HW 6: Due November 5

1. Consider a chain in 3D with fixed bond lengths $\|\boldsymbol{a}_i\| = a$, free dihedral angles ϕ_i, and fixed bond supplements $\theta_i = \theta$. Show that in the long chain limit, $n \to \infty$, that

$$C_\infty = \frac{1+\cos(\theta)}{1-\cos(\theta)}.$$

   Evaluate your result for terahedrally bonded chains, $\cos(\theta) = 1/3$, and observe that the value is well below the experimentally observed range of 5 to 10. Note; $C_\infty \equiv \lim_{n\to\infty}\langle \boldsymbol{R}\cdot\boldsymbol{R}\rangle/na^2$.

2. Consider a chain in 3D with identical independent bonds where the bond lengths are fixed at a, the bond supplements are fixed at θ, and the dihedral angles are restricted by a potential of the form $V(\phi) = \frac{V_o}{2}(1-\cos(3\phi)) + V_o(\phi/\pi)^2$, where the function is defined over $\phi \in [-\pi, \pi]$ and is 2π periodic.

   (a) Show that

$$C_\infty = \left(\frac{1+\cos(\theta)}{1-\cos(\theta)}\right)\left(\frac{1+\langle\cos(\phi)\rangle}{1-\langle\cos(\phi)\rangle}\right).$$

   (b) Assume now that $V_o = 2$ kcal/mol and compute C_∞. Are you in within the experimental range (assume $\cos(\theta) = 1/3$).

   (c) Assume that the dihedral angles are restricted to the discrete values defined by the three minima of $V(\cdot)$; this is called the rotational isomeric state approximation. Recompute C_∞. Is the approximation reasonable in that does it reasonably approximate the value you obtained when you utilized the full potential?[1]

3. Consider a freely jointed chain in 3D in a strain-ensemble with fixed bond lengths a. Plot $\langle f\rangle a/kT$ versus $\|\boldsymbol{R}\|/na$ for chains with $n \in \{2, 3, 5, 10\}$ links. On the same plot, include the $n \to \infty$ (Gaussian limit) case as well as the stress-ensemble (inverse Langevin) case.

[1] The next level of sophistication in chain models is to acknowledge that bonds are not independent of each other and to include nearest neighbor interactions along the chain.