Supporting Information

Phase Behavior of Temperature-Responsive Polymers with Tunable LCST: An Equation-of-State Approach

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PEO/water model

Chemical potential of the polymer $\mu_2 = \mu_{2,LF} + \mu_{2,HB}$, as follows from (22), is given by

$$\frac{\mu_{2,LF}}{k_B T} = \ln\phi_2 + \left(1 - \frac{r_2}{r_1}\right)\phi_1 + r_2\tilde{\rho}\theta_1^2 X_{21} + \\ + r_2\left\{\frac{\tilde{P}_2\tilde{v} - \tilde{\rho}}{\tilde{T}_2} + (\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r_2}\ln\frac{\tilde{\rho}}{\omega_2}\right\} \tag{S.1}$$

$$\frac{\mu_{2,HB}}{k_B T} = r_2(\nu_{11} + \nu_{12}) + {a_2}^2 \ln\left(1 - \frac{r\nu_{12}}{{a_2}^2 x_2}\right) \tag{S.2}$$

and chemical potential of the solvent (H_2O) $\mu_1 = \mu_{1,LF} + \mu_{1,HB}$ is given by

$$\frac{\mu_{1,LF}}{k_B T} = \ln\phi_1 + \left(1 - \frac{r_1}{r_2}\right)\phi_2 + r_1\tilde{\rho}\theta_2^2 X_{12} + \\ + r_1\left\{\frac{\tilde{P}_1\tilde{v} - \tilde{\rho}}{\tilde{T}_1} + (\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r_1}\ln\frac{\tilde{\rho}}{\omega_1}\right\} \tag{S.3}$$

$$\frac{\mu_{1,HB}}{k_B T} = r_1(\nu_{11} + \nu_{12}) + {d_1}^1 \ln\left(1 - \frac{r(\nu_{11} + \nu_{12})}{{d_1}^1 x_1}\right) + \\ + {a_1}^1 \ln\left(1 - \tfrac{r\nu_{11}}{{a_1}^1 x_1}\right) \tag{S.4}$$

Equations of state have the following form

$$\begin{cases} \tilde{\rho}^2 + \tilde{P} + \tilde{T}\left(\ln(1 - \tilde{\rho}) + \tilde{\rho}\left(1 - \frac{1}{\bar{r}}\right)\right) = 0 \\ \mathcal{D}_1\mathcal{A}_1 - r\nu_{11}A_{11} = 0 \\ \mathcal{D}_1\mathcal{A}_2 - r\nu_{12}A_{12} = 0 \end{cases} \tag{S.5}$$

where

$$\begin{aligned}\mathcal{D}_1 &= {d_1}^1 x_1 - r(\nu_{11} + \nu_{12}) \\ \mathcal{A}_1 &= {a_1}^1 x_1 - r\nu_{11} \\ \mathcal{A}_2 &= {a_2}^2 x_2 - r\nu_{12}\end{aligned} \quad \begin{aligned} A_{11} &= r\tilde{v}\exp\left({G_{11}}^0/RT\right) \\ A_{12} &= r\tilde{v}\exp\left({G_{12}}^0/RT\right)\end{aligned} \tag{S.6}$$

In a binary case the model has two independent variables - composition x_2 and temperature T and the number of parameters, including external pressure P. External pressure is always kept constant in our considerations thus it is treated as a parameter rather than a variable.

Let us notice some functional dependencies, clearly r given by (2), as well as the segment and surface fractions, are all functions of composition x_2

$$r = r[x_2], \quad \phi_{1,2} = \phi_{1,2}[x_2], \quad \theta_{1,2} = \theta_{1,2}[x_2], \tag{S.7}$$

consequently, from equation (25) we have

$$v^* = v^*[x_2], \quad \epsilon^* = \epsilon^*[x_2] \tag{S.8}$$

Reduced pressure $\tilde{P}$ and reduced temperature $\tilde{T}$ defined by (14) depend on ϵ^* and v^*, thus

$$\begin{aligned}\tilde{P} &= \tilde{P}[v^*(x_2), \epsilon^*(x_2)] = \tilde{P}[x_2] \\ \tilde{T} &= \tilde{T}[\epsilon^*(x_2), T] = \tilde{T}[x_2, T]\end{aligned} \tag{S.9}$$

finally, auxiliary functions

$$A_{11} = A_{11}[x_2, \tilde{\rho}, T], \quad A_{12} = A_{12}[x_2, \tilde{\rho}, T] \tag{S.10}$$

Equations (S.1-S.2, S.3-S.4) and (S.5) suggest that chemical potential can be treated as a composite function

$$\mu_{1,2} = \mu_{1,2}[x_2, \tilde{\rho}(x_2, T), \nu_{11}(x_2, T), \nu_{12}(x_2, T), T] \tag{S.11}$$

Binodal

At a given temperature T mole fraction points ${x_2}^A$ and ${x_2}^B$ belong to the binodal curve if the following condition is satisfied

$$\begin{cases} \mu_1({x_2}^A, \tilde{\rho}^A, {\nu_{11}}^A, {\nu_{12}}^A, T) - \mu_1({x_2}^B, \tilde{\rho}^B, {\nu_{11}}^B, {\nu_{12}}^B, T) = 0 \\ \mu_2({x_2}^A, \tilde{\rho}^A, {\nu_{11}}^A, {\nu_{12}}^A, T) - \mu_2({x_2}^B, \tilde{\rho}^B, {\nu_{11}}^B, {\nu_{12}}^B, T) = 0 \end{cases} \tag{S.12}$$

Thus finding the binodal points at given temperature T involves solving of the system of 8 nonlinear equations – 2 binodal condition equations (S.12), 3 equations of state (S.5) at point ${x_2}^A$ and another 3 equations of state (S.5) at ${x_2}^B$:

$$\begin{cases} \mu_1({x_2}^A, \tilde{\rho}^A, {\nu_{11}}^A, {\nu_{12}}^A, T) - \mu_1({x_2}^B, \tilde{\rho}^B, {\nu_{11}}^B, {\nu_{12}}^B, T) = 0 \\ \mu_2({x_2}^A, \tilde{\rho}^A, {\nu_{11}}^A, {\nu_{12}}^A, T) - \mu_2({x_2}^B, \tilde{\rho}^B, {\nu_{11}}^B, {\nu_{12}}^B, T) = 0 \\ (\tilde{\rho}^A)^2 + \tilde{P}^A + \tilde{T}^A \left(\ln(1-\tilde{\rho}^A) + \tilde{\rho}^A \left(1 - \frac{1}{\bar{r}^A}\right)\right) = 0 \\ ({d_1}^1 {x_1}^A - r^A({\nu_{11}}^A + {\nu_{12}}^A))({a_1}^1 {x_1}^A - r^A {\nu_{11}}^A) - r^A {\nu_{11}}^A {A_{11}}^A = 0 \\ ({d_1}^1 {x_1}^A - r^A({\nu_{11}}^A + {\nu_{12}}^A))({a_2}^2 {x_2}^A - r^A {\nu_{12}}^A) - r^A {\nu_{12}}^A {A_{12}}^A = 0 \\ (\tilde{\rho}^B)^2 + \tilde{P}^B + \tilde{T}^B \left(\ln(1-\tilde{\rho}^B) + \tilde{\rho}^B \left(1 - \frac{1}{\bar{r}^B}\right)\right) = 0 \\ ({d_1}^1 {x_1}^B - r^B({\nu_{11}}^B + {\nu_{12}}^B))({a_1}^1 {x_1}^B - r^B {\nu_{11}}^B) - r^B {\nu_{11}}^B {A_{11}}^B = 0 \\ ({d_1}^1 {x_1}^B - r^B({\nu_{11}}^B + {\nu_{12}}^B))({a_2}^2 {x_2}^B - r^B {\nu_{12}}^B) - r^B {\nu_{12}}^B {A_{12}}^B = 0 \end{cases} \tag{S.13}$$

Spinodal

At a given temperature T the spinodal is determined by

$$\frac{\mathrm{d}}{\mathrm{d}x_2} \mu_2(x_2, \tilde{\rho}, \nu_{11}, \nu_{12}, T) = 0 \tag{S.14}$$

For this system the full x-derivative is given by

$$\frac{\mathrm{d}}{\mathrm{d}x_2} = \frac{\partial}{\partial x_2} + \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\partial}{\partial \tilde{\rho}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial}{\partial \nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial}{\partial \nu_{12}} \tag{S.15}$$

Thus

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}x_2} = \frac{\partial \mu_2}{\partial x_2} + \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\partial \mu_2}{\partial \tilde{\rho}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial \mu_2}{\partial \nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial \mu_2}{\partial \nu_{12}}, \tag{S.16}$$

where

$$\frac{\partial \mu_2}{\partial x_2} = \frac{\partial \mu_{2,LF}}{\partial x_2} + \frac{\partial \mu_{2,HB}}{\partial x_2} \tag{S.17}$$

$$\frac{\partial \mu_{2,LF}}{\partial x_2} = \frac{1}{\phi_2}\frac{\partial \phi_2}{\partial x_2} + \left(1 - \frac{r_2}{r_1}\right)\frac{\partial \phi_1}{\partial x_2} + 2r_2\tilde{\rho}X_{21}\theta_1\frac{\partial \theta_1}{\partial x_2} \tag{S.18}$$

$$\frac{\partial \mu_{2,HB}}{\partial x_2} = {a_2}^2 \frac{\nu_{12}\left(r - x_2\frac{\partial r}{\partial x_2}\right)}{x_2({a_2}^2 x_2 - r\nu_{12})} \tag{S.19}$$

$$\begin{aligned}\frac{\partial \mu_2}{\partial \tilde{\rho}} &= \frac{\partial \mu_{2,LF}}{\partial \tilde{\rho}} = \\ &= r_2 X_{21}{\theta_1}^2 + r_2\left(\frac{1}{\tilde{\rho}}\left(\frac{1}{r_2} - 1\right) - \frac{\tilde{P}_2}{\tilde{T}_2\tilde{\rho}^2} - \frac{1}{\tilde{T}_2} - \frac{\ln 1 - \tilde{\rho}}{\tilde{\rho}^2}\right)\end{aligned} \tag{S.20}$$

$$\frac{\partial \mu_2}{\partial \nu_{11}} = \frac{\partial \mu_{2,HB}}{\partial \nu_{11}} = r_2 \tag{S.21}$$

$$\frac{\partial \mu_2}{\partial \nu_{12}} = \frac{\partial \mu_{2,HB}}{\partial \nu_{12}} = r_2 - \frac{{a_2}^2 r}{{a_2}^2 x_2 - r\nu_{12}} \tag{S.22}$$

Equation (S.16) implies that

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}x_2} = \frac{\mathrm{d}\mu_2}{\mathrm{d}x_2}\left[x_2, \tilde{\rho}, \nu_{11}, \nu_{12}, \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}, \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}, \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}, T\right]$$

Notice that x-derivatives of reduced density and H-bond fractions are needed for spinodal calculation. These derivatives can be obtained by solving the following equations:

$$\begin{cases} \dfrac{\mathrm{d}}{\mathrm{d}x_2}\left[\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left(\ln(1-\tilde{\rho}) + \tilde{\rho}\left(1 - \dfrac{1}{\bar{r}}\right)\right)\right] = 0 \\ \dfrac{\mathrm{d}}{\mathrm{d}x_2}\left[\mathcal{D}_1\mathcal{A}_1 - r\nu_{11}A_{11}\right] = 0 \\ \dfrac{\mathrm{d}}{\mathrm{d}x_2}\left[\mathcal{D}_1\mathcal{A}_2 - r\nu_{12}A_{12}\right] = 0 \end{cases} \tag{S.23}$$

Equations (S.23) in explicit form are given by

$$\begin{cases} 2\tilde{\rho}\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2} + \frac{\mathrm{d}\tilde{P}}{\mathrm{d}x_2} + \frac{\mathrm{d}\tilde{T}}{\mathrm{d}x_2}\left[\ln(1-\tilde{\rho}) + \tilde{\rho}\left(1 - \frac{1}{\bar{r}}\right)\right] + \\ \quad + \tilde{T}\left[\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\left(\frac{\tilde{\rho}}{\tilde{\rho}-1} - \frac{1}{\bar{r}}\right) + \frac{\tilde{\rho}}{\bar{r}^2}\frac{\mathrm{d}\bar{r}}{\mathrm{d}x_2}\right] = 0 \\ \frac{\mathrm{d}\mathcal{D}_1}{\mathrm{d}x_2}\mathcal{A}_1 + \frac{\mathrm{d}\mathcal{A}_1}{\mathrm{d}x_2}\mathcal{D}_1 - A_{11}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{11} + r\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\right) - r\nu_{11}\frac{\mathrm{d}A_{11}}{\mathrm{d}x_2} = 0 \\ \frac{\mathrm{d}\mathcal{D}_1}{\mathrm{d}x_2}\mathcal{A}_2 + \frac{\mathrm{d}\mathcal{A}_2}{\mathrm{d}x_2}\mathcal{D}_1 - A_{12}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{12} + r\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\right) - r\nu_{12}\frac{\mathrm{d}A_{12}}{\mathrm{d}x_2} = 0 \end{cases} \tag{S.24}$$

where

$$\begin{aligned} \frac{\mathrm{d}\mathcal{D}_1}{\mathrm{d}x_2} &= -{d_1}^1 - \frac{\mathrm{d}r}{\mathrm{d}x_2}(\nu_{11}+\nu_{12}) - r\left(\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\right) \\ \frac{\mathrm{d}\mathcal{A}_1}{\mathrm{d}x_2} &= -{a_1}^1 - \frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{11} - r\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2} \\ \frac{\mathrm{d}\mathcal{A}_2}{\mathrm{d}x_2} &= {a_2}^2 - \frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{12} - r\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2} \end{aligned} \tag{S.25}$$

$$\begin{aligned} \frac{\mathrm{d}\tilde{P}}{\mathrm{d}x_2} &= \frac{\partial\tilde{P}}{\partial x_2} = \frac{P}{\epsilon^{*2}}\left(\frac{\partial v^*}{\partial x_2}\epsilon^* - v^*\frac{\partial\epsilon^*}{\partial x_2}\right) \\ \frac{\mathrm{d}\tilde{T}}{\mathrm{d}x_2} &= \frac{\partial\tilde{T}}{\partial x_2} = \frac{-RT}{\epsilon^{*2}}\frac{\partial\epsilon^*}{\partial x_2} \end{aligned} \tag{S.26}$$

$$\begin{aligned} \frac{\partial\epsilon^*}{\partial x_2} &= \frac{\partial\phi_1}{\partial x_2}\epsilon_1^* + \frac{\partial\phi_2}{\partial x_2}\epsilon_2^* - RTX_{12}\left(\frac{\partial\phi_1}{\partial x_2}\theta_2 + \frac{\partial\theta_2}{\partial x_2}\phi_1\right) \\ \frac{\partial v^*}{\partial x_2} &= \frac{\partial\phi_1}{\partial x_2}v_1^* + \frac{\partial\phi_2}{\partial x_2}v_2^* \end{aligned} \tag{S.27}$$

$$\begin{aligned} \frac{\partial\phi_2}{\partial x_2} &= \frac{r_2}{r} - \frac{\phi_2}{r}\frac{\partial r}{\partial x_2}, \quad \frac{\partial\phi_1}{\partial x_2} = 1 - \frac{\partial\phi_2}{\partial x_2} \\ \frac{\partial\theta_2}{\partial x_2} &= \frac{\partial\phi_2}{\partial x_2}\left(\frac{s_1}{s_2}\right)\left(\frac{\theta_2}{\phi_2}\right)^2, \quad \frac{\partial\theta_1}{\partial x_2} = 1 - \frac{\partial\theta_2}{\partial x_2} \end{aligned} \tag{S.28}$$

$$\begin{aligned} \frac{\mathrm{d}r}{\mathrm{d}x_2} &= \frac{\partial r}{\partial x_2} = r_2 - r_1 \\ \frac{\mathrm{d}\bar{r}}{\mathrm{d}x_2} &= \frac{1}{(1-r\nu_H)^2}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2} + r^2\frac{\mathrm{d}\nu_H}{\mathrm{d}x_2}\right) \end{aligned} \tag{S.29}$$

$$\begin{aligned} \frac{\mathrm{d}A_{11}}{\mathrm{d}x_2} &= \frac{1}{\tilde{\rho}^2}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\tilde{\rho} - r\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)\exp\left(\frac{{G_{11}}^0}{RT}\right) \\ \frac{\mathrm{d}A_{12}}{\mathrm{d}x_2} &= \frac{1}{\tilde{\rho}^2}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\tilde{\rho} - r\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)\exp\left(\frac{{G_{12}}^0}{RT}\right) \end{aligned} \tag{S.30}$$

Thus finding a concentration and a temperature of a spinodal point is equivalent to solving the system of 7 equations – 1 spinodal condition equation (S.14), 3 equations of state (S.5) and 3 derivatives of equations of state (S.24).

Critical point

The extremum of the spinodal curve, corresponding to the critical point of the system, is given by

$$\frac{\mathrm{d}^2\mu_2}{\mathrm{d}x_2^2} = 0 \tag{S.31}$$

Full second derivative in x_2 is given by

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}x_2^2} = \frac{\partial^2}{\partial x_2^2} &+ \left\{\frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}x_2^2}\frac{\partial}{\partial\tilde{\rho}} + \frac{\mathrm{d}^2\nu_{11}}{\mathrm{d}x_2^2}\frac{\partial}{\partial\nu_{11}} + \frac{\mathrm{d}^2\nu_{12}}{\mathrm{d}x_2^2}\frac{\partial}{\partial\nu_{12}}\right\} + \\ &+ \left\{\left(\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)^2\frac{\partial^2}{\partial\tilde{\rho}^2} + \left(\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\right)^2\frac{\partial^2}{\partial\nu_{11}^2} + \left(\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\right)^2\frac{\partial^2}{\partial\nu_{12}^2}\right\} + \\ &+2\left\{\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\partial^2}{\partial x_2\partial\tilde{\rho}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial^2}{\partial x_2\partial\nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2}{\partial x_2\partial\nu_{12}}\right\} + \\ &+2\left\{\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial^2}{\partial\tilde{\rho}\partial\nu_{11}} + \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2}{\partial\tilde{\rho}\partial\nu_{12}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2}{\partial\nu_{11}\partial\nu_{12}}\right\}\end{aligned} \tag{S.32}$$

Thus

$$\begin{aligned}\frac{\mathrm{d}^2\mu_2}{\mathrm{d}x_2^2} = \frac{\partial^2\mu_2}{\partial x_2^2} &+ \left\{\frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\tilde{\rho}} + \frac{\mathrm{d}^2\nu_{11}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{11}} + \frac{\mathrm{d}^2\nu_{12}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{12}}\right\} + \\ &+ \left\{\left(\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\tilde{\rho}^2} + \left(\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{11}^2} + \left(\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{12}^2}\right\} + \\ &+2\left\{\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\tilde{\rho}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{12}}\right\} + \\ &+2\left\{\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{11}} + \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{12}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{11}\partial\nu_{12}}\right\}\end{aligned} \tag{S.33}$$

where

$$\frac{\partial^2\mu_2}{\partial x_2^2} = \frac{\partial^2\mu_{2,LF}}{\partial x_2^2} + \frac{\partial^2\mu_{2,HB}}{\partial x_2^2} \tag{S.34}$$

$$\frac{\partial^2 \mu_{2,LF}}{\partial x_2^2} = -\left(\frac{1}{\phi_2}\frac{\partial \phi_2}{\partial x_2}\right)^2 + \frac{1}{\phi_2}\frac{\partial^2 \phi_2}{\partial x_2^2} + \left(1 - \frac{r_2}{r_1}\right)\frac{\partial^2 \phi_1}{\partial x_2^2} + \\ +2r_2\tilde{\rho}X_{21}\left(\left(\frac{\partial \theta_1}{\partial x_2}\right)^2 + \theta_1\frac{\partial^2 \theta_1}{\partial x_2^2}\right) \tag{S.35}$$

$$\frac{\partial^2 \mu_{2,HB}}{\partial x_2^2} = {a_2}^2 \frac{\left(x_2\nu_{12}\frac{\partial r}{\partial x_2} - r\nu_{12}\right)\left(2{a_2}^2 x_2 - x_2\nu_{12}\frac{\partial r}{\partial x_2} - r\nu_{12}\right)}{\left(x_2({a_2}^2 x_2 - r\nu_{12})\right)^2} \tag{S.36}$$

$$\frac{\partial^2 \mu_2}{\partial \tilde{\rho}^2} = \frac{\partial^2 \mu_{2,LF}}{\partial \tilde{\rho}^2} = \\ = r_2\left(\frac{2}{\tilde{\rho}^3}\left(\frac{\tilde{P}_2}{\tilde{T}_2} + \ln(1-\tilde{\rho})\right) + \frac{1}{\tilde{\rho}^2}\left(\frac{1}{1-\tilde{\rho}} - \frac{1}{r_2} + 1\right)\right) \tag{S.37}$$

$$\frac{\partial^2 \mu_2}{\partial \tilde{\nu}_{11}^2} = \frac{\partial^2 \mu_{2,HB}}{\partial \tilde{\nu}_{11}^2} = 0 \tag{S.38}$$

$$\frac{\partial^2 \mu_2}{\partial \tilde{\nu}_{12}^2} = \frac{\partial^2 \mu_{2,HB}}{\partial \tilde{\nu}_{12}^2} = \frac{-{a_2}^2 r^2}{({a_2}^2 x_2 - r\nu_{12})^2} \tag{S.39}$$

$$\frac{\partial^2 \mu_2}{\partial x_2 \partial \tilde{\rho}} = \frac{\partial^2 \mu_{2,LF}}{\partial x_2 \partial \tilde{\rho}} = 2r_2 X_{21}\theta_1\frac{\partial \theta_1}{\partial x_2} \tag{S.40}$$

$$\frac{\partial^2 \mu_2}{\partial x_2 \partial \nu_{11}} = \frac{\partial^2 \mu_{2,HB}}{\partial x_2 \partial \nu_{11}} = 0 \tag{S.41}$$

$$\frac{\partial^2 \mu_2}{\partial x_2 \partial \nu_{12}} = \frac{\partial^2 \mu_{2,HB}}{\partial x_2 \partial \nu_{12}} = ({a_2}^2)^2\frac{r - x_2\frac{\partial r}{\partial x_2}}{(r\nu_{12} - {a_2}^2 x_2)^2} \tag{S.42}$$

$$\frac{\partial^2 \mu_2}{\partial \tilde{\rho} \partial \nu_{11}} = \frac{\partial^2 \mu_{2,LF}}{\partial \tilde{\rho} \partial \nu_{11}} = 0 \tag{S.43}$$

$$\frac{\partial^2 \mu_2}{\partial \tilde{\rho} \partial \nu_{12}} = \frac{\partial^2 \mu_{2,LF}}{\partial \tilde{\rho} \partial \nu_{12}} = 0 \tag{S.44}$$

$$\frac{\partial^2 \mu_2}{\partial \nu_{11} \partial \nu_{12}} = \frac{\partial^2 \mu_{2,HB}}{\partial \nu_{11} \partial \nu_{12}} = 0 \tag{S.45}$$

and first derivatives of the chemical potential are given by equations (S.17), (S.20), (S.21), (S.22). Equation (S.33) implies that

$$\frac{\mathrm{d}^2 \mu_2}{\mathrm{d}x_2^2} = \frac{\mathrm{d}^2 \mu_2}{\mathrm{d}x_2^2}\left(x_2, \tilde{\rho}, \nu_{11}, \nu_{12}, \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}, \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}, \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}, \frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}x_2^2}, \frac{\mathrm{d}^2\nu_{11}}{\mathrm{d}x_2^2}, \frac{\mathrm{d}^2\nu_{12}}{\mathrm{d}x_2^2}, T\right)$$

Notice that second x-derivatives of reduced density and H-bond fractions are needed for critical point calculation. These derivatives can be obtained by solving the following equations:

$$\begin{cases} \frac{\mathrm{d}^2}{\mathrm{d}x_2^2}\left[\tilde{\rho}^2+\tilde{P}+\tilde{T}\left(\ln(1-\tilde{\rho})+\tilde{\rho}\left(1-\frac{1}{\bar{r}}\right)\right)\right]=0 \\ \frac{\mathrm{d}^2}{\mathrm{d}x_2^2}\left[\mathcal{D}_1\mathcal{A}_1-r\nu_{11}A_{11}\right]=0 \\ \frac{\mathrm{d}^2}{\mathrm{d}x_2^2}\left[\mathcal{D}_1\mathcal{A}_2-r\nu_{12}A_{12}\right]=0 \end{cases} \tag{S.46}$$

Equations (S.46) in explicit form are given by

$$\begin{cases} 2\left(\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)^2+2\tilde{\rho}\frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}x_2^2}+\frac{\mathrm{d}^2\tilde{P}}{\mathrm{d}x_2^2}+\frac{\mathrm{d}^2\tilde{T}}{\mathrm{d}x_2^2}\left[\ln(1-\tilde{\rho})+\tilde{\rho}\left(1-\frac{1}{\bar{r}}\right)\right]+ \\ 2\frac{\mathrm{d}\tilde{T}}{\mathrm{d}x_2}\left[\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\left(\frac{\tilde{\rho}}{\tilde{\rho}-1}-\frac{1}{\bar{r}}\right)+\frac{\tilde{\rho}}{\bar{r}^2}\frac{\mathrm{d}\bar{r}}{\mathrm{d}x_2}\right]+ \\ \tilde{T}\left[-\frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}x_2^2}\left(\frac{\tilde{\rho}}{1-\tilde{\rho}}+\frac{1}{\bar{r}}\right)-\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\left(\frac{\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}}{(1-\tilde{\rho})^2}-\frac{2}{\bar{r}^2}\frac{\mathrm{d}\bar{r}}{\mathrm{d}x_2}\right)\right]+ \\ +\frac{\tilde{\rho}\tilde{T}}{\bar{r}^2}\left[\frac{\mathrm{d}^2\bar{r}}{\mathrm{d}x_2^2}-\frac{2}{\bar{r}}\left(\frac{\mathrm{d}\bar{r}}{\mathrm{d}x_2}\right)^2\right]=0 \\ \frac{\mathrm{d}^2\mathcal{D}_1}{\mathrm{d}x_2^2}\mathcal{A}_1+2\frac{\mathrm{d}\mathcal{A}_1}{\mathrm{d}x_2}\frac{\mathrm{d}\mathcal{D}_1}{\mathrm{d}x_2}+\frac{\mathrm{d}^2\mathcal{A}_1}{\mathrm{d}x_2^2}\mathcal{D}_1-A_{11}\left(2\frac{\mathrm{d}r}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}+r\frac{\mathrm{d}^2\nu_{11}}{\mathrm{d}x_2^2}\right)- \\ -2\frac{\mathrm{d}A_{11}}{\mathrm{d}x_2}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{11}+r\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\right)-r\nu_{11}\frac{\mathrm{d}^2A_{11}}{\mathrm{d}x_2^2}=0 \\ \frac{\mathrm{d}^2\mathcal{D}_1}{\mathrm{d}x_2^2}\mathcal{A}_2+2\frac{\mathrm{d}\mathcal{A}_2}{\mathrm{d}x_2}\frac{\mathrm{d}\mathcal{D}_1}{\mathrm{d}x_2}+\frac{\mathrm{d}^2\mathcal{A}_2}{\mathrm{d}x_2^2}\mathcal{D}_1-A_{12}\left(2\frac{\mathrm{d}r}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}+r\frac{\mathrm{d}^2\nu_{12}}{\mathrm{d}x_2^2}\right)- \\ -2\frac{\mathrm{d}A_{12}}{\mathrm{d}x_2}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{12}+r\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\right)-r\nu_{12}\frac{\mathrm{d}^2A_{12}}{\mathrm{d}x_2^2}=0 \end{cases} \tag{S.47}$$

where

$$\begin{aligned} \frac{\mathrm{d}^2\mathcal{D}_1}{\mathrm{d}x_2^2}&=-2\frac{\mathrm{d}r}{\mathrm{d}x_2}\left(\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}+\frac{\mathrm{d}\nu_{12}}{dx}\right)-r\left(\frac{\mathrm{d}^2\nu_{11}}{\mathrm{d}x_2^2}+\frac{\mathrm{d}^2\nu_{12}}{\mathrm{d}x_2^2}\right) \\ \frac{\mathrm{d}^2\mathcal{A}_1}{\mathrm{d}x_2^2}&=-2\frac{\mathrm{d}r}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}-r\frac{\mathrm{d}^2\nu_{11}}{\mathrm{d}x_2^2} \\ \frac{\mathrm{d}^2\mathcal{A}_2}{\mathrm{d}x_2^2}&=-2\frac{\mathrm{d}r}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}-r\frac{\mathrm{d}^2\nu_{12}}{\mathrm{d}x_2^2} \end{aligned} \tag{S.48}$$

$$\begin{aligned} \frac{\mathrm{d}^2\tilde{P}}{\mathrm{d}x_2^2}&=\frac{\partial^2\tilde{P}}{\partial x_2^2}=\frac{P}{\epsilon^{*2}}\left(\frac{\partial^2 v^*}{\partial x_2^2}\epsilon^*-\frac{\partial^2\epsilon^*}{\partial x_2^2}v^*\right)-\frac{2}{\epsilon^*}\frac{\partial\epsilon^*}{\partial x_2}\frac{\partial\tilde{P}}{\partial x_2} \\ \frac{\mathrm{d}^2\tilde{T}}{\mathrm{d}x_2^2}&=\frac{\partial^2\tilde{T}}{\partial x_2^2}=\frac{-RT}{\epsilon^{*2}}\left(\frac{\partial^2\epsilon^*}{\partial x_2^2}-\frac{2}{\epsilon^*}\left(\frac{\partial\epsilon^*}{\partial x_2}\right)^2\right) \end{aligned} \tag{S.49}$$

$$
\begin{aligned}
\frac{\partial^2 \epsilon^*}{\partial x_2^2} &= \frac{\partial^2 \phi_1}{\partial x_2^2}\epsilon_1^* + \frac{\partial^2 \phi_2}{\partial x_2^2}\epsilon_2^* - \\
&\quad -RTX_{12}\left(\frac{\partial^2 \phi_1}{\partial x_2^2}\theta_2 + 2\frac{\partial \phi_1}{\partial x_2}\frac{\partial \theta_2}{\partial x_2} + \frac{\partial^2 \theta_2}{\partial x_2^2}\phi_1\right) \\
\frac{\partial^2 v^*}{\partial x_2^2} &= \frac{\partial^2 \phi_1}{\partial x_2^2}v_1^* + \frac{\partial^2 \phi_2}{\partial x_2^2}v_2^*
\end{aligned} \tag{S.50}
$$

$$
\begin{aligned}
\frac{\partial^2 \phi_2}{\partial x_2^2} &= \frac{-2}{r}\frac{\partial r}{\partial x_2}\frac{\partial \phi_2}{\partial x_2}, \qquad \frac{\partial^2 \phi_1}{\partial x_2^2} = 1 - \frac{\partial^2 \phi_2}{\partial x_2^2} \\
\frac{\partial^2 \theta_2}{\partial x_2^2} &= \left(\frac{s_1}{s_2}\right)\left[\frac{\partial^2 \phi_2}{\partial x_2^2}\left(\frac{\theta_2}{\phi_2}\right)^2 + \frac{2\theta_2}{{\phi_2}^3}\frac{\partial \phi_2}{\partial x_2}\left(\frac{\partial \theta_2}{\partial x_2}\phi_2 - \theta_2\frac{\partial \phi_2}{\partial x_2}\right)\right] \\
\frac{\partial^2 \theta_1}{\partial x_2^2} &= 1 - \frac{\partial^2 \theta_2}{\partial x_2^2}
\end{aligned} \tag{S.51}
$$

$$
\frac{\mathrm{d}^2 \bar{r}}{\mathrm{d}x_2^2} = \frac{2\bar{r}}{r^3}\frac{\mathrm{d}r}{\mathrm{d}x_2}\left(\frac{\mathrm{d}\bar{r}}{\mathrm{d}x_2}r - \frac{\mathrm{d}r}{\mathrm{d}x_2}\bar{r}\right) + 2\bar{r}\frac{\mathrm{d}r}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_H}{\mathrm{d}x_2} + \bar{r}^2\frac{\mathrm{d}^2 \nu_H}{\mathrm{d}x_2^2} \tag{S.52}
$$

$$
\begin{aligned}
\frac{\mathrm{d}^2 A_{11}}{\mathrm{d}x_2^2} &= \frac{1}{\tilde{\rho}^3}\left(2r\left(\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)^2 - 2\tilde{\rho}\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}r}{\mathrm{d}x_2} - r\tilde{\rho}\frac{\mathrm{d}^2 \tilde{\rho}}{\mathrm{d}x_2^2}\right)\exp\left(\frac{{G_{11}}^0}{RT}\right) \\
\frac{\mathrm{d}^2 A_{12}}{\mathrm{d}x_2^2} &= \frac{1}{\tilde{\rho}^3}\left(2r\left(\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)^2 - 2\tilde{\rho}\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}r}{\mathrm{d}x_2} - r\tilde{\rho}\frac{\mathrm{d}^2 \tilde{\rho}}{\mathrm{d}x_2^2}\right)\exp\left(\frac{{G_{12}}^0}{RT}\right)
\end{aligned} \tag{S.53}
$$

Thus critical point can be found as a solution to the system of 11 equations – 1 critical point condition equation (S.31), 1 spinodal condition equation (S.14), 3 equations of state (S.5), 3 first derivatives of the equations of state (S.24) and 3 second derivatives of the equations of state (S.47). Needless to say that equations (S.31), (S.14), (S.24), (S.47), as well as equations (S.13), can only be solved numerically.

P(EO-EE)/water model

Esters

The modification of PEO/water model via the combination rule (30) leaves lattice-fluid part unchanged, except for the modified dimensionless parameters (30), and introduces additional terms and equations to hydrogen-bonding part. Now total H-bond fraction is given by

$$
\nu_H = \nu_{11} + \nu_{12} + \nu_{13} \tag{S.54}
$$

and chemical potentials of the polymer and the solvent change accordingly:

$$\frac{\mu_{2,HB}}{k_BT} = r_2\nu_H + {a_2}^2 \ln\left(1 - \frac{r\nu_{12}}{{a_2}^2 x_2}\right) + {a_3}^2 \ln\left(1 - \frac{r\nu_{13}}{{a_3}^2 x_2}\right) \tag{S.55}$$

$$\begin{aligned}\frac{\mu_{1,HB}}{k_BT} &= r_1\nu_H + {d_1}^1 \ln\left(1 - \frac{r(\nu_{11}+\nu_{12}+\nu_{13})}{{d_1}^1 x_1}\right) + \\ &+{a_1}^1 \ln\left(1 - \frac{r\nu_{11}}{{a_1}^1 x_1}\right)\end{aligned} \tag{S.56}$$

$\mu_{2,LF}$ and $\mu_{1,LF}$ are given by (S.1) and (S.3) respectively. In the equations of state the lattice-fluid reduced density equation has the same form (S.5.1) and the hydrogen-bonding part gains additional equation governing new H-bond fraction and has the following form

$$\begin{cases} \mathcal{D}_1\mathcal{A}_1 - r\nu_{11}A_{11} = 0 \\ \mathcal{D}_1\mathcal{A}_2 - r\nu_{12}A_{12} = 0 \\ \mathcal{D}_1\mathcal{A}_3 - r\nu_{13}A_{13} = 0 \end{cases} \tag{S.57}$$

where

$$\begin{aligned} \mathcal{D}_1 &= {d_1}^1 x_1 - r(\nu_{11}+\nu_{12}+\nu_{13}) \\ \mathcal{A}_1 &= {a_1}^1 x_1 - r\nu_{11} \\ \mathcal{A}_2 &= {a_2}^2 x_2 - r\nu_{12} \\ \mathcal{A}_3 &= {a_3}^2 x_2 - r\nu_{13} \end{aligned} \qquad \begin{aligned} A_{11} &= r\tilde{v}\exp\left({G_{11}}^0/RT\right) \\ A_{12} &= r\tilde{v}\exp\left({G_{12}}^0/RT\right) \\ A_{13} &= r\tilde{v}\exp\left({G_{13}}^0/RT\right) \end{aligned} \tag{S.58}$$

Notice that $\mathcal{D}_1$ changes to include ν_{13}. With additional equation of state, finding binodal point at given temperature is equivalent to solving the system of 10 equations. Introduction of another variable changes the form of full x-derivate, thus

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}x_2} = \frac{\partial\mu_2}{\partial x_2} + \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\tilde{\rho}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\nu_{12}} + \frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\nu_{13}} \tag{S.59}$$

where

$$\frac{\partial\mu_{2,HB}}{\partial x_2} = {a_2}^2 \frac{\nu_{12}\left(r - x_2\frac{\partial r}{\partial x_2}\right)}{x_2({a_2}^2 x_2 - r\nu_{12})} + {a_3}^2 \frac{\nu_{13}\left(r - x_2\frac{\partial r}{\partial x_2}\right)}{x_2({a_3}^2 x_2 - r\nu_{13})} \tag{S.60}$$

$$\frac{\partial\mu_2}{\partial\nu_{13}} = \frac{\partial\mu_{2,HB}}{\partial\nu_{13}} = r_2 - \frac{{a_3}^2 r}{{a_3}^2 x_2 - r\nu_{13}} \tag{S.61}$$

$\partial\mu_{2,LF}/\partial x_2$, $\partial\mu_2/\partial\rho$, $\partial\mu_2/\partial\nu_{11}$, $\partial\mu_2/\partial\nu_{12}$ are given by (S.18),(S.20),(S.21),(S.22) respectively. First x-derivatives of the equations of state are needed to proceed further with the spinodal calculation. Derivative of the reduced density equation of state, as well as the derivatives of first two equations for H-bond fractions, with $\mathcal{D}_1$, $\mathcal{A}_1$, $\mathcal{A}_2$, $\mathcal{A}_3$ given by (S.58), do not change and have the form identical to (S.24), the derivative of the third H-bond fractions equation is given by the following familiar form

$$\frac{\mathrm{d}\mathcal{D}_1}{\mathrm{d}x_2}\mathcal{A}_3 + \frac{\mathrm{d}\mathcal{A}_3}{\mathrm{d}x_2}\mathcal{D}_1 - A_{13}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{13} + r\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\right) - r\nu_{13}\frac{\mathrm{d}A_{13}}{\mathrm{d}x_2} = 0 \tag{S.62}$$

Derivatives of other quantities calculated in (S.26)-(S.30) all preserve their functional form, taking into account that ν_H is now given by (S.54). Now we have to solve 9 equation to calculate a point on the spinodal curve. Second derivate of the chemical potential needed for critical point calculation has the following form

$$\begin{aligned}\frac{\mathrm{d}^2\mu_2}{\mathrm{d}x_2^2} = &\frac{\partial^2\mu_2}{\partial x_2^2} + \frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\tilde{\rho}} + \frac{\mathrm{d}^2\nu_{11}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{11}} + \frac{\mathrm{d}^2\nu_{12}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{12}} + \\ &+ \frac{\mathrm{d}^2\nu_{13}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{13}} + \left(\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\tilde{\rho}^2} + \left(\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{11}^2} + \\ &+ \left(\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{12}^2} + \left(\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{13}^2} + \\ &+2\left\{\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\tilde{\rho}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{12}}\right\} + \\ &+2\left\{\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{13}} + \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{11}} + \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{12}}\right\} + \\ &+2\left\{\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{13}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{11}\partial\nu_{12}}\right\} + \\ &+2\left\{\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{11}\partial\nu_{13}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{12}\partial\nu_{13}}\right\}\end{aligned} \tag{S.63}$$

where

$$\begin{aligned}\frac{\partial^2\mu_{2,HB}}{\partial x_2^2} = &{a_2}^2\frac{\left(x_2\nu_{12}\frac{\partial r}{\partial x_2} - r\nu_{12}\right)\left(2{a_2}^2x_2 - x_2\nu_{12}\frac{\partial r}{\partial x_2} - r\nu_{12}\right)}{\left(x_2({a_2}^2x_2 - r\nu_{12})\right)^2} + \\ &+{a_3}^2\frac{\left(x_2\nu_{13}\frac{\partial r}{\partial x_2} - r\nu_{13}\right)\left(2{a_3}^2x_2 - x_2\nu_{13}\frac{\partial r}{\partial x_2} - r\nu_{13}\right)}{\left(x_2({a_3}^2x_2 - r\nu_{13})\right)^2}\end{aligned} \tag{S.64}$$

$$\frac{\partial^2\mu_2}{\partial\tilde{\nu}_{13}^2} = \frac{-{a_3}^2r^2}{({a_3}^2x_2 - r\nu_{13})^2}, \tag{S.65}$$

$$\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{13}} = ({a_3}^2)^2\frac{r - x_2\frac{\partial r}{\partial x_2}}{(r\nu_{13} - {a_3}^2x_2)^2}, \tag{S.66}$$

$$\frac{\partial^2 \mu_2}{\partial\tilde{\rho}\partial\nu_{13}} = \frac{\partial^2 \mu_2}{\partial\nu_{11}\partial\nu_{13}} = \frac{\partial^2 \mu_2}{\partial\nu_{12}\partial\nu_{13}} = 0 \tag{S.67}$$

and the rest of the second partial derivatives of the chemical potential are given by equations (S.35)-(S.45). Second derivative of the additional equation of state needed for the critical point calculation has the form of

$$\begin{aligned}&\frac{\mathrm{d}^2\mathcal{D}_1}{\mathrm{d}x_2^2}\mathcal{A}_3 + 2\frac{\mathrm{d}\mathcal{A}_3}{\mathrm{d}x_2}\frac{\mathrm{d}\mathcal{D}_1}{\mathrm{d}x_2} + \frac{\mathrm{d}^2\mathcal{A}_3}{\mathrm{d}x_2^2}\mathcal{D}_1 - A_{13}\left(2\frac{\mathrm{d}r}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2} + r\frac{\mathrm{d}^2\nu_{13}}{\mathrm{d}x_2^2}\right) - \\ &-2\frac{\mathrm{d}A_{13}}{\mathrm{d}x_2}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{13} + r\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\right) - r\nu_{13}\frac{\mathrm{d}^2A_{13}}{\mathrm{d}x_2^2} = 0\end{aligned} \tag{S.68}$$

Second derivatives of the other functions are given by (S.49)-(S.53), and the critical point can be found as a solution to the system of 14 equations.

Amides

More H-bonds, same parameters. Now total H-bond fraction is given by

$$\nu_H = \nu_{11} + \nu_{12} + \nu_{13} + \nu_{21} \tag{S.69}$$

Once again this modification leaves lattice-fluid part of the model unchanged, but introduces additional terms and equations to hydrogen-bonding part. Chemical potentials of the polymer and the solvent have the following form

$$\begin{aligned}\frac{\mu_{2,HB}}{k_BT} &= r_2\nu_H + {d_2}^2\ln\left(1 - \frac{r\nu_{21}}{{d_2}^2x_2}\right) + \\ &+{a_2}^2\ln\left(1 - \frac{r\nu_{12}}{{a_2}^2x_2}\right) + {a_3}^2\ln\left(1 - \frac{r\nu_{13}}{{a_3}^2x_2}\right)\end{aligned} \tag{S.70}$$

$$\begin{aligned}\frac{\mu_{1,HB}}{k_BT} &= r_1\nu_H + {d_1}^1\ln\left(1 - \frac{r(\nu_{11}+\nu_{12}+\nu_{13})}{{d_1}^1x_1}\right) + \\ &+{a_1}^1\ln\left(1 - \frac{r(\nu_{11}+\nu_{21})}{{a_1}^1x_1}\right)\end{aligned} \tag{S.71}$$

with $\mu_{2,LF}$ and $\mu_{1,LF}$ are given by (S.1) and (S.3) respectively. Analogously to the previous case the system of the equations of state gain yet another equation

$$\begin{cases} \mathcal{D}_1\mathcal{A}_1 - r\nu_{11}A_{11} = 0 \\ \mathcal{D}_1\mathcal{A}_2 - r\nu_{12}A_{12} = 0 \\ \mathcal{D}_1\mathcal{A}_3 - r\nu_{13}A_{13} = 0 \\ \mathcal{D}_2\mathcal{A}_1 - r\nu_{21}A_{21} = 0 \end{cases} \tag{S.72}$$

where

$$\begin{aligned} \mathcal{D}_1 &= {d_1}^1x_1 - r(\nu_{11}+\nu_{12}+\nu_{13}) \\ \mathcal{D}_2 &= {d_2}^2x_1 - r\nu_{21} \\ \mathcal{A}_1 &= {a_1}^1x_1 - r\nu_{11} \\ \mathcal{A}_2 &= {a_2}^2x_2 - r\nu_{12} \\ \mathcal{A}_3 &= {a_3}^2x_2 - r\nu_{13} \end{aligned} \qquad \begin{aligned} A_{11} &= r\tilde{v}\exp\left({G_{11}}^0/RT\right) \\ A_{12} &= r\tilde{v}\exp\left({G_{12}}^0/RT\right) \\ A_{13} &= r\tilde{v}\exp\left({G_{13}}^0/RT\right) \\ A_{21} &= r\tilde{v}\exp\left({G_{21}}^0/RT\right) \end{aligned} \tag{S.73}$$

which brings the number of equations needed for finding a pair of binodal points at a given temperature up to 12. Full x-derivative of the chemical potential changes to be

$$\begin{aligned} \frac{\mathrm{d}\mu_2}{\mathrm{d}x_2} = \frac{\partial\mu_2}{\partial x_2} + \frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\tilde{\rho}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\nu_{12}} + \\ + \frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\nu_{13}} + \frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\frac{\partial\mu_2}{\partial\nu_{21}} \end{aligned} \tag{S.74}$$

where

$$\begin{aligned} \frac{\partial\mu_{2,HB}}{\partial x_2} = {d_2}^2\frac{\nu_{21}\left(r - x_2\frac{\partial r}{\partial x_2}\right)}{x_2({d_2}^2x_2 - r\nu_{21})} + {a_2}^2\frac{\nu_{12}\left(r - x_2\frac{\partial r}{\partial x_2}\right)}{x_2({a_2}^2x_2 - r\nu_{12})} + \\ + {a_3}^2\frac{\nu_{13}\left(r - x_2\frac{\partial r}{\partial x_2}\right)}{x_2({a_3}^2x_2 - r\nu_{13})} \end{aligned} \tag{S.75}$$

$$\frac{\partial\mu_2}{\partial\nu_{21}} = r_2 - \frac{{d_2}^2r}{{d_2}^2x_2 - r\nu_{21}} \tag{S.76}$$

with the rest of partial derivatives of the chemical potential given by (S.18)-(S.22) and (S.61). First derivative of the additional equation of state has the following form

$$\frac{\mathrm{d}\mathcal{D}_2}{\mathrm{d}x_2}\mathcal{A}_1 + \frac{\mathrm{d}\mathcal{A}_1}{\mathrm{d}x_2}\mathcal{D}_2 - A_{21}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{21} + r\frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\right) - r\nu_{21}\frac{\mathrm{d}A_{21}}{\mathrm{d}x_2} = 0 \tag{S.77}$$

while the rest of the derivatives of the equations of state is given by (S.24) and (S.62), with $\mathcal{D}$'s and $\mathcal{A}$'s redefined in (S.73). Derivatives of other quantities calculated in (S.26)-(S.30) all preserve their functional form, taking into account that ν_H is now given by (S.69). A point on the spinodal can now be found as a solution to the system of 11 equations. Second derivative of the chemical potential now has the following form

$$\begin{aligned}
\frac{\mathrm{d}^2\mu_2}{\mathrm{d}x_2^2} &= \frac{\partial^2\mu_2}{\partial x_2^2} + \frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\tilde{\rho}} + \\
&+ \frac{\mathrm{d}^2\nu_{11}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{11}} + \frac{\mathrm{d}^2\nu_{12}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{12}} + \frac{\mathrm{d}^2\nu_{13}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{13}} + \frac{\mathrm{d}^2\nu_{21}}{\mathrm{d}x_2^2}\frac{\partial\mu_2}{\partial\nu_{21}} + \\
&+ \left(\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\tilde{\rho}^2} + \left(\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{11}^2} + \\
&+ \left(\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{12}^2} + \left(\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{13}^2} + \left(\frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\right)^2\frac{\partial^2\mu_2}{\partial\nu_{21}^2} + \\
&+ 2\left\{\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\tilde{\rho}} + \frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{12}}\right\} + \\
&+ 2\left\{\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{13}} + \frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial x_2\partial\nu_{21}}\right\} + \\
&+ 2\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\left\{\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{11}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{12}}\right\} + \\
&+ 2\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x_2}\left\{\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{13}} + \frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\tilde{\rho}\partial\nu_{21}}\right\} + \\
&+ 2\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\left\{\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{11}\partial\nu_{12}} + \frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{11}\partial\nu_{13}}\right\} + \\
&+ 2\frac{\mathrm{d}\nu_{11}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{11}\partial\nu_{21}} + \\
&+ 2\left\{\frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{13}\partial\nu_{13}} + \frac{\mathrm{d}\nu_{12}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{12}\partial\nu_{21}}\right\} + \\
&+ \frac{\mathrm{d}\nu_{13}}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\frac{\partial^2\mu_2}{\partial\nu_{13}\partial\nu_{21}}
\end{aligned} \tag{S.78}$$

where

$$\begin{aligned}
\frac{\partial^2\mu_{2,HB}}{\partial x_2^2} &= {d_2}^2\frac{\left(x_2\nu_{21}\frac{\partial r}{\partial x_2} - r\nu_{21}\right)\left(2{d_2}^2x_2 - x_2\nu_{21}\frac{\partial r}{\partial x_2} - r\nu_{21}\right)}{\left(x_2({d_2}^2x_2 - r\nu_{21})\right)^2} + \\
&+ {a_2}^2\frac{\left(x_2\nu_{12}\frac{\partial r}{\partial x_2} - r\nu_{12}\right)\left(2{a_2}^2x_2 - x_2\nu_{12}\frac{\partial r}{\partial x_2} - r\nu_{12}\right)}{\left(x_2({a_2}^2x_2 - r\nu_{12})\right)^2} + \\
&+ {a_3}^2\frac{\left(x_2\nu_{13}\frac{\partial r}{\partial x_2} - r\nu_{13}\right)\left(2{a_3}^2x_2 - x_2\nu_{13}\frac{\partial r}{\partial x_2} - r\nu_{13}\right)}{\left(x_2({a_3}^2x_2 - r\nu_{13})\right)^2}
\end{aligned} \tag{S.79}$$

$$\frac{\partial^2\mu_2}{\partial\tilde{\nu}_{21}^2} = \frac{-{d_2}^2r^2}{({d_2}^2x_2 - r\nu_{21})^2}, \tag{S.80}$$

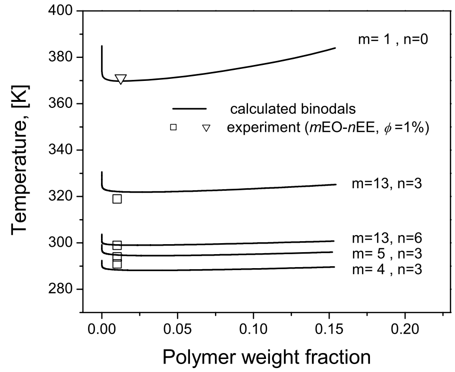

Fig. S1. Binodals for the polyester copolymer series calculated for the experimental values of M_w as described in section 3.3, and the corresponding experimental cloud point temperatures of the $1wt\%$ polymer solution.

$$\frac{\partial^2 \mu_2}{\partial x_2 \partial \nu_{21}} = ({d_2}^2)^2 \frac{r - x_2 \frac{\partial r}{\partial x_2}}{(r\nu_{21} - {d_2}^2 x_2)^2}, \tag{S.81}$$

$$\frac{\partial^2 \mu_2}{\partial \tilde{\rho} \partial \nu_{21}} = \frac{\partial^2 \mu_2}{\partial \nu_{11} \partial \nu_{21}} = \frac{\partial^2 \mu_2}{\partial \nu_{12} \partial \nu_{21}} = \frac{\partial^2 \mu_2}{\partial \nu_{13} \partial \nu_{21}} = 0 \tag{S.82}$$

and the rest of the second partial derivatives of the chemical potential are given by equations (S.35)-(S.45) and (S.65)-(S.67). Second derivative of the additional equation of state needed for the critical point calculation has the form of

$$\begin{aligned} &\frac{\mathrm{d}^2 \mathcal{D}_2}{\mathrm{d}x_2^2}\mathcal{A}_1 + 2\frac{\mathrm{d}\mathcal{A}_1}{\mathrm{d}x_2}\frac{\mathrm{d}\mathcal{D}_2}{\mathrm{d}x_2} + \frac{\mathrm{d}^2\mathcal{A}_1}{\mathrm{d}x_2^2}\mathcal{D}_2 - A_{21}\left(2\frac{\mathrm{d}r}{\mathrm{d}x_2}\frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2} + r\frac{\mathrm{d}^2\nu_{21}}{\mathrm{d}x_2^2}\right) - \\ &-2\frac{\mathrm{d}A_{21}}{\mathrm{d}x_2}\left(\frac{\mathrm{d}r}{\mathrm{d}x_2}\nu_{21} + r\frac{\mathrm{d}\nu_{21}}{\mathrm{d}x_2}\right) - r\nu_{21}\frac{\mathrm{d}^2 A_{21}}{\mathrm{d}x_2^2} = 0 \end{aligned} \tag{S.83}$$

Second derivatives of the other functions are given by (S.49)-(S.53), and the critical point can be found as a solution to the system of 17 equations.

Example binodals

Figure S1 shows calculated binodal curves for PEO and for selected polyester copolymers (for the experimental molecular weights, as described in section 3.3). In support of the hydrophilic/hydrophobic “superposition” argument, one can see no significant difference in the shape of the binodals with polymer composition (m, n) despite the large shift in critical temperature.