**Polymer Physics**
**Homework 3**
**January 28, 2022 (Due February 1 Lunar New Years)**

The persistence length or Kuhn length of a synthetic polymer is determined by bond rotations and chemical structure and topology.  For synthetic vinyl polymers such as polypropylene or polybutylene-1 the chain tacticity can have a strong impact on chain rigidity, often leading to a helical chain structure.  A number of authors have investigated the impact of tacticity on chain persistence, for instance, Tzounis, Argyropoulou, Anogiannakis and Theodorou *Tacticity Effect on the Conformational Properties of Polypropylene and Poly(ethylene−propylene) Copolymers* Macromolecules **51** 6878-6891 (2018) used Monte Carlo simulations of a single chain to quantify the impact of tacticity on persistence, Figure 2.  Recently, Chen and Luo How asymmetric chirality and chain density affect chain stiffness of polymer melts Comp. Mat. Sci. **203** 111071 (2022) used atomistic molecular dynamics to describe the impact of tacticity and tacticity distribution on a melt of 50 chains of 50 units or 100 chains of 100 units.

a)  Tacticity for polymers describes the chirality or "handedness" of polymer units.  For vinyl polymers each carbon atom has tetrahedral bonds (like a tripod with a flagpole).  Two of the bonds are attached to the polymer chain. For polypropylene one of the bonds has a methyl group (for polybutylene a ethyl group) which can be to the left or to the right as one progresses down the chain.  For two mer units with matched handedness we say we have a meso dyad, for opposite a racemic (or mixed) dyad.  NMR is used to determine tacticity and it can only measure groups of three mer units (or higher odd groupings), so we traditionally talk of the tacticity for triads, pentads, and higher odd groupings of mer units.  Explain what isotactic, syndiotactic, heterotactic, atactic mean.  For a description of persistence what would be the optimal number of mer units to consider and why?

b)  There are three main simulation methods that have been used to describe persistence, the simplest is coarse grain molecular dynamics which involves a series of beads representing molecular units that have bond and rotational (angular) potentials.  For instance, studies of the impact of short branches on persistence have been studied using CGMD simulations. Tzounis used single chain atomic Monte Carlo simulations which involves allowing bond rotation subject to minimization of the Helmholtz free energy (free energy with constant volume) after random rotations subject to steric interactions with the possibility of some random rotations.  MC simulations are the simplest way to observe things such as phase separation.  MC simulations would be difficult for a system of many chains since such a system requires fixing the temperature with a "thermostat" and fixing the pressure with a "barostat" so that the density is realistic.  These are achieved by the application of a decay function for deviations of temperature (energy kT) and density (N/V) in addition to random thermal motion of atoms and random thermal rotation of bonds subject to transport equations.  Chen uses such atomic MD simulations to consider the impact of tacitcity on the chain persistence using the biopolymer software GROMACS (https://www.gromacs.org/About_Gromacs).  GROMACS allows the description of maps of dihedral bond angle, Figures 3-5, which is common in biophysics to describe the presence of alpha helix or beta sheets and other tertiary structures.  Chen uses this to describe right- and left-handed helices in polypropylene and polybutylene-1 (figures 4 and 5).

On page 2 Chen describes the simulation method. From the Wikipedia page describe the OPLS force field. Remember a spring constant is described by $F = k_{spr} x = dE/dx$, and the Leonard-Jones potential is commonly used for non-bonded interactions (https://en.wikipedia.org/wiki/OPLS). How can a cut-off distance speed up the simulation? What is a leap-frog algorithm? Explain what is involved in a steepest decent method (such as the Cauchy method you may have used) to solve differential equations? What is a canonical ensemble? (You can use Wikipedia for most of these things, very short answers are appropriate.)

c) Equation 1 is used to determine the persistence length. Explain what this equation means and why it might make sense. You could refer to Hsu, Paul and Binder *Standard Definitions of Persistence Length Do Not Describe the Local "Intrinsic" Stiffness of Real Polymer Chains Macromolecules* **43***, 3094–3102* (2010) if you are interested or just work out what the equation means. Remember the dot product of two vectors is the product of the absolute values times the cosine of the angle between the vectors and <cos> = 0 for a random relationship and 1 for perfect alignment.

d) Compare Chen's Figure 2 with Tzounis' Figures 2 and 3. Do the two techniques agree? The experimental measurement of persistence length or Kuhn length involves the measurement of an average value. From Chen's results, how can such an average value for the chain be misleading? Consider both the chain end effects and the effect of local chain tacticity. Comment on the time dependence that is available from Chen's simulation in Figure 3.

e) Explain what a "dihedral pair" means on page 4. Plots such as figures 4 and 5 are common in the description of protein structure but uncommon in synthetic polymers. Explain Figure 4, what is the difference between the different positions on the chain in terms of the helicity?