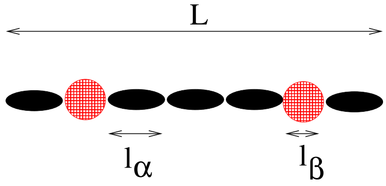


Problem 1: 2-component model

We consider the 2-component model of a polymer chain which consists of M segments of two different types α, β (internal degrees of freedom are neglected). The number of configurations with length L is given by the Binomial distribution

$$\Omega(L, M, T) = \frac{M!}{M_\alpha!(M - M_\alpha)!} \qquad L = M_\alpha l_\alpha + (M - M_\alpha) l_\beta$$

(a) Make use of the asymptotic expansion of the logarithm of the Gamma function

$$\ln(\Gamma(z)) = (\ln z - 1)z + \ln(\sqrt{2\pi}) - \frac{1}{2}\ln z + \frac{1}{12z} + O(z^{-3})$$

$$N! = \Gamma(N+1)$$

to calculate the leading terms of the force-extension relation which is obtained from

$$\kappa = \frac{\partial}{\partial L}(-kT \ln \Omega(L, M, T))$$

Discuss the error of Stirling's approximation for $M = 1000$ and $l_\beta / l_\alpha = 2$

(b) Now switch to an ensemble with constant force κ . The corresponding partition function is

$$Z(\kappa, M, T) = \sum_L e^{\kappa L/kT} \Omega(L, M, T)$$

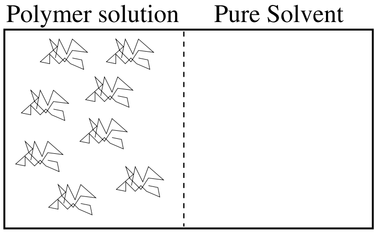
Calculate the first two moments of the length

$$\overline{L} = -\frac{\partial}{\partial \kappa}(-kT \ln Z) = Z^{-1} kT \frac{\partial}{\partial \kappa} Z$$

$$\overline{L^2} = Z^{-1}(kT)^2 \frac{\partial^2}{\partial \kappa^2} Z$$

and discuss the relative uncertainty $\sigma = \frac{\sqrt{\overline{L^2} - \overline{L}^2}}{\overline{L}}$. Determine the maximum of σ.

Problem 2: Osmotic pressure of a Polymer solution



$\mu_1(P,T) = \mu_1^0(P',T)$

Calculate the osmotic pressure $\Pi = P - P'$ for the Flory-Huggins model of a polymer solution The difference of the chemical potential of the solvent $\mu_1(P,T) - \mu_1^0(P,T)$ can be obtained from the free enthalpy change

$$\Delta G_m = kT\left(\phi_1 \ln \phi_1 + \frac{\phi_2}{M} \ln \phi_2 + \chi \phi_1 \phi_2\right)$$

and the osmotic pressure is given by

$$\mu_1^0(P',T) - \mu_1^0(P,T) = -\Pi \frac{\partial \mu_1^0}{\partial P}$$

Taylor series expansion gives the virial expansion of the osmotic pressure as a series of powers of ϕ_2. Truncate after the quadratic term and discuss qualitatively the dependence on the interaction parameter χ (and hence also on temperature).

Problem 3: Polymer mixture

Consider a mixture of two types of polymers with chain lengths M_1 and M_2. Show that the free enthalpy change is given by

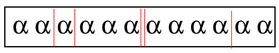
$$\Delta G_m = kT\left(\frac{\phi_1}{M_1} \ln \phi_1 + \frac{\phi_2}{M_2} \ln \phi_2 + \chi \phi_1 \phi_2\right)$$

Determine the critical values ϕ_c and χ_c .Discuss the phase diagram for the symmetrical case $M_1 = M_2$.

Problem 4: Some combinatorial factor

Consider a string of N identical characters. Show that the number of possibilities to divide the string into M blocks each containing $0 \cdots N$ characters is given by the number of different ways to arrange the $M + N$ objects which is given by

$$\frac{(M+N)!}{M!N!}$$



N=12 M=6