Chemistry C3102-2006: Polymers Section

HOMEWORK #5

Due Tuesday, June 6

1. A polymer brush in good solvent forms a layer of thickness L that scales with number of monomers, N and grafting density σ as $L \sim aN\sigma^{1/3}$. How does the polymer thickness scale in poor solvent?

   In poor solvent, an isolated chain will collapse to a small sphere of size $R \sim N^{1/3}a$. So if the chains were grafted a distance D apart where $D > R$, then the surface will be dotted with "mushrooms" of size $R \sim N^{1/3}a$ that contain monomer and no solvent. Thus, the thickness of the polymer will not be homogeneous when the polymer is grafted dilutely on the surface in the presence of poor solvent. In that case, $L = 0$ or $L = R \sim N^{1/3}a$, and is independent of the grafting density when $\sigma = (D/a)^{-2}$ is in the range $0 < \sigma < (R/a)^{-2}$. Notice that the highest grafting density at which the molten globules remain isolated, $\sigma = (R/a)^{-2}$, scales as $N^{-2/3}$ (this you can see by replacing R with the scaling $N^{1/3}a$) so that as the chain gets larger, this upper grafting limit gets smaller.

   On the other hand, if $D < R$, then the globules will coalesce so as to form a homogeneous layer which minimise polymer contact with the solvent. In this case, as each chain is grafted to the surface within an area D^2, and the volume of the collapsed chain is the number of monomrs times the voluem of each monomer, then the layer thickness is

   $$\frac{1 \text{ chain}}{D^2 \text{ area}} \times \frac{Na^3 \text{ volume}}{\text{chain}} = L$$

   or

   $$\begin{aligned} L &= \frac{Na^3}{D^2} \\ &= \frac{Na^3/a^2}{D^2/a^2} \\ &= aN\sigma. \end{aligned}$$

   That is, under poor solvent conditions the layer thickness depends linearly upon the grafting density.

2. A researcher suggests a new model for the phase separation of a binary mixture of solvent (species 1) and solute (species 2). The researcher has written this new solution thery, "the three-hump model", in a lengthy manuscript for publication. You are given the job of reviewing the manuscript and informing the editor of its correctness or incorrectness. You have not read the researcher's *excessively* long description, but one of his figures (reproduced below) rings "alarm bells", signalling that the model violates fundamental thermodynamics. Using only the researchers figure, explain to the editor why this manuscript should not be published. Describe all incorrrect aspects of this figure.

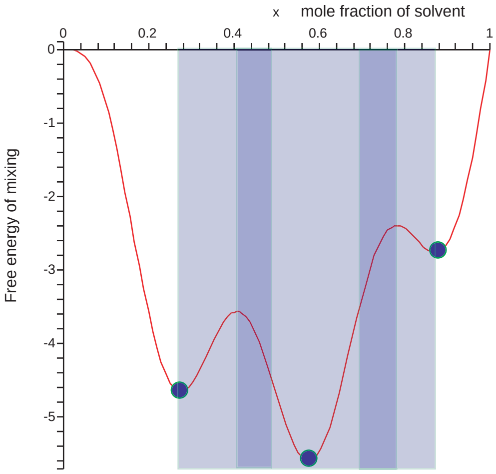


Figure 1: ΔF^m, free energy of mixing, versus x_1, mole fraction of solvent as predicted from the new Three-hump Model of Solution Thermodynamics: $\Delta F^m/RT = \sin(6\pi x_1) - 6\pi x_1(1-x_1)$. Shown is the model predictions at a given temperature where three phases, whose energy and composition are given by closed circles, coexist in the unstable concentration range (shaded area). The darker shaded regions show the metastable region where you can create a solution containing either 1 homogeneously mixed phase, or 2 partially-mixed phases that exist over short times before they slowly decompose into the three lowest energy phases via the process of spinodal decomposition.

- It is not possible to have a two component system separate into more than 2 phases. You can understand this using the phase rule, where F, the number of degrees of freedom of the system is given by the number of components, C, and phases, P: $F = C - P + 2$. So for a two component system, $F = 4 - P$. If we had a one phase, there would be $F = 3$ degrees of freedom required to specify the system: these being temperature, pressure, and mole fraction of solute. If we had two phases, there would be $F = 2$ degrees of freedom required to specify the system: these being temperature and pressure (You don't need to specify mole fraction as the equal chemical potentials across phases determines this). For three phases, there would be only $F = 1$ degree of freedom, an insufficient number of degrees of freedom OR, you can note for this specific model that it is impossible to construct a line, tangent to the ΔG^m curve at three different binodal compositions - which would be necessary for the co-existence of three phases.
- Completely unstable regions should be marked by regions of the ΔG^m curve that have negative curvature. Compositions for which $\partial^2 \Delta G^m/\partial x_1^2 < 0$ will spontaneously de-mix.
- Metastable regions are compositional regions where $\partial^2 \Delta G^m/\partial x_1^2 < 0$ and where compositions will eventually de-mix, but do so using the slower kinetics of nucleation & growth.
- Unstable regions are usually bounded by metastable regions and not the other way around as indicated in the shading of the figure.

3. Using Flory-Huggins solution theory for polymer-solvent solutions containing chains of length $\mathcal{N} = 100$ monomers, and a critical temperature of $T_c = 332$ K , show (using Maple for needed efficiency)

(a) Predictions of $\Delta G^m/(NRT)$ versus ϕ_2, volume fraction of monomer, for $T = 275$, 300, 325, 332, 350, 400 K.

The Flory-Huggins Solution model is

$$\frac{\Delta G^m}{NRT} = \chi\phi_1\phi_2 + \phi_1 \ln \phi_1 + \frac{\phi_2}{\mathcal{N}} \ln \phi_2.$$

You are not given χ, but you are told that the chains are of length $\mathcal{N}$ and $T_c = 332$K. This is sufficient to determine χ over a range of temperatures. The value of χ at the critical temperature, where spinodals and binodals merge and above which the solution is homogeneous, is given by

$$\chi_c \equiv \frac{1}{2} + \frac{1}{2\mathcal{N}} + \frac{1}{\sqrt{\mathcal{N}}},$$

or $\chi_c \equiv \chi(T_c) = 0.605$. Then, as

$$\chi(T) = \frac{\mathcal{B}}{RT}$$

and

$$\chi(T_c) = \frac{\mathcal{B}}{RT_c},$$

then

$$\chi(T) = \chi(T_c) \times \frac{T_c}{T}.$$

Thus, The Flory-Huggins model reduces to:

$$\frac{\Delta G^m}{NRT} = \left(0.605 \times \frac{T_c}{T}\right)(1-\phi_2)\phi_2 + (1-\phi_2)\ln(1-\phi_2) + \frac{\phi_2}{\mathcal{N}} \ln \phi_2.$$

```
> G300:=y->0.605*332/300*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y);
```

$$G300 := y \mapsto 0.6695333333\, y\,(1-y) + (1-y)\ln(1-y) + \tfrac{1}{100}\, y \ln(y)$$

```
> G325:=y->0.605*332/325*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y);
```

$$G325 := y \mapsto 0.6180307692\, y\,(1-y) + (1-y)\ln(1-y) + \tfrac{1}{100}\, y \ln(y)$$

```
> G332:=y->0.605*332/332*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y);
```

$$G332 := y \mapsto 0.6050000000\, y\,(1-y) + (1-y)\ln(1-y) + \tfrac{1}{100}\, y \ln(y)$$

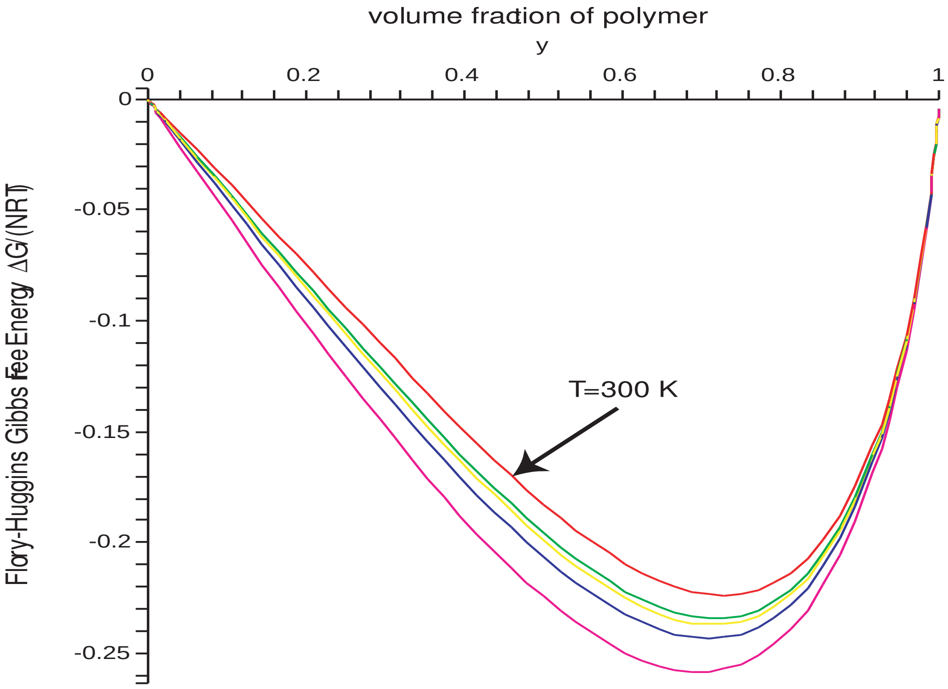
```
> G350:=y->0.605*332/350*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y);
```

$$G350 := y \mapsto 0.5738857143\, y\,(1-y) + (1-y)\ln(1-y) + \tfrac{1}{100}\, y \ln(y)$$

```
> G400:=y->0.605*332/400*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y);
```

$$G400 := y \mapsto 0.5021500000\, y\,(1-y) + (1-y)\ln(1-y) + \tfrac{1}{100}\, y \ln(y)$$

```
> plot([G300(y),G325(y), G332(y), G350(y), G400(y)], y=0..1);
```

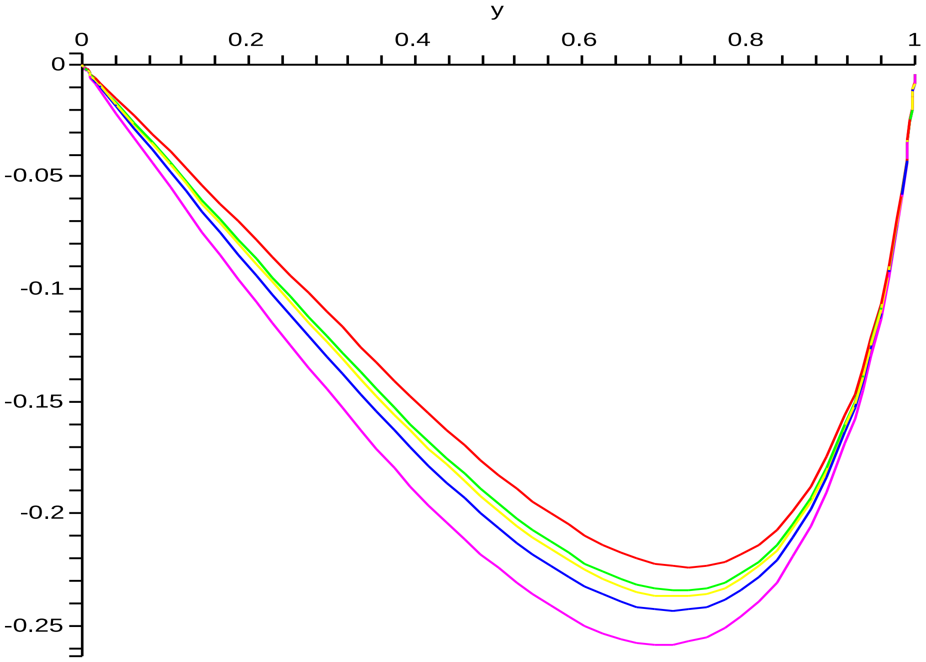


Alternatively, you can express a procedure, which I call g, which takes values of y, volume fraction of polymer, and T, temperature, and generate a procedural function that you can plot, derivitize (if that is a word), or solve:

```
> g:=proc(y, T) description "free energy";
> 0.605*332/T*y*(1-y)+(1-y)*ln(1-y)  + y/100*ln(y)
> end proc;
```

$$g := \textbf{proc}(yT)\textbf{description}\ \text{“}free\ energy''; \qquad 332 * .605 * y * (1-y) * T^{-1} + (1-y) * ln(1-y) + 1/100 * y * ln(y)\textbf{end proc};$$

```
> plot( [g(y, 300),g(y,325), g(y,332), g(y,350), g(y,400)], y=0..1);
```



You might not be able to discern easily any inflexion points, but the next exercise will show that they are definitely there; and indeed you can see them by plotting over a reduced range of y.

(b) Spinodal compositions for the temperature range, $275K < T < 400K$

The spinodal compositions at any $T \leq T_c$ satisfy

$$\frac{\partial^2 \Delta G^m/(NRT)}{\partial \phi_2^2} = 0.$$

The easiest way to demonstrate these spinodal composition is to plot the second derivative of the free energy expression versus composition: spinodal compositions are found as those compositions where the second derivative curve crosses the composition coordinate.

```
> ddG300:=y->diff(diff(0.605*332/300*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y)
y), y);
```

$$ddG300 := y \mapsto -1.339066667 + (1-y)^{-1} + \frac{1}{100}\, y^{-1}$$

```
> ddG325:=y->diff(diff(0.605*332/325*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y)
y), y);
```

$$ddG325 := y \mapsto -1.236061538 + (1-y)^{-1} + \frac{1}{100}\, y^{-1}$$

```
> ddG332:=y->diff(diff(0.605*332/332*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y)
y),y);
```

$$ddG332 := y \mapsto -1.210000000 + (1-y)^{-1} + \frac{1}{100}\, y^{-1}$$

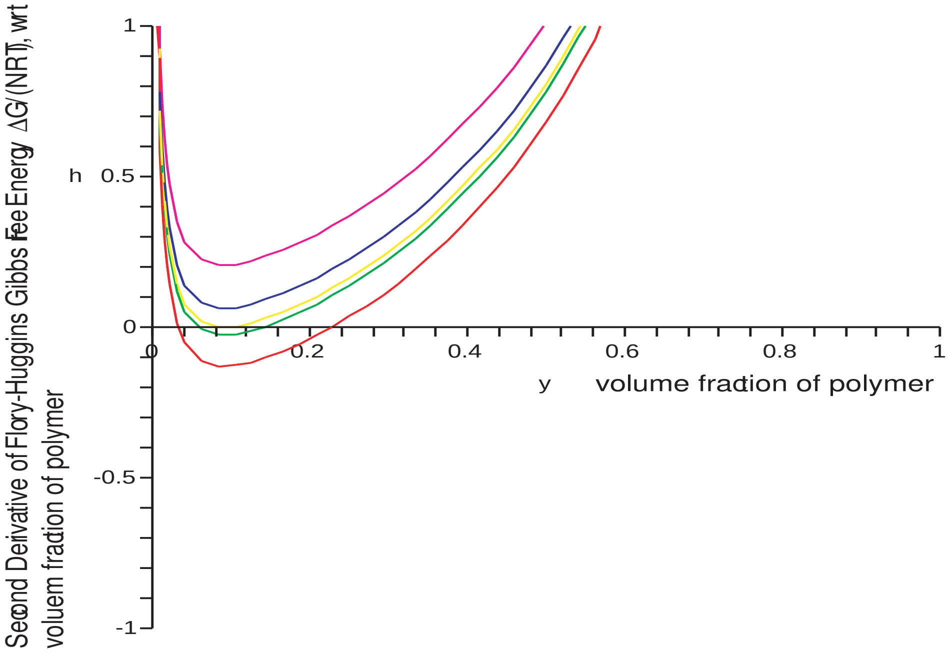
```
> ddG350:=y->diff(diff(0.605*332/350*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y)
y),y);
```

$$ddG350 := y \mapsto -1.147771429 + (1-y)^{-1} + \frac{1}{100}\, y^{-1}$$

```
> ddG400:=y->diff(diff(0.605*332/400*y*(1-y) + (1-y)*ln(1-y) + y/100*ln(y)
y);
```

$$ddG400 := y \mapsto -1.004300000 + (1-y)^{-1} + \frac{1}{100}\, y^{-1}$$

```
> plot([ddG300(y),ddG325(y), ddG332(y), ddG350(y), ddG400(y)], y=0..1, h=-1
```



You can solve for the spinodal compositions at each temperature:

```
> solve( ddG300(y)=0, y);
```

0.03276645143, 0.2279126287

```
> solve( ddG325(y)=0, y);
```

0.05690933409, 0.1421596689

```
> solve( ddG332(y)=0, y);
```

0.09090909091, 0.09090909091

Alternatively, you could again resort to formulating procedures, which is much easier and can yield in a few lines the complete spinodal curve as a function of temperature

```
> dg:= proc(y, t); diff(g(y,t), y) end proc;
```

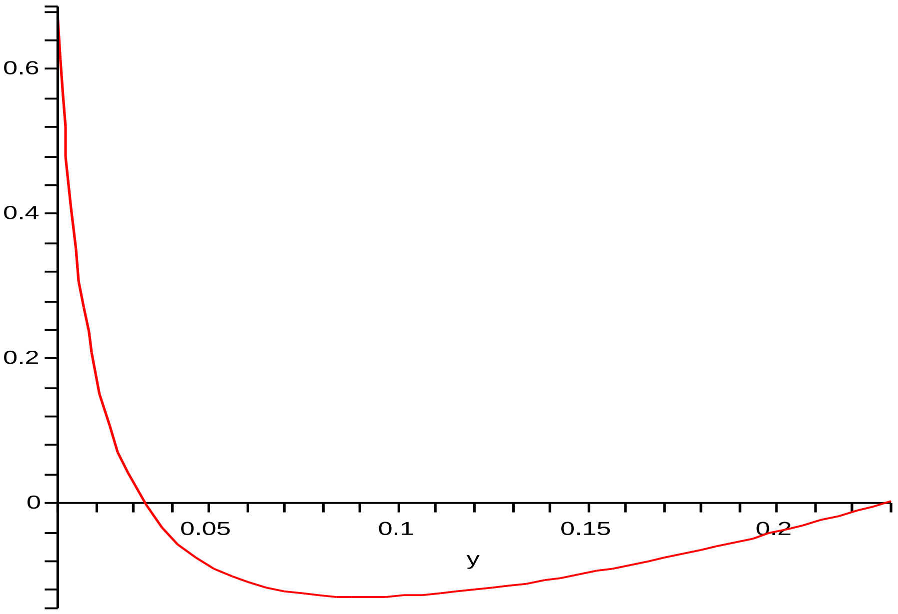
$dg := \textbf{proc}(yt) \quad \mathit{diff}(g(y, t), y)\textbf{end proc};$

```
> dgg:= proc(y,t); diff(dg(y,t), y) end proc;
```

$dgg := \textbf{proc}(yt) \quad \mathit{diff}(dg(y, t), y)\textbf{end proc};$

Here I simply created procedures for calculating the $dg \equiv \partial(G^m/NRT)/\partial y$ for values of polymer volume fraction, y, and temperature, as well as $dgg \equiv \partial^2(G^m/NRT)/\partial y^2$. Then I plot the second derivative at $T = 300$ simply to show that there is indeed 2 inflection or spinodal points.

```
> plot( dgg(y, 300), y=0.01..0.23);
```



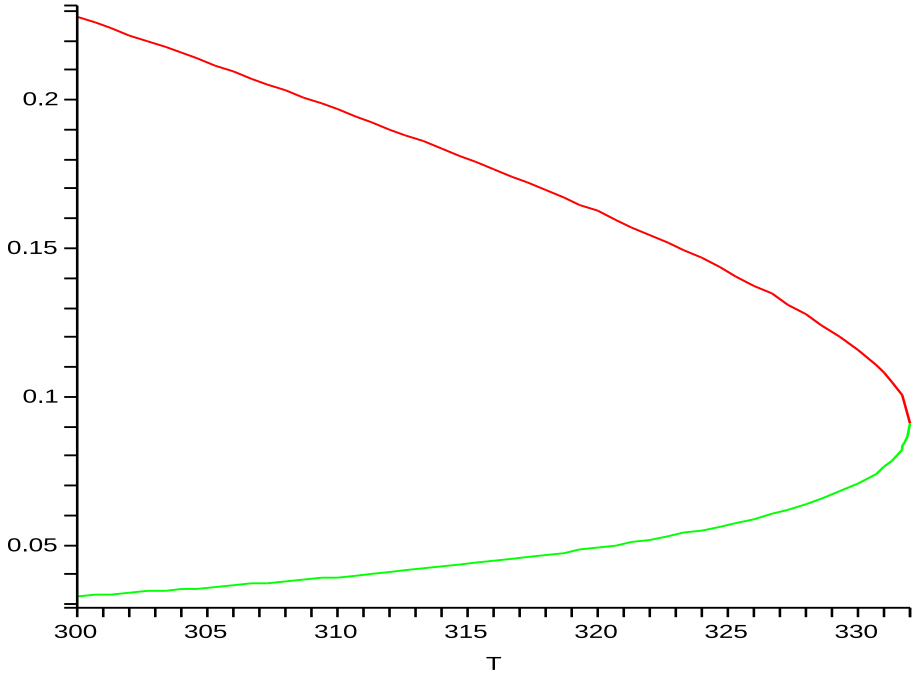
Now what we can do is solve for the two values of polymer volume fraction for which $dgg = 0$ at arbitrary temperature:

```
>  solve( dgg(y, T) =0, y);
```

$$0.5 - 0.001232201533\,T + 0.0001369112815\,\sqrt{13337104.0 - 67064.0\,T + 81.0\,T^2},\ 0.5 - 0.001232201533\,T - 0.0001369112815\,\sqrt{13337104.0 - 67064.0\,T + 81.0\,T^2}$$

These are the 2 spinodals at any T (which correspond to two roots of a polynomial) which I can plot as a function of temperature. I will plot only for temperatures up to T_c as mixtures above T_c are homogenous at all compositions. I simply copy the maple output into the plot function:

```
>  plot( [.5-0.1232201533e-2*T+0.1369112815e-3*(13337104.-67064.*T+81.*T^2)^(1/2), .5-0.1232201533e-2*T-0.1369112815e-3*(13337104.-67064.*T+81.*T^
T=300..332);
```



And the result is the envelope of spinodals as a function of T. Notice that the spinodals are low polymer volume fractions.

(c) Binodal compositions for the same temperature range, and

The binodals correspond to where the $\Delta G^m/(NRT)$ versus ϕ_2 curve is tangent to the line whose compositional intercepts are the chemical potentials. In other words, if the chemical potentials are given by:

$$\frac{\mu_1 - \mu_1^\circ}{RT} = \Delta G^m/(NRT) + \phi_2\Big(\frac{\partial(\Delta G^m/(NRT))}{\partial \phi_1}\Big) \tag{1}$$

and

$$\frac{\mu_2 - \mu_2^\circ}{RT} = \Delta G^m/(NRT) + \phi_1\Big(\frac{\partial(\Delta G^m/(NRT))}{\partial \phi_2}\Big), \tag{2}$$

then the spinodal fractions of the two phases, which we denote $\{\phi_1^\dagger, \phi_2^\dagger\}$ and $\{\phi_1^\ddagger, \phi_2^\ddagger\}$ are those at which

$$\frac{\mu_1^\dagger - \mu_1^\circ}{RT} = \frac{\mu_1 \ddagger - \mu_1^\circ}{RT},$$

and

$$\frac{\mu_2^\dagger - \mu_2^\circ}{RT} = \frac{\mu_2^\ddagger - \mu_2^\circ}{RT}.$$

So, inserting the F-H expression for eq 1 and 2, we get

$$\frac{\mu_1 - \mu_1^\circ}{RT} = \chi\phi_2^2 + \ln(1-\phi_2) + \phi_2\Big(1 - \frac{1}{\mathcal{N}}\Big)$$

and

$$\frac{\mu_2 - \mu_2^\circ}{RT} = \chi(1-\phi_2)^2 + \frac{1}{\mathcal{N}}\ln(\phi_2) + (1-\phi_2)\Big(\frac{1}{\mathcal{N}} - 1\Big).$$

Thus, there are 2 equations, $\mu_1^\dagger = \mu_1^\ddagger$ and $\mu_2^\dagger = \mu_2^\ddagger$, and 2 unknowns, $\phi_2^\dagger$ and $\phi_2^\ddagger$ to solve. These equations are:

$$\begin{aligned}
\chi\phi_2^{2\dagger} + \ln\left(1-\phi_2^\dagger\right) + \phi_2^\dagger\left(1-\frac{1}{\mathcal{N}}\right) &= \chi\phi_2^{2\ddagger} + \ln\left(1-\phi_2^\ddagger\right) + \phi_2^\ddagger\left(1-\frac{1}{\mathcal{N}}\right) \\
\chi(1-\phi_2^\dagger)^2 + \frac{1}{\mathcal{N}}\ln\left(\phi_2^\dagger\right) + (1-\phi_2^\dagger)\left(\frac{1}{\mathcal{N}}-1\right) &= \chi(1-\phi_2^\ddagger)^2 + \frac{1}{\mathcal{N}}\ln\left(\phi_2^\ddagger\right) + (1-\phi_2^\ddagger)\left(\frac{1}{\mathcal{N}}-1\right)
\end{aligned}$$

Now $\chi = 0.605 \times 332/T$, so these above equations provide for each temperature $T < T_c = 332$, the binodals or the compositions of the two phases, $\phi_2^\dagger$ and $\phi_2^\ddagger$. These are also the phase diagram requested below. Note that the binodals are not found as the polyemr volume fractions which minimise ΔG^m, although these minima are excellent first guesses in an iterative solution of the above 2 equations.

(d) T-ϕ_2 phase diagram This is the T versus $\phi_2^\dagger$ and T versus $\phi_2^\ddagger$ plots..

Discuss how these predictions would be altered for a solution of chains of higher molecular weight.

With higher molecular weight chains, the polymer becomes even more difficult to homogenously mix. You need to go to even higher temperatures in order to get the chains to mix homogeneously. That is T_c increases with molecular weight or $\mathcal{N}$. Moreover, the composition at the critical point , ϕ_2c, is smaller for larger $\mathcal{N}$. See figure in Section 5.3.3