## Suspensions and polymer solutions

## Solution of Exercise 8

1. In class we obtained

$$\phi_{\text{spin}1,2} = \frac{N(2\chi - 1) \pm \sqrt{[N(2\chi - 1) + 1]^2 - 8\chi N}}{4\chi N},$$
(1)

and

$$\chi_{\rm c} = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{N},\tag{2}$$

as the critical value of  $\chi$  for which the expression in the square root of Eq. (1) vanishes, i.e.,  $\phi_{\text{spin1}} = \phi_{\text{spin2}}$ . From Eq. (1) we have

$$\phi_{\rm spin2} - \phi_{\rm spin1} = \frac{\sqrt{[N(2\chi - 1) + 1]^2 - 8\chi N}}{2\chi N}.$$
(3)

We now substitute in Eq. (3)  $\chi = \chi_c(1 + \epsilon)$  and expand to leading order in small  $\epsilon$ , recalling that the expression vanishes for  $\chi = \chi_c$ . The result is

$$\phi_{\mathrm{spin2}} - \phi_{\mathrm{spin1}} \simeq \sqrt{2 - \frac{1}{\chi_{\mathrm{c}}} - \frac{1}{N\chi_{\mathrm{c}}}} \epsilon^{1/2}$$

Finally, substituting  $\chi_c$  from Eq. (2), we obtain to leading order in small  $\epsilon$  and large N,

$$\phi_{\text{spin}2} - \phi_{\text{spin}1} \simeq 2N^{-1/4} \epsilon^{1/2}.$$
 (4)

2. The Flory-Huggins free energy of a polymer solution, as derived in class, is

$$\Delta F = k_{\rm B} T \left[ \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi) \right], \tag{5}$$

where N is the number of monomers in a polymer chain and  $\phi$  the polymer volume fraction. Recall that this is the free energy *per lattice site*. The total free energy is

$$F_{\rm tot} = \frac{V}{a^3} \Delta F,$$

where V is the total volume, and  $a^3$  the volume of a lattice cell (monomer volume). We recall also that

$$\phi = \frac{NN_{\rm c}a^3}{V},$$

where  $N_{\rm c}$  is the number of polymer chains. To calculate the pressure we will need to take the derivative of  $F_{\rm tot}$  with respect to V while keeping T and  $N_{\rm c}$  constant. This is equivalent to

$$\left(\frac{\partial}{\partial V}\right)_{T,N_{\rm c}} = \left(\frac{\partial\phi}{\partial V}\right)_{T,N_{\rm c}} \left(\frac{\partial}{\partial\phi}\right)_{T,N_{\rm c}} = -\frac{\phi}{V} \left(\frac{\partial}{\partial\phi}\right)_{T,N_{\rm c}}$$

Hence,

$$p = -\left(\frac{\partial F_{\text{tot}}}{\partial V}\right)_{T,N_{\text{c}}} = -\frac{1}{a^3} \left[\Delta F + V\left(\frac{\partial \Delta F}{\partial V}\right)_{T,N_{\text{c}}}\right] = \frac{1}{a^3} \left(\phi \frac{\partial \Delta F}{\partial \phi} - \Delta F\right).$$
(6)

(a) i. We use Eq. (5) in Eq. (6) to get

$$p = -\frac{k_{\rm B}T}{a^3} [\ln(1-\phi) + \chi \phi^2],$$

which, to 2nd order in  $\phi \ll 1$ , gives

$$p \simeq \frac{k_{\rm B}T}{a^3} \left[ \frac{\phi}{N} + \frac{1}{2} (1 - 2\chi) \phi^2 \right] = \frac{k_{\rm B}T}{a^3} \left( \frac{\phi}{N} + \frac{1}{2} \frac{v}{a^3} \phi^2 \right),\tag{7}$$

where  $v = a^3(1 - 2\chi)$  is the excluded-volume parameter.

- ii. Since  $\phi = NN_c a^3/V$ , the 1st-order term in Eq. (7) is equal to  $k_B T N_c/V = k_B T/V_c$ , where  $V_c = V/N_c$  is the volume per chain. To leading order, therefore, the pressure is equal to  $k_B T$  per molecular volume, in accord with van't Hoff's law.
- iii. The 2nd-order term will start dominating when  $\phi > (a^3/v)N^{-1}$ . We obtained for the overlap volume fraction  $\phi^* \sim (a^3/v)^{0.6}N^{-0.8}$ . When N is very large, therefore, we get that the 2nd-order term dominates at volume fractions much smaller than  $\phi^*$ . This does not make sense, because at  $\phi \ll \phi^*$  we expect the system to behave as a dilute solution of isolated chains, which is exactly what the 1st-order (van't Hoff) term describes! This is a failure of the mean-field Flory-Huggins theory, which assumes a uniform distribution of monomers throughout the solution, i.e., it ignores the correlations between monomers belonging to the same chain. This assumption of uniformity leads to an overestimation of the monomer-monomer repulsions and, thus, to a dominance of the interaction term at concentrations which are far too low.
- iv. Nevertheless, if we stick to the Flory-Huggins theory, then at  $\phi > \phi^*$  the 2nd-order term surely dominates, and we get

$$p \simeq \frac{k_{\rm B}T}{a^3} \frac{v}{a^3} \phi^2. \tag{8}$$

(Note that, since the solution is assumed semi-dilute, we still have  $\phi \ll 1$ , and an expansion in  $\phi$  is still valid.)

(b) In class we did a scaling analysis for a semi-dilute polymer solution in a good solvent, obtaining for the blob size

$$\xi \sim a \left(\frac{v}{a^3}\right)^{\frac{2\nu-1}{1-3\nu}} \phi^{\frac{\nu}{1-3\nu}}$$

Recall that in this analysis the blobs form a "rescaled melt", i.e., the volume available for a blob is the volume of the blob itself. Hence, applying van't Hoff's law for the blobs, we get

$$p \sim \frac{k_{\rm B}T}{\xi^3} \sim \frac{k_{\rm B}T}{a^3} \left(\frac{v}{a^3}\right)^{\frac{3(2\nu-1)}{3\nu-1}} \phi^{\frac{3\nu}{1-3\nu}} \sim \frac{k_{\rm B}T}{a^3} \left(\frac{v}{a^3}\right)^{0.70} \phi^{2.3}.$$
 (9)

Comparing Eqs. (8) and (9), we see that the correlations inside the chains lead to a stronger dependence of the pressure on  $\phi$ .