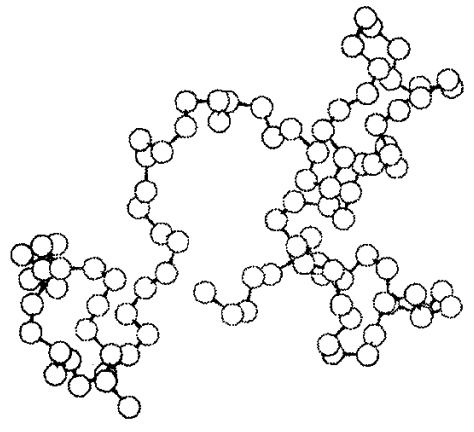


What is the Volume occupied by a single polymer chain?

In practice, a very simple and useful model for the path traced out by following along the backbone of the chain is a

Random Walk:



The polymer chain consists of n bonds. Each bond is a "step" of length l in a random direction after the previous step.

- The full ("contour") length of the path is: $L = nl$
- The average distance from one end of the path to the other is related by: $\langle r^2 \rangle = nl^2$
- The average distance of each junction from the center of mass is related by: $\langle s^2 \rangle = \frac{1}{6} nl^2$

Compare the volume of the "envelope" which surrounds the polymer chain with the sum total volume of all the "atoms" of the chain:

$$V_{\text{envelope}} \propto [\langle s^2 \rangle]^{3/2} = K_1 n^{3/2} l^3$$

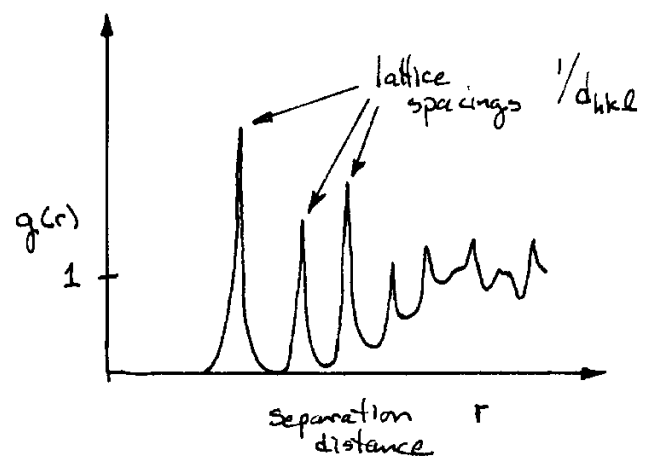
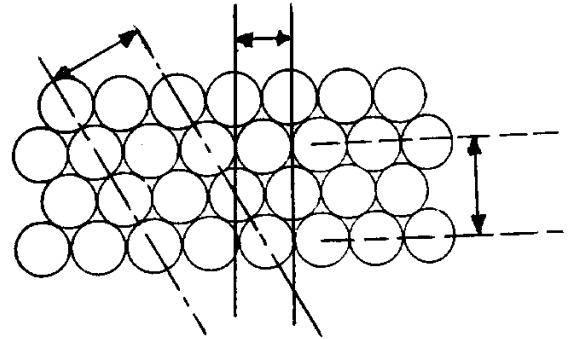
$$V_{\text{atoms}} \propto nl^3$$

$$V_{\text{atoms}}/V_{\text{envelope}} \propto n^{-1/2}$$

For polymers, n is typically very large, on the order of $10^5 - 10^7$ so the space inside the envelope is mostly empty! For realistic densities of amorphous polymers, polymer chains must be highly intertwined.

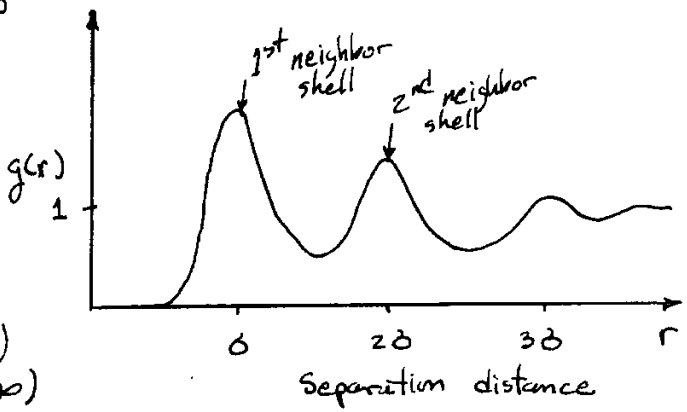
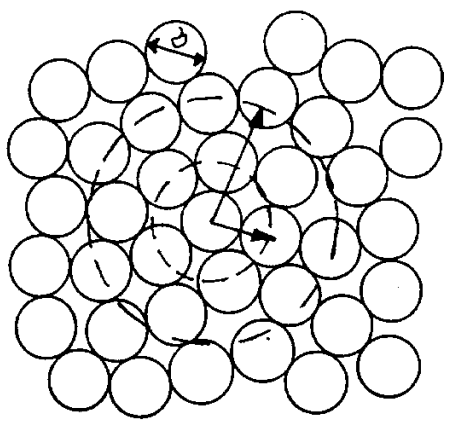
The Pair Distribution Function $g(r)$ is used to give a quantitative description of atom structure in dense phases. It is a plot of the (normalized) population of atoms at a distance r from a central, reference atom. In a highly ordered phase like a crystal, atoms are located at well-defined lattice sites, which are separated by exact lattice spacings.

These give rise to sharp peaks in the Pair Distribution Function (or PDF). In a perfect, infinite crystal, these peaks are Dirac delta spikes and persist to very large values of r . In a real crystal, thermal motion of the atoms, imperfections in the crystal lattice, and finite crystallite sizes limit the distance r to which these sharp peaks persist, causing them to eventually "smear out" so in a homogeneous phase.



In a dense but amorphous liquid or glass phase, atoms are not localized to discrete lattice sites. The atoms may undergo long range motion (liquid) or not (glass) but on average describe a fairly

close-packed structure characterized by "shells" of neighboring atoms, referred to as nearest-neighbor and next-nearest-neighbor shells, etc. Each shell is roughly one atomic diameter further out radially from the reference atom than the previous shell. Because the packing is imperfect in the amorphous phase, each shell is not fully occupied and there is considerable broadening of each peak. At large values of r the atoms appear uniformly distributed, with equal population at any (large) distance ($g(r) \rightarrow 1$ as $r \rightarrow \infty$)



Mathematically, the PDF may be written:

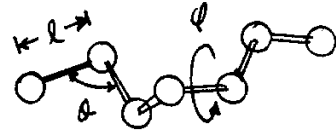
$$g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(r - d_{ij}) \right\rangle$$

Dirac delta: $\delta(x) = 1$ if $x=0$
 $= 0$ if $x \neq 0$

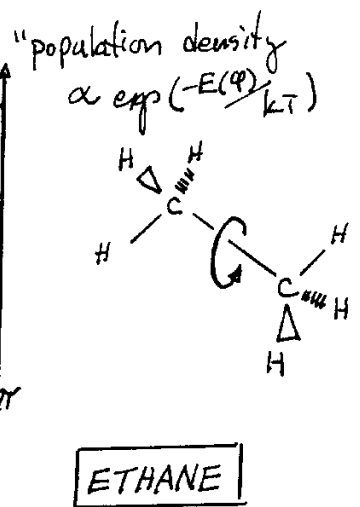
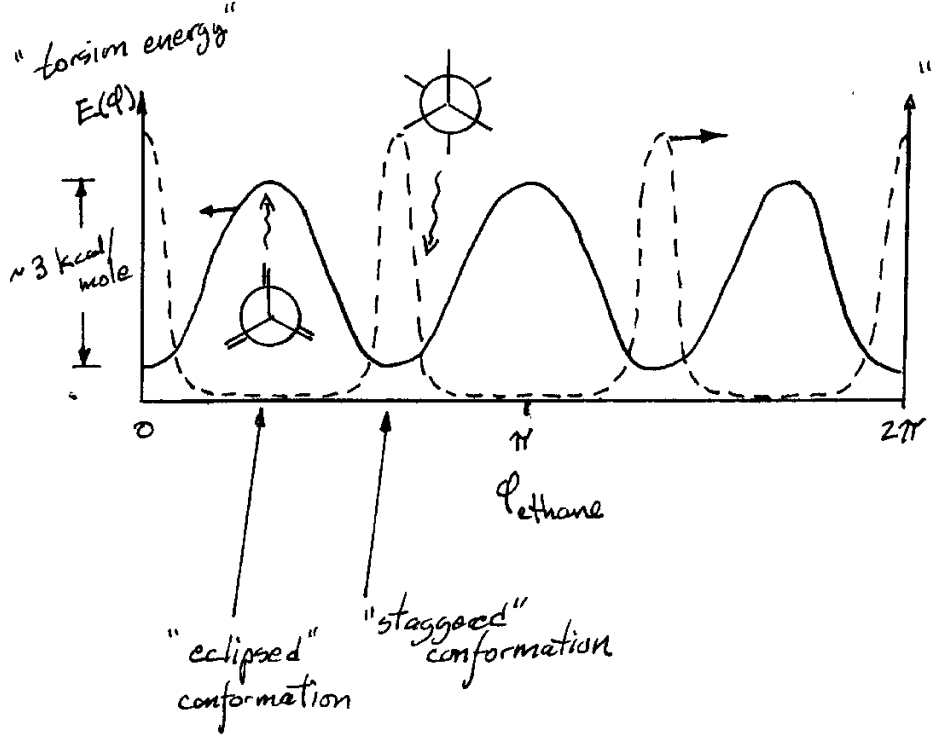
N is the number of atoms used in the summation, V is volume, the brackets indicate an average over all pairs of atoms i & j whose distance of separation is d_{ij} , and N^2/V is a normalization constant.

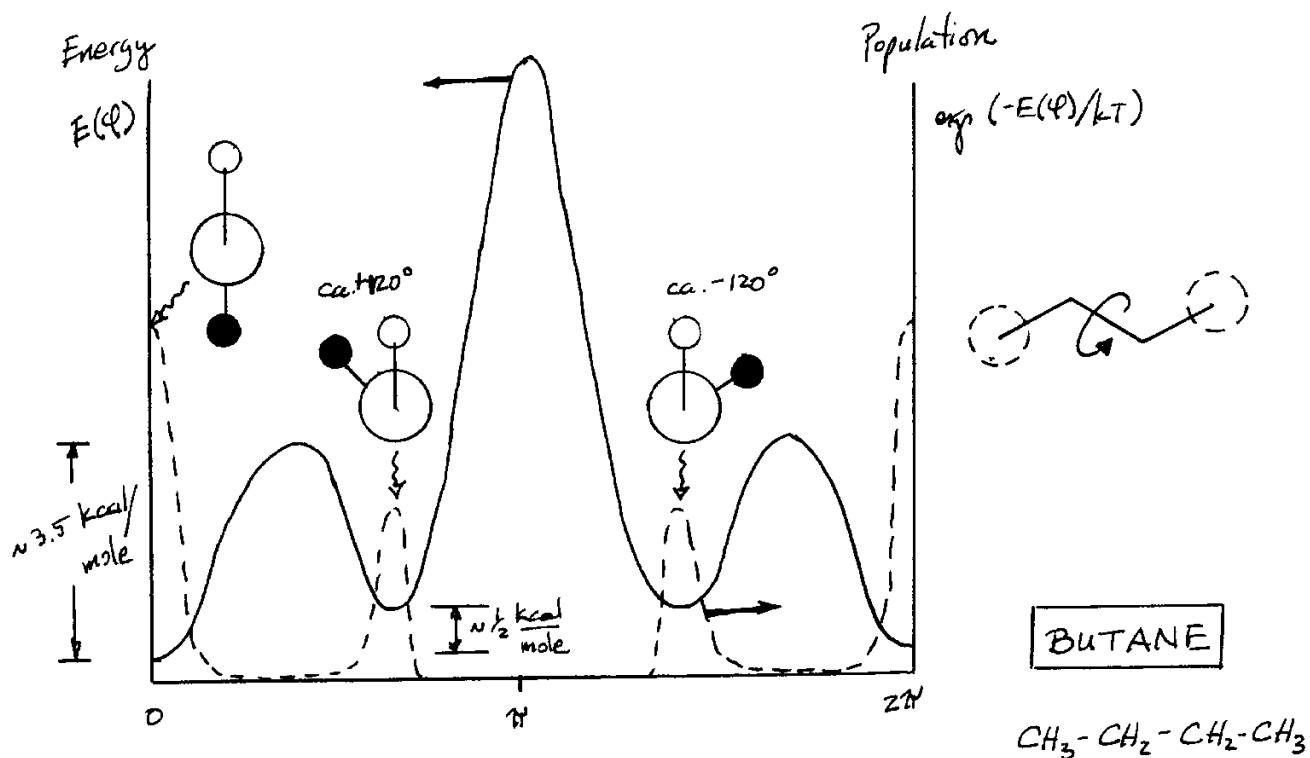
The Conformation of a polymer chain describes the spatial arrangement of all the atoms of the chain. Unless the polymer chain has long "branches" or "side chains", the conformation is well-defined by the path of the polymer "backbone" or "main chain".

The conformation depends on bond lengths (l) and bond angles (θ) but these are usually very tightly constrained. It also depends on the torsions



(ϕ) of each bond. The conformation is a strong function both of the particular values of ϕ_i (i =each bond in the chain) and also of the sequence of ϕ_i 's. As an example of preferred values for ϕ , consider the case of the simplest such alkane: ethane (C_2H_6)

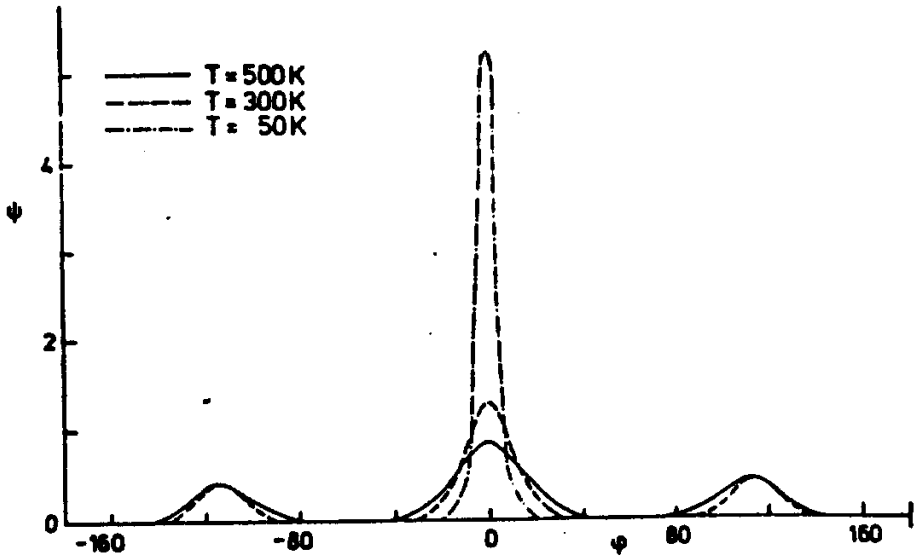
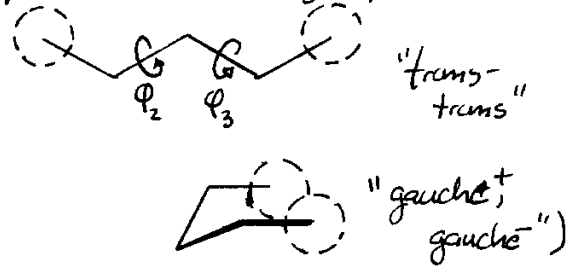




Just like ethane, butane has 3 strong minima (values of ϕ where the torsion energy $E(\phi)$ is low). Because of the "crowding" energy when the two $-CH_3$ groups come close together, very few torsions will have values of $\phi = 180^\circ$. In fact, all values of ϕ_i will cluster around the 3 minima: 0 , $+120^\circ$ and -120° . In ethane, these are equally populated ($\propto \exp(-E(\phi)/kT)$). In butane, even partial crowding makes $\phi_i \approx 0$ (called "trans") more stable than either $\phi_i \approx +120^\circ$ (called "gauche plus") or $\phi_i \approx -120^\circ$ (called "gauche minus").

n-PENTANE

Here too, to a first approximation, each torsion clusters around 3 values independent of the other torsion. However, one conformation (g^+g^- or g^-g^+) sees additional crowding of terminal $-CH_3$ groups:



Shown below is a ~~topographic~~ "topographic" map of the torsion energy $E(\phi_2, \phi_3)$

