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Addition/Correction

Addition to “Phase-Separating Binary Polymer Mixtures: The Degeneracy of the Virial Coefficients and Their Extraction from Phase Diagrams”

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Regarding our previous publication entitled “Phase-Separating Binary Polymer Mixtures: The Degeneracy of the Virial Coefficients and Their Extraction from Phase Diagrams”,[1] we wish to add a short discussion on the following topics: (1) a practical expression for the slope of the tangent to binodal and spinodal in the critical point, (2) an extension on how to find the virial coefficients, when the critical point is known, (3) a demonstration that eq 37 from ref 1 is always met by the solution of the coexistence equations, and (4) an extension on how to find the virial coefficients when the composition of two coexisting phases is known.

The main advantage for the new equations presented in this Addition is that they are expressed directly in experimentally accessible quantities: the coordinates of the critical point or the compositions of the coexisting phases.

1. PRACTICAL EXPRESSION FOR THE SLOPE OF THE TANGENT TO BINODAL AND SPINODAL IN THE CRITICAL POINT

It was recently noted that eq 20 in ref 1, which expresses the stability requirement in the critical point

$$B_{22}\sqrt{S_c}^{\,3} + B_{12}\sqrt{S_c}^{\,2} - B_{12}\sqrt{S_c} - B_{11} = 0 \tag{1}$$

where -S_c is the slope of the tangent of the binodal and spinodal in the critical point and (B_{11}, B_{12}, B_{22}) are the virial coefficients for the mixture can be rewritten as

$$S_c^{3/2} = \left(\frac{B_{12}S_c - B_{11}}{\frac{B_{12}}{S_c} - B_{22}}\right) \tag{2}$$

As a result, by using eqs 24 and 25 in ref 1, it is found that

$$S_c = \left(\frac{c_{2,c}}{c_{1,c}}\right)^{2/3} \tag{3}$$

Here ($c_{1,c}$, $c_{2,c}$) are the coordinates of the critical point in molar concentration units. This is a useful relation in the case where the critical point is known. In addition, eq 3 is an expression for S_c that explicitly shows that it satisfies the transformation $(B_{11}, B_{12}, B_{22}, S_c) \rightarrow (B_{22}, B_{12}, B_{11}, 1/S_c)$. This property was already clear from eqs 20−21 in ref 1 but was not obvious from the explicit solutions as presented in eqs 22−23 in ref 1.

2. AN EXPLICIT EXPRESSION FOR THE VIRIAL COEFFICIENTS WHEN THE CRITICAL POINT IS KNOWN

From eq 29 in ref 1, it follows that all triplets of virial coefficients (B_{11}^*, B_{12}^*, B_{22}^*) that correspond to a certain critical point ($c_{1,c}$, $c_{2,c}$) can be written in vector notation as

$$\begin{pmatrix} B_{11}^* \\ B_{12}^* \\ B_{22}^* \end{pmatrix} = \begin{pmatrix} B_{11} \\ B_{12} \\ B_{22} \end{pmatrix} + \lambda_1 \begin{pmatrix} S_c \\ 1 \\ 1/S_c \end{pmatrix} \tag{4}$$

Here, -S_c is the slope of the tangent of the binodal and spinodal in the critical point; λ_1 can be any real number provided $\frac{B_{12}^{*2}}{B^*_{11}B^*_{22}} > 1$. Equation 3 has the interesting consequence that when combined with a rearranged version of equations originally provided by Edmond and Ogston[2] (eqs 26−27 in ref 1)

$$B_{11} = B_{12}\left(\frac{c_{2,c}}{c_{1,c}}\right)^{2/3} - \frac{1}{2c_{1,c}} \tag{5}$$

$$B_{22} = B_{12}\left(\frac{c_{1,c}}{c_{2,c}}\right)^{2/3} - \frac{1}{2c_{2,c}} \tag{6}$$

it allows one to rewrite eq 4 in a form that solely contains the location of the critical point ($c_{1,c}$, $c_{2,c}$):

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$$\begin{pmatrix} B_{11}^* \\ B_{12}^* \\ B_{22}^* \end{pmatrix} = \begin{pmatrix} -\dfrac{1}{2c_{1,c}} \\ 0 \\ -\dfrac{1}{2c_{2,c}} \end{pmatrix} + \lambda_2 \begin{pmatrix} \left(\dfrac{c_{2,c}}{c_{1,c}}\right)^{2/3} \\ 1 \\ \left(\dfrac{c_{1,c}}{c_{2,c}}\right)^{2/3} \end{pmatrix} \tag{7}$$

This expression gives all possible values for the virial coefficients (B_{11}^*, B_{12}^*, B_{22}^*) leading to the same critical point ($c_{1,c}$, $c_{2,c}$). Here $\lambda_2 > 1/(2(c_{1,c}{}^{2/3}c_{2,c}{}^{1/3} + c_{1,c}{}^{1/3}c_{2,c}{}^{2/3}))$ to satisfy the phase separation criterion $\frac{B_{12}^{2*}}{B_{11}^*B_{22}^*} > 1$. The advantage of this method is that no prior knowledge of the virial coefficients is needed, in contrast to eq 29 in ref 1.

3. CONSISTENCY CHECK FOR THE SOLUTION OF THE COEXISTENCE EQUATIONS

The coexistence equations with (B_{11}, B_{12}, B_{22}) as unknowns (adapted from eqs 15−17) from ref 1 read:

$$\begin{aligned}(c_1^{\mathrm{I}} - c_1^{\mathrm{II}}) + B_{11}(c_1^{\mathrm{I}^2} - c_1^{\mathrm{II}^2}) + 2B_{12}(c_1^{\mathrm{I}}c_2^{\mathrm{I}} - c_1^{\mathrm{II}}c_2^{\mathrm{II}}) \\ = -((c_2^{\mathrm{I}} - c_2^{\mathrm{II}}) + B_{22}(c_2^{\mathrm{I}^2} - c_2^{\mathrm{II}^2}))\end{aligned} \tag{8}$$

$$(\ln c_1^{\mathrm{II}} - \ln c_1^{\mathrm{I}}) = 2B_{11}(c_1^{\mathrm{I}} - c_1^{\mathrm{II}}) + 2B_{12}(c_2^{\mathrm{I}} - c_2^{\mathrm{II}}) \tag{9}$$

$$(\ln c_2^{\mathrm{II}} - \ln c_2^{\mathrm{I}}) = 2B_{22}(c_2^{\mathrm{I}} - c_2^{\mathrm{II}}) + 2B_{12}(c_1^{\mathrm{I}} - c_1^{\mathrm{II}}) \tag{10}$$

Since the determinant of this set of equations is zero, there are either zero or an infinite number of solutions. The requirement that there needs to be an infinite number of solutions leads to the condition:

$$\begin{aligned}&(c_1^{\mathrm{II}} - c_1^{\mathrm{I}}) + (c_2^{\mathrm{II}} - c_2^{\mathrm{I}}) \\ &= \frac{1}{2}(c_1^{\mathrm{I}} + c_1^{\mathrm{II}})\cdot\ln\left(\frac{c_1^{\mathrm{II}}}{c_1^{\mathrm{I}}}\right) + \frac{1}{2}(c_2^{\mathrm{I}} + c_2^{\mathrm{II}})\cdot\ln\left(\frac{c_2^{\mathrm{II}}}{c_2^{\mathrm{I}}}\right)\end{aligned} \tag{11}$$

Here it will be demonstrated that eq 11 (corresponding to eq 37 from ref 1) is always fulfilled by the solution of the coexistence eqs 8−10. Equation 11 can be rewritten as

$$\begin{aligned}&(c_1^{\mathrm{II}} - c_1^{\mathrm{I}}) - \frac{1}{2}(c_1^{\mathrm{I}} + c_1^{\mathrm{II}})\cdot(\ln(c_1^{\mathrm{II}}) - \ln(c_1^{\mathrm{I}})) \\ &= -\left((c_2^{\mathrm{II}} - c_2^{\mathrm{I}}) - \frac{1}{2}(c_2^{\mathrm{I}} + c_2^{\mathrm{II}})\cdot(\ln(c_2^{\mathrm{II}}) - \ln(c_2^{\mathrm{I}}))\right)\end{aligned} \tag{12}$$

Substituting eqs 9−10 in eq 12 leads to

$$\begin{aligned}&(c_1^{\mathrm{II}} - c_1^{\mathrm{I}}) - (c_1^{\mathrm{I}} + c_1^{\mathrm{II}})\cdot(B_{11}(c_1^{\mathrm{I}} - c_1^{\mathrm{II}}) + B_{12}(c_2^{\mathrm{I}} - c_2^{\mathrm{II}})) \\ &= -((c_2^{\mathrm{II}} - c_2^{\mathrm{I}}) - (c_2^{\mathrm{I}} + c_2^{\mathrm{II}})\cdot(B_{22}(c_2^{\mathrm{I}} - c_2^{\mathrm{II}}) \\ &\quad + B_{12}(c_1^{\mathrm{I}} - c_1^{\mathrm{II}})))\end{aligned} \tag{13}$$

Summing eqs 8 and 13 gives

$$\begin{aligned}&-(c_1^{\mathrm{I}} + c_1^{\mathrm{II}})\cdot(B_{12}(c_2^{\mathrm{I}} - c_2^{\mathrm{II}})) + 2B_{12}(c_1^{\mathrm{I}}c_2^{\mathrm{I}} - c_1^{\mathrm{II}}c_2^{\mathrm{II}}) \\ &= (c_2^{\mathrm{I}} + c_2^{\mathrm{II}})\cdot(B_{12}(c_1^{\mathrm{I}} - c_1^{\mathrm{II}}))\end{aligned} \tag{14}$$

and further simplification leads to the identity

$$c_1^{\mathrm{I}}c_2^{\mathrm{I}} - c_1^{\mathrm{II}}c_2^{\mathrm{I}} + c_1^{\mathrm{I}}c_2^{\mathrm{II}} + c_1^{\mathrm{II}}c_2^{\mathrm{II}} = c_1^{\mathrm{I}}c_2^{\mathrm{I}} + c_1^{\mathrm{I}}c_2^{\mathrm{II}} - c_1^{\mathrm{II}}c_2^{\mathrm{I}} + c_1^{\mathrm{II}}c_2^{\mathrm{II}} \tag{15}$$

confirming that eq 11 always holds for the solutions as obtained from eqs 8−10.

4. OBTAINING THE VIRIAL COEFFICIENTS FROM THE COMPOSITION OF TWO COEXISTING PHASES

In the previous section, it was shown that eq 11 holds for every solution of the coexistence equations, and consequently an infinite number of solutions for the virial coefficients (B_{11}, B_{12}, B_{22}) can be found from eqs 8−10. This means that (at least) one of these equations can be written as a linear combination of the other two. Indeed, multiplying eq 9 by $1/2(c_1^{\mathrm{I}} + c_1^{\mathrm{II}})$ and eq 10 by $1/2(c_2^{\mathrm{I}} + c_2^{\mathrm{II}})$ leads to

$$\begin{aligned}&\frac{1}{2}(c_1^{\mathrm{I}} + c_1^{\mathrm{II}})(\ln c_1^{\mathrm{I}} - \ln c_1^{\mathrm{II}}) + B_{11}(c_1^{\mathrm{I}} + c_1^{\mathrm{II}})(c_1^{\mathrm{I}} - c_1^{\mathrm{II}}) \\ &\quad + B_{12}(c_1^{\mathrm{I}} + c_1^{\mathrm{II}})(c_2^{\mathrm{I}} - c_2^{\mathrm{II}}) = 0\end{aligned} \tag{16}$$

$$\begin{aligned}&\frac{1}{2}(c_2^{\mathrm{I}} + c_2^{\mathrm{II}})(\ln c_2^{\mathrm{I}} - \ln c_2^{\mathrm{II}}) + B_{22}(c_2^{\mathrm{I}} - c_2^{\mathrm{II}})(c_2^{\mathrm{I}} + c_2^{\mathrm{II}}) \\ &\quad + B_{12}(c_1^{\mathrm{I}} - c_1^{\mathrm{II}})(c_2^{\mathrm{I}} + c_2^{\mathrm{II}}) = 0\end{aligned} \tag{17}$$

Equation 8 is recovered by addition of eqs 16−17 and substitution of eq 11. As a result, eqs 16−17 can be used to solve for (B_{11}, B_{12}, B_{22}) and lead to

$$\begin{pmatrix} B_{11} \\ B_{12} \\ B_{22} \end{pmatrix} = \begin{pmatrix} -\dfrac{(\ln c_1^{\mathrm{I}} - \ln c_1^{\mathrm{II}})}{2(c_1^{\mathrm{I}} - c_1^{\mathrm{II}})} \\ 0 \\ -\dfrac{(\ln c_2^{\mathrm{I}} - \ln c_2^{\mathrm{II}})}{2(c_2^{\mathrm{I}} - c_2^{\mathrm{II}})} \end{pmatrix} + \lambda_3 \begin{pmatrix} \dfrac{c_2^{\mathrm{I}} - c_2^{\mathrm{II}}}{c_1^{\mathrm{I}} - c_1^{\mathrm{II}}} \\ 1 \\ \dfrac{c_1^{\mathrm{I}} - c_1^{\mathrm{II}}}{c_2^{\mathrm{I}} - c_2^{\mathrm{II}}} \end{pmatrix} \tag{18}$$

This expression gives all possible values for the virial coefficients (B_{11}, B_{12}, B_{22}) leading to the same coexisting phases (c_1^{I}, c_2^{I}, c_1^{II}, c_2^{II}). Here $\lambda_3 < (1/2)(\ln c_1^{\mathrm{I}} - \ln c_1^{\mathrm{II}})(\ln c_2^{\mathrm{I}} - \ln c_2^{\mathrm{II}})/((c_2^{\mathrm{I}} - c_2^{\mathrm{II}})(\ln c_2^{\mathrm{I}} - \ln c_2^{\mathrm{II}}) + (c_1^{\mathrm{I}} - c_1^{\mathrm{II}})(\ln c_1^{\mathrm{I}} - \ln c_1^{\mathrm{II}}))$ in order to satisfy the phase separation criterion $\frac{B_{12}^2}{B_{11}B_{22}} > 1$. The advantage of this method is that no prior knowledge of the virial coefficients is needed, in contrast to eq 69 in ref 1.

■ REFERENCES

(1) Bot, A.; Dewi, B. P. C.; Venema, P. Phase-Separating Binary Polymer Mixtures: The degeneracy of the virial coefficients and their extraction from phase diagrams. *ACS Omega* **2021**, *6*, 7862−7878.

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