Supplementary Information (SI) for Molecular Systems Design & Engineering.

PhaseTime: A Flory–Huggins-Based Computational Framework for Predicting Time-Dependent Phase Diagrams of Reactive Polymer Blends

Supplemental Material

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Contents

S1. Chemical potentials of the constituents i1 and 2j

Consider a quasibinary polymer blend comprising two polydisperse species, labeled 1 and 2. Species 1 consists of constituents 1i with chain size N_{1i} and volume fraction φ_{1i}, while species 2 consists of constituents 2j with chain size N_{2j} and volume fraction φ_{2j}. The total number of segments is:

$$N_{\text{tot}} = \sum_i n_{1i} N_{1i} + \sum_j n_{2j} N_{2j} \tag{S1.1}$$

Assuming identical segment sizes, the volume fraction of the constituents is

$$\varphi_{1i} = \frac{n_{1i} N_{1i}}{N_{\text{tot}}}, \quad \varphi_{2j} = \frac{n_{2j} N_{2j}}{N_{\text{tot}}} \tag{S1.2}$$

and the total volume fractions of the two species are

$$\varphi_1 = \sum_i \varphi_{1i}, \quad \varphi_2 = \sum_j \varphi_{2j}.$$

By applying the incompressibility assumption:

$$\varphi_1 + \varphi_2 = 1$$

In the context of the Flory–Huggins framework with temperature- and composition-dependent interactions,[1] the normalized free energy of mixing per lattice site is:

$$f_{\text{m}} = \sum_i \frac{\varphi_{1i}}{N_{1i}} \ln \varphi_{1i} + \sum_j \frac{\varphi_{2j}}{N_{2j}} \ln \varphi_{2j} + g \varphi_1 \varphi_2 \tag{S1.3}$$

with $g = g(T, \varphi_2)$ being an interaction parameter dependent on composition and temperature, and is commonly expressed in terms of an interaction parameter $\chi(T, \varphi_2)$ defined via chemical potentials[2]. The two are related as:[2,3]

$$\chi = g - g_\varphi \varphi_1 \tag{S1.4}$$

where we have invoked the short-hand notation:

$$g_\varphi = \left. \frac{\partial g}{\partial \varphi_2} \right|_T .$$

For any constituent $a \in (1i, 2j)$, the dimensionless chemical potential is:

$$\frac{\Delta\mu_a}{k_\mathrm{B}T} = \left.\frac{\partial\left[N_\mathrm{tot} f_\mathrm{m}\right]}{\partial n_a}\right|_{n_{a\neq k},T,P} = f_\mathrm{m}\frac{\partial N_\mathrm{tot}}{\partial n_a} + N_\mathrm{tot}\sum_b f_{\mathrm{m},\varphi_b}\frac{\partial \varphi_b}{\partial n_a} \tag{S1.5}$$

where we have invoked the short-hand notation, $f_{\mathrm{m},\varphi_b} = \frac{\partial f_\mathrm{m}}{\partial \varphi_b}$.

Let’s compute these terms one by one:

$$\frac{\partial N_\mathrm{tot}}{\partial n_a} = N_a \tag{S1.6}$$

$$\frac{\partial \varphi_b}{\partial n_a} = \frac{\partial}{\partial n_a}\left[\frac{n_b N_b}{N_\mathrm{tot}}\right] = \frac{N_b}{N_\mathrm{tot}}\frac{\partial n_b}{\partial n_a} - n_b N_b \frac{1}{N_\mathrm{tot}{}^2}\frac{\partial N_\mathrm{tot}}{\partial n_a} = \frac{N_a}{N_\mathrm{tot}}\left(\delta_{ab} - \varphi_b\right) \tag{S1.7}$$

Substituting eqns (S1.6) and (S1.7) to eqn (S1.5):

$$\begin{aligned} \frac{\Delta\mu_a}{k_\mathrm{B}T} &= f_\mathrm{m} N_a + N_\mathrm{tot}\sum_b f_{\mathrm{m},\varphi_b}\left[\frac{N_a}{N_\mathrm{tot}}\left(\delta_{ab} - \varphi_b\right)\right] \\ &= f_\mathrm{m} N_a + \sum_b f_{\mathrm{m},\varphi_b}\left[N_a \delta_{ab}\right] - \sum_b f_{\mathrm{m},\varphi_b}\left[N_a \varphi_b\right] \\ &= N_a\left[f_\mathrm{m} + f_{\mathrm{m},\varphi_a} - \sum_b f_{\mathrm{m},\varphi_b}\varphi_b\right] \end{aligned} \tag{S1.8}$$

The common constraint term in eqn (S1.8) can be expressed as:

$$\sum_b f_{\mathrm{m},\varphi_b}\varphi_b = \sum_{1i} f_{\mathrm{m},\varphi_{1i}}\varphi_{1i} + \sum_{2j} f_{\mathrm{m},\varphi_{2j}}\varphi_{2j} \tag{S1.9}$$

By substituting the partial derivatives of free energy for constituents 1*i* and 2*j*,:

$$\frac{\partial f_\mathrm{m}}{\partial \varphi_{1i}} = \frac{1}{N_{1i}}\left(\ln\varphi_{1i} + 1\right) + g\varphi_2, \tag{S1.10}$$

$$\frac{\partial f_\mathrm{m}}{\partial \varphi_{2j}} = \frac{1}{N_{2j}}\left(\ln\varphi_{2j} + 1\right) + g\varphi_1 + g_\varphi \varphi_1 \varphi_2, \tag{S1.11}$$

to eqn (S1.8) we get:

$$\begin{aligned}\sum_b f_{\mathrm{m},\varphi_b}\varphi_b &= \sum_{1i}\frac{\varphi_{1i}}{N_{1i}}\left(\ln\varphi_{1i}+1\right)+\sum_{2j}\frac{\varphi_{2j}}{N_{2j}}\left(\ln\varphi_{2j}+1\right)+2g\varphi_1\varphi_2+g_\varphi\varphi_1\varphi_2{}^2 \\ &= S+\sum_{1i}\frac{\varphi_{1i}}{N_{1i}}\ln\varphi_{1i}+\sum_{2j}\frac{\varphi_{2j}}{N_{2j}}\ln\varphi_{2j}+2g\varphi_1\varphi_2+g_\varphi\varphi_1\varphi_2{}^2\end{aligned} \tag{S1.12}$$

where,

$$\rho_{\mathrm{ch}}=\sum_{1i}\frac{\varphi_{1i}}{N_{1i}}+\sum_{2j}\frac{\varphi_{2j}}{N_{2j}}=\frac{\varphi_1}{N_{1\mathrm{n}}}+\frac{\varphi_2}{N_{2\mathrm{n}}}. \tag{S1.13}$$

is the total dimensionless molecular-number density, with $N_{1\mathrm{n}}$ and $N_{2\mathrm{n}}$ being the number averages of the corresponding size-distributions.

The chemical potential of the constituent 1*i* can be obtained by substituting eqns (S1.3), (S1.10) and (S1.12) to eqn (S1.8):

$$\begin{aligned}\frac{\Delta\mu_{1i}}{k_{\mathrm{B}}T}\frac{1}{N_{1i}} &= f_{\mathrm{m}}+f_{\mathrm{m},\varphi_{1i}}-\sum_b f_{\mathrm{m},\varphi_b}\varphi_b \\ &= \sum_i\frac{\varphi_{1i}}{N_{1i}}\ln\varphi_{1i}+\sum_j\frac{\varphi_{2j}}{N_{2j}}\ln\varphi_{2j}+g\varphi_1\varphi_2 \\ &\quad+\frac{1}{N_{1i}}\left(\ln\varphi_{1i}+1\right)+g\varphi_2 \\ &\quad-\rho_{\mathrm{ch}}-\sum_{1i}\frac{\varphi_{1i}}{N_{1i}}\ln\varphi_{1i}-\sum_{2j}\frac{\varphi_{2j}}{N_{2j}}\ln\varphi_{2j}-2g\varphi_1\varphi_2-g_\varphi\varphi_1\varphi_2{}^2 \\ &= \frac{1}{N_{1i}}\left(\ln\varphi_{1i}+1\right)-\rho_{\mathrm{ch}}+g\varphi_2{}^2-g_\varphi\varphi_1\varphi_2{}^2\end{aligned}$$

or

$$\frac{\Delta\mu_{1i}}{k_{\mathrm{B}}T}=\ln\varphi_{1i}+1-N_{1i}\rho_{\mathrm{ch}}+N_{1i}\varphi_2{}^2\left(g-g_\varphi\varphi_1\right) \tag{S1.14}$$

Similarly, the chemical potential of the constituent 2*j* can be obtained by substituting eqns (S1.3), (S1.11) and (S1.12) to eqn (S1.8):

$$\begin{aligned}\frac{\Delta\mu_{2j}}{k_{\mathrm{B}}T}\frac{1}{N_{2j}} &= f_{\mathrm{m}} + f_{\mathrm{m},\varphi_{2j}} - \sum_b f_{\mathrm{m},\varphi_b}\varphi_b \\ &= \sum_i \frac{\varphi_{1i}}{N_{1i}}\ln\varphi_{1i} + \sum_j \frac{\varphi_{2j}}{N_{2j}}\ln\varphi_{2j} + g\varphi_1\varphi_2 \\ &\quad + \frac{1}{N_{2j}}\left(\ln\varphi_{2j}+1\right) + g\varphi_1 + g_\varphi\varphi_1\varphi_2 \\ &\quad -\rho_{\mathrm{ch}} - \sum_{1i}\frac{\varphi_{1i}}{N_{1i}}\ln\varphi_{1i} - \sum_{2j}\frac{\varphi_{2j}}{N_{2j}}\ln\varphi_{2j} - 2g\varphi_1\varphi_2 - g_\varphi\varphi_1{\varphi_2}^2 \\ &= +\frac{1}{N_{2j}}\left(\ln\varphi_{2j}+1\right) + g_\varphi\varphi_1\varphi_2 - \rho_{\mathrm{ch}} + g{\varphi_1}^2 - g_\varphi\varphi_1{\varphi_2}^2 \\ &= +\frac{1}{N_{2j}}\left(\ln\varphi_{2j}+1\right) - \rho_{\mathrm{ch}} + g{\varphi_1}^2 + g_\varphi{\varphi_1}^2\varphi_2\end{aligned} \tag{S1.15}$$

or

$$\frac{\Delta\mu_{2j}}{k_{\mathrm{B}}T} = \ln\varphi_{2j} + 1 - N_{2j}\rho_{\mathrm{ch}} + N_{2j}{\varphi_1}^2\left(g + g_\varphi\varphi_2\right). \tag{S1.16}$$

Equations (S1.14) and (S1.16) are identical to the expressions reported in refs.1,4.

For convenience, equations (S1.14) and (S1.16) can be reexpressed in terms of $\chi(T, \varphi_2)$ as:

$$\begin{aligned}\frac{\Delta\mu_{1i}}{k_{\mathrm{B}}T} &= \ln\varphi_{1i} + 1 - N_{1i}\rho_{\mathrm{ch}} + N_{1i}{\varphi_2}^2\chi \\ \frac{\Delta\mu_{2j}}{k_{\mathrm{B}}T} &= \ln\varphi_{2j} + 1 - N_{2j}\rho_{\mathrm{ch}} - N_{2j}\varphi_2\left(1-\varphi_2\right)\chi + N_{2j}\int_{\varphi_2}^{1}\chi\, d\varphi\end{aligned} \tag{S1.17}$$

Regarding the derivation of $\Delta\mu_{2j}$, note that,

$$\begin{aligned}{\varphi_1}^2\left(g + \varphi_2 g_\varphi\right) &= -\varphi_1 g + {\varphi_1}^2 g + {\varphi_1}^2\varphi_2 g_\varphi + \varphi_1 g \\ &= -\varphi_2\varphi_1 g + {\varphi_1}^2\varphi_2 g_\varphi + \left(1-\varphi_2\right)g \\ &= -\varphi_2\varphi_1\left(g - g_\varphi\varphi_1\right) + \left(1-\varphi_2\right)g \\ &= -\varphi_2\varphi_1\chi + \int_{\varphi_2}^{1}\chi\, d\varphi.\end{aligned}$$

S2. Cloud-point equations

Flory’s separation factors for species 1 and 2:

$$\sigma_1 = N_{1i}^{\ -1}\left(\ln\varphi''_{1i} - \ln\varphi'_{1i}\right) \tag{S2.1}$$

$$\sigma_2 = N_{2j}^{\ -1}\left(\ln\varphi''_{2j} - \ln\varphi'_{2j}\right). \tag{S2.2}$$

Across the coexistence boundary, the chemical potentials of constituents 1i in the parent (′) and shadow (″) phases are equal:

$$\begin{aligned}
&\Delta\mu''_{1i} = \Delta\mu'_{1i} \rightarrow \\
&\ln\varphi''_{1i} + 1 - N_{1i}\rho''_{\text{ch}} + N_{1i}\varphi''^{2}_{2}\chi\left(\varphi''_2\right) = \ln\varphi'_{1i} + 1 - N_{1i}\rho'_{\text{ch}} + N_{1i}\varphi'^{2}_{2}\chi\left(\varphi'_2\right) \rightarrow \\
&\ln\varphi''_{1i} - \ln\varphi'_{1i} + N_{1i}\left(\rho'_{\text{ch}} - \rho''_{\text{ch}}\right) + N_{1i}\left[\chi\left(\varphi''_2\right)\varphi''^{2}_{2} - \chi\left(\varphi'_2\right)\varphi'^{2}_{2}\right] = 0
\end{aligned}$$

By substituting eqn (S2.1), we get:

$$N_{1i}\sigma_1 + N_{1i}\left(\rho'_{\text{ch}} - \rho''_{\text{ch}}\right) + N_{1i}\left(\chi\left(\varphi''_2\right)\varphi''^{2}_{2} - \chi\left(\varphi'_2\right)\varphi'^{2}_{2}\right) = 0$$

or

$$\sigma_1 = \left(\rho''_{\text{ch}} - \rho'_{\text{ch}}\right) + \chi\left(\varphi'_2\right)\varphi'^{2}_{2} - \chi\left(\varphi''_2\right)\varphi''^{2}_{2} \tag{S2.3}$$

Similarly, for the constituents 2*j*:

$$\begin{aligned}
&\Delta\mu''_{2j} = \Delta\mu'_{2j} \rightarrow \\
&\ln\varphi''_{2j} + 1 - N_{2j}\rho''_{\text{ch}} - N_{2j}\varphi''_2\left(1-\varphi''_2\right)\chi\left(\varphi''_2\right) + N_{2j}\int_{\varphi''_2}^{1}\chi d\varphi = \ln\varphi'_{2j} + 1 - N_{2j}\rho'_{\text{ch}} - N_{2j}\varphi'_2\left(1-\varphi'_2\right)\chi\left(\varphi'_2\right) + N_{2j}\int_{\varphi'_2}^{1}\chi d\varphi \rightarrow \\
&\ln\varphi''_{2j} - \ln\varphi'_{2j} + N_{2j}\left(\rho'_{\text{ch}} - \rho''_{\text{ch}}\right) + N_{2j}\left[\varphi'_2\left(1-\varphi'_2\right)\chi\left(\varphi'_2\right) - \varphi''_2\left(1-\varphi''_2\right)\chi\left(\varphi''_2\right)\right] + N_{2j}\int_{\varphi''_2}^{\varphi'_2}\chi d\varphi = 0
\end{aligned}$$

By substituting eqn (S2.2), we get:

$$N_{2j}\sigma_2 + N_{2j}\left(\rho'_{\text{ch}} - \rho''_{\text{ch}}\right) + N_{2j}\left[\varphi'_2\left(1-\varphi'_2\right)\chi\left(\varphi'_2\right) - \varphi''_2\left(1-\varphi''_2\right)\chi\left(\varphi''_2\right)\right] + N_{2j}\int_{\varphi''_2}^{\varphi'_2}\chi d\varphi = 0$$

or

$$\sigma_2 = \left(\rho''_{\mathrm{ch}} - \rho'_{\mathrm{ch}}\right) + \varphi''_2\left(1-\varphi''_2\right)\chi\left(\varphi''_2\right) - \varphi'_2\left(1-\varphi'_2\right)\chi\left(\varphi'_2\right) - \int_{\varphi''_2}^{\varphi'_2} \chi d\varphi \tag{S2.4}$$

First cloud-point equation:

$$\begin{aligned}\sigma_2 - \sigma_1 &= \left(\rho''_{\mathrm{ch}} - \rho'_{\mathrm{ch}}\right) + \left(\varphi''_2\left(1-\varphi''_2\right)\chi\left(\varphi''_2\right) - \varphi'_2\left(1-\varphi'_2\right)\chi\left(\varphi'_2\right)\right) - \int_{\varphi''_2}^{\varphi'_2} \chi d\varphi \\ &\quad - \left(\rho''_{\mathrm{ch}} - \rho'_{\mathrm{ch}}\right) - \left(\varphi'^2_2\chi\left(\varphi'_2\right) - \varphi''^2_2\chi\left(\varphi''_2\right)\right) \\ &= \chi\left(\varphi''_2\right)\varphi''_2 - \chi\left(\varphi''_2\right)\varphi''^2_2 - \chi\left(\varphi'_2\right)\varphi'_2 + \chi\left(\varphi'_2\right)\varphi'^2_2 - \chi\left(\varphi'_2\right)\varphi'^2_2 + \chi\left(\varphi''_2\right)\varphi''^2_2 - \int_{\varphi''_2}^{\varphi'_2} \chi d\varphi\end{aligned} \tag{S2.5}$$

or

$$\sigma_2 - \sigma_1 = \chi\left(\varphi''_2\right)\varphi''_2 - \chi\left(\varphi'_2\right)\varphi'_2 - \int_{\varphi''_2}^{\varphi'_2} \chi d\varphi \tag{S2.6}$$

Note that eqn (S2.6) has opposite sign as compared to the first cloud-point equations reported in refs. [1,4].

Second cloud-point equation:

$$\begin{aligned}\sigma_1\left(\varphi'_1 + \varphi''_1\right) + \sigma_2\left(\varphi'_2 + \varphi''_2\right) &= \left(\varphi'_1 + \varphi''_1\right)\left(\rho''_{\mathrm{ch}} - \rho'_{\mathrm{ch}}\right) + \left(\varphi'_1 + \varphi''_1\right)\left(\chi\left(\varphi_2\right)\varphi'^2_2 - \chi\left(\varphi''_2\right)\varphi''^2_2\right) \\ &\quad + \left(\varphi'_2 + \varphi''_2\right)\left(\rho''_{\mathrm{ch}} - \rho'_{\mathrm{ch}}\right) + \left(\varphi'_2 + \varphi''_2\right)\left(\varphi''_2\left(1-\varphi''_2\right)\chi\left(\varphi''_2\right) - \varphi'_2\left(1-\varphi'_2\right)\chi\left(\varphi_2\right)\right) \\ &\quad - \left(\varphi'_2 + \varphi''_2\right)\int_{\varphi''_2}^{\varphi'_2} \chi d\varphi \\ &= \left(\varphi'_1 + \varphi''_1\right)\left(\rho''_{\mathrm{ch}} - \rho'_{\mathrm{ch}}\right) + \left(2 - \varphi'_2 - \varphi''_2\right)\left(\varphi'^2_2\chi\left(\varphi_2\right) - \varphi''^2_2\chi\left(\varphi''_2\right)\right) \\ &\quad + \left(\varphi'_2 + \varphi''_2\right)\left(\rho''_{\mathrm{ch}} - \rho'_{\mathrm{ch}}\right) + \left(\varphi'_2 + \varphi''_2\right)\left(\varphi''_2\chi\left(\varphi''_2\right) - \varphi''^2_2\chi\left(\varphi''_2\right) - \varphi'_2\chi\left(\varphi_2\right) + \varphi'^2_2\chi\left(\varphi_2\right)\right) \\ &\quad - \left(\varphi'_2 + \varphi''_2\right)\int_{\varphi''_2}^{\varphi'_2} \chi d\varphi\end{aligned}$$

then,

$$\begin{aligned}\sigma_1\left(\varphi_1'+\varphi_1''\right)+\sigma_2\left(\varphi_2'+\varphi_2''\right)=2\left(\rho_{\mathrm{ch}}''-\rho_{\mathrm{ch}}'\right)+&\\
&2\varphi_2'^2\chi\left(\varphi_2\right)-2\varphi_2''^2\chi\left(\varphi_2''\right)-\varphi_2'^3\chi\left(\varphi_2\right)+\varphi_2'\varphi_2''^2\chi\left(\varphi_2''\right)-\varphi_2'^2\varphi_2''\chi\left(\varphi_2\right)+\varphi_2''^3\chi\left(\varphi_2''\right)\\
&+\varphi_2'\varphi_2''\chi\left(\varphi_2''\right)-\varphi_2'\varphi_2''^2\chi\left(\varphi_2''\right)-\varphi_2'^2\chi\left(\varphi_2\right)+\varphi_2'^3\chi\left(\varphi_2\right)\\
&+\varphi_2''^2\chi\left(\varphi_2''\right)-\varphi_2''^3\chi\left(\varphi_2''\right)-\varphi_2'\varphi_2''\chi\left(\varphi_2\right)+\varphi_2'^2\varphi_2''\chi\left(\varphi_2\right)\\
&-\left(\varphi_2'+\varphi_2''\right)\int_{\varphi_2''}^{\varphi_2'}\chi d\varphi\\
&=2\left(\rho_{\mathrm{ch}}''-\rho_{\mathrm{ch}}'\right)+\varphi_2'^2\chi\left(\varphi_2\right)-\varphi_2''^2\chi\left(\varphi_2''\right)+\varphi_2'\varphi_2''\chi\left(\varphi_2''\right)-\varphi_2'\varphi_2''\chi\left(\varphi_2\right)-\left(\varphi_2'+\varphi_2''\right)\int_{\varphi_2''}^{\varphi_2'}\chi d\varphi\end{aligned}$$

and thus, we get

$$\sigma_1\left(\varphi_1'+\varphi_1''\right)+\sigma_2\left(\varphi_2'+\varphi_2''\right)=2\left(\rho_{\mathrm{ch}}''-\rho_{\mathrm{ch}}'\right)-\left(\varphi_2''-\varphi_2'\right)\left(\chi\left(\varphi_2\right)\varphi_2'+\chi\left(\varphi_2''\right)\varphi_2''\right)-\left(\varphi_2'+\varphi_2''\right)\int_{\varphi_2''}^{\varphi_2'}\chi d\varphi \quad \text{(S2.7)}$$

which is identical with the one reported in refs. 1,4.

S3. Flory–Stockmayer distribution implemented in PhaseTime

S3.1. Scope and assumptions

The Flory–Stockmayer distribution implemented in *PhaseTime* describes the molecular population generated by the reaction of complementary multifunctional groups. The formulation follows the classical Flory–Stockmayer[5–7] framework and the notation by Macosko & Miller[8] and Odle et al.[9], in conjunction with the extensions proposed by Bachmann and Bendler[10] for the evaluation of molecular-weight moments of cross-linked copolymers and branched polycondensates. The same moment structure is used in reduced Flory–Huggins units.

For each reactive species, the initial mixture contains A-type and B-type precursor classes. A-type groups react only with B-type groups. The labels A and B therefore refer to complementary reactive functionalities within the considered species; they are not the two quasibinary blend species.

The model assumes equal reactivity of functional groups of the same type and neglects intramolecular ring formation in finite molecular species. These are assumptions of the Flory–Stockmayer molecular-distribution model and are independent of the subsequent Flory–Huggins phase-equilibrium calculation.

S3.2. Notation and relation to PhaseTime variables

Let A_{f_i} denote the initial amount of A-type precursor class i, carrying f_i reactive A groups, and let B_{g_j} denote the initial amount of B-type precursor class j, carrying g_j reactive B groups. The total initial amounts of A- and B-type functional groups are

$$F_A = \sum_i f_i A_{f_i}, \quad F_B = \sum_j g_j B_{g_j}. \tag{S3.1}$$

The fractions of A and B groups that belong to each precursor class are

$$a_{f_i} = \frac{f_i A_{f_i}}{F_A}, \quad b_{g_j} = \frac{g_j B_{g_j}}{F_B} \tag{S3.2}$$

To avoid confusion with the scalar reaction variable used in the present manuscript, we denote these same quantities by

$$\alpha_i \equiv a_{f_i}, \quad \beta_j \equiv b_{g_j}.$$

Thus,

$$\alpha_i = \frac{f_i A_{f_i}}{\sum_i f_i A_{f_i}}, \quad \beta_j = \frac{g_j B_{g_j}}{\sum_j g_j B_{g_j}} \tag{S3.3}$$

In the original molecular-weight formulation, M_{Af_i} and M_{Bg_j} are molecular weights. In the current implementation, these quantities are replaced by reduced molecular volumes,

$$M_{Af_i} \rightarrow N_i^A, \quad M_{Bg_j} \rightarrow N_j^B$$

where N_i^A and N_j^B are expressed in units of the Flory–Huggins reference volume.

S3.3. Parameters of the Flory–Stockmayer distribution

For each reactive species described by the Flory–Stockmayer model, the required inputs define the initial reactive mixture and the numerical representation of the resulting molecular population. The chemical parameters are the initial amounts of the A- and B-type precursor classes, A_{f_i} and B_{g_j}, their functionalities, f_i and g_j, and their reduced molecular volumes, N_i^A and N_j^B. The scalar reaction variable a specifies the reaction state and determines the corresponding group conversions p_A and p_B, as described below.

The numerical parameters control the finite representation of the otherwise infinite Flory–Stockmayer distribution. These include the maximum precursor multiplicities used in the enumeration and the cutoff w_min, below which molecular species are omitted from the retained distribution. Optionally, the moment-correction procedure may be activated to approximately restore the omitted contribution of the truncated tail.

The quantities N_i^A and N_j^B are reduced molecular volumes, not true molar masses. They are expressed relative to the Flory–Huggins reference volume and therefore define the chain-size contribution of each precursor class to the entropy of mixing. The “generic” mode supports multiple A- and B-type precursor classes, whereas the “binary” mode is the corresponding single-A/single-B specialization. Both modes generate the same output representation, $\{N_k, w_k\}$, for use in the polydisperse Flory–Huggins calculation.

Table S1. Parameters of the Flory–Stockmayer distribution in PhaseTime. The reduced sizes N_i^A and N_j^B are expressed in Flory–Huggins lattice units.

parameter	**variable**	**type**	**description**
A_{f_i}	CA[i]	vector	Initial amount of A-type precursor class i
B_{g_j}	CB[j]	vector	Initial amount of B-type precursor class j
f_i	ff[i]	vector	Functionality of A-type precursor class i
g_j	gg[j]	vector	Functionality of B-type precursor class j
N_i^A	MA[i]	vector	Reduced molecular volume of A-type precursor class i
N_j^B	MB[j]	vector	Reduced molecular volume of B-type precursor class j
a	aa	float	Scalar reaction variable, $a=p_\mathrm{A}p_\mathrm{B}$
m_max	mm_max	int	Maximum precursor multiplicity used in the enumeration
n_max	nn_max	int	Maximum B-type precursor multiplicity in the binary specialization
w_min	ww_min	float	Minimum relative volume-fraction contribution required for retention
	match_moment	bool	Activates the optional moment correction
	model	string	Choice between “binary” and “generic” enumeration

S3.4. Conversion variables

Let p_A and p_B denote the fractions of reacted A- and B-type groups. Since each bond consumes one A group and one B group,

$$p_A F_A = p_B F_B \tag{S3.4}$$

Defining

$$r_f = \frac{F_A}{F_B} \tag{S3.5}$$

one obtains

$$p_B = r_f\, p_A. \tag{S3.6}$$

The scalar reaction variable used here is

$$a = p_A p_B \tag{S3.7}$$

The physically admissible range of *a* is constrained by

$$0 \le p_A \le 1, \quad 0 \le p_B \le 1$$

The gel-denominator appearing in the recursive moment equations (see Section S3.8) is

$$D = 1 - a\left(f_w - 1\right)\left(g_w - 1\right). \tag{S3.8}$$

The corresponding Flory–Stockmayer mean-field gel point, expressed in terms of the reaction variable, is obtained in the limit $D \to 0$:

$$a_{\text{gel}} = \frac{1}{\left(f_w - 1\right)\left(g_w - 1\right)}, \tag{S3.9}$$

hence, we can reexpress eqn (S3.8) as

$$D = 1 - \frac{a}{a_{\text{gel}}}. \tag{S3.10}$$

S3.5. Functionality moments and auxiliary quantities

Following the notation by Bachmann and Bendler,[10] the functionality-weighted first and second moments are

$$f_w = \sum_i f_i \alpha_i, \quad g_w = \sum_j g_j \beta_j \tag{S3.11}$$

$$f_z = \sum_i f_i^2 \alpha_i, \quad g_z = \sum_j g_j{}^2 \beta_j \tag{S3.12}$$

The corresponding reduced-size moments are

$$M_{1a} = \sum_i N_i^A \alpha_i, \qquad M_{1b} = \sum_j N_j^B \beta_j,$$
$$M_{2a} = \sum_i \left(N_i^A\right)^2 \alpha_i, \quad M_{2b} = \sum_j \left(N_j^B\right)^2 \beta_j,$$
$$M_{fa} = \sum_i f_i N_i^A \alpha_i, \quad M_{gb} = \sum_j g_j \left(N_j^B\right)^2 \beta_j.$$

Following the functional-unit representation of Bachmann and Bendler, we define the effective reduced volume per functional group as

$$N_{c,A} = \frac{M_{1a}}{f_w}, \quad N_{c,B} = \frac{M_{1b}}{g_w} \tag{S3.13}$$

In the notation of the implementation,

$$N_{c,A} \equiv M_{c,A}, \quad N_{c,B} \equiv M_{c,B}. \tag{S3.14}$$

This is a reduced-volume analogue of assigning an effective molecular weight to a functional unit. If the reduced precursor volumes scale with functionality, this representation is exact. Otherwise, it should be interpreted as an effective functional-unit approximation used for the analytical moment correction.

S3.6. Discrete Flory–Stockmayer molecular population

A molecular species is specified by two integer vectors,

$$\mathbf{m} = \left(m_1, m_2, \ldots, m_{\max}\right), \quad \mathbf{n} = \left(n_1, n_2, \ldots, n_{n_{\max}}\right),$$

where m_i is the number of A-type precursor units of class i, and n_j is the number of B-type precursor units of class j.

By defining:

$$M_A(\mathbf{m}) = \sum_i m_i, \quad M_B(\mathbf{n}) = \sum_j n_j, \tag{S3.15}$$

and

$$F_A(\mathbf{m}) = \sum_i f_i m_i, \quad F_B(\mathbf{n}) = \sum_j g_j n_j, \tag{S3.16}$$

the Stockmayer[6,7] population of molecules with composition (**m**, **n**) is written as

$$\mathcal{N}_{\mathbf{m},\mathbf{n}} = \mathcal{K} \frac{\left(F_A(\mathbf{m}) - M_A(\mathbf{m})\right)! \left(F_B(\mathbf{n}) - \sum_j n_j\right)!}{\left(F_A(\mathbf{m}) - M_A(\mathbf{m}) - M_B(\mathbf{n}) + 1\right)! \left(F_B(\mathbf{n}) - M_B(\mathbf{n}) - M_A(\mathbf{m}) + 1\right)!} \prod_i \frac{\xi_i^{m_i}}{m_i!} \prod_j \frac{\eta_j^{n_j}}{n_j!}, \quad \text{(S3.17)}$$

whereas, the terms for which any factorial argument is negative are excluded.

The coefficients are

$$\xi_i = \alpha_i \frac{p_B (1 - p_A)^{f_i - 1}}{1 - p_B} \quad \text{(S3.18)}$$

$$\eta_j = \beta_j \frac{p_A (1 - p_B)^{g_i - 1}}{1 - p_A} \quad \text{(S3.19)}$$

and

$$\mathcal{K} = F_A \frac{(1 - p_A)(1 - p_B)}{p_B} = F_B \frac{(1 - p_A)(1 - p_B)}{p_A} \quad \text{(S3.20)}$$

The size of a molecule composed of m_i A-type precursors and n_j B-type precursors is therefore:

$$N_{\mathbf{m},\mathbf{n}} = \sum_i m_i N_i^A + \sum_j n_j N_j^B. \quad \text{(S3.21)}$$

For each molecular species (**m**,**n**), the Stockmayer expression gives the number population $\mathcal{N}_{\mathbf{m},\mathbf{n}}$. The corresponding reduced volume carried by this molecular constituent is therefore

$$\mathcal{N}_{\mathbf{m},\mathbf{n}} N_{\mathbf{m},\mathbf{n}}$$

The relative volume-fraction contribution computed directly from the Stockmayer population, before final normalization or moment correction is defined as

$$\tilde{w}_{\mathbf{m},\mathbf{n}} = \frac{\mathcal{N}_{\mathbf{m},\mathbf{n}} N_{\mathbf{m},\mathbf{n}}}{\sum_i A_{f_i} N_i^A + \sum_j B_{g_j} N_j^B}, \quad \text{(S3.22)}$$

where the denominator is the total initial reduced volume of the corresponding reactive species. Note that $\tilde{w}_{\mathbf{m},\mathbf{n}}$ is a relative volume fraction inside that species, not the absolute volume fraction of the constituent in the full blend. Since the multi-index (**m**,**n**) labels the molecular species generated by the Flory–Stockmayer enumeration, the retained species are subsequently re-indexed by a single constituent index *k*. Thus, any species-specific quantities such as chain size and relative volume fraction may be written equivalently as $N_k \equiv N_{\mathbf{m},\mathbf{n}}$, and $w_k \equiv w_{\mathbf{m},\mathbf{n}}$, respectively.

If the Flory–Stockmayer distribution describes quasibinary species *c*, whose total volume fraction in the blend is φ_c, then the actual volume fraction of constituent $k \in (1i, 2j)$ entering the polydisperse Flory–Huggins formulation is

$$\varphi_{c,k} = \varphi_c w_{c,k}$$

where $w_{c,k}$ is the normalized or moment-corrected relative volume fraction of constituent *k* within species *c*. Therefore,

$$\sum_k w_{c,k} = 1, \quad \sum_k \varphi_{c,k} = \varphi_c$$

In the complete, untruncated pre-gel Flory–Stockmayer distribution, the sum of all relative volume-fraction contributions is unity. In the numerical implementation, however, only a finite set of species is retained, as will be discussed in Section S3.9.

S3.7. Moment definitions for the retained distribution

For a discrete volume-weighted distribution, the moments are

$$M_q = \sum_k w_k N_k{}^q \tag{S3.23}$$

The moments required for the average reduced chain sizes are the M_{-1}, M_0, M_1 and M_2. The number-, weight-, and z-average reduced chain sizes are then.

$$N_n = \frac{M_0}{M_{-1}}, \quad N_w = \frac{M_1}{M_0}, \quad N_z = \frac{M_2}{M_1}. \tag{S3.24}$$

Note that for a normalized volume-fraction distribution, $M_0 = 1$; therefore, $N_\mathrm{n} = 1/M_{-1}$ and $N_\mathrm{w} = M_1$.

S3.8. Analytical full-distribution moments

The analytical moments of the full, untruncated Flory–Stockmayer distribution are denoted by M_q^{full}. The (–1)-moment follows from the total number of molecules divided by the total reduced volume. Since each A–B bond reduces the number of molecules by one,

$$M_{-1}^{\text{full}} = \frac{\sum_i A_{f_i} + \sum_j B_{g_j} - p_A F_A}{\sum_i A_{f_i} N_i^A + \sum_j B_{g_j} N_j^B}. \tag{S3.25}$$

The zeroth moment is just:

$$M_0^{\text{full}} = 1. \tag{S3.26}$$

The first moment corresponding to the reduced weight-average chain size, is

$$M_1^{\text{full}} = \frac{r_f N_{c,A}{}^2 f_w + N_{c,B}{}^2 g_w}{r_f N_{c,A} + N_{c,B}} + \frac{p_B\left[p_A\left(f_w - 1\right) N_{c,B}{}^2 g_w{}^2 + p_B\left(g_w - 1\right) N_{c,A}{}^2 f_w{}^2 + 2N_{c,A} N_{c,B} f_w g_w \right]}{\left(r_f N_{c,A} + N_{c,B}\right) D} \tag{S3.27}$$

c.f. eqn (12) in ref. [10] in conjunction with eqns (S3.6) and (S3.8), herein.

The second moment M_2^{full}, required for N_z, is evaluated using the recursive expectation relations of Bachmann and Bendler. First define the outgoing-branch expectations[8,10]

$$E_A = E\left(W_A^{out}\right) = \frac{p_\mathrm{A} M_{1b} + p_A p_B \left(g_w - 1\right) M_{1a}}{D},$$
$$E_A = E\left(W_B^{out}\right) = \frac{p_\mathrm{B} M_{1a} + p_A p_B \left(f_w - 1\right) M_{1b}}{D},$$

The corresponding within-node second moments are

$$\begin{aligned} W_A^{(2)} &= \sum_i a_{f_i} E\left(W_{A_{f_i}}^{in}\right)^2 = M_{2a} + 2\left(M_{fa} - M_{1a}\right) E_A + \left(f_z - 2f_w + 1\right) E_A{}^2 \\ W_B^{(2)} &= \sum_j b_{g_j} E\left(W_{B_{g_j}}^{in}\right)^2 = M_{2b} + 2\left(M_{gb} - M_{1b}\right) E_B + \left(g_z - 2g_w + 1\right) E_B{}^2 \end{aligned} \tag{S3.28}$$

The second outgoing-branch expectations are

$$\begin{aligned} E_A^{(2)} &= E\left(\left(W_A^{out}\right)^2\right) = \frac{p_A}{D}\left[p_B\left(g_w-1\right)W_A^{(2)} - \left(g_w-1\right)E_B{}^2 + W_B^{(2)} - p_B\left(f_w-1\right)\left(g_w-1\right)E_A{}^2 \right] \\ E_B^{(2)} &= E\left(\left(W_B^{out}\right)^2\right) = \frac{p_B}{D}\left[p_A\left(f_w-1\right)W_B^{(2)} - \left(f_w-1\right)E_A{}^2 + W_A^{(2)} - p_A\left(f_w-1\right)\left(g_w-1\right)E_B{}^2 \right]. \end{aligned} \tag{S3.29}$$

By invoking the functional-unit representation,

$$\begin{gathered} m_{1a} = N_{c,A}, \qquad m_{1b} = N_{c,B}, \\ m_{3a} = N_{c,A}{}^3 f_z, \quad m_{3b} = N_{c,B}{}^3 g_z, \end{gathered}$$

we obtain the full second moment as follows:

$$\begin{aligned} M_2^{\text{full}} = &\frac{r_f\left[m_{3a} + 2M_{2a}E_A + M_{fa}E_A{}^2 + M_{1a}\left(E_A^{(2)} - E_A{}^2\right)\right]}{r_f m_{1a} + m_{1b}} \\ &+ \frac{\left[m_{3b} + 2M_{2b}E_B + M_{gb}E_B{}^2 + M_{1b}\left(E_B^{(2)} - E_B{}^2\right)\right]}{r_f m_{1a} + m_{1b}} \end{aligned} \tag{S3.30}$$

S3.9. Renormalization of the truncated distribution and moment correction

The relative volume-fraction contributions $\tilde{w}_{\mathbf{m},\mathbf{n}}$ defined above are evaluated before final normalization of the retained finite distribution. In the complete pre-gel Flory–Stockmayer distribution,

$$\sum_{\mathbf{m},\mathbf{n}} \tilde{w}_{\mathbf{m},\mathbf{n}} = 1, \quad \tilde{w}_{\mathbf{m},\mathbf{n}} = w_{\mathbf{m},\mathbf{n}}$$

In practice, the distribution is truncated by enumerating molecular species only up to prescribed precursor multiplicities and by discarding species whose relative volume-fraction contribution is smaller than the cutoff $w_{\min}$. As a result, the retained head of the distribution generally satisfies

$$M_0^{\text{head}} = \sum_{k\in\text{head}} \tilde{w}_k < 1,$$

and the missing volume fraction,

$$\Delta M_0 = M_0^{\text{full}} - M_0^{\text{head}}.$$

is part of the omitted long-chain tail. More generally, the omitted contribution to the q-th moment is

$$\Delta M_q = M_q^{\text{full}} - M_q^{\text{head}}$$

where

$$M_q^{\text{head}} = \sum_{k \in \text{head}} \tilde{w}_k N_k^q .$$

In situations where the moment correction is not applied, the retained relative volume-fraction contributions are normalized directly:

$$w_k = \frac{\tilde{w}_k}{M_0^{\text{head}}}$$

In this case, the omitted tail is not represented explicitly; its missing volume fraction is redistributed over the retained species by normalization.

When moment matching is activated, the framework approximates the omitted tail by two effective constituents with reduced sizes N_a and N_b, and volume-fraction weights u and v. The four quantities are chosen so that the augmented distribution reproduces the four target moments

$$M_{-1}^{\text{full}}, \quad M_0^{\text{full}}, \quad M_1^{\text{full}}, \quad M_2^{\text{full}}$$

Thus, the effective tail satisfies

$$\begin{aligned}
&\frac{u}{N_a} + \frac{v}{N_b} = \Delta M_{-1}, \\
&u + v = \Delta M_0, \\
&uN_a + vN_b = \Delta M_1, \\
&uN_a{}^2 + vN_b{}^2 = \Delta M_2 .
\end{aligned}$$

After solution of these moment-matching equations, the augmented finite distribution satisfies

$$M_q^{\text{corr}} = M_q^{\text{full}}, \quad q = -1, 0, 1, 2$$

This directly preserves the number-, weight-, and z-average reduced chain sizes. The correction is applied only when the missing moment contribution can be represented by positive effective sizes and non-negative weights. Therefore, the added constituents should not be interpreted as physical molecular species, but as a compact moment-preserving representation of the truncated long-chain tail. The implementation follows this two-species construction and checks that the augmented distribution reproduces the target moments.

S4. Segmentation algorithm

Some calculated spinodal and binodal curves may be multivalued in a chosen projection, for example when represented as $t(\varphi_2)$. *PhaseTime* therefore includes a numerical segmentation step that separates such curves into single-valued branches. This is used both for plotting and within the objective function used when fitting spinodal or binodal curves to reference data. In the fitting workflow, the model curve is segmented before being compared with the corresponding experimental or target segments.

The algorithm operates on a generic set of points,

$$\mathcal{S} = \left\{ \left(x_k , y_k \right) \right\}_{k=1}^{n} ,$$

where (x, y) denotes the selected curve representation. Non-finite points are first removed. Nearly duplicate points are then collapsed using small tolerances in both coordinates. Importantly, points with similar x-values but clearly different y-values are kept distinct, so that separate branches are not accidentally averaged.

For approximately double-valued curves, *PhaseTime* can determine the split automatically. Candidate split values are chosen as midpoints between consecutive distinct y-values. For each candidate value y_s, the curve is divided into a lower and an upper part,

$$\mathcal{S}^{-} = \left\{ \left(x_k , y_k \right) : y_k \le y_s \right\},$$
$$\mathcal{S}^{+} = \left\{ \left(x_k , y_k \right) : y_k > y_s \right\}.$$

The optimal split is the one that minimizes the total scaled path length of the two resulting branches,

$$\mathcal{L}\left(y_s \right) = \mathcal{L}\left(\mathcal{S}^{-} \right) + \mathcal{L}\left(\mathcal{S}^{+} \right)$$

Here, $\mathcal{L}$ is the polyline length after sorting the points by x, with both coordinates scaled by their total ranges. This criterion favors the split that produces two smooth branches rather than one artificially folded curve.

Manual segmentation is also available for plotting purposes. In this case, one supplies one or more split values along either the x- or y-axis. The curve is then divided into the corresponding intervals, and any segment with too few points is discarded. This option is useful for more complicated curve shapes, or when the desired branch separation is known from the structure of the phase diagram.

The segmentation step is purely numerical. It does not modify the thermodynamic model or the computed equilibrium conditions; it only organizes the calculated points into branches suitable for plotting, interpolation, and fitting.

S5. Reaction-composition phase diagrams without moment-matching

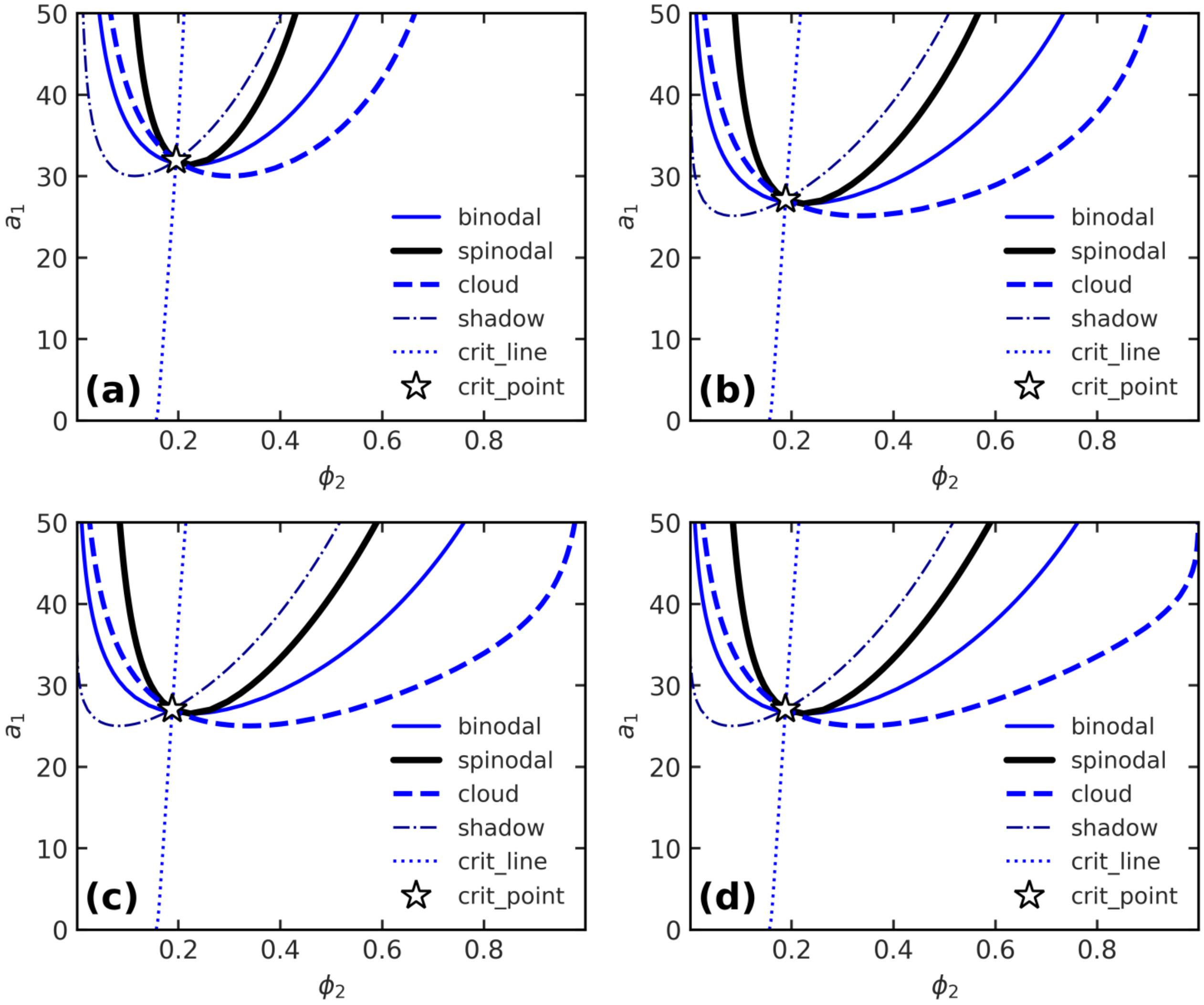

Figure S1. Reaction-composition phase diagrams of the representative polydisperse reactive blend obtained without moment matching for different cutoff values: **(a)** $n_{\max}$=$m_{\max}$=5, **(b)** 10, **(c)** 20, and **(d)** 40. Each panel includes the cloud and shadow curves, spinodal, critical line, critical point, and effective monodisperse binodal. The cutoff dependence is strongest at low nmax and decreases as the cutoff is increased.

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