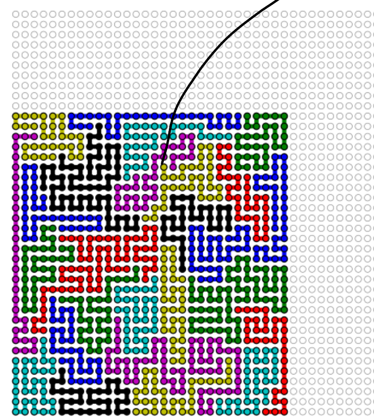
Flory-Huggins theory for polymer solutions

solution

S higher

melt



separated phase

Energy?

N_{sites} : number of sites (volume)

N : number of beads / polymer

N_p : number of polymers

q : coordination number

$j-1$ polymers present.

Polymer j : 1st bead : $N_{sites} - (j-1)N$

2nd bead : $q\, P_{unocc} = q \dfrac{N_{sites} - (j-1)N - 1}{N_{sites}}$ mean-field.

3rd bead : $(q-1)\, P_{unocc} = (q-1) \dfrac{N_{sites} - (j-1)N - 2}{N_{sites}}$

k-th bead : $(q-1)\, P_{unocc} = (q-1) \dfrac{N_{sites} - (j-1)N - k + 1}{N_{sites}}$

$\vdots$

All in all, for polymer j

$$\left(N_{sites} - (j-1)N\right) q \left(\frac{N_{sites} - (j-1)N - 1}{N_{sites}}\right) \cdot (q-1) \frac{N_{sites} - (j-1)N - 2}{N_{sites}} \cdots (q-1) \frac{N_{sites} - (j-1)N - N + 1}{N_{sites}}$$

$$\frac{q_z (q_z-1)^{N-2}}{(N_{sites})^{N-1}} \frac{(N_{sites}-(j-1)N)!}{(N_{sites}-jN)!} \equiv \Omega_j$$

For <u>all</u> polymers: $\frac{1}{N_p!} \prod_{j=1}^{N_p} \Omega_j$

$$= \frac{1}{N_p!} \frac{q_z^{N_p}(q_z-1)^{(N-2)N_p}}{(N_{sites})^{N_p(N-1)}} \frac{N_{sites}!}{\cancel{(N_{sites}-N)!}} \frac{\cancel{(N_{sites}-N)!}}{\cancel{(N_{sites}-2N)!}} \frac{\cancel{(N_{sites}-2N)!}}{\cancel{(N_{sites}-3N)!}} \cdots \frac{\cancel{(N_{sites}-(N_p-1)N)!}}{(N_{sites}-N_pN)!}$$

$$= \frac{1}{N_p!} \frac{q_z^{N_p}(q_z-1)^{(N-2)N_p}}{(N_{sites})^{N_p(N-1)}} \frac{N_{sites}!}{(N_{sites}-N_pN)!} = \Omega_{sol}$$

$$\Omega_{sep} \underset{\uparrow}{=} \frac{1}{N_p!} \frac{q_z^{N_p}(q_z-1)^{(N-2)N_p}}{(NN_p)^{N_p(N-1)}} (NN_p)!$$

$N_{sites} = NN_p$

$$\frac{\Delta S}{k_B} = \frac{S_{sol}-S_{sep}}{k_B} = \ln\frac{\Omega_{sol}}{\Omega_{sep}} = \ln\left[\left(\frac{NN_p}{N_{sites}}\right)^{N_p(N-1)} \frac{N_{sites}!}{\underbrace{(N_{sites}-N_pN)!}_{(1-\Phi)N_{sites}}\underbrace{(NN_p)!}_{\phi N_{sites}}}\right]$$

Define $\Phi = \left(\frac{NN_p}{N_{sites}}\right)$ polymer fraction.

$$\frac{\Delta S}{k_B} = \underbrace{N_p}_{\frac{\Phi N_{sites}}{N}}\underbrace{(N-1)}_{\phi N_{sites}}\ln\Phi + N_{sites}\ln N_{sites} - N_{sites}(1-\phi)\ln N_{sites}(1-\Phi) - N_{sites}\phi\ln N_{sites}\Phi$$

$$\underline{\frac{\Delta S}{N_{sites}k_B} = -\frac{\Phi}{N}\ln\Phi - \ln(1-\Phi)}$$

Energy, solution

J_{SS} : solvent – solvent : $\dfrac{N_{sites}\, q}{2} J_{SS} (1-\Phi)^2$

J_{SP} : solvent – polymer : $\underbrace{N N_p}_{N_{sites} \cdot \Phi} (q-2)(1-\Phi) J_{SP}$

J_{PP} : polymer - polymer ; $\dfrac{N N_p (q-2)}{2} \Phi J_{PP}$

$$\mathcal{E}_{sol} = \frac{N_{sites}\, q}{2} J_{SS}(1-\Phi)^2 + N_{sites}(q-2)\Phi(1-\Phi) J_{SP} + N_{sites} \Phi^2 \frac{(q-2)}{2} J_{PP}.$$

$$\mathcal{E}_{sep} = \frac{(q-2)}{2} J_{PP} N_{sites} \Phi + N_{sites}(1-\Phi) \frac{q}{2} J_{SS}$$

$$\frac{\Delta \mathcal{E}}{N_{sites}} = \frac{\mathcal{E}_{sol} - \mathcal{E}_{sep}}{N_{sites}} = \Phi(1-\Phi)\Big[\underbrace{-\frac{q}{2} J_{SS} + (q-2) J_{SP} - \frac{q-2}{2} J_{PP}}_{k_B T \chi \quad \text{Flory-Huggins param.}}\Big]$$

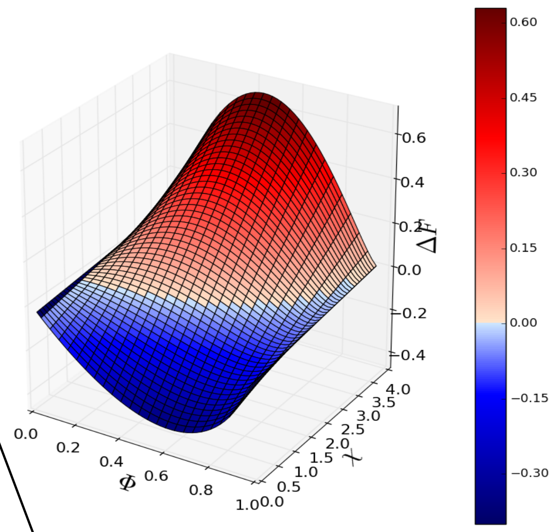
Recall: $\dfrac{\Delta S}{N_{sites}\, k_B} = -\dfrac{\Phi}{N} \ln \Phi - \ln(1-\Phi)$

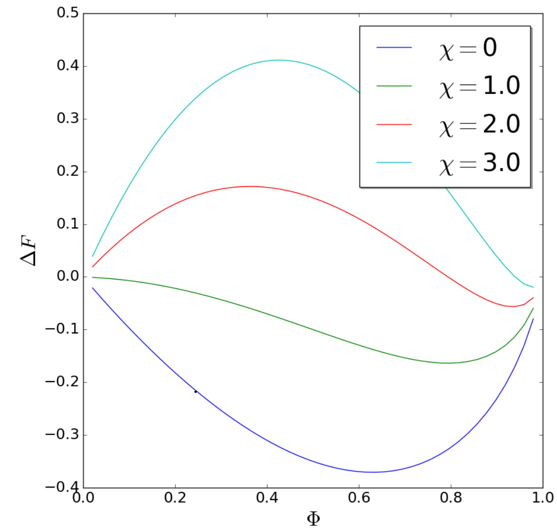
$$\frac{\Delta F}{N_{sites} k_B T} = \underline{\Phi(1-\Phi)\chi + \frac{\Phi}{N} \ln \Phi - (1-\Phi)\ln(1-\Phi)} = \frac{F_{sol} - F_{sep}}{N_{sites}\, k_B T}$$

$\Delta F \leq 0$; sol stable

≥ 0 : sep stable

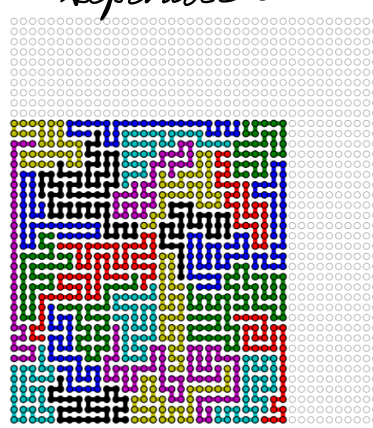
$$\frac{\Delta F}{N_{sites} k_B T} = \Phi(1-\Phi)\chi + \frac{\Phi}{N} \ln \Phi - (1-\Phi)\ln(1-\Phi)$$





solution

separated



ϕ : polymer fraction $(N_p N / N_{sites})$

χ : Flory Huggins parameter $\chi = \frac{1}{k_B T}\left[-\frac{q}{2} J_{ss} + (q-2) J_{sp} - \frac{q-2}{2} J_{PP}\right]$