Deriving κ for FH

Binary

Our FH expression is

$$g(\phi_1, \phi_2) = \frac{\phi_1}{N_1}\ln(\phi_1) + \frac{\phi_2}{N_2}\ln(\phi_2) + \chi\phi_1\phi_2 \tag{1}$$

We have our Free energy functional which looks like:

$$\mathcal{G} = \int_V g(\phi_1, \phi_2) + \frac{\kappa}{2}(\nabla\phi_1)^2 \; dV \tag{2}$$

We can split g and κ into Entropic and Enthalpic contributions i.e., $g = g_{ideal} + g_{residual}$ and $\kappa = \kappa_{entropic} + \kappa_{enthalpic}$.

To derive $\kappa_{entropic}$ first, we introduce a perturbation of the form

$$\bar{\phi}_i = \phi_i - \epsilon_i, \quad \epsilon_i = \frac{R^2_{G,i}}{6}\nabla^2\phi_i. \tag{3}$$

We need some basic algebraic identities to make progress on the expansion.

Helpful aside 1: Expansion of $\ln{(x-\epsilon)}$

Consider $\ln{(x-\epsilon)}$, we can rewrite it as

$$\begin{aligned} \ln{(x-\epsilon)} &= \ln{\left(x(1-\frac{\epsilon}{x})\right)} \\ &= \ln{(x)} + \ln{\left(1-\frac{\epsilon}{x}\right)} \end{aligned} \tag{4}$$

We can use a Taylor series expansion for the second term by introducing a transformation $u = \frac{\epsilon}{x}$, which neatly gives us the expansion

$$\ln{(1-u)} = -u - \frac{u^2}{2} - \frac{u^3}{3} + \ldots \tag{5}$$

We are only interested in the first order terms. So we get

$$\ln{(x-\epsilon)} = \ln{(x)} - \frac{\epsilon}{x} + \ldots \tag{6}$$

Back to things!

Starting with

$$\int_V \frac{\phi_1-\epsilon_1}{N_1}\ln{(\phi_1-\epsilon_1)} + \frac{\phi_2-\epsilon_2}{N_2}\ln{(\phi_2-\epsilon_2)}\, dV \tag{7}$$

And inserting our expansion result

$$\int_V \frac{1}{N_1}\left((\phi_1-\epsilon_1)\left(\ln\phi_1 - \frac{\epsilon_1}{\phi_1}\right)\right) + \frac{1}{N_2}\left((\phi_2-\epsilon_2)\left(\ln\phi_2 - \frac{\epsilon_2}{\phi_2}\right)\right) \; dV \tag{8}$$

Expanding out more and retaining terms of $\mathcal{O}(\epsilon)$,

$$\int_V \frac{1}{N_1}(\phi_1 \ln \phi_1 - \epsilon_1 \ln \phi_1 - \epsilon_1) + \frac{1}{N_2}(\phi_2 \ln \phi_2 - \epsilon_2 \ln \phi_2 - \epsilon_2)\ dV \tag{9}$$

Splitting up

$$\begin{gathered}
\mathcal{O}(1): \\
\int_V \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2\ dV \\
\mathcal{O}(\epsilon): \\
\int_V -\frac{1}{N_1}\epsilon_1 \ln \phi_1 - \frac{\epsilon_1}{N_1} - \frac{1}{N_2}\epsilon_2 \ln \phi_2 - \frac{\epsilon_2}{N_2}\ dV
\end{gathered} \tag{10}$$

We thus want to unpack the $\mathcal{O}(\epsilon)$ terms because the $\mathcal{O}(1)$ terms directly correspond to $\int_V g(\phi_1, \phi_2)$.

Recall that $\epsilon_i = \frac{R_{G,i}^2}{6}\nabla^2 \phi_i$, we also note that $\phi_1 = 1 - \phi_2$. Therefore

$$\epsilon_2 = \frac{R_{G,2}^2}{6}\nabla^2 \phi_2 = -\frac{R_{G,2}^2}{6}\nabla^2 \phi_1 \tag{11}$$

Factoring out $\nabla^2 \phi_1$,

$$\int_V \frac{1}{6}\left(\frac{R_{G,2}^2}{N_2}\ln(1-\phi_1) - \frac{R_{G,1}^2}{N_1}\ln \phi_1 + \frac{R_{G,2}^2}{N_2} - \frac{R_{G,1}^2}{N_1}\right)\nabla^2 \phi_1 \tag{12}$$

Helpful Aside 2: Integration by Parts and Divergence Theorem

Recall integration by parts for higher dimensions:

$$\int_V u\nabla \cdot (\mathbf{V})\, dV = \int_S u\mathbf{V}\cdot \mathbf{n}\, dS - \int_V \nabla u \cdot \mathbf{V}\, dV \tag{13}$$

By specifying suitable BCs, the surface integral disappears. We also want to recall the following Vector Calc identity:

$$\nabla^2 \phi = \nabla \cdot (\nabla \phi) \tag{14}$$

Back to our problem.

$$\begin{aligned}
\int_V \ln(1-\phi_1)\nabla^2\phi_1 &= -\int_V \nabla(\ln(1-\phi_1))\cdot \nabla\phi_1\ dV \\
&= -\int_V \frac{-1}{1-\phi_1}\nabla\phi_1\cdot\nabla\phi_1\ dV \\
&= \int_V \frac{1}{1-\phi_1}(\nabla\phi_1)^2
\end{aligned} \tag{15}$$

$$\int_V \ln\phi_1 \nabla^2\phi_1 = -\int_V \frac{1}{\phi_1}\nabla(\phi_1)^2 \tag{16}$$

$$\int_V \nabla^2\phi_1 = \int_V \nabla 1\cdot\nabla\phi_1 = 0 \tag{17}$$

So our unitary terms disappear.

We thus have:

$$\int_V \frac{1}{6}\left(\frac{R_{G,2}^2}{N_2(1-\phi_1)} + \frac{R_{G,1}^2}{N_1\phi_1}\right)(\nabla\phi_1)^2 \tag{18}$$

We thus recover

$$\kappa_{entropic} = \frac{1}{3}\left(\frac{R_{G,1}^2}{N_1\phi_1} + \frac{R_{G,2}^2}{N_2(1-\phi_1)}\right) \tag{19}$$

Doing the same process for $\kappa_{enthalpic}$,

$$\int_V \chi\phi_1\phi_2 \; dV \tag{20}$$

Inserting our perturbation

$$\begin{aligned}&\int_V \chi(\phi_1-\epsilon_1)(\phi_2-\epsilon_2)\; dV \\ &= \int_V \chi\phi_1\phi_2 - \chi(\epsilon_2\phi_1+\epsilon_1\phi_2)\; dV\end{aligned} \tag{21}$$

Focusing $\mathcal{O}(\epsilon)$,

$$\begin{aligned}&-\frac{\chi}{6}\int_V -\phi_1 R_{G,2}^2\nabla^2\phi_1 + R_{G,1}^2(1-\phi_1)\nabla^2\phi_1\; dV \\ &= \frac{\chi}{6}\int_V R_{G,2}^2\phi_1\nabla^2\phi_1 + R_{G,1}^2\phi_1\nabla^2\phi_1 - R_{G,1}^2\nabla^2\phi_1\; dV \\ &= \frac{\chi}{6}\int_V \left(R_{G,1}^2 + R_{G,2}^2\right)(\nabla\phi)^2\end{aligned} \tag{22}$$

By inspection,

$$\kappa_{enthalpic} = \frac{\chi}{3}\left(R_{G,1}^2 + R_{G,2}^2\right) \tag{23}$$

Ternary

For the ternary system, the Free energy functional looks like

$$\begin{aligned}&\mathcal{G}(\phi_1,\phi_2,\phi_3) = \\ &\int_V g(\phi_1,\phi_2,\phi_3) + \frac{\kappa_1}{2}(\nabla^2\phi_1) + \frac{\kappa_2}{2}(\nabla^2\phi_2) + \kappa_{12}(\nabla\phi_1)(\nabla\phi_2)\; dV\end{aligned} \tag{24}$$

We start with

$$\int_V \frac{\phi_1}{N_1}\ln\phi_1 + \frac{\phi_2}{N_2}\ln\phi_2 + \frac{\phi_3}{N_3}\ln\phi_3\; dV \tag{25}$$

Inserting the perturbations

$$\begin{aligned}&\int_V \left(\frac{(\phi_1-\epsilon_1)}{N_1}\ln(\phi_1-\epsilon_1) + \frac{(\phi_2-\epsilon_2)}{N_2}\ln(\phi_2-\epsilon_2) \right.\\ &\left. + \frac{(\phi_3-\epsilon_3)}{N_3}\ln(\phi_3-\epsilon_3)\right)\; dV\end{aligned} \tag{26}$$

Expanding and similarly retaining terms of $\mathcal{O}(\epsilon)$,

$$\int_V -\frac{1}{N_1}\epsilon_1\ln\phi_1 - \frac{\epsilon_1}{N_1} - \frac{1}{N_2}\epsilon_2\ln\phi_2 - \frac{\epsilon_2}{N_2} - \frac{1}{N_3}\epsilon_3\ln\phi_3 - \frac{\epsilon_3}{N_3}\; dV \tag{27}$$

Inserting our expressions for ϵ,

$$\int_V \left(\frac{-1}{N_1}\frac{R_{G,1}^2}{6}\nabla^2\phi_1 \ln\phi_1 - \frac{R_{G,1}^2}{6N_1}\nabla^2\phi_1 - \frac{1}{N_2}\frac{R_{G,2}^2}{6}\nabla^2\phi_2 \ln\phi_2 - \frac{R_{G,2}^2}{6N_2}\nabla^2\phi_2 \right. \\ \left. - \frac{1}{N_3}\frac{R_{G,3}^2}{6}\nabla^2\phi_3 \ln\phi_3 - \frac{R_{G,3}^2}{6N_3}\nabla^2\phi_3 \right) \, dV \tag{28}$$

Doing this term by term

$$\int_V \frac{-1}{N_1}\frac{R_{G,1}^2}{6}\nabla^2\phi_1 \ln\phi_1 - \frac{R_{G,1}^2}{6N_1}\nabla^2\phi_1 \, dV \\ = \int_V \frac{R_{G,1}^2}{6}\frac{1}{N_1\phi_1}(\nabla\phi_1)^2 \, dV \tag{29}$$

$$\int_V -\frac{1}{N_2}\frac{R_{G,2}^2}{6}\nabla^2\phi_2 \ln\phi_2 - \frac{R_{G,2}^2}{6N_2}\nabla^2\phi_2 \, dV \\ = \int_V \frac{R_{G,2}^2}{6}\frac{1}{N_2\phi_2}(\nabla\phi_2)^2 \tag{30}$$

$$\int_V -\frac{1}{N_3}\frac{R_{G,3}^2}{6}\nabla^2\phi_3 \ln\phi_3 - \frac{R_{G,3}^2}{6N_3}\nabla^2\phi_3 \, dV \\ \text{Dropping the second term because it disappears} \\ = -\frac{R_{G,3}^2}{6N_3}\int_V \nabla^2(1-\phi_1-\phi_2)\ln(1-\phi_1-\phi_2) \, dV \\ = \frac{R_{G,3}^2}{6N_3}\int_V \frac{1}{1-\phi_1-\phi_2}\left((\nabla\phi_1)^2 + (\nabla\phi_2)^2 + 2\nabla\phi_1\cdot\nabla\phi_2\right) \tag{31}$$

Adding things up:

$$\int_V \frac{1}{6}\left(\frac{R_{G,1}^2}{N_1\phi_1} + \frac{R_{G,3}^2}{N_3(1-\phi_1-\phi_2)}\right)(\nabla\phi_1)^2 + \\ \frac{1}{6}\left(\frac{R_{G,2}^2}{N_2\phi_2} + \frac{R_{G,3}^2}{N_3(1-\phi_1-\phi_2)}\right)(\nabla\phi_2)^2 + \\ \frac{1}{3}\frac{R_{G,3}^2}{N_3}\frac{1}{1-\phi_1-\phi_2}(\nabla\phi_1\cdot\nabla\phi_2) \, dV \tag{32}$$

We thus get

$$\kappa_{1,entropic} = \frac{1}{3}\left(\frac{R_{G,1}^2}{N_1\phi_1} + \frac{R_{G,3}^2}{N_3(1-\phi_1-\phi_2)}\right) \tag{33}$$

$$\kappa_{2,entropic} = \frac{1}{3}\left(\frac{R_{G,2}^2}{N_2\phi_2} + \frac{R_{G,3}^2}{N_3(1-\phi_1-\phi_2)}\right) \tag{34}$$

$$\kappa_{12,entropic} = \frac{1}{3}\frac{R_{G,3}^2}{N_3}\frac{1}{1-\phi_1-\phi_2} \tag{35}$$

For the Enthalpic component,

$$\int_V \chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_3 + \chi_{23}\phi_2\phi_3 \tag{36}$$

Introducing our perturbation

$$\int_V \chi_{12}(\phi_1 - \epsilon_1)(\phi_2 - \epsilon_2) + \chi_{13}(\phi_1 - \epsilon_1)(\phi_3 - \epsilon_3) + \chi_{23}(\phi_2 - \epsilon_2)(\phi_3 - \epsilon_3)\, dV \tag{37}$$

Expanding out and retain terms of $\mathcal{O}(\epsilon)$ and below,

$$\begin{aligned}\int_V \chi_{12}\left(\phi_1\phi_2 - \epsilon_2\phi_1 - \epsilon_1\phi_2\right) + \chi_{13}(\phi_1\phi_3 - \epsilon_3\phi_1 - \epsilon_1\phi_3) \\ + \chi_{23}(\phi_2\phi_3 - \epsilon_3\phi_2 - \epsilon_2\phi_3)\end{aligned} \tag{38}$$

$\mathcal{O}(\epsilon)$,

$$\begin{aligned}\int_V -\chi_{12}\frac{R_{G,2}^2}{6}\phi_1\nabla^2\phi_2 - \chi_{12}\frac{R_{G,1}^2}{6}\phi_2\nabla^2\phi_1 \\ - \chi_{13}\frac{R_{G,3}^2}{6}\phi_1\nabla^2\phi_3 - \chi_{13}\frac{R_{G,1}^2}{6}\phi_3\nabla^2\phi_1 \\ - \chi_{23}\frac{R_{G,3}^2}{6}\phi_2\nabla^2\phi_3 - \chi_{23}\frac{R_{G,2}^2}{6}\phi_3\nabla^2\phi_2\, dV\end{aligned} \tag{39}$$

Expanding out ϕ_3 terms

$$\begin{aligned}\int_V -\chi_{12}\frac{R_{G,2}^2}{6}\phi_1\nabla^2\phi_2 - \chi_{12}\frac{R_{G,1}^2}{6}\phi_2\nabla^2\phi_1 \\ - \chi_{13}\frac{R_{G,3}^2}{6}\phi_1\left(-\nabla^2\phi_1 - \nabla^2\phi_2\right) - \chi_{13}\frac{R_{G,1}^2}{6}(1 - \phi_1 - \phi_2)\nabla^2\phi_1 \\ - \chi_{23}\frac{R_{G,3}^2}{6}\phi_2(-\nabla^2\phi_1 - \nabla^2\phi_2) - \chi_{23}\frac{R_{G,2}^2}{6}(1 - \phi_1 - \phi_2)\nabla^2\phi_2\, dV\end{aligned} \tag{40}$$

Dropping constant coefficient terms because they disappear

$$\begin{aligned}\int_V -\chi_{12}\frac{R_{G,2}^2}{6}\phi_1\nabla^2\phi_2 - \chi_{12}\frac{R_{G,1}^2}{6}\phi_2\nabla^2\phi_1 \\ + \chi_{13}\frac{R_{G,3}^2}{6}\phi_1\nabla^2\phi_1 + \chi_{13}\frac{R_{G,3}^2}{6}\phi_1\nabla^2\phi_2 \\ \chi_{13}\frac{R_{G,1}^2}{6}\phi_1\nabla^2\phi_1 + \chi_{13}\frac{R_{G,1}^2}{6}\phi_2\nabla^2\phi_1 \\ + \chi_{23}\frac{R_{G,3}^2}{6}\phi_2\nabla^2\phi_1 + \chi_{23}\frac{R_{G,3}^2}{6}\phi_2\nabla^2\phi_2 \\ + \chi_{23}\frac{R_{G,2}^2}{6}\phi_1\nabla^2\phi_2 + \chi_{23}\frac{R_{G,2}^2}{6}\phi_2\nabla^2\phi_2\, dV\end{aligned} \tag{41}$$

Grouping terms

$$\begin{aligned}\int_V \left(\chi_{13}\frac{R_{G,3}^2}{6} + \chi_{13}\frac{R_{G,1}^2}{6}\right)\phi_1\nabla^2\phi_1 \\ + \left(\chi_{23}\frac{R_{G,3}^2}{6} + \chi_{23}\frac{R_{G,2}^2}{6}\right)\phi_2\nabla^2\phi_2 \\ + \left(-\chi_{12}\frac{R_{G,2}^2}{6} + \chi_{13}\frac{R_{G,3}^2}{6} + \chi_{23}\frac{R_{G,2}^2}{6}\right)\phi_1\nabla^2\phi_2 \\ + \left(-\chi_{12}\frac{R_{G,1}^2}{6} + \chi_{13}\frac{R_{G,1}^2}{6}\chi_{23}\frac{R_{G,3}^2}{6}\right)\phi_2\nabla^2\phi_1\, dV\end{aligned} \tag{42}$$

Integrating by parts and getting our κ

$$\kappa_{1,enthalpic} = \frac{\chi_{13}}{3}(R_{G,1}^2 + R_{G,3}^2) \tag{43}$$

$$\kappa_{2,enthalpic} = \frac{\chi_{23}}{3}(R_{G,2}^2 + R_{G,3}^2) \tag{44}$$

$$\kappa_{12,enthalpic} = \frac{1}{6}\Big((R_{G,1}^2 + R_{G,3}^2)\chi_{13} + (R_{G,2}^2 + R_{G,3}^2)\chi_{23} - (R_{G,1}^2 + R_{G,2}^2)\chi_{12}\Big) \tag{45}$$

Some Comments

- Using the perturbation approach outlined here, we are able to generate the $\kappa_{enthalpic}$ terms correctly
  - See https://doi.org/10.1002/(SICI)1099-0488(20000515)38:10%3C1301::AID-POLB50%3E3.0.CO;2-M, https://doi.org/10.1002/polb.1990.09028121
- However, the entropic terms are a bit off from the same works:
  - For the binary mixture, in one paper, the expression matches correctly: https://doi.org/10.1002/polb.1989.090271306
  - However for the polymer-solvent and polymer-polymer-solvent systems, they do not match up.
- The method used by Ariyapadi (https://doi.org/10.1002/polb.1990.090281216) only introduces $N-1$ ϵ terms, which means that information (i.e., $R_{G,N}$)about the Nth species is not captured which leaves me suspicious.