UNIVERSITY OF CALIFORNIA BERKELEY
Department of Civil Engineering
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Structural Engineering,
Mechanics and Materials
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HW 4: Due October 31

1. Write a computer program (MATLAB is probably best) to compute and plot a random walk in *three* dimensions with fixed step size. Repeatedly run your program with chains having 1000 bonds to get a sense of what random walks look like. Use your program to find the mean end-to-end distance for chains with 50 bonds and 5000 bonds.

2. 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; $C_\infty \equiv \lim_{n\to\infty} \langle \boldsymbol{R} \cdot \boldsymbol{R} \rangle / na^2$.

3. 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 $V(\phi) = \frac{V_o}{2}(1 - \cos(3\phi) + \sin(\phi/2))$, where the function is defined over $\phi \in [0, 2\pi]$ and is defined to repeat periodically for ϕ outside of this domain.

   (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 $\cos(\theta) = 1/3$). Note you may have to compute the integral numerically.

   (c) Assume now 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 For this case compute C_∞. Are you in within the experimental range (assume $\cos(\theta) = 1/3$). [1]

4. 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.