

Supplementary Material

May 28, 2021

1 Solving for the association fraction in PC-SAFT

The association fraction is obtained by solving a system of non-linear equations given by:

$$X_{i,a} = \frac{1}{1 + \rho \sum_j \sum_b^{n_j^{\text{assoc}}} n_{j,b} x_j X_{j,b} \Delta_{ij,ab}}, \quad (1)$$

where n_i^{assoc} is the number of types of sites on species i , ρ is the number density of the system, $n_{i,a}$ is the number of sites of type a on species i , $X_{i,a}$ is the fraction of sites of type a on species i not bonded to any other site and $\Delta_{ij,ab}$ is the association strength between site of type a on species i and site of type b on species j . Whilst one could solve for the above equation using standard root-finding algorithms such as Newton–Raphson, a commonly-used approach is to imply solve the above equation iteratively such that:

$$X_{i,a}^{(k+1)} = \frac{1}{1 + \rho \sum_j \sum_b^{n_j^{\text{assoc}}} n_{j,b} x_j X_{j,b}^{(k)} \Delta_{ij,ab}}, \quad (2)$$

where the superscript (k) denotes a particular iteration; $X_{i,a}^{(0)}$ is typically assigned a value of 1 for all sites and species. Solving the above equation directly often results in oscillatory convergence; this is avoided by introducing a damping factor, α :

$$X_{i,a}^{(k+1)} = \alpha X_{i,a}^{(k)} + (1 - \alpha) \frac{1}{1 + \rho \sum_j \sum_b^{n_j^{\text{assoc}}} n_{j,b} x_j X_{j,b}^{(k)} \Delta_{ij,ab}}, \quad (3)$$

where α is usually given a value of 0.5. With this, it typically takes 5-10 iterations for the value of $X_{i,a}$ to converge.

2 Estimation of k_{ij} for polymer blends

In order to estimate the binary interaction parameter, k_{ij} , between polymers used in PC-SAFT, regression to experimental liquid–liquid equilibrium data is performed. Table 1 summarises the available data in literature for the polymer blends studied in this work.

The data provided in Tripathi¹'s work gives the composition at the liquid-liquid envelope, thus, as one can obtain such data from PC-SAFT (i.e. $x_i^\alpha(T, P; k_{ij})$, where α indexes the phase and i and j indexes the species), it is possible to define the following objective function:

$$\min_{k_{ij}} \sum_n (x_{i,n}^{\alpha, \text{exp}} - x_i^\alpha(T_n, P_n; k_{ij}))^2. \quad (4)$$

Using the standard steepest-descent algorithm, it is possible to determine the value of k_{ij} . It was found that the objective function was convex, as such, using the values obtained from the Hudson-McCoubrey combining rule as an initial guess, the locally optimal parameter obtained can be assumed to be the globally optimal parameter.

However, the data provided by Kressler *et al.*² details whether, at a given temperature and composition, phase-splitting is observed. In order to use this data to obtain k_{ij} , the objective function is redefined as:

$$\min_{k_{ij}} \left(1 - \frac{N_{p,c}(k_{ij})}{N_p} \right). \quad (5)$$

Table 1: Summary of polymer blend LLE data used and k_{ij} values obtained.

Polymer blend (molecular weight)	Refs	k_{ij}
PS(1344)/PB(1104)	Tripathi ¹	0.00034276
PS(1672)/PB(1104)	Tripathi ¹	-0.0003567
PS(4368)/PB(1104)	Tripathi ¹	-0.001414
PS(1344)/PB(2585)	Tripathi ¹	0.000721
PS(1672)/PB(2585)	Tripathi ¹	-0.0001737
PS(2950)/PMMA(10550)	Callaghan and Paul ³	0.01404
PS(2950)/PMMA(4250)	Callaghan and Paul ³	0.01415
PS(9200)/PMMA(2400)	Callaghan and Paul ³	0.01301
PS(9200)/PMMA(4250)	Callaghan and Paul ³	0.01288
PS(1250)/PMMA(6350)	Kressler <i>et al.</i> ²	0.01629
PS(1390)/PMMA(6350)	Kressler <i>et al.</i> ²	0.01603
PS(1390)/PMMA(12000)	Kressler <i>et al.</i> ²	0.01605

where N_p is the number of point and $N_{p,c}$ counts the number of times where, at a given composition and temperature, PC-SAFT predicts the same phase as the experimental data. Unfortunately, this function is not smooth; as such, a gradient-free algorithm was used instead.

The k_{ij} values obtained from these procedures are given in table 1.

3 Derivation of κ

Following the methodology of Ariyapadi and Nauman⁴, the value of the gradient energy parameter κ can be derived from the Gibbs free energy of mixing function. This methodology can be used to identify a suitable expression for κ when more complex free energy functions are used. For this section, we use a simple quartic polynomial as an illustrative example.

In terms of both the averaged volume fractions of species 1 and 2 over all lattice sites $\bar{\phi}_1$ and $\bar{\phi}_2$ respectively, the Gibbs energy of mixing can be written as follows:

$$\tilde{g}_m(\bar{\phi}_1, \bar{\phi}_2) = A\bar{\phi}_1^2\bar{\phi}_2^2, \quad (6)$$

where A is a constant that is often fitted or specified as a model parameter. The relationship between $\bar{\phi}_i$ and the normal volume fraction ϕ_i is written as follows:

$$\phi_i(\mathbf{r}) = \bar{\phi}_i + \epsilon_i, \quad \epsilon_i = \frac{R_{G,i}^2}{6}(\nabla^2 \phi_i), \quad (7)$$

where $R_{G,i}$ is the radius of gyration for species i . It should be noted that when the system is homogeneous, $\bar{\phi}$ and ϕ are identical.

The total Gibbs energy of the system G_{System} can be evaluated by integrating eq. (6) over the entire volume:

$$G_{\text{System}} = \int_{\tilde{V}} A\bar{\phi}_1^2\bar{\phi}_2^2 d\tilde{V}. \quad (8)$$

Upon introducing the expression given in eq. (7) and discarding terms of ϵ^2 or higher, we can write down the following expression for G_{System} :

$$G_{\text{System}} = \int_{\tilde{V}} A(\phi_1^2\phi_2^2 - 2\epsilon_2\phi_2\phi_1^2 - 2\epsilon_1\phi_1\phi_2^2) d\tilde{V}. \quad (9)$$

At this stage, we can consider how the Landau–Ginzburg free energy functional which is written as follows:

$$G_{\text{System}} = \int_{\tilde{V}} g(\phi_1) + \frac{\kappa}{2}(\nabla\phi_1)^2 d\tilde{V}, \quad (10)$$

consists of both a uniform (U) and non-uniform (NU) contribution:

$$G_{\text{System}} = G_U + G_{\text{NU}} \quad (11)$$

The uniform contribution can be simply written as follows:

$$G_U = \int_{\tilde{V}} A \phi_1^2 \phi_2^2 d\tilde{V}, \quad (12)$$

while the non-uniform contribution can be written as follows:

$$G_{NU} = A \int_{\tilde{V}} \left(\frac{-R_{G,1}^2}{3} + 2\phi_1 \left(\frac{2R_{G,1}^2}{3} + \frac{R_{G,2}^2}{3} \right) - 3\phi_1^2 \left(\frac{R_{G,1}^2}{3} + \frac{R_{G,2}^2}{3} \right) \right) (\nabla \phi_1)^2 d\tilde{V}. \quad (13)$$

A direct comparison between eq. (13) and eq. (10) enables us to write down the following expression for κ :

$$\frac{\kappa}{2} = A \left(\frac{-R_{G,1}^2}{3} + 2\phi_1 \left(\frac{2R_{G,1}^2}{3} + \frac{R_{G,2}^2}{3} \right) - 3\phi_1^2 \left(\frac{R_{G,1}^2}{3} + \frac{R_{G,2}^2}{3} \right) \right). \quad (14)$$

We can note that this expression for κ is comparatively complicated and it introduces a compositional dependence which is typically neglected by most studies. In contrast, when only the residual free energy component of the Gibbs free energy of mixing given by the Flory–Huggins equation is considered, κ can be written quite cleanly:

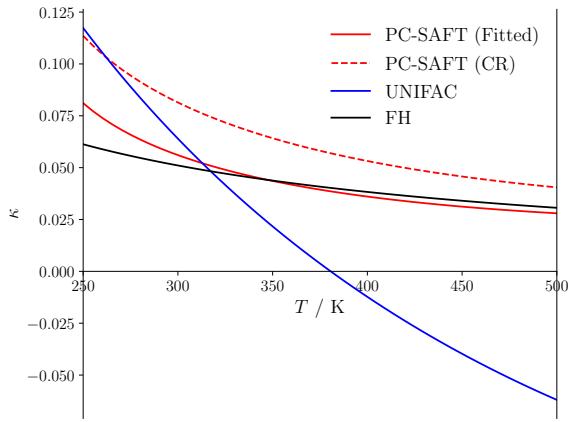
$$\frac{\kappa}{2} = \chi_{12} \left(\frac{R_{G,1}^2}{6} + \frac{R_{G,2}^2}{6} \right). \quad (15)$$

It must be noted that the residual / excess component of the zeroth order Redlich–Kistler approximation for \tilde{g}_m takes on the same form as the residual component of the Flory–Huggins equation when the polymers are of same length.

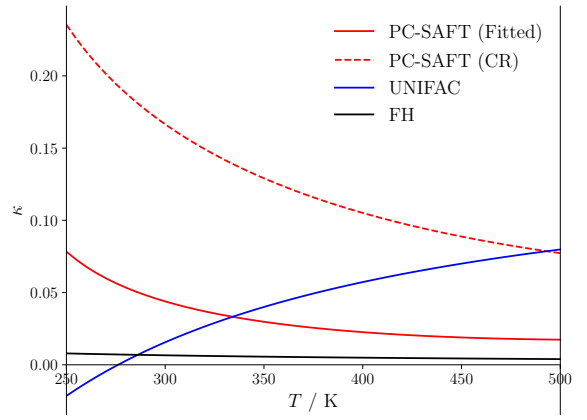
In order to obtain κ for UNIFAC-FV and the PC-SAFT models studied, one should, in principle, obtain it by repeating the process used to obtain equation 15. However, due to lengthy equations involved in these models, this is quite complex and introduces additional non-linearities to the Cahn–Hilliard equation. As such, in order to approximate κ , we will be approximating both UNIFAC-FV and PC-SAFT by the Flory–Huggins equation such that:

$$\min_{\chi_{12}} \sum_n \left(\chi_{12} - \frac{\Delta g_{\text{mix},m}(\phi_{i,n}) - \sum_i \phi_{i,n} \ln(\phi_{i,n}/N_i)}{\phi_{i,n}(1 - \phi_{i,n})} \right)^2, \quad (16)$$

where n indexes the number of points where $\Delta g_{\text{mix},m}$ is evaluated in the range of ϕ_i between zero and one. Using the polyfit function provided in the numpy module, one hundred points are used to fit χ_{12} for UNIFAC-FV and PC-SAFT. The resulting values for κ in the cases studied are given in figure 1.



(a) Fitted κ (using equation 16) for a of a PS/PB blend where $N_1 = N_2 = 50$. For PC-SAFT: $k_{ij}^{\text{Fitted}} = -0.0014$ and $k_{ij}^{\text{CR}} = 0.0001$.



(b) Fitted κ (using equation 16) for a of a PS/PMMA blend where $N_1 = N_2 = 500$. For PC-SAFT: $k_{ij}^{\text{Fitted}} = 0.0125$ and $k_{ij}^{\text{CR}} = 0.0180$.

Figure 1: Fitted κ (using equation 16) for different polymer blends of interest using the PC-SAFT with k_{ij} estimated from either the Hudson-McCoubrey combining rule (red, dashed) or equation 64, in main text, (red, solid), UNIFAC (blue, solid) and Flory-Huggins (black, solid) equations.(color online)

References

- [1] J. B. P. Tripathi, *PhD thesis*, Imperial College London, 1979.
- [2] J. Kressler, N. Higashida, K. Shimomai, T. Inoue and T. Ougizawa, *Macromolecules*, 1994, **27**, 2448–2453.
- [3] T. A. Callaghan and D. R. Paul, *Macromolecules*, 1993, **26**, 2439–2450.
- [4] M. V. Ariyapadi and E. B. Nauman, *Journal of Polymer Science Part B: Polymer Physics*, 1990, **28**, 2395–2409.