Polymers are huge molecules constructed out of many identical building blocks called monomers. Here we shall restrict ourselves to linear molecules in which every monomer has one successor and/or predecessor. The number of monomers per polymer may vary from a few hundreds to many thousands.

Figure 1. Polyethylene in the all-trans configuration

The polymer is drawn here in the trans conformation. Many other conformations exist, and it is the aim of the RIS model to describe the statistics of these conformations.

We shall describe the conformation of the polymer by giving the position vectors of its backbone atoms, in this case the carbon atoms. The positions of the remaining atoms then usually follow by simple chemical rules. So, suppose we have N+1 monomers, then we have N+1 position vectors

We then have N-1 bond vectors

and N-2 dihedral angles

The dihedral angle $\phi_i$ is the angle between the plane of the vectors $r_{i-1}$ and $r_i$ and the plane of the vectors $r_i$ and $r_{i+1}$. In order to completely specify the conformation we
should also give the \( N-1 \) angles and the \( N \) bond lengths. This description leaves six variables to fix the centre of mass and the orientation of the molecule.

As a model of the dihedral angle in polyethylene we can consider the case of n-butane. We have but one dihedral angle and the energy as a function of this angle can be calculated using DFT methods. Shown is the relative energy as a function of dihedral angle calculated using models of butane created using insightII.

The conformation with \( f = 180^\circ \) is called the trans conformation (\( t \)), the one with \( f = 240^\circ \) is called gauche plus (\( g^+ \)), and the one with \( f = 120^\circ \) is called gauche minus (\( g^- \)). Notice that at room temperature only the three minima will be populated which makes it possible to restrict interest to three conformations called \( t, g^+ \) and \( g^- \).

Now let us try to write down the energy of a polymer as a function of the angles \( f_i \). In order to do so we start with the molecule in its all trans conformation i.e. \( f_i = t \) for all \( i \). Next we successively bring the angles \( f_0, f_1, ..., f_{N-2} \) to their actual values. Every angle will then contribute to the total energy like in the case of butane i.e.
In doing so we have neglected the fact that for example the sequence $f_i = g^+ \cdot f_{i+1} = g^-$ brings the monomers $i$-2 and $i$+2 virtually to the same position, which leads to a larger positive contribution to the energy. The same holds true for the sequence $f_i = g^-$, $f_{i+1} = g^+$. This phenomenon is called the "pentane" effect because pentane is the smallest molecule in which it may occur. In order to incorporate the pentane effect into our formalism we write

It is clear that the above is also only part of the story because we have neglected the possibility that monomers $i$ and $i+n \ (n>4)$ will occupy the same position. We may say that we have included the short range excluded volume effect, but not the long range excluded volume. Short range and long range here refer to the distance along the chain. However, the treatment of long range effects is beyond the length scale appropriate for DFT methods. Here we focus on the calculation of energy parameters for statistical mechanical models of polymers. More information can be found at the website http://www.tn.utwente.nl/cdr/PolymeerDictaat/node1.html.