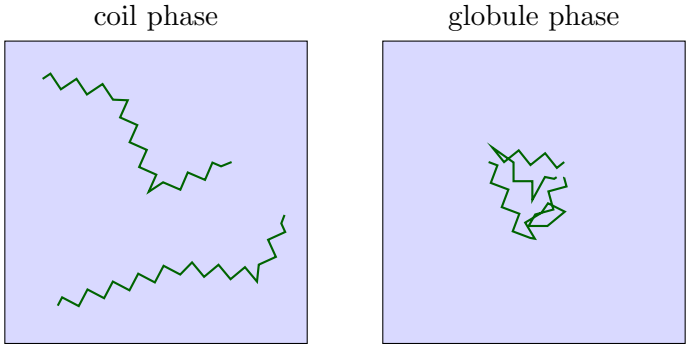
Coil-Globule Phase Transition

A polymer is a chain-like molecule consisting of individual monomer units bonded together in a repeating fashion. Polymers are known to go through very interesting phase transitions between various states; this problem is meant to explore one of these in very basic detail by using Landau theory.

Let's begin by considering the case of a single polymer chain of N_{P} monomers. If we have a region of volume V, and each monomer has a volume v, by defining $N = v/V$, we can crudely model the polymer as occupying N_{P} out of N sites on a lattice. Define $\phi = N_{\mathrm{P}}/N$. The remainder of the sites on the lattice, $(1-\phi)N$, are occupied by solvent molecules. Experimentalists have observed that polymer solutions tend to exist in two phases: a *coil* phase, in which the polymer dissolves well and is loosely coiled throughout the solvent, and a *globule phase*, in which the polymers are tightly wound up and do not intermingle much with the solvent.



Using the generalized formula for entropy, one can estimate that the entropy of this configuration is[1]

$$S = Nk_{\mathrm{B}}\left(-\frac{1}{N}\phi\log\phi - (1-\phi)\log(1-\phi)\right).$$

Typically there is a (net) repulsive energy of interaction, described by a parameter χ, between the polymer and the solvent:

$$E = Nk_{\mathrm{B}}T\chi\phi(1-\phi).$$

(a) Show that the free energy is given by, taking the limit $N \to \infty$ as well as ignoring linear terms in ϕ,[2]

$$F = Nk_{\mathrm{B}}T\left[\left(\frac{1}{2}-\chi\right)\phi^2 + \frac{1}{6}\phi^3 + \cdots\right].$$

(b) For what χ_{c} do we observe a phase transition? Note that this is not a phase transition that occurs by changing temperatures. For $\chi < \chi_{\mathrm{c}}$ are we in the coil phase or globule phase, and why?

[1] The extra factor of $1/N$ is meant to try and retain some of the fact that the polymer is a chain, and thus doesn't truly occupy uniformly randomly distributed lattice sites.

[2] This is because these terms can be absorbed into the "self" free energy of the polymer species; it will have no effect on the interactions.