

Supplementary Information for
A Unified Approach to Phase Equilibria in Multi-Component
Polymer Systems with Effective Chemical Potential

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SUPPLEMENTARY NOTE S1. TWO-PHASE EQUILIBRIUM

To facilitate the understanding of our derivation process, we consider the coexistence of two phases denoted α and β , in a binary blend consisting of two components, denoted 1 and 2, for illustration.

At two-phase equilibrium, the chemical potentials of components 1 and 2 are equal in each coexistence phase, α and β ,

$$\mu_1^\alpha = \mu_1^\beta \quad (\text{S1})$$

$$\mu_2^\alpha = \mu_2^\beta \quad (\text{S2})$$

Subtracting Eq. S2 from Eq. S1 leads to,

$$\mu_1^\alpha - \mu_2^\alpha = \mu_1^\beta - \mu_2^\beta \quad (\text{S3})$$

Thus we can define an "effective chemical potential" for component 1 by taking the chemical potential of component 2 as a reference,

$$\tilde{\mu}_1 \equiv \mu_1 - \mu_2 \quad (\text{S4})$$

Consequently, at two-phase equilibrium, the effective chemical potential of component 1 must satisfy,

$$\tilde{\mu}_1^\alpha = \tilde{\mu}_1^\beta \quad (\text{S5})$$

where $\tilde{\mu}_1^\alpha$ and $\tilde{\mu}_1^\beta$ denote the effective chemical potentials of component 1 in phases α and β , respectively.

According to Eq. S4, we can express the chemical potentials of component 1 as follows,

$$\mu_1 = \tilde{\mu}_1 + \mu_2 \quad (\text{S6})$$

For practical computational considerations, volume fractions (ϕ) often serve as more convenient independent variables than mole numbers. The system's canonical ensemble (CE) free energy can be expressed in terms of volume fractions as,

$$\tilde{F}(\phi_1, \phi_2) = \frac{1}{n} F(n_1, n_2) \quad (\text{S7})$$

Here, \tilde{F} represents the CE free energy as a function of the dimensionless volume fractions, while F denotes the CE free energy expressed in terms of the number of moles of the components. The total mole number is given by $n = n_1 + n_2$, such that the volume fractions are defined as $\phi_1 = \frac{n_1}{n}$ and $\phi_2 = \frac{n_2}{n}$, with the constraint $\phi_1 + \phi_2 = 1$.

Under two-phase coexistence conditions, the following condition must be satisfied[1],

$$\tilde{F}^\alpha - \tilde{F}^\beta = \sum_{i=1}^2 \mu_i (\phi_i^\alpha - \phi_i^\beta) \quad (\text{S8})$$

Substituting Eq. S6 into Eq. S8, we can obtain,

$$\begin{aligned} \tilde{F}^\alpha - \tilde{F}^\beta &= (\tilde{\mu}_1 + \mu_2)(\phi_1^\alpha - \phi_1^\beta) + \mu_2(\phi_2^\alpha - \phi_2^\beta) \\ &= \tilde{\mu}_1(\phi_1^\alpha - \phi_1^\beta) \end{aligned} \quad (\text{S9})$$

From this, we can rewrite Eq. S9. This also demonstrates that in the free energy curve, $\tilde{F}(\phi)$ versus the volume fraction, ϕ_1 as the independent variable, the slope of the common tangent line physically represents the effective chemical potential of component 1, $\tilde{\mu}_1$ under two-phase equilibrium conditions in a binary blend.

$$\tilde{\mu}_1^\alpha = \tilde{\mu}_1^\beta = \frac{\tilde{F}^\alpha - \tilde{F}^\beta}{\phi_1^\alpha - \phi_1^\beta} \quad (\text{S10})$$

Here, Eq. S5 and Eq. S10 together constitute the two-phase coexistence condition from the perspective of "effective chemical potentials".

For ternary blends with components 1,2 and 3 in phases α and β , where component 3 chosen as the reference, the effective chemical potentials of components 1 and 2 are expressed as,

$$\tilde{\mu}_1 = \mu_1 - \mu_3 \quad (\text{S11})$$

$$\tilde{\mu}_2 = \mu_2 - \mu_3 \quad (\text{S12})$$

Similar to the binary case (Eq. S5), at two-phase equilibrium, the effective chemical potential must satisfy,

$$\tilde{\mu}_1^\alpha = \tilde{\mu}_1^\beta \quad (\text{S13})$$

$$\tilde{\mu}_2^\alpha = \tilde{\mu}_2^\beta \quad (\text{S14})$$

And the common tangent plane conditions can be derived from the original coordinate (μ_1, μ_2, μ_3) system [1],

$$\begin{aligned} \tilde{F}^\alpha - \tilde{F}^\beta &= \sum_{i=1}^{n_c=3} \mu_i (\phi_i^\alpha - \phi_i^\beta) \\ &= (\tilde{\mu}_1 + \mu_3)(\phi_1^\alpha - \phi_1^\beta) + (\tilde{\mu}_2 + \mu_3)(\phi_2^\alpha - \phi_2^\beta) + \mu_3(\phi_3^\alpha - \phi_3^\beta) \\ &= \tilde{\mu}_1(\phi_1^\alpha - \phi_1^\beta) + \tilde{\mu}_2(\phi_2^\alpha - \phi_2^\beta) + \mu_3[(\phi_1^\alpha - \phi_1^\beta) + (\phi_2^\alpha - \phi_2^\beta) + (\phi_3^\alpha - \phi_3^\beta)] \quad (\text{S15}) \\ &= \tilde{\mu}_1(\phi_1^\alpha - \phi_1^\beta) + \tilde{\mu}_2(\phi_2^\alpha - \phi_2^\beta) + \mu_3[(\phi_1^\alpha + \phi_2^\alpha + \phi_3^\alpha) - (\phi_1^\beta + \phi_2^\beta + \phi_3^\beta)] \\ &= \tilde{\mu}_1(\phi_1^\alpha - \phi_1^\beta) + \tilde{\mu}_2(\phi_2^\alpha - \phi_2^\beta) + \mu_3(1 - 1) \\ &= \tilde{\mu}_1(\phi_1^\alpha - \phi_1^\beta) + \tilde{\mu}_2(\phi_2^\alpha - \phi_2^\beta) \end{aligned}$$

By rearranging Eq. S15, we can explicitly express the common tangent condition for the coexistence of the ternary system as follows,

$$\tilde{F}^\alpha - \tilde{F}^\beta = \sum_{i=1}^2 \tilde{\mu}_i (\phi_i^\alpha - \phi_i^\beta) \quad (\text{S16})$$

Therefore, Eq. S13, S14 and S16 together constitute the complete set of phase equilibrium conditions for the three-component system.

SUPPLEMENTARY NOTE S2. EFFECTIVE CHEMICAL POTENTIALS AND CHEMICAL POTENTIALS

Next, we will show how to obtain the effective chemical potentials starting from the free energy of the canonical ensemble. The chemical potential of component 1, μ_1 can be derived into an alternative expression.

$$\begin{aligned}
\mu_1 &= \left(\frac{\partial F}{\partial n_1} \right)_{n_2} \\
&= \left[\frac{\partial(n\tilde{F})}{\partial n_1} \right]_{n_2} \\
&= \left(\frac{\partial n}{\partial n_1} \right)_{n_2} \tilde{F} + n \left(\frac{\partial \tilde{F}}{\partial n_1} \right)_{n_2} \\
&= \left(\frac{\partial n}{\partial n_1} \right)_{n_2} \tilde{F} + n \left[\left(\frac{\partial \tilde{F}}{\partial \phi_1} \right)_{\phi_2} \left(\frac{\partial \phi_1}{\partial n_1} \right)_{n_2} + \left(\frac{\partial \tilde{F}}{\partial \phi_2} \right)_{\phi_1} \left(\frac{\partial \phi_2}{\partial n_1} \right)_{n_2} \right]
\end{aligned} \tag{S17}$$

The total mole number $n = n_1 + n_2$, implies $dn = dn_1 + dn_2$. Holding n_2 constant ($dn_2 = 0$) yields $\frac{\partial n}{\partial n_1} = 1$.

Applying the chain rule, we derive the following partial derivatives of the volume fractions,

$$\left(\frac{\partial \phi_1}{\partial n_1} \right)_{n_2} = \frac{\partial}{\partial n_1} \left(\frac{n_1}{n} \right) = \frac{1}{n} - \frac{n_1}{n^2} = \frac{n_2}{n^2} = \frac{\phi_2}{n} \tag{S18}$$

$$\left(\frac{\partial \phi_2}{\partial n_1} \right)_{n_2} = \frac{\partial}{\partial n_1} \left(\frac{n_2}{n} \right) = -\frac{n_2}{n^2} = -\frac{\phi_2}{n} \tag{S19}$$

Combining these results with Eq. S17, the chemical potential μ_1 simplifies to,

$$\begin{aligned}
\mu_1 &= \tilde{F} + n \left[\frac{\phi_2}{n} \left(\frac{\partial \tilde{F}}{\partial \phi_1} \right)_{\phi_2} - \frac{\phi_2}{n} \left(\frac{\partial \tilde{F}}{\partial \phi_2} \right)_{\phi_1} \right] \\
&= \tilde{F} + \phi_2 \left[\left(\frac{\partial \tilde{F}}{\partial \phi_1} \right)_{\phi_2} - \left(\frac{\partial \tilde{F}}{\partial \phi_2} \right)_{\phi_1} \right]
\end{aligned} \tag{S20}$$

Similarly, the chemical potential of component 2 is given by,

$$\mu_2 = \tilde{F} + \phi_1 \left[\left(\frac{\partial \tilde{F}}{\partial \phi_2} \right)_{\phi_1} - \left(\frac{\partial \tilde{F}}{\partial \phi_1} \right)_{\phi_2} \right] \tag{S21}$$

By subtracting Eq. S21 from Eq. S20, it implies that the effective chemical potential of component 1 can be expressed,

$$\tilde{\mu}_1 = \left(\frac{\partial \tilde{F}}{\partial \phi_1} \right)_{\phi_2} - \left(\frac{\partial \tilde{F}}{\partial \phi_2} \right)_{\phi_1} \quad (\text{S22})$$

For a binary blend, the effective chemical potential $\tilde{\mu}_1$ of component 1 is the total derivative of the CE free energy \tilde{F} with respect to the volume fraction ϕ_1 .

$$\tilde{\mu}_1 = \frac{d\tilde{F}}{d\phi_1} \quad (\text{S23})$$

As introduced in Eq.(4) of the main text, we define the γ_p for convenience, here, we can obtain,

$$\gamma_1 = \left(\frac{\partial \tilde{F}}{\partial \phi_1} \right)_{\phi_2}, \gamma_2 = \left(\frac{\partial \tilde{F}}{\partial \phi_2} \right)_{\phi_1} \quad (\text{S24})$$

γ_1 and γ_2 represent the response of the free energy \tilde{F} to changes in ϕ_1 (holding ϕ_2 fixed) and ϕ_2 (holding ϕ_1 fixed), respectively. And γ_1 and γ_2 are independent.

Combining Eq. S22 and Eq. S24, the effective chemical potentials $\tilde{\mu}_1$ can be expressed as,

$$\tilde{\mu}_1 = \gamma_1 - \gamma_2 \quad (\text{S25})$$

The introduction of the parameter γ can simplify the calculation of the effective chemical potentials.

To demonstrate this, we consider a binary homopolymer blend system as an example. According to Flory-Huggins theory, the CE free energy density of a DIS phase is given by,

$$\tilde{F}(\phi_1, \phi_2) = \frac{\phi_1}{\alpha_1} \ln \phi_1 + \frac{\phi_2}{\alpha_2} \ln \phi_2 + \chi N \phi_1 \phi_2 \quad (\text{S26})$$

where $\alpha_i = N_i/N$ ($i = 1, 2$) represents the relative chain length of component i .

According to Eq. S24,

$$\gamma_1 = \left(\frac{\partial \tilde{F}}{\partial \phi_1} \right)_{\phi_2} = \frac{1}{\alpha_1} + \frac{1}{\alpha_1} \ln \phi_1 + \chi N \phi_2 \quad (\text{S27})$$

$$\gamma_2 = \left(\frac{\partial \tilde{F}}{\partial \phi_2} \right)_{\phi_1} = \frac{1}{\alpha_2} + \frac{1}{\alpha_2} \ln \phi_2 + \chi N \phi_1 \quad (\text{S28})$$

Substituting Eq. S27 and Eq. S28 into Eq. S25 yields the effective chemical potential $\tilde{\mu}_1$,

$$\begin{aligned}\tilde{\mu}_1 &= \gamma_1 - \gamma_2 \\ &= \frac{1}{\alpha_1} + \frac{1}{\alpha_1} \ln \phi_1 + \chi N \phi_2 - \left(\frac{1}{\alpha_2} + \frac{1}{\alpha_2} \ln \phi_2 + \chi N \phi_1 \right) \\ &= \frac{1}{\alpha_1} \ln \phi_1 - \frac{1}{\alpha_2} \ln(1 - \phi_1) + \chi N(1 - 2\phi_1) + \frac{1}{\alpha_1} - \frac{1}{\alpha_2}\end{aligned}\quad (\text{S29})$$

For comparison, the free energy of a binary system is typically expressed as a function of a single independent composition variable in a classical approach,

$$\hat{F}(\phi_1) = \frac{\phi_1}{\alpha_1} \ln \phi_1 + \frac{1 - \phi_1}{\alpha_2} \ln(1 - \phi_1) + \chi N \phi_1(1 - \phi_1) \quad (\text{S30})$$

To clarify the distinction between the different free energy formulations while maintaining thermodynamic rigor, we present the following refined notation by applying the mass conservation constraint,

$$\hat{F}(\phi_1) \equiv \tilde{F}(\phi_1, 1 - \phi_1) \quad (\text{S31})$$

According to Eq. S23, the effective chemical potential $\tilde{\mu}_1$ can be expressed as the first derivative of \hat{F} with respect to the volume fraction ϕ_1 .

$$\begin{aligned}\tilde{\mu}_1 &= \frac{d\hat{F}}{d\phi_1} \\ &= \frac{1}{\alpha_1} + \frac{1}{\alpha_1} \ln \phi_1 + \frac{1}{\alpha_2} [1 + \ln(1 - \phi_1)] \cdot (-1) + \chi N(1 - \phi_1) + \chi N \phi_1 \cdot (-1) \\ &= \frac{1}{\alpha_1} \ln \phi_1 - \frac{1}{\alpha_2} \ln(1 - \phi_1) + \chi N(1 - 2\phi_1) + \frac{1}{\alpha_1} - \frac{1}{\alpha_2}\end{aligned}\quad (\text{S32})$$

This approach is considerably more cumbersome, particularly for ternary or multi-component polymer blend systems, where the number of steps for derivation increases substantially.

To further illustrate this point, we proceed with a proof for ternary systems. Consider a three-component polymer blend with components 1, 2 and 3 (where $\phi_1 + \phi_2 + \phi_3 = 1$). The CE free energy $\tilde{F}(\phi_1, \phi_2, \phi_3)$ is given by,

$$\tilde{F}(\phi_1, \phi_2, \phi_3) = \frac{\phi_1}{\alpha_1} \ln \phi_1 + \frac{\phi_2}{\alpha_2} \ln \phi_2 + \frac{\phi_3}{\alpha_3} \ln \phi_3 + \chi_{12} N \phi_1 \phi_2 + \chi_{13} N \phi_1 \phi_3 + \chi_{23} N \phi_2 \phi_3 \quad (\text{S33})$$

where $\alpha_i = N_i/N$ ($i = 1, 2, 3$) represents the relative chain length of component i , $\chi_{ij}N$ is the Flory-Huggins parameters. We select component 3 as reference, the effective chemical potentials $\tilde{\mu}_i$ ($i = 1, 2$) is given by,

$$\tilde{\mu}_1 = \gamma_1 - \gamma_3 \quad (\text{S34})$$

$$\tilde{\mu}_2 = \gamma_2 - \gamma_3 \quad (\text{S35})$$

Here, we compute γ_i ($i = 1, 2, 3$),

$$\gamma_1 = \left(\frac{\partial \tilde{F}}{\partial \phi_1} \right)_{\phi_2, \phi_3} = \frac{1}{\alpha_1} \ln \phi_1 + \frac{1}{\alpha_1} + \chi_{12}N\phi_2 + \chi_{13}N\phi_3 \quad (\text{S36})$$

$$\gamma_2 = \left(\frac{\partial \tilde{F}}{\partial \phi_2} \right)_{\phi_1, \phi_3} = \frac{1}{\alpha_2} \ln \phi_2 + \frac{1}{\alpha_2} + \chi_{12}N\phi_1 + \chi_{23}N\phi_3 \quad (\text{S37})$$

$$\gamma_3 = \left(\frac{\partial \tilde{F}}{\partial \phi_3} \right)_{\phi_1, \phi_2} = \frac{1}{\alpha_3} \ln \phi_3 + \frac{1}{\alpha_3} + \chi_{13}N\phi_1 + \chi_{23}N\phi_2 \quad (\text{S38})$$

Therefore, the final expression of the effective chemical potentials $\tilde{\mu}_i$ can be obtained by substituting Eq. S36, Eq. S37 and Eq. S38 into Eq. S34 and Eq. S35, respectively.

$$\begin{aligned} \tilde{\mu}_1 &= \gamma_1 - \gamma_3 \\ &= \frac{1}{\alpha_1} \ln \phi_1 + \frac{1}{\alpha_1} - \left(\frac{1}{\alpha_3} \ln \phi_3 + \frac{1}{\alpha_3} \right) + (\chi_{12}N - \chi_{23}N)\phi_2 + \chi_{13}N(\phi_3 - \phi_1) \end{aligned} \quad (\text{S39})$$

$$\begin{aligned} \tilde{\mu}_2 &= \gamma_2 - \gamma_3 \\ &= \frac{1}{\alpha_2} \ln \phi_2 + \frac{1}{\alpha_2} - \left(\frac{1}{\alpha_3} \ln \phi_3 + \frac{1}{\alpha_3} \right) + (\chi_{12}N - \chi_{13}N)\phi_1 + \chi_{23}N(\phi_3 - \phi_2) \end{aligned} \quad (\text{S40})$$

The derivation presented above maintains clarity, whereas directly computing partial derivatives of the free energy would lead to more cumbersome calculations.

$$\begin{aligned} \hat{F}(\phi_1, \phi_2, 1 - \phi_1 - \phi_2) &= \frac{\phi_1}{\alpha_1} \ln \phi_1 + \frac{\phi_2}{\alpha_2} \ln \phi_2 + \frac{1 - \phi_1 - \phi_2}{\alpha_3} \ln (1 - \phi_1 - \phi_2) \\ &+ \chi_{12}N\phi_1\phi_2 + \chi_{13}N\phi_1(1 - \phi_1 - \phi_2) + \chi_{23}N\phi_2(1 - \phi_1 - \phi_2) \end{aligned} \quad (\text{S41})$$

And the effective chemical potential $\tilde{\mu}_1$ is,

$$\begin{aligned}
\tilde{\mu}_1 &= \left(\frac{\partial \hat{F}}{\partial \phi_1} \right)_{\phi_2} \\
&= \frac{1}{\alpha_1} \ln \phi_1 + \frac{1}{\alpha_1} + \frac{\partial}{\partial \phi_1} \left[\frac{(1 - \phi_1 - \phi_2)}{\alpha_3} \ln(1 - \phi_1 - \phi_2) \right] \\
&\quad + \chi_{12} N \phi_2 + \chi_{13} (1 - \phi_1 - \phi_2) + \chi_{13} \phi_1 \frac{\partial(1 - \phi_1 - \phi_2)}{\partial \phi_1} + \chi_{23} N \phi_2 \frac{\partial(1 - \phi_1 - \phi_2)}{\partial \phi_1}
\end{aligned} \tag{S42}$$

A critical term in Eq. S42 can be derived that,

$$\begin{aligned}
&\frac{\partial}{\partial \phi_1} \left[\frac{(1 - \phi_1 - \phi_2)}{\alpha_3} \ln(1 - \phi_1 - \phi_2) \right] \\
&= -\frac{1}{\alpha_3} \ln(1 - \phi_1 - \phi_2) + \frac{1 - \phi_1 - \phi_2}{\alpha_3} \cdot \frac{-1}{1 - \phi_1 - \phi_2} \\
&= -\frac{1}{\alpha_3} [\ln(1 - \phi_1 - \phi_2) + 1]
\end{aligned} \tag{S43}$$

By substituting Eq. S43 into Eq. S42, we derive the complete expression for the effective chemical potential of component 1, $\tilde{\mu}_1$:

$$\begin{aligned}
\tilde{\mu}_1 &= \left(\frac{\partial \hat{F}}{\partial \phi_1} \right)_{\phi_2} \\
&= \frac{1}{\alpha_1} \ln \phi_1 + \frac{1}{\alpha_1} - \frac{1}{\alpha_3} (\ln(1 - \phi_1 - \phi_2) + 1) \\
&\quad + \chi_{12} N \phi_2 + \chi_{13} (1 - \phi_1 - \phi_2) + \chi_{13} \phi_1 (-1) + \chi_{23} N \phi_2 (-1) \\
&= \frac{1}{\alpha_1} \ln \phi_1 + \frac{1}{\alpha_1} - \left(\frac{1}{\alpha_3} \ln(1 - \phi_1 - \phi_2) + \frac{1}{\alpha_3} \right) \\
&\quad + (\chi_{12} N - \chi_{23} N) \phi_2 + \chi_{13} N (1 - 2\phi_1 - \phi_2)
\end{aligned} \tag{S44}$$

The derivation of $\tilde{\mu}_2$ is similar. It can be seen that direct derivation of partial derivatives of the free energy may lead to cumbersome procedures. By introducing γ , the tedious derivation process can be divided into simple and consistent operations, thereby simplifying derivation, enhancing clarity of expression, and being more friendly for programming.

REFERENCES

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