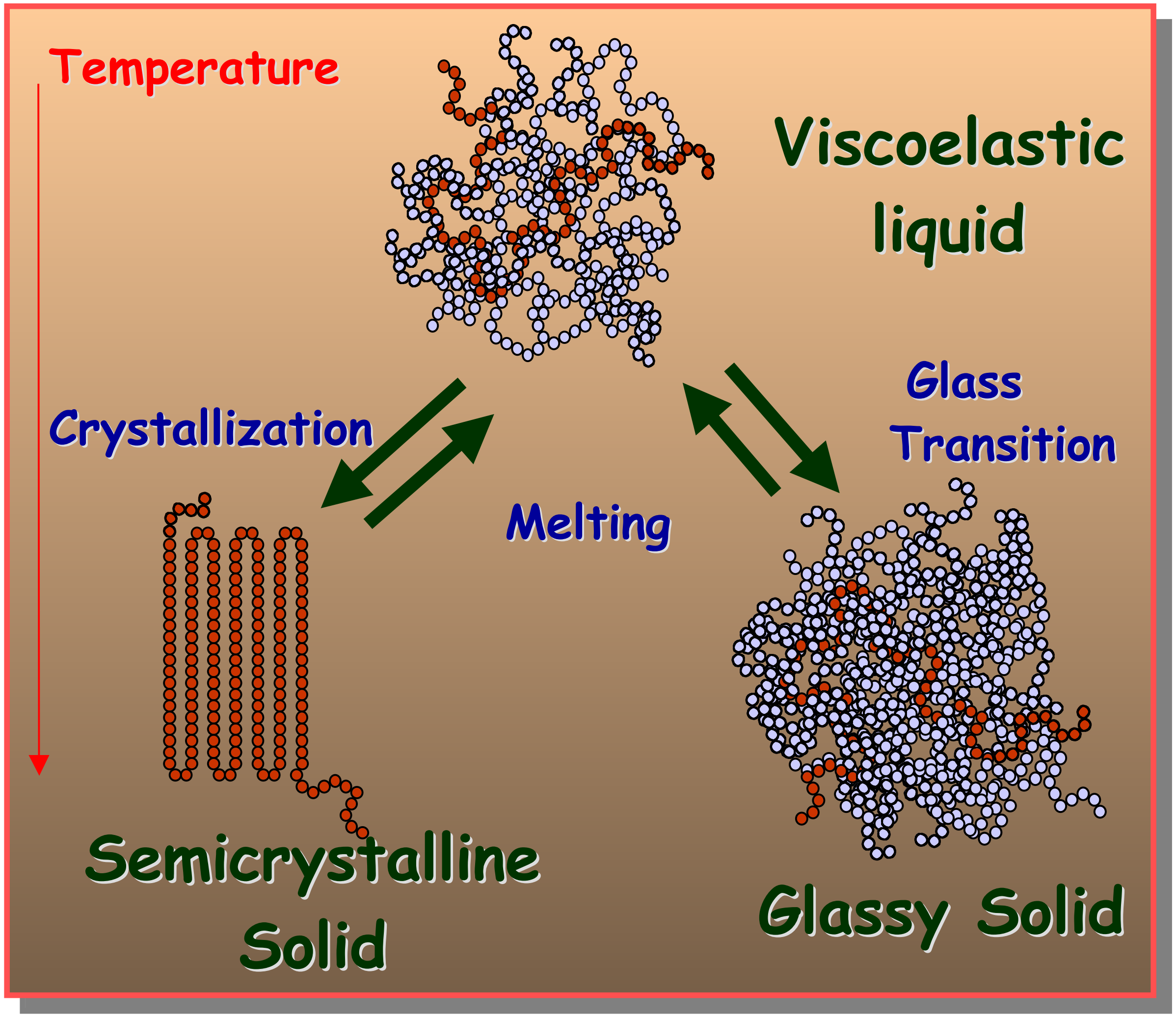
Topics to be Covered

- *The Extraordinary Properties of Rubber*
- *Chain Conformations*
- *Cross-linking*

Chapters 1 & 7 in CD (Polymer Science and Engineering)

Polymer Solid State



Rubber and Other Elastomers

~ 1500 Columbus Stumbles Across Haiti

~ 1600 Missionaries Observe Indians Making Crude Rubber Shoes (Caoutchouc)

1700 Joseph Priestly Invents a Name

1820 1st Rubber Shoes

1832 Mackintosh

1833 Goodyear Starts Work on Rubber

1844 Vulcanization

1875 Henry Wickham -- Pirate or Con-Man?

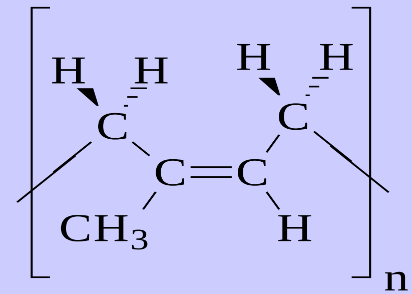
1922 Stevenson Plan

1942 Synthetic Rubber Project

1988 Penn State Rubber Project

Natural Rubber

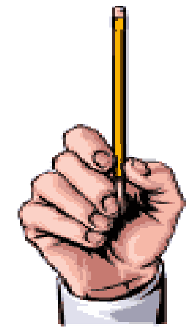
~1496



cis-1,4-polyisoprene

The Origin of a Name

Priestley was a member of the Lunar Society, which met in Birmingham, England, on Monday evenings closest to the full moon, so that the members could find their way home in the dark. Fellow "lunatics" included Mathew Boulton (of steam engine fame), Joshia Wedgwood (founder of the potteries) and Erasmus Darwin. Benjamin Franklin was a Corresponding Member. Priestley's nonconformist religious and political views resulted in an attack on his house by a mob, which burnt it down. Priestley and his family barely escaped to London and decided to emigrate to the U.S., where he settled in Northumberland, Pennsylvannia, on the banks of the Susquehanna.



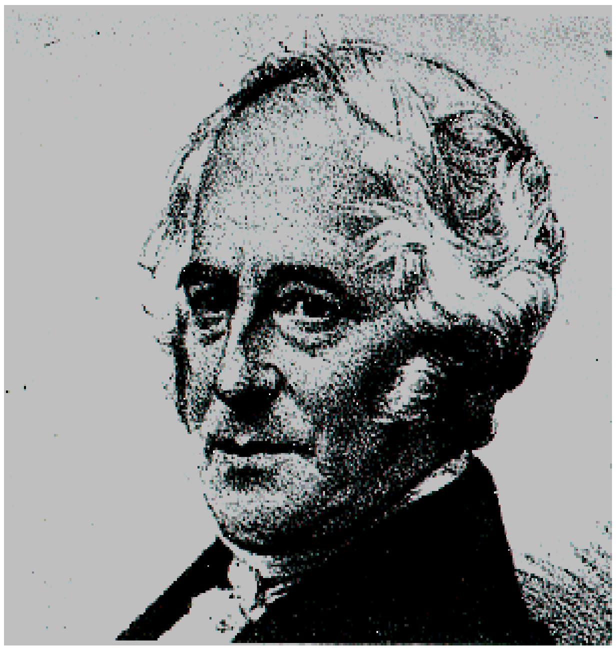
~1770

First Applications

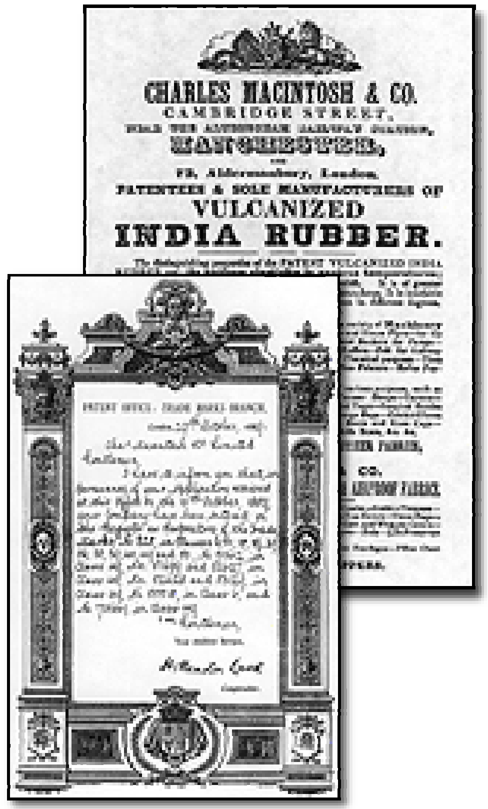
Early 1800's

Hancock and Macintosh

Early 1800's

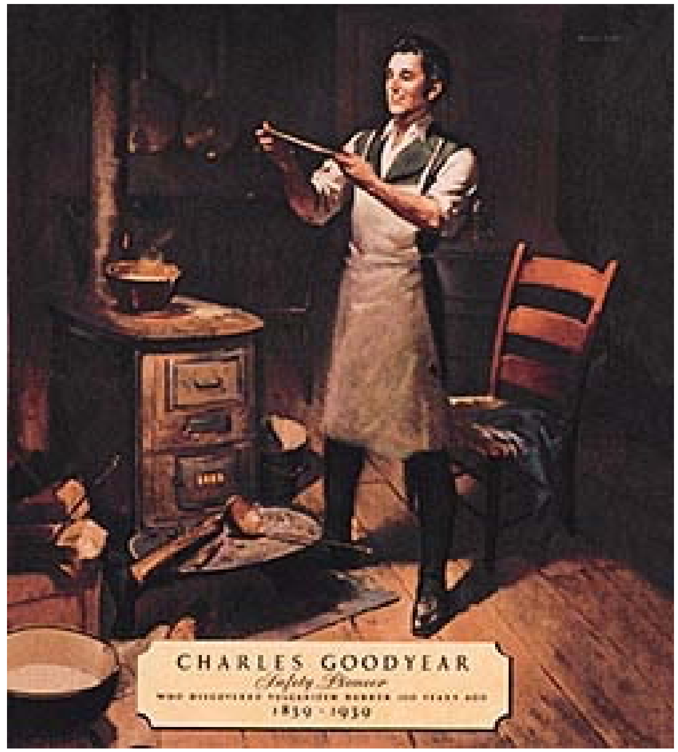


Thomas Hancock



Charles Macintosh

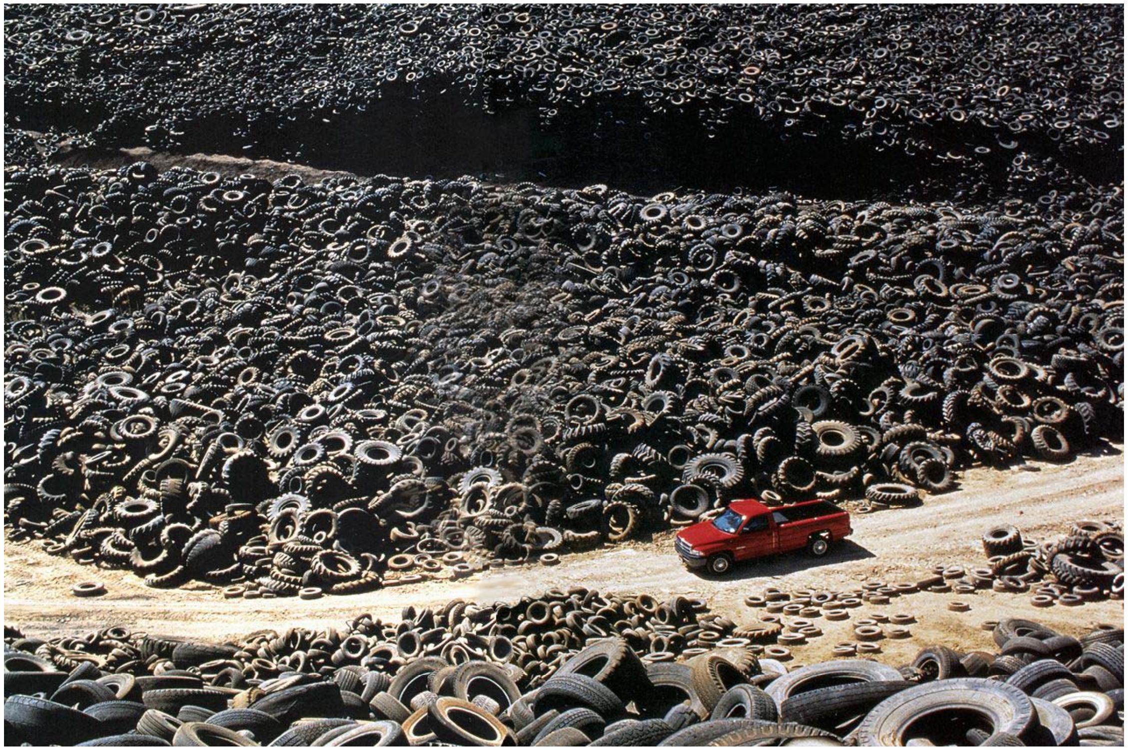
Goodyear



~ 1840's

The Rubber Tire

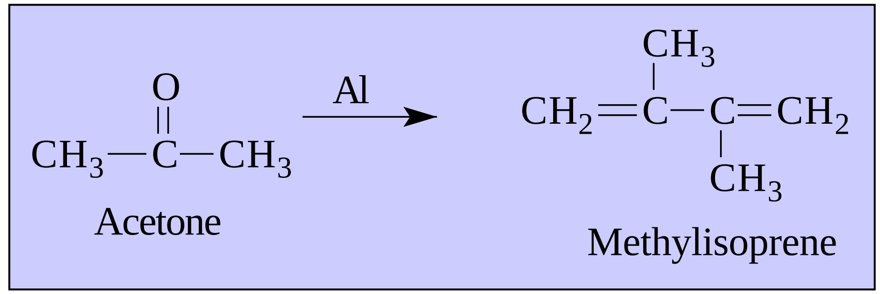
~ 1880's



John Dunlop

The Stevenson Plan

Methyl Rubber

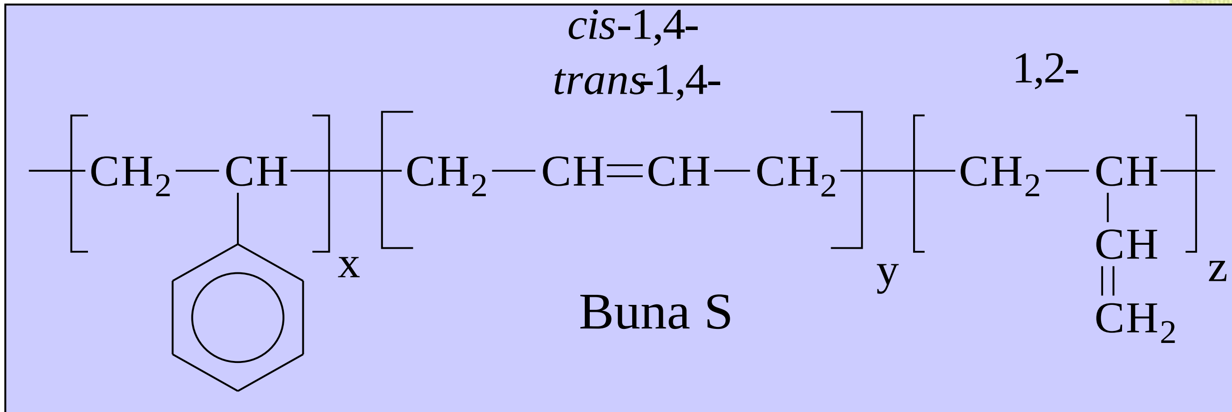


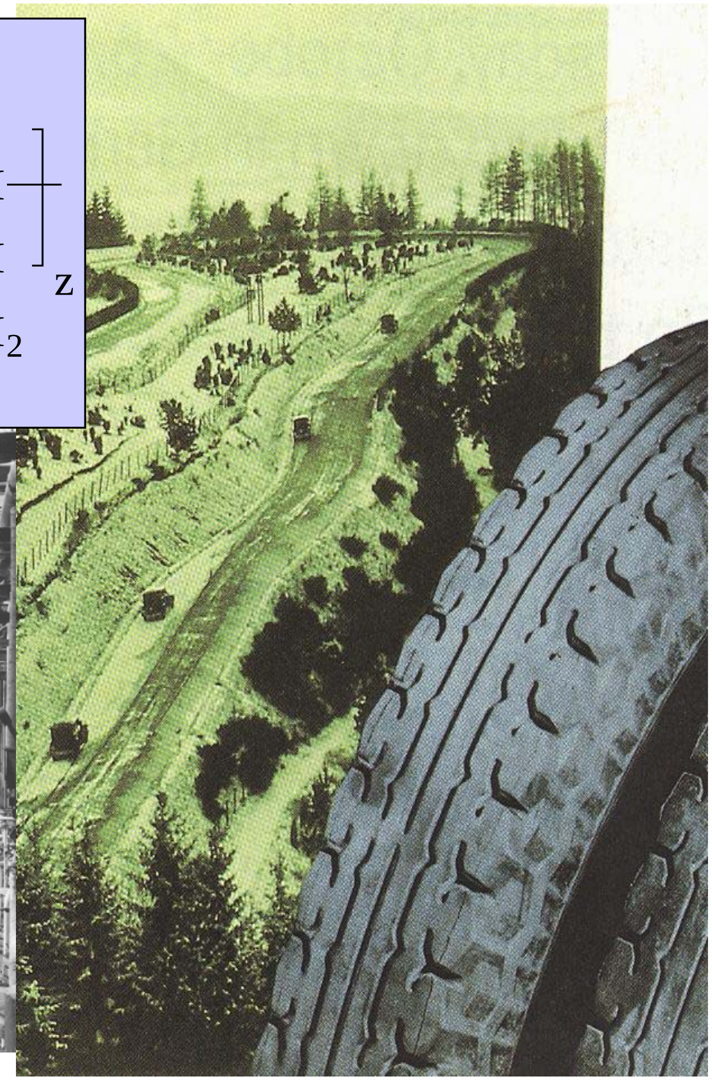
Carl Duisberg at 22 years of age

Original samples of Bayer's methyl rubber preserved for over 70 years.

Kaiser Wilhelm II was one of the first to have tires made out of Bayer's methyl rubber.

Buna S Rubber





The famed Nürburgring racing course where Buna rubber was tested.

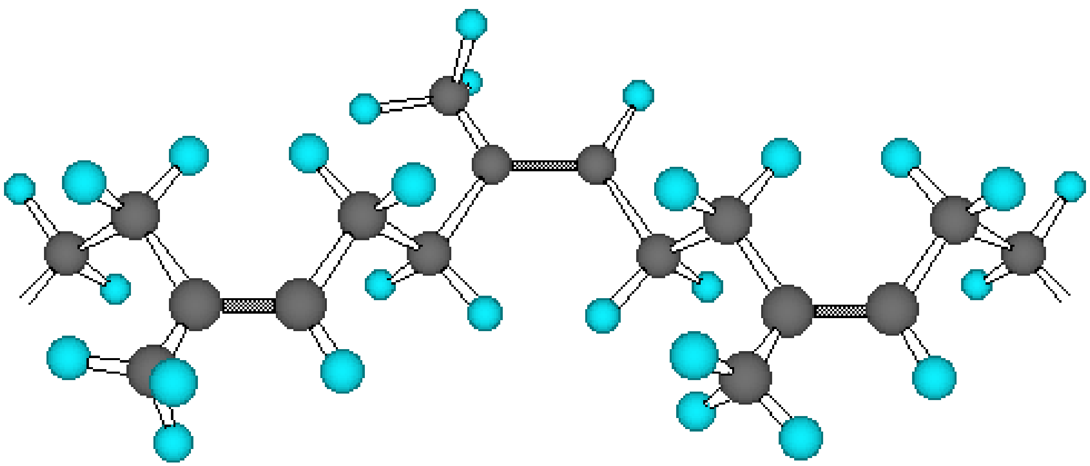
WW II

"If we fail to secure quickly a large new rubber supply, our war effort and our domestic economy will both collapse."—Baruch Committee report, September 1942

Still an Art ?

A Firestone employee examining a truck tire

Firestone/Bridgestone truck tire prior to curing



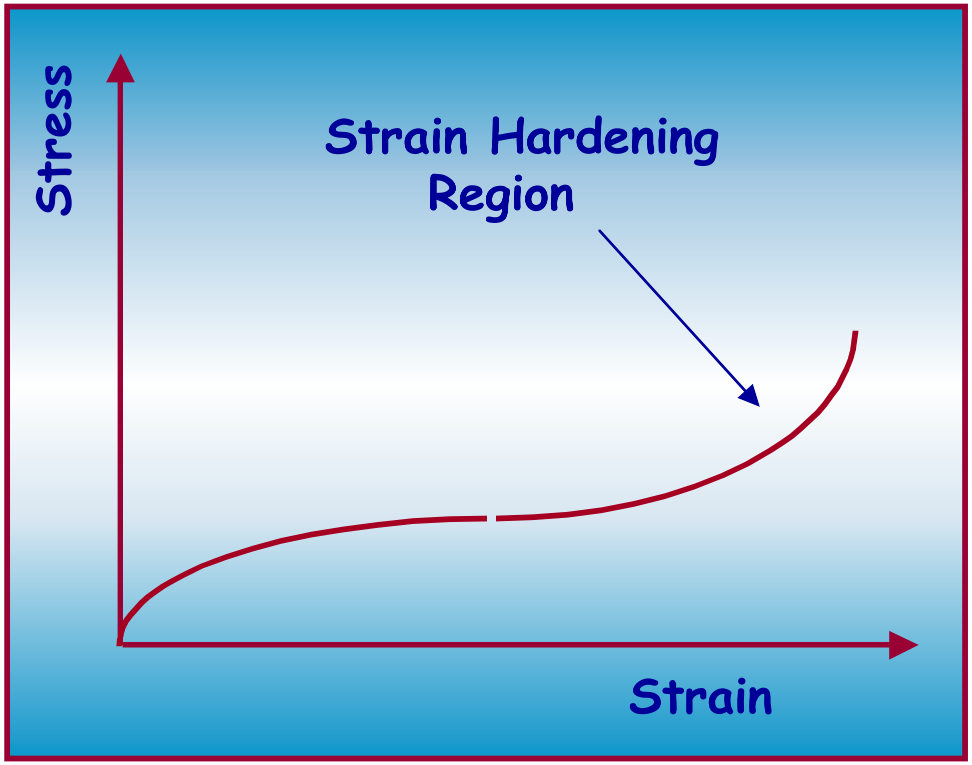
A modern Firestone/Bridgestone facility

Another Application

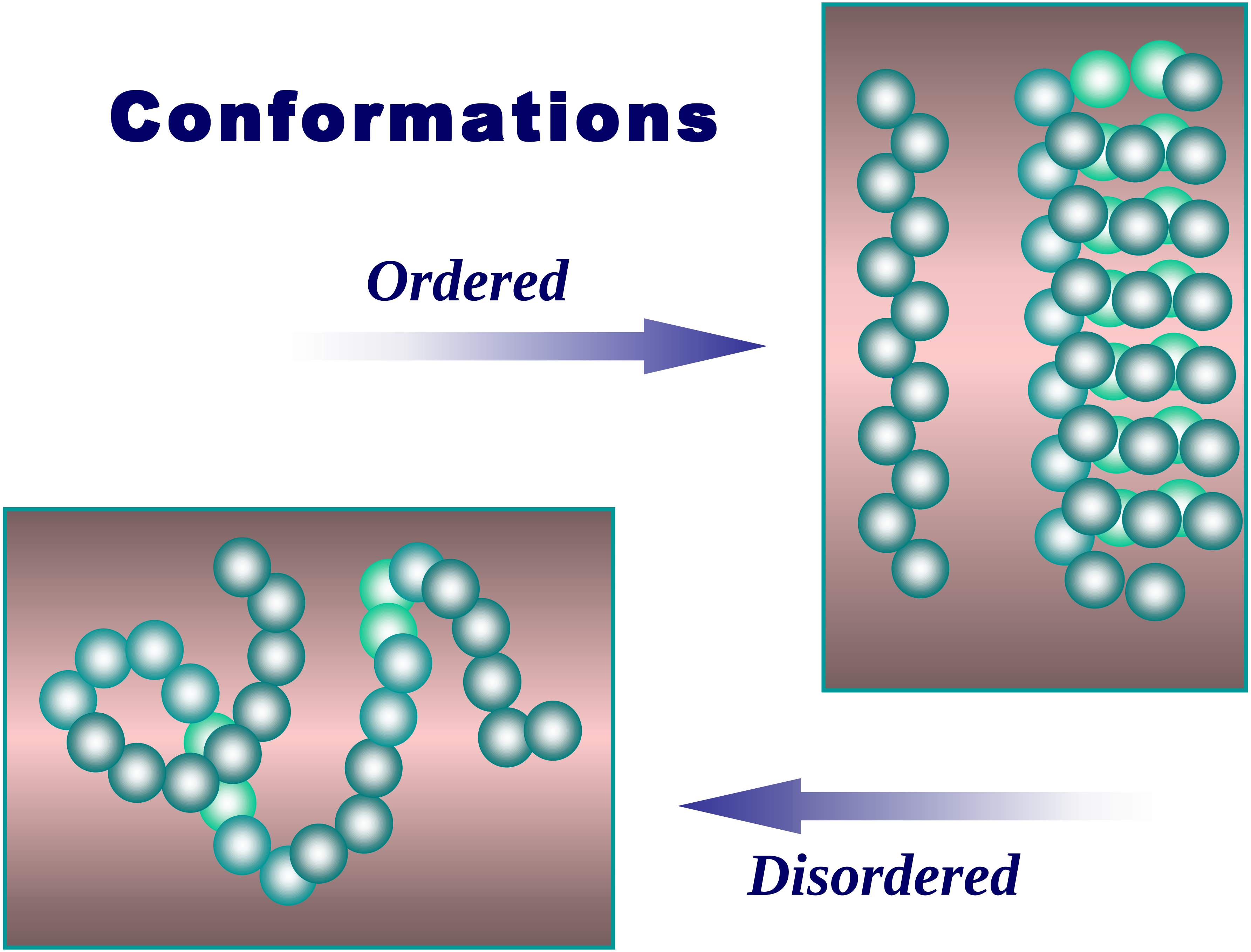
Charles II

Harrison Experiment

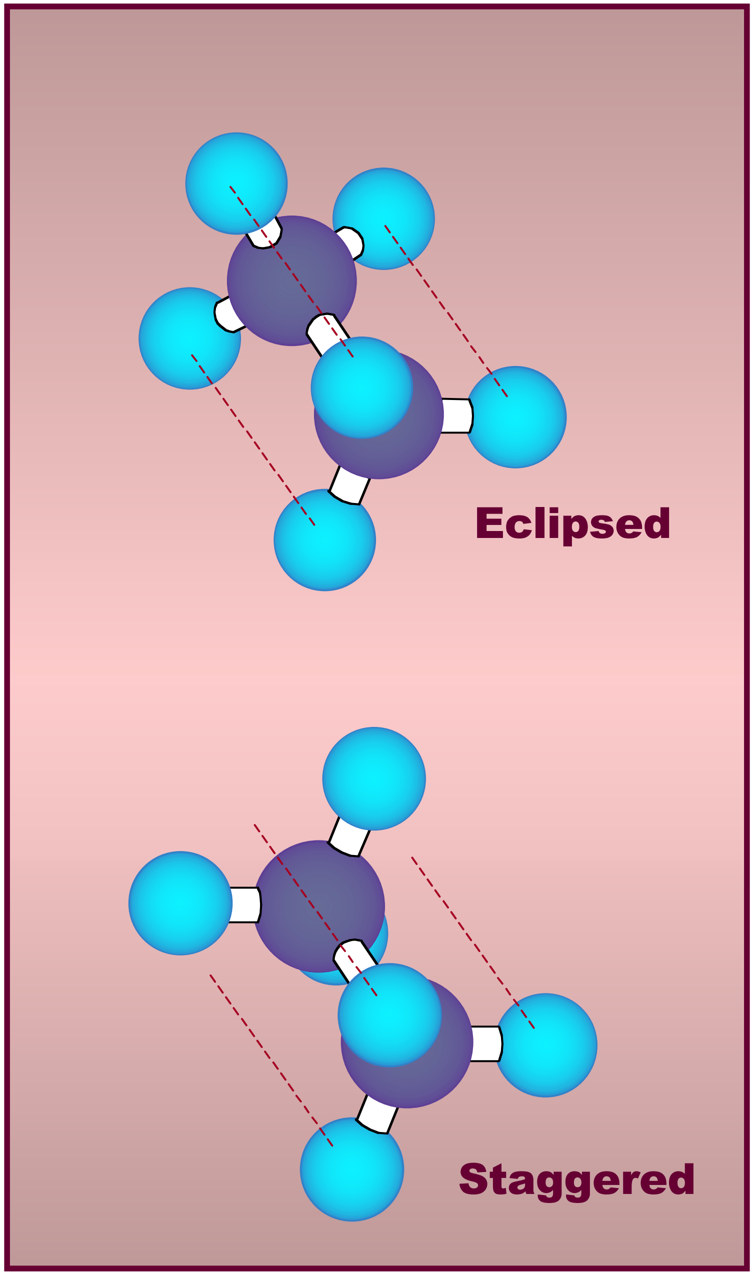
- Material Derived from Trojan-Enz
- Samples Cut Out With a Dog Bone Cutter
- Test -- Tensile Elongation (1 cm per minute)
- Uniaxial Deformation
  ~ 1,000 %
- Biaxial Deformation
  ~ 300 %
- Estimated Burst Pressure
- ~ 57 psi ~ 4 atm.

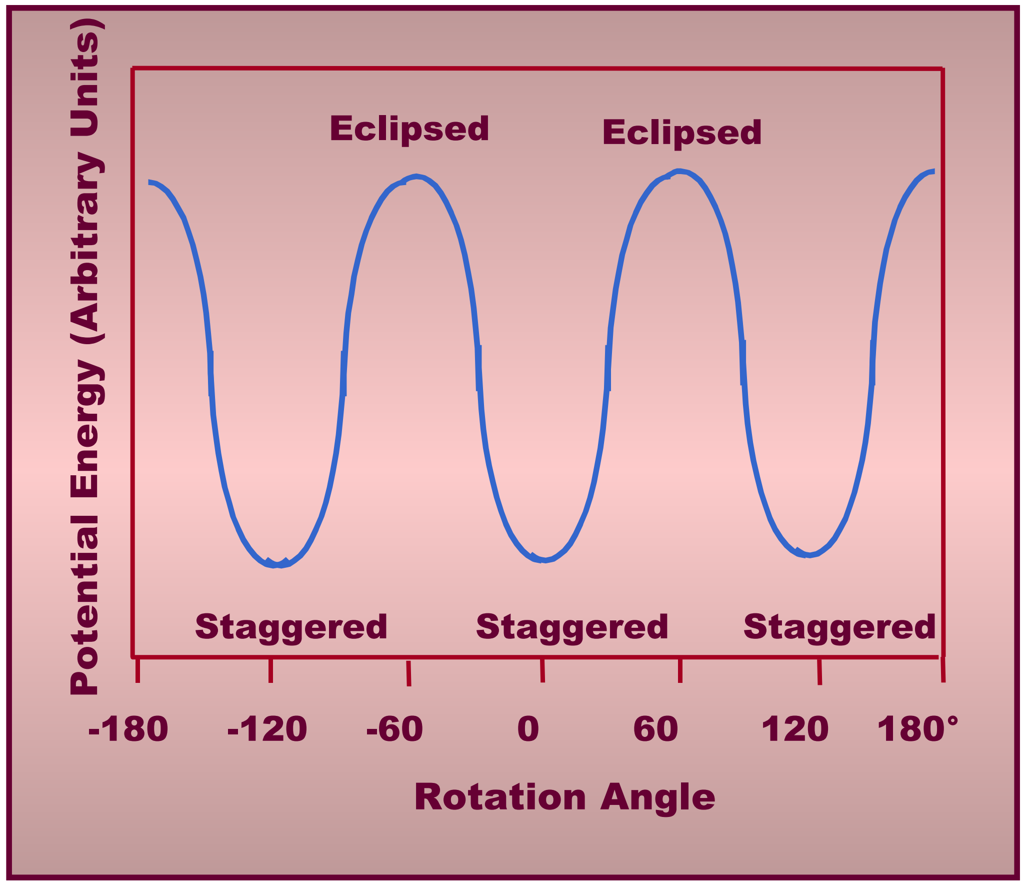


Conformations

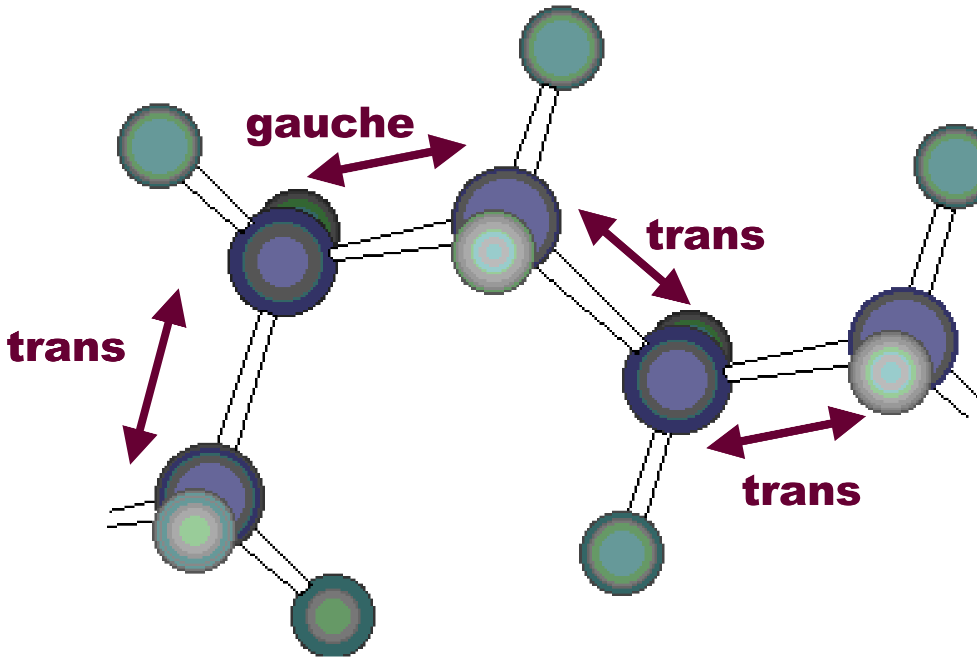


Conformations

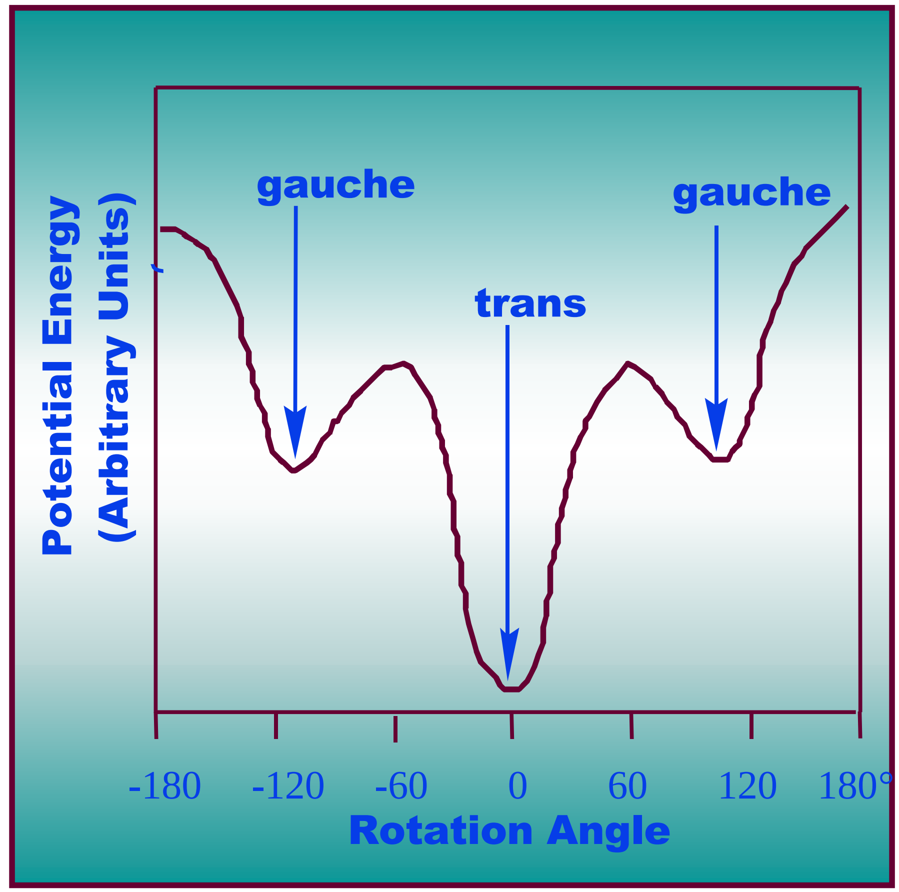




Conformations; or how do Chains Fold

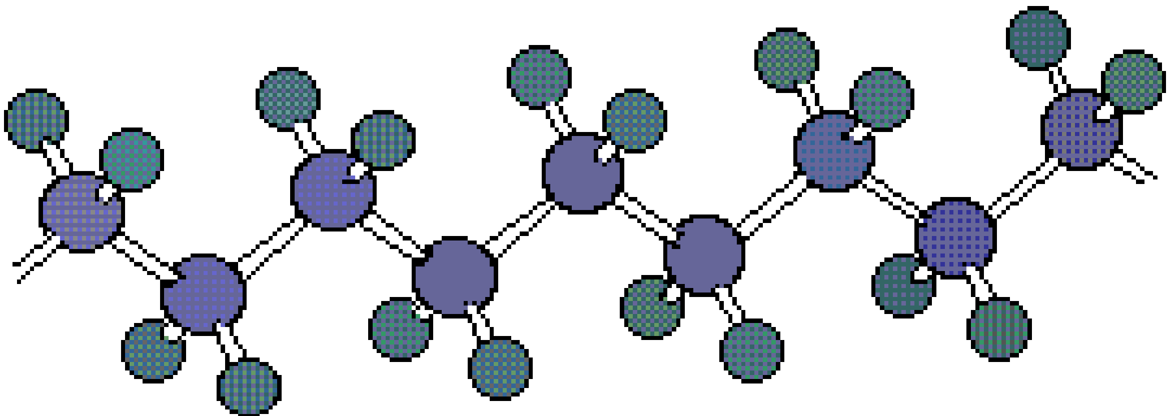


Polyethylene



Interesting Questions

- *Why Doesn't the Chain Just Sit in its Minimum Energy Conformation?*
  - *e.g. polyethylene*



- *What is the Effect of Thermal Motion ?*

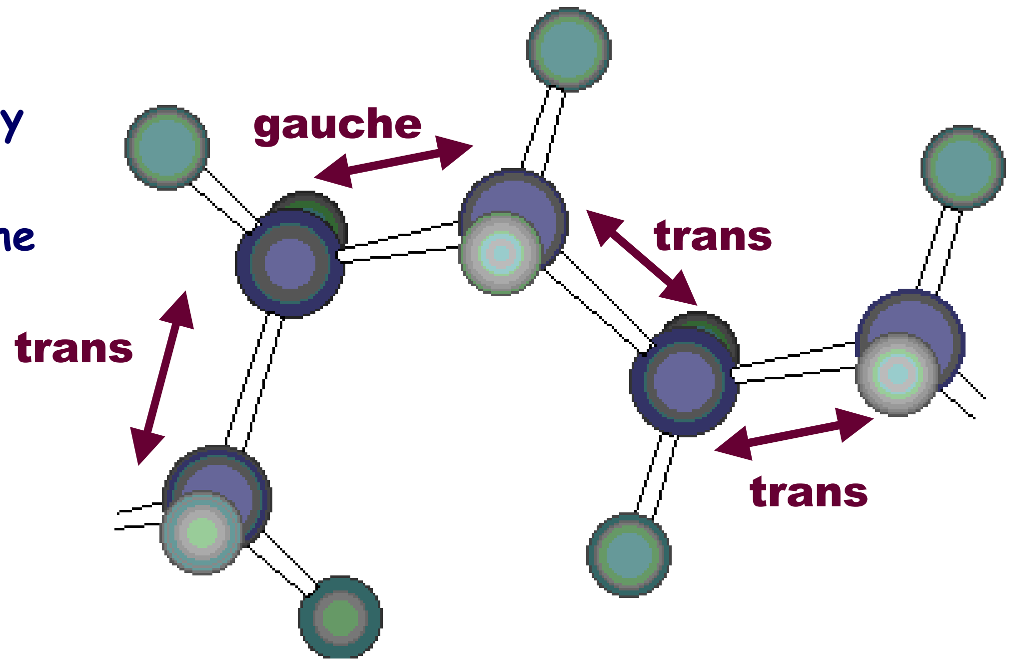
- *How Many Shapes or Conformations are Available to a Chain ?*

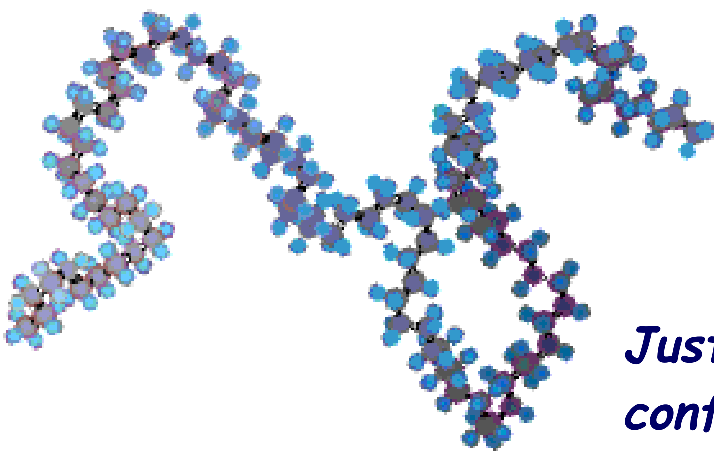
How Many Shapes or Conformations are Available to a Chain ?

A Simple Estimate

- *Assume each bond in the chain is only allowed to be in one of three conformations, trans, gauche and the other gauche*

- *Assume each of these conformations has the same energy*



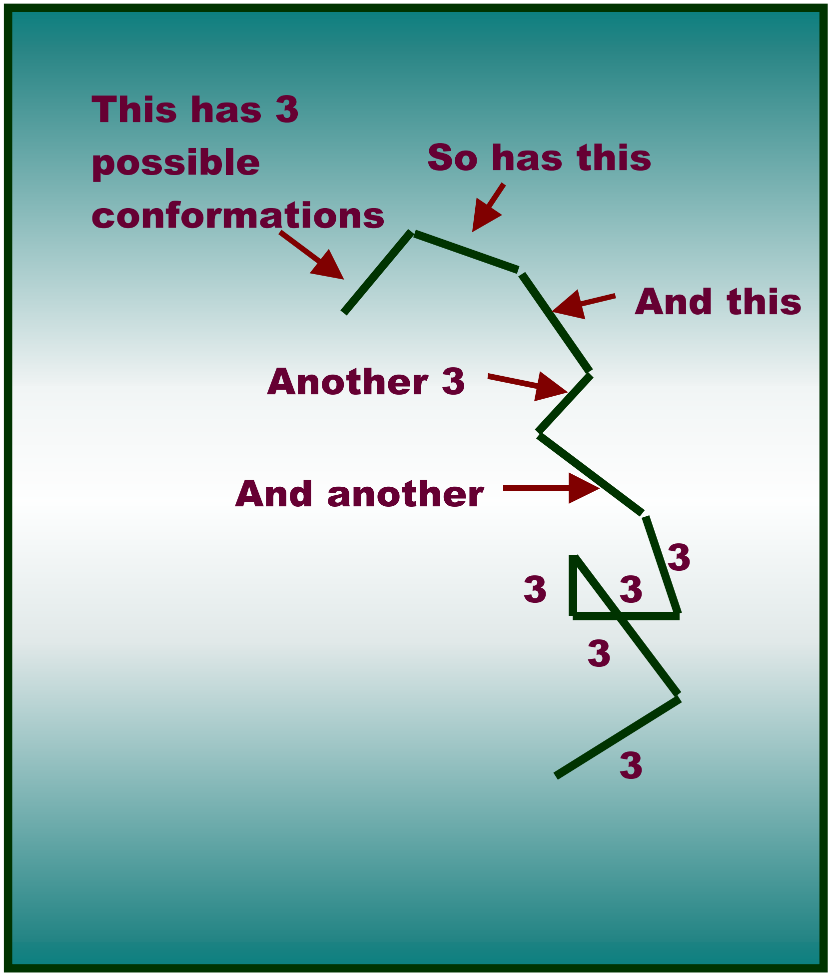


Just one of many conformations or configurations

How Many Conformations are Available to a Chain?

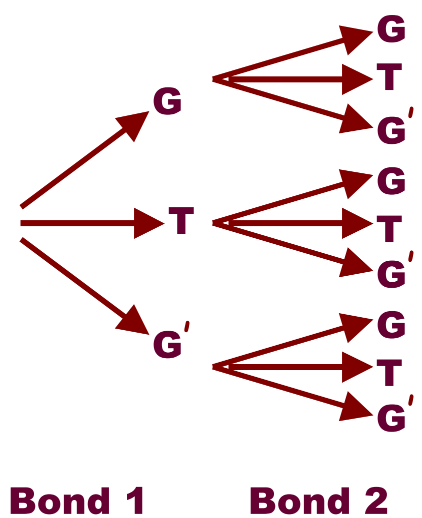
The first bond can therefore be found in any one of three conformations, as can the second, the third, and so on. How many configurations are available to the first two bonds taken together (ignoring redundancies).

A. 3+3=6
B. 3x3=9

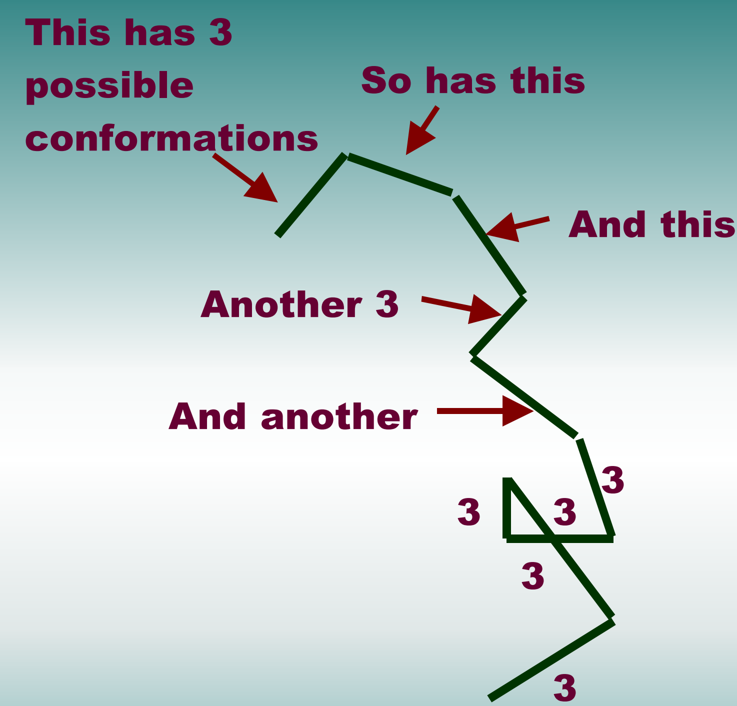


How Many Conformations are Available to a Chain?

Pascal's triangle



How many arrangements are there for a chain with 10,000 bonds ?



For this chain of 10 bonds there are 3.3.3.3.3.3.3.3.3.3 = 3^{10} possible arrangements. Or have we over-counted?

How Many Conformations are Available to a Chain Consisting of 10,000 Bonds ?

The answer would seem to be simple;

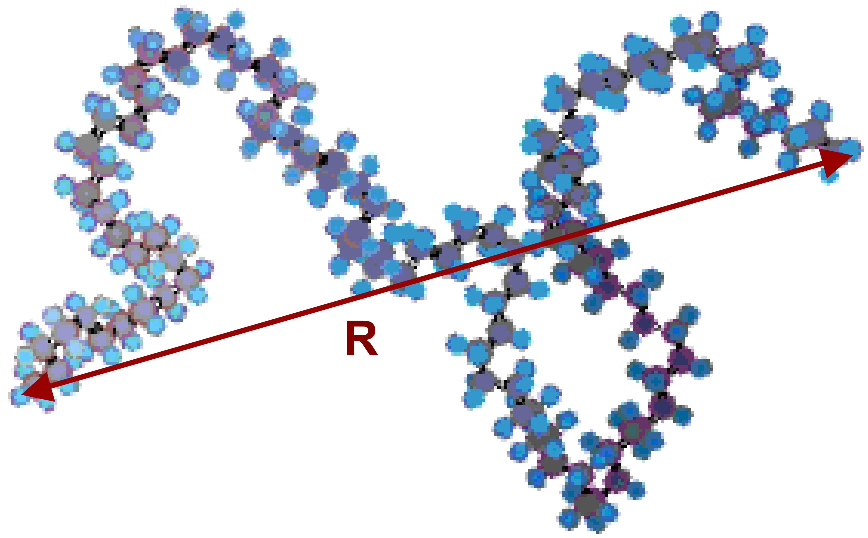
$$3^{10,000} = 10^{4,771}$$

But you have to be careful in doing these types of calculations. You have to account for redundancies.

Crucial Point; even after accounting for redundancies there are one hell of a lot of (distinguishable) configurations available to a chain. So, how on earth can we relate structure, or in this case the absence of structure, to properties?

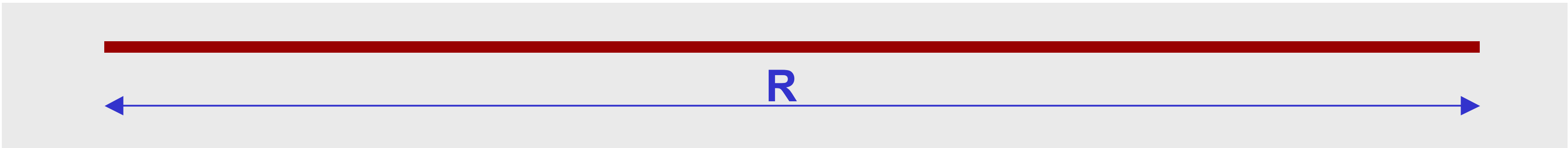
The Chain End-to-End Distance

- *It is the enormous number that saves us as it permits a statistical approach.*
- *But we will need a parameter that tells us something about the shape of the chain.*

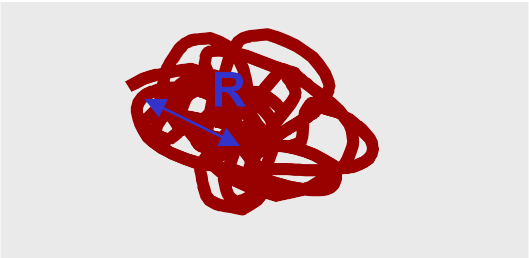


The Chain End-to-End Distance

The distance between the ends will be equal to the chain length if the chain is fully stretched out;



But may approach zero if the chain is squished in on itself forming a compact ball.



Intuitively, one would expect most chains to lie somewhere between these extremes.

Random Walks and Random Flights

Redrawn from J. Perrin, Atoms, *English translation by D. L. Hammick, Constable and Company, London, 1916.*

Random Walks and Random Flights

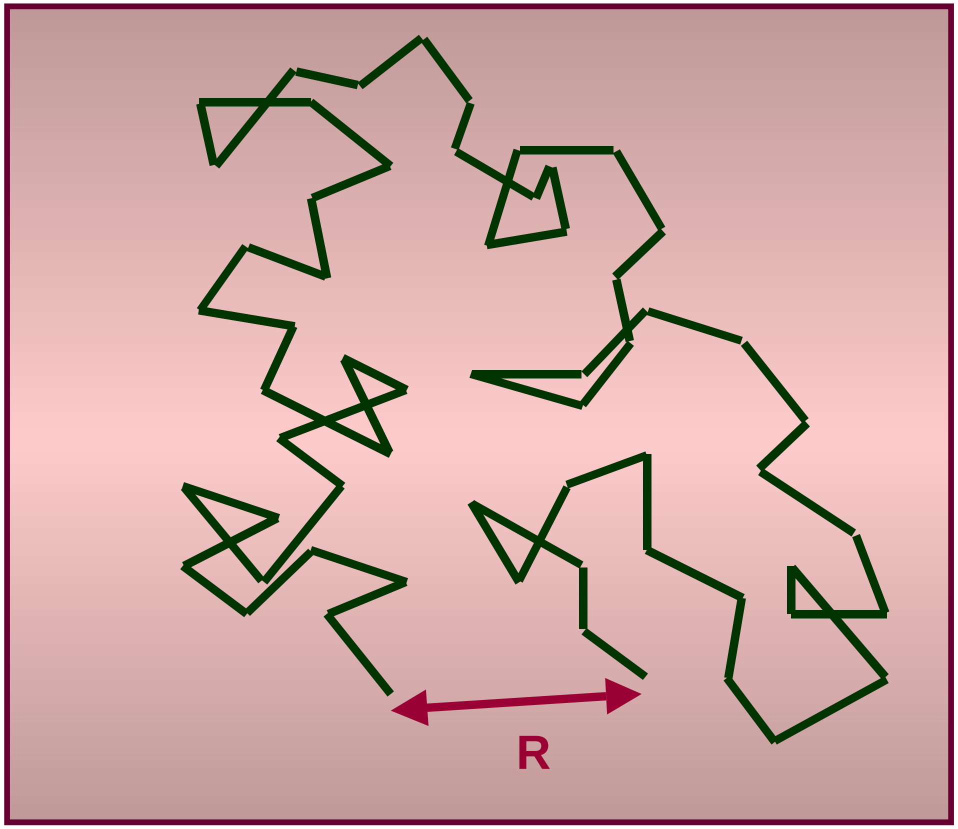
For a polymer chain;

- Consider steps of equal length, defined by the chemical bonds.

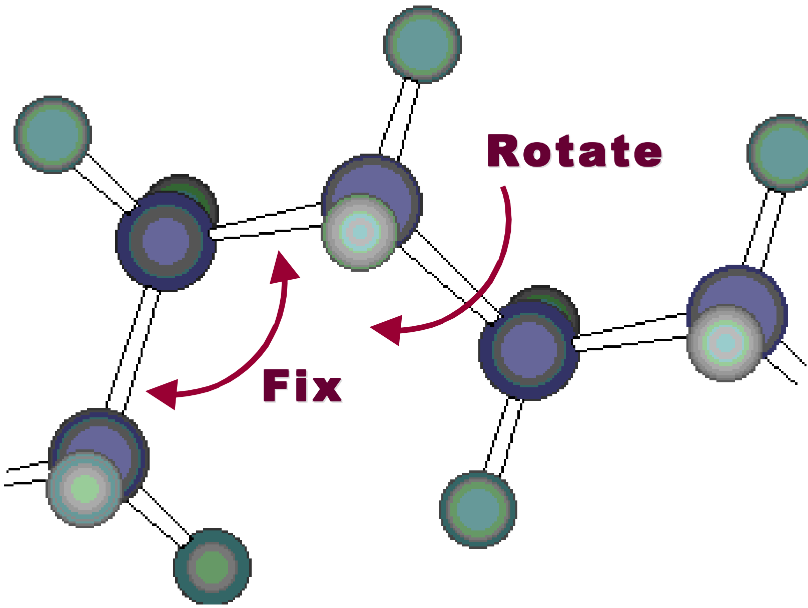
Complications;

- A polymer chain is sterically excluded from an element of volume occupied by other bits of itself.

- The "steps" taken by a chain are constrained by the nature of the covalent bond and the steric limitations placed on bond rotations.

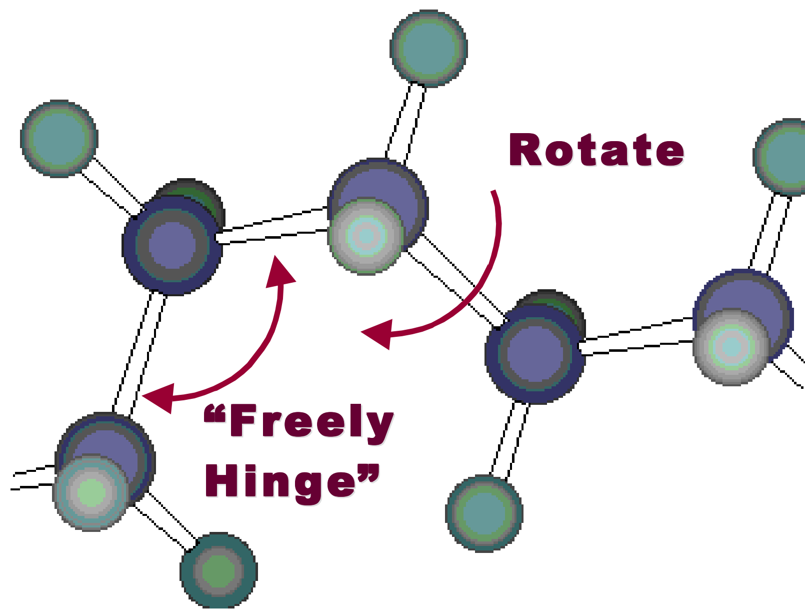


The Freely Jointed Chain



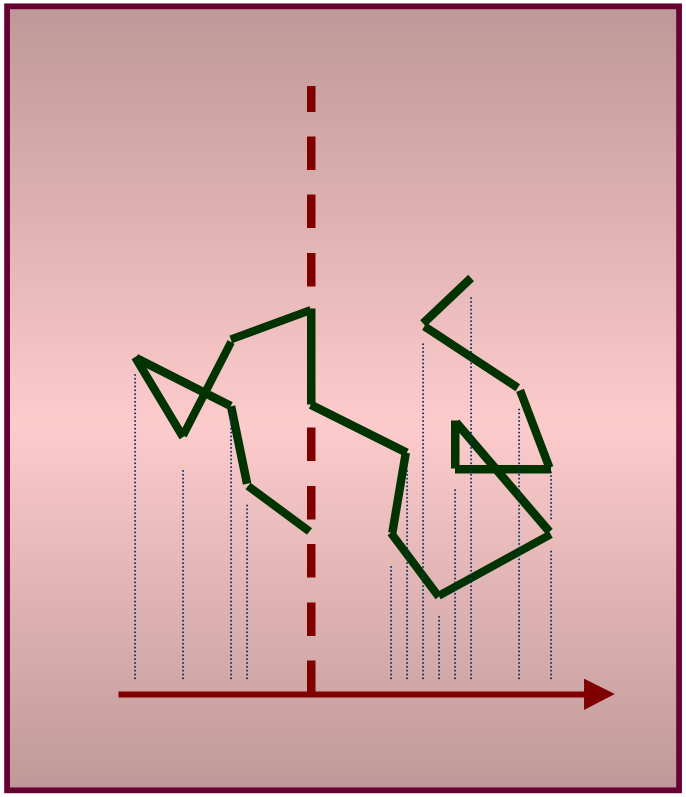
What we will assume and still get the right answer . . . more or less

The way it really is . . . more or less



Random Walks and Random Flights

- To begin with we are only going to consider a one- dimensional walk.
- Actually, that is all we really need.
- Imagine a three dimensional walk projected onto (say) the x-axis of a Cartesian system
- There will be some average value of the bond length <l>, that we can use*.
- We can then sum the contributions of projections in all three spatial directions (remember Pythagoras ?) to get the end -to - end distance R



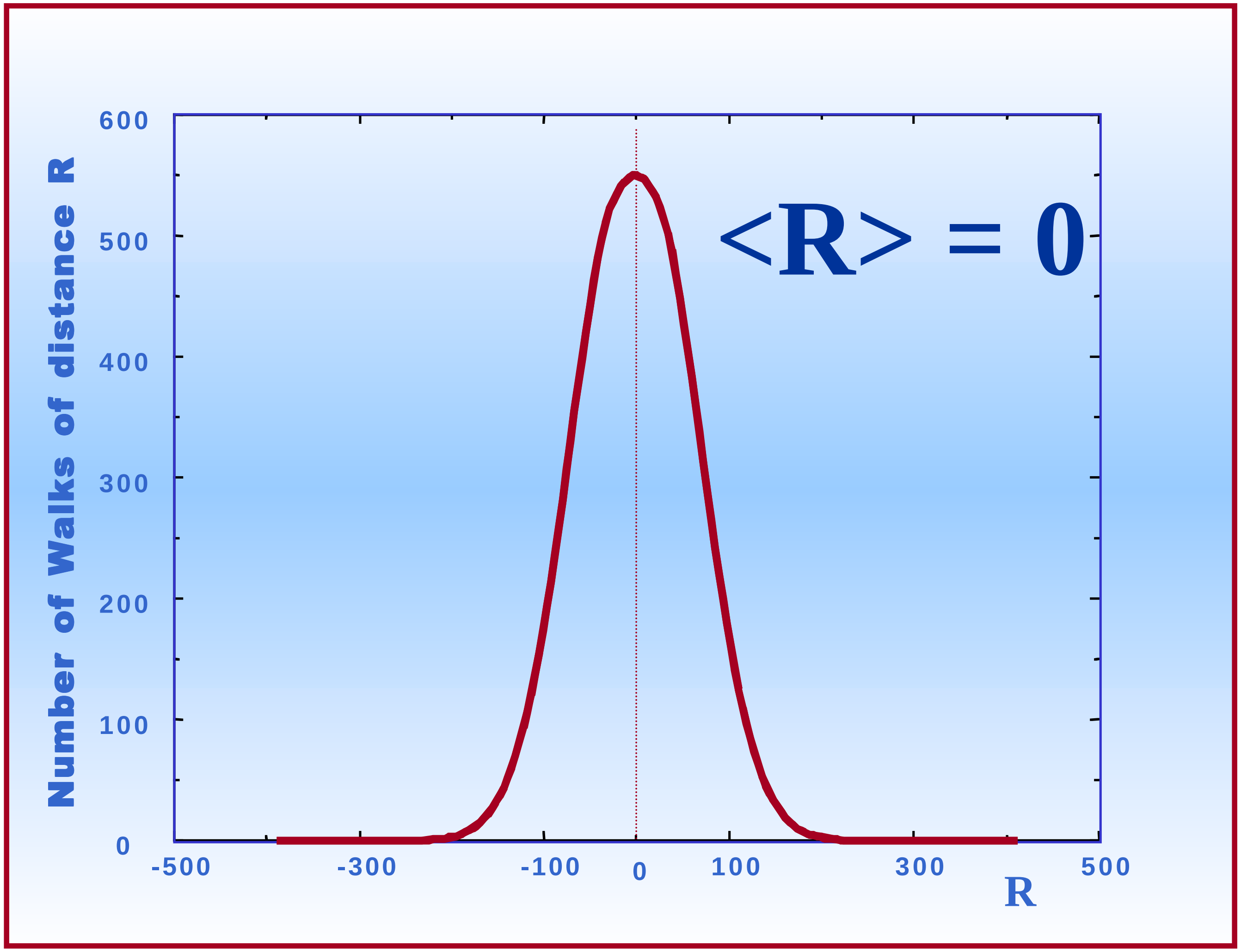
* This is actually calculated using the same arguments as we are going to use for the random walk!

A One-Dimensional Drunken Walk

Q: *What is the average distance traveled from the Pub for drunken walks of N steps? (Assume each step is 1 unit in length).*

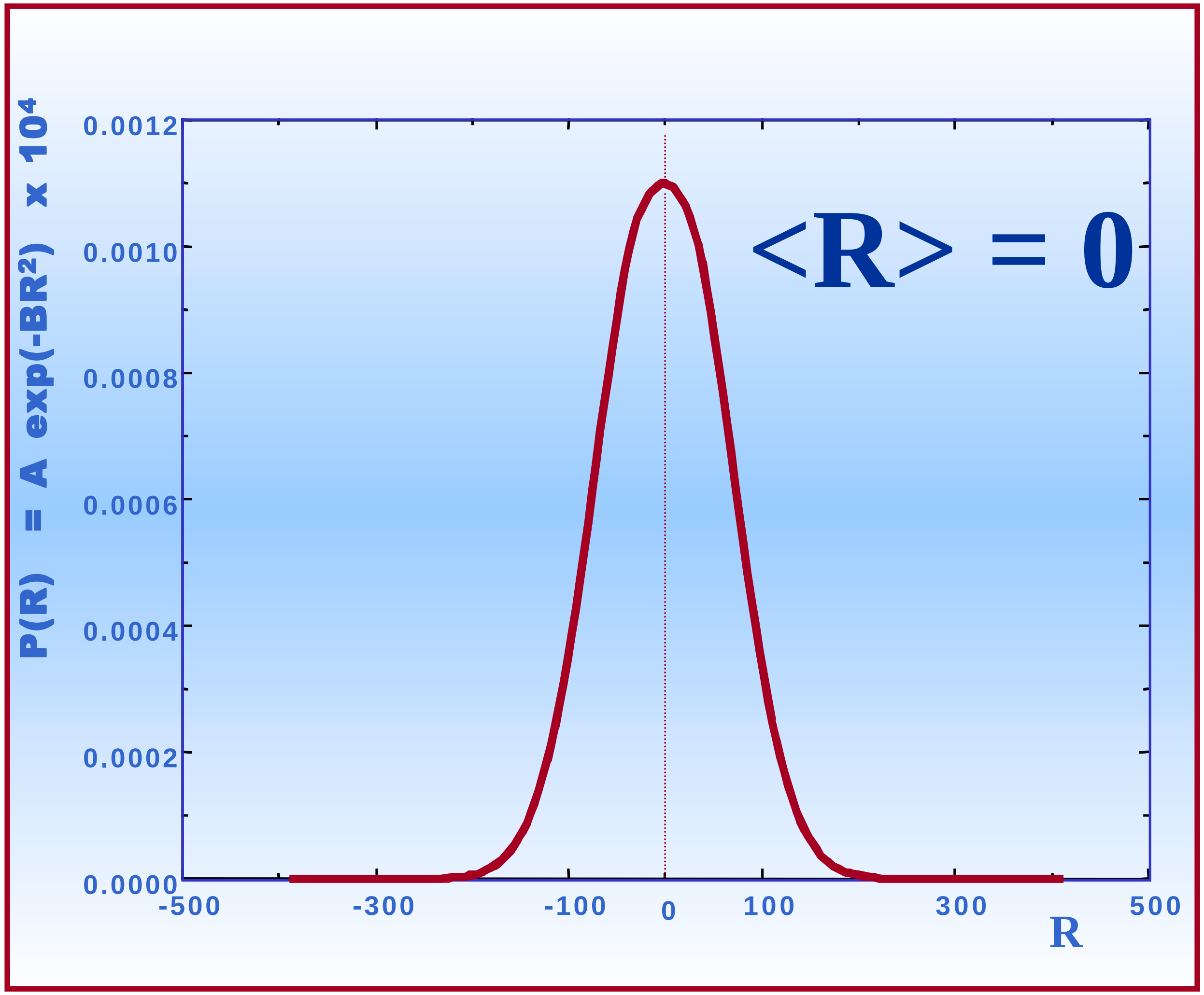
WALK	R
1	+30
2	+50
3	-40
4	-50
5	+40
6	-30
.	.
.	.

Intuitive Answer



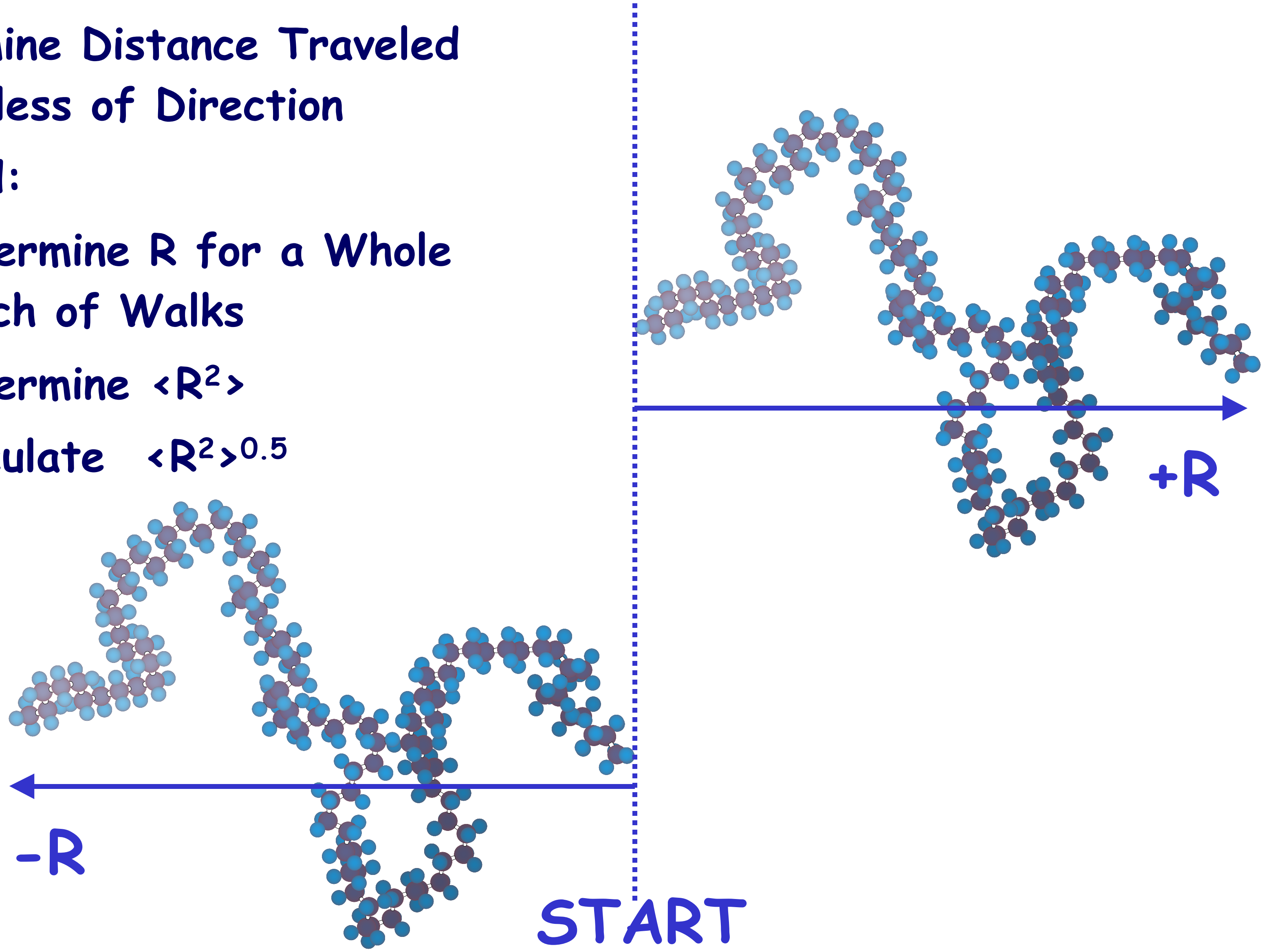
Probability Distributions

- Another way to graph this is to plot the *fraction* of walks that end up a distance R from the pub.
- Each of these values then also represents the probability that a walk of N steps will have an end - to-end distance R.
- This is a probability distribution, P(R), and if you know some statistics you may guess that the shape of the curve will be Gaussian (for large N). (See equation on y-axis). We'll come back to this.

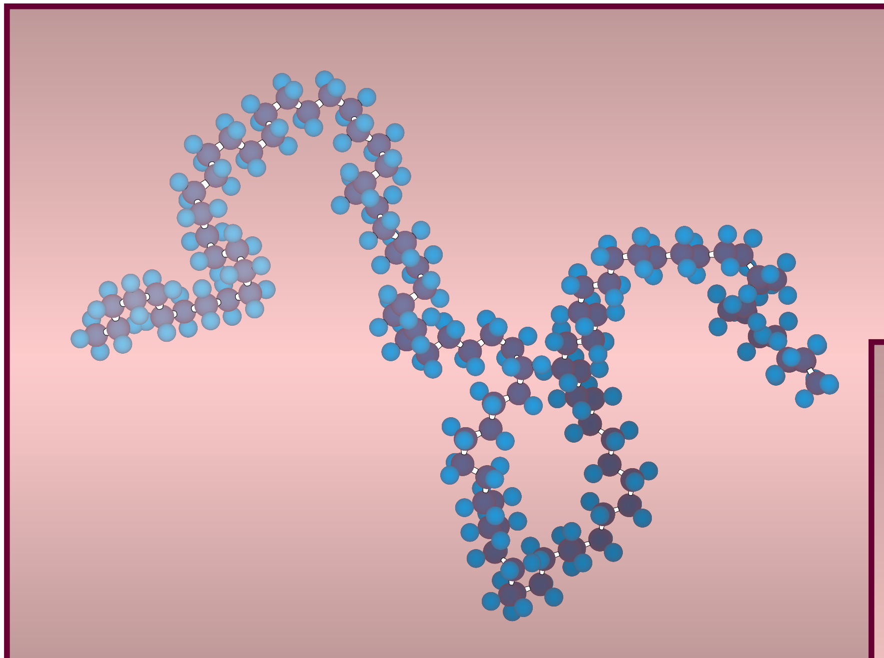


What We Need To Do

- Determine Distance Traveled Regardless of Direction
- Method:
  - Determine R for a Whole Bunch of Walks
  - Determine $\langle R^2 \rangle$
  - Calculate $\langle R^2 \rangle^{0.5}$

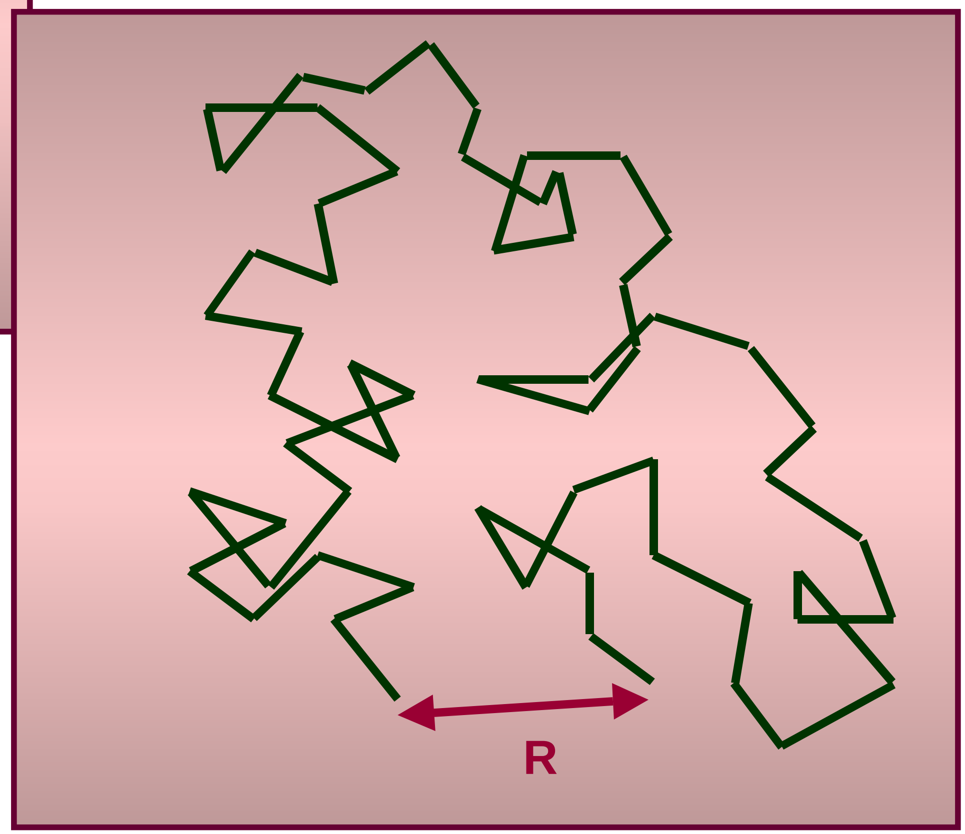


The Root-Mean-Square End-to-End Distance



$\langle R^2 \rangle = N\,l^2$

$\langle R^2 \rangle^{0.5} = N^{0.5}\,l$



If $N = 10{,}000$, $l = 1$;

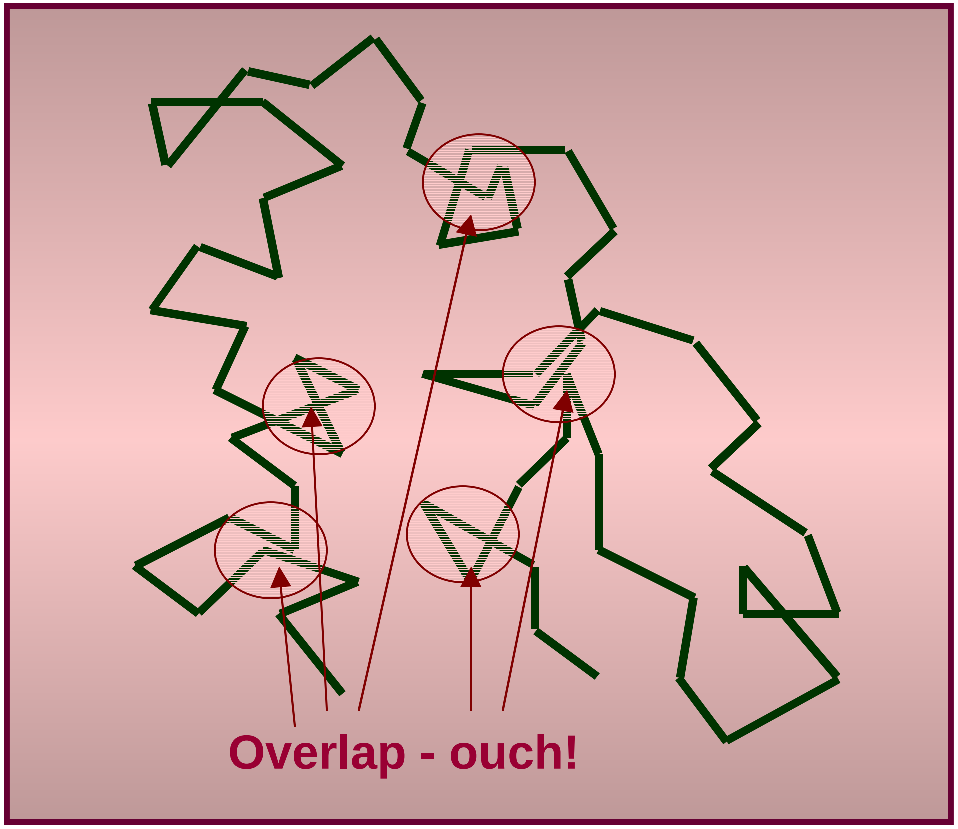
$\langle R^2 \rangle^{0.5} = 100$! ! !

Real Chains

- Even sterically allowed bond rotation angles will not be independent of one another. Local overlap can occur

- Incorporate corrections (using the Rotational Isomeric States Model) into a general factor C_∞ , and we can now write;

$$< R^2 >= C_\infty N l^2$$



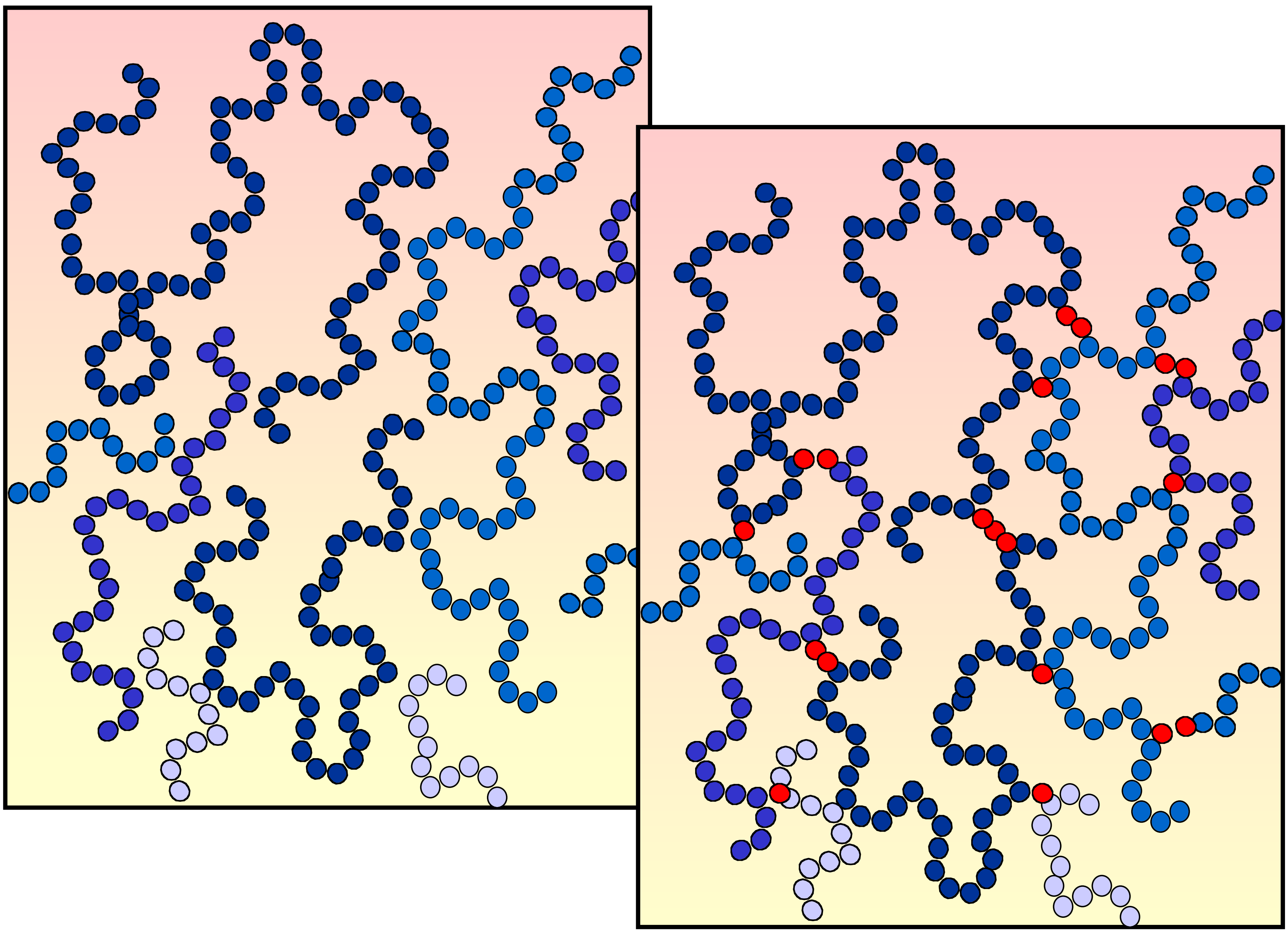
Crucial Points

- *We have figured out a way to Describe a collection of random Chains*

- *A qualitative understanding of Rubber elasticity immediatly follows*

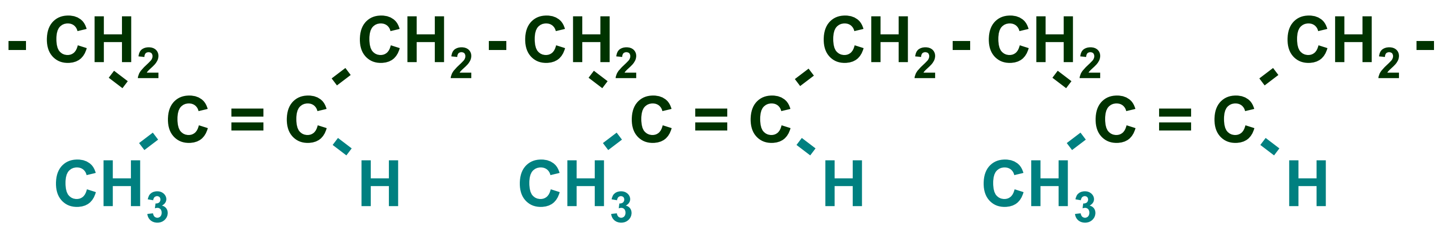
- *A pathway to more rigorous and quantitative work is opened up*

The Importance of Cross-Linking



Network formation by cross-linking

An example of cross linking is the reaction of natural rubber or poly(isoprene) ;



with sulfur (or, as we prefer, sulphur) . The sulfur interconnects the chains by reacting with the double bonds.

Network formation by cross-linking

This is the process originally discovered by Charles Goodyear, (*vulcanization*). Note that the linkages shown on the right actually consist of short chains of sulfur atoms) Cross - linking is crucial in making elastomers with useful properties, as it prevents the chains from slipping past one another.