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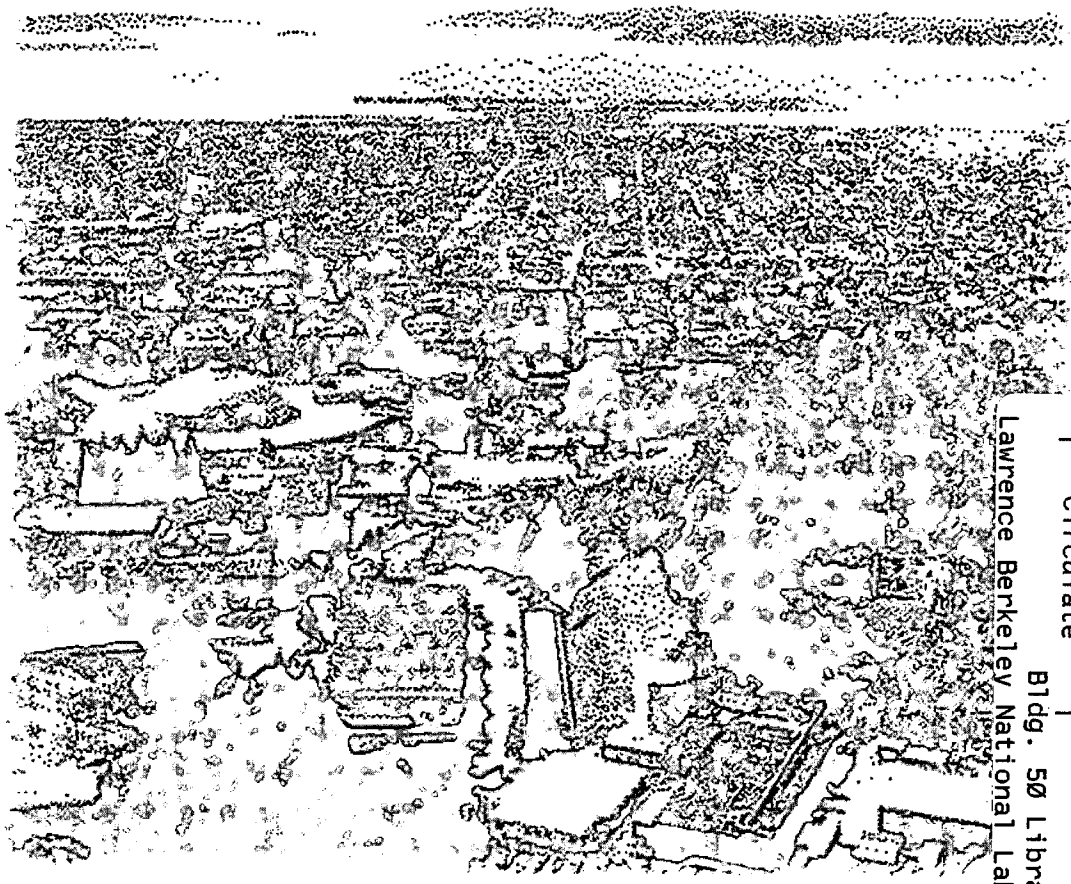

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STABILITY THEORY FOR POLYDISPERSE FLUID MIXTURES

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Abstract

Based on discrete multicomponent stability theory, a new method is developed for obtaining analytical expressions for spinodal and critical-point criteria for polydisperse fluid mixtures. This method is based on a theorem that follows from the classical theory of stability. Coupled with constraints (e.g. mole-fraction balance), this theorem yields analytical stability criteria for several multicomponent systems: a system containing one homologous series; a system containing one homologous series and one discrete component; and finally, a system containing an arbitrary number of homologous series and an arbitrary number of discrete components. The calculation procedure is much simpler than that using the classical determinant method.

Keywords : equation of state, lattice model, critical state, spinodal, continuous thermodynamics

I. INTRODUCTION

The theory of stability plays an important role in phase-equilibrium thermodynamics because it provides quantitative information on spinodals, i.e., the limit of instability, and on critical points, where two coexisting phases become indistinguishable. For multicomponent systems, especially those with very many components (e.g. petroleum, shale oil, coal-tar derived liquids, vegetable oils, polymer solutions and polymer blends), continuous thermodynamics is often useful; a comprehensive review by Cotterman and Prausnitz [1] discusses bubble-point, dew-point, flash and liquid-liquid-separation calculations. However, for such systems, application of stability theory is far from complete.

Most published work concerning stability for polydisperse systems was developed for polymer solutions and polymer blends, based on lattice models. Two different procedures have been established. The first one, the discrete multicomponent procedure, considers various species as discrete components. Expressions for spinodals and critical points are derived for a polydisperse polymer system by solving determinants from classical thermodynamics based on various lattice models, while the continuous distribution function for polymer species is only used for calculations of various moments of this function [2,3,4,5,6]. The second, more recent, procedure is the functional method developed primarily by Kehlen, Ratzsch and coworkers

[7,8,9,10]. In their framework, thermodynamic functions were defined for continuous mixtures. Expressions for spinodals and critical points based on lattice models were derived using functional theory where the second-order variation of the Gibbs function of mixing was obtained by using the Lagrange method of undetermined multipliers. More recently, Hu, Ying, Wu and Prausnitz [11,12,13] adopted both procedures for a close-packed lattice model and a lattice-fluid model, as well as a generalized molecular-thermodynamic model based on lattice theory. They found that the two procedures give exactly the same results.

For engineering application for mixtures containing a very large number of components, it is desirable to apply multicomponent stability theory to an equation of state. Browarzik and Kehlen [14] successfully extended the functional method to polydisperse fluid mixtures containing one homologous series. Hu and Ying [15] also obtained analytical expressions for the same system using the discrete multicomponent method.

The discrete multicomponent approach is intuitive and rigorous. The calculation procedure conforms with classical theory. However, because of the huge number of components, the dimension of the determinants approaches infinity. To obtain analytical expressions for real systems, the derivation procedure is very tedious, often prohibitive, even though the computational complexities are usually not evident until one tries to use them for a realistic mixture. On the other hand, the functional method is attractive due to its mathematical integrity and simplicity. However, its reliability must be checked with results by the discrete approach; because the components are discretely distributed, a continuous distribution function for the description of composition is at best a good approximation. In this work, we develop a new method based on the discrete multicomponent theory. With a theorem that follows from the classical criterion of stability, we obtain analytical expressions for the spinodals and the critical points for multicomponent systems containing one homologous series; or one homologous series and one discrete component; or an arbitrary number of homologous series and an arbitrary number of discrete components. Spinodals and critical points are easily derived by solving a set of linear equations. The new method can be used for both lattice models and equation-of-state models.

II. A THEOREM FOR STABILITY CALCULATIONS

We consider a molar Helmholtz function A_m for a K-component mixture; A_m is a function of temperature T, molar volume V_m, and mole fractions x_i, i=1,2,...,K-1. At constant temperature, we propose a virtual process starting from an equilibrium state: volume is varied by δV_m, and mole fractions are varied by δx_i . The resulting change in A_m , δA_m , can be calculated by expanding A_m in a Taylor series about the conditions of the original state, provided that all those variations of volume and mole fractions are small perturbations [16]:

$$\delta A_m = \delta^{(1)} A_m + \frac{1}{2!}\delta^{(2)} A_m + \frac{1}{3!}\delta^{(3)} A_m + \ldots \tag{1}$$

where $\delta^{(k)}A_m$ is the kth-order variation of A_m. Here $\delta^{(1)}A_m$ and $\delta^{(2)}A_m$ are expressed by

$$\delta^{(1)} A_m = \sum_{i=1}^{K-1} A_i \delta x_i + A_V \delta V_m \tag{2}$$

$$\delta^{(2)} A_m = \sum_{i=1}^{K-1}\sum_{j=1}^{K-1} A_{ij}\delta x_i \delta x_j + 2\sum_{i=1}^{K-1} A_{iV}\delta x_i \delta V_m + A_{VV}(\delta V_m)^2 \tag{3}$$

Expressions for higher-order variations can be written accordingly. In eqs (2) and (3), A_i and A_V are first-order partial derivatives of A_m with respect to x_i and V_m; A_{ij}, A_{iV} and A_{VV} are second-order partial derivatives of A_m with respect to x_i and x_j, x_i and V_m, and V_m alone, respectively. At constant temperature, the spinodals and the critical points are determined by:

$$\delta^{(2)} A_m = 0 \qquad \text{spinodal criterion} \tag{4}$$

and

$$\delta^{(3)} A_m = 0 \qquad \text{critical-point criterion} \tag{5}$$

respectively. To satisfy eq.(4), it is necessary and sufficient that the coefficient determinant of eq.(3) should be zero. Therefore, the spinodal criterion can be written as:

$$D_{sp} = \begin{vmatrix} A_{VV} & A_{V1} & A_{V2} & \cdots\cdots & A_{V,K-1} \\ A_{1V} & A_{11} & A_{12} & \cdots\cdots & A_{1,K-1} \\ A_{2V} & A_{21} & A_{22} & \cdots\cdots & A_{2,K-1} \\ \cdots & \cdots & \cdots & \cdots\cdots & \cdots \\ A_{K-1,V} & A_{K-1,1} & A_{K-1,2} & \cdots\cdots & A_{K-1,K-1} \end{vmatrix} = 0 \tag{6}$$

The critical-point criterion can be expressed by a similar determinant. It is difficult to obtain analytical expressions from those determinant when K approaches infinity.

We now introduce a theorem that follows from the spinodal criterion which is useful for obtaining analytical expressions for the spinodal and critical-point criteria. The verification of this theorem is shown in Appendix I.

Theorem: At constant temperature, the partial derivatives of second-order variation of the molar Helmholtz function, $\delta^{(2)}A_m$, with respect to variations of volume and mole fractions, δV_m and δx_i , should be zero on the spinodal surface. The theorem can be expressed by two equations:

$$\left(\frac{\partial(\delta^{(2)} A_m)}{\partial(\delta V_m)}\right)_{T,\delta x} = 0 \tag{7}$$

$$\left(\frac{\partial(\delta^{(2)} A_m)}{\partial(\delta x_i)}\right)_{T,\delta V,\delta x[i]} = 0 \qquad i=1, 2,..., K\text{-}1 \tag{8}$$

where $\delta x[i]$ in the subscript means that all δx_j except δx_i and δx_K are kept constant.

This theorem is equivalent to the spinodal criterion $\delta^{(2)}A_m$=0 or to eq.(6). Upon using this theorem coupled with constraints, we find that the subsequent calculation procedure for obtaining analytical expressions for the stability criterion is much simpler than that based on the classical method, i.e., to solve the very large determinant.

III. POLYDISPERSE FLUID MIXTURES CONTAINING ONE HOMOLOGOUS SERIES DESCRIBED BY AN EQUATIONS OF STATE

For a K-component polydisperse fluid mixture composed of one homologous series (e.g. mixtures of normal alkanes), the Helmholtz function can be expressed:

$$A_m = \sum_i^K x_i A_{m,i}^{o} + \sum_i^K x_i RT \ln x_i + A_m^r(T, V_m, a, b, c) = A_m^{id} + A_m^r \tag{9}$$

where $A^{o}_{m,i}$, A^{r}_{m} and A^{id}_{m} are, respectively, the molar Helmholtz function for pure component i in its standard state, the residual molar Helmholtz function for the mixture and the ideal-solution contribution to the molar Helmholtz function. The second summation term refers to the ideal Helmholtz function of mixing. The residual molar Helmholtz function is a function of temperature, molar volume and characteristic parameters of a relevant equation of state, a, b and c for the mixture. These parameters are functions of composition determined by mixing rules. Because we are concerned with a mixture containing a homologous series, the parameters for pure components can be considered as molar mass (M) dependent. Parameters for the mixture are then functions of the temperature and the average molar mass $\overline{M}$ of the mixture as shown by Cottermann and Prausnitz (1991),

$$a = a(T,\overline{M}) \quad , \quad b = b(T,\overline{M}) \quad , \quad c = c(T,\overline{M}) \tag{10}$$

where

$$\overline{M} = \sum_{i=1}^{K} x_i M_i \quad . \tag{11}$$

Spinodal Criterion: On the spinodal surface at constant temperature, the second-order variation of A_m can be expressed by variations δx_i, $\delta\overline{M}$ and δV_m.

$$\delta^{(2)} A_m = \sum_{i=1}^{K-1}\sum_{j=1}^{K-1} \frac{\partial^2 A^{id}_m}{\partial x_i \partial x_j}\delta x_i \delta x_j + A_{MM}(\delta\overline{M})^2 + 2A_{VM}\delta\overline{M}\delta V_m + A_{VV}(\delta V_m)^2 = 0 \tag{12}$$

where

$$\frac{\partial^2 A^{id}_m}{\partial x_i \partial x_j} = \frac{RT}{x_K} = j_K \tag{13}$$

$$\frac{\partial^2 A^{id}_m}{\partial x_i^2} = \frac{RT}{x_i} + \frac{RT}{x_K} = j_i + j_K \tag{14}$$

$$A_{VM} = \frac{\partial^2 A^r_m}{\partial V_m \partial \overline{M}} \tag{15}$$

$$A_{MM} = \frac{\partial^2 A^r_m}{\partial \overline{M}^2} \quad . \tag{16}$$

Eq.(12) can then be rewritten:

$$\delta^{(2)} A_m = \sum_{i=1}^{K-1} j_i(\delta x_i)^2 + j_K(\delta x_K)^2 + A_{MM}(\delta\overline{M})^2 + 2A_{VM}\delta\overline{M}\delta V_m + A_{VV}(\delta V_m)^2 \quad . \tag{17}$$

Variations of mole fractions and average molar mass in eqs (12) and (17) are subject to the constraints:

$$\sum_{i=1}^{K}\delta x_i = 0 \qquad \text{or} \qquad \delta x_K = -\sum_{i=1}^{K-1}\delta x_i \tag{18}$$

$$\delta\overline{M} = \sum_{i=1}^{K} M_i\,\delta x_i \quad = \sum_{i=1}^{K-1} M_i^{+}\delta x_i \tag{19}$$

where $M_i^{+} = M_i - M_K$.

Now we use our theorem. Substituting eq.(17) into eqs.(7) and (8) , we obtain

$$A_{VM}\delta\overline{M} + A_{VV}\delta V_m = 0 \tag{20}$$

$$j_i\delta x_i - j_K\delta x_K + A_{MM}(\delta\overline{M})M_i^+ + A_{VM}(\delta V_M)M_i^+ = 0 \tag{21}$$

We then consider the two constraints, eqs.(18) and (19). Substitution of eq.(21) into eq.(18) yields

$$j_K\delta x_K = (A_{MM}\delta\overline{M} + A_{VM}\delta V_M)\overline{M^+} \tag{22}$$

where $\overline{M^+} = \sum_{i=1}^{K-1} x_i M_i^+$. Substitution of eq.(21) into eq.(19) yields

$$j_K\delta x_K = [RT\delta\overline{M} + \overline{M^{+2}}(A_{MM}\delta\overline{M} + A_{VM}\delta V_M)] / \overline{M^+} \tag{23}$$

where $\overline{M^{+2}} = \sum_{i=1}^{K-1} x_i M_i^{+2}$. Variables $\overline{M^+}$ and $\overline{M^{+2}}$ can be related with the average molar mass $\overline{M}$ and the average square molar mass $\overline{M^2}$ through the second-order central moment $\mu_{(2)}$ as follows:

$$\mu_{(2)} = \sum_{i=1}^{K} x_i(M_i - \overline{M})^2 = \overline{M^2} - \overline{M}^2 = \sum_{i=1}^{K} x_i(M_i^+ - \overline{M^+})^2 = \overline{M^{+2}} - \overline{M^+}^2 \tag{24}$$

where $\overline{M^2}$ is the defined by

$$\overline{M^2} = \sum_{i=1}^{K} x_i M_i^2 \tag{25}$$

Combining eqs.(22)(23) and (24), we have

$$\delta\overline{M} = -\frac{A_{VM}\mu_{(2)}}{RT + A_{MM}\mu_{(2)}}\delta V_m \tag{26}$$

Now we have two equations connecting $\delta\overline{M}$ and δV_m, eqs.(20) and (26). The former is directly derived from eq.(7) of the theorem. The latter comes from eq.(8) of the theorem and the two constraints. Combining eqs.(20) and (26) and eliminating δV_m yields the spinodal criterion.

$$F_{sp} = A_{VV}RT - \mu_{(2)}(A_{VM}^2 - A_{MM}A_{VV}) = 0 \tag{27}$$

or

$$\mu_{(2)} = RTA_{VV} / B \tag{28}$$

where

$$B = A_{VM}^2 - A_{VV}A_{MM} \tag{29}$$

Eqs.(27) or (28) are exactly the same as those derived by solving the determinant, eq.(6), as shown earlier by Hu and Ying [15] by a lengthy derivation. Also, it is the same in form as that from Browarzik and Kehlen [14] using a functional procedure.

Critical-Point Criterion: We use eq.(5), $\delta^{(3)}A_m$=0, for the critical-point criterion. Because F_{sp} is a function of volume, average molar mass and average square molar mass, $\delta^{(3)}A_m$=0 is equivalent to

$$\delta F_{sp} = \frac{\partial F_{sp}}{\partial V_m}\delta V_m + \frac{\partial F_{sp}}{\partial \overline{M}}\delta\overline{M} + \frac{\partial F_{sp}}{\partial \overline{M^2}}\delta\overline{M^2} = 0 \tag{30}$$

All those partial derivatives in eq.(30) can be obtained from eq.(27):

$$\partial F_{sp} / \partial V_m = A_{VVV}RT - \mu_{(2)}(2A_{VM}A_{VVM} - A_{VVV}A_{MM} - A_{VV}A_{MMV}) \tag{31}$$

$$\partial F_{sp} / \partial \overline{M} = A_{VVM} RT - \mu_{(2)}(2A_{VM} A_{VMM} - A_{VVM} A_{MM} - A_{VV} A_{MMM}) + 2\overline{M}(A_{VM}^2 - A_{VV} A_{MM}) \tag{32}$$

$$\partial F_{sp} / \partial \overline{M^2} = -(A_{VM}^2 - A_{VV} A_{MM}) \tag{33}$$

where A_{VVV}, A_{VVM}, A_{MMV} and A_{VMM} are third-order derivatives of A_m^r with respect to corresponding subscripts. For eliminating those variations, we need relations between $\delta\overline{M}$, $\delta\overline{M^2}$ and δV_m .The relation between $\delta\overline{M}$ and δV_m is shown in eq.(26). For $\delta\overline{M^2}$, from eq.(25),

$$\delta\overline{M^2} = \sum_{i=1}^{K} M_i^2 \delta x_i = \sum_{i=1}^{K-1} M_i^{+2} \delta x_i + 2M_K \delta\overline{M} \tag{34}$$

By using eqs.(20), (21) and (22), and replacing δx_i and $\delta\overline{M}$ by δV_m, we have from eq.(34),

$$\delta\overline{M^2} = \frac{1}{RT}\left(-\frac{A_{MM} A_{VM} \mu_{(2)}}{RT + A_{MM}\mu_{(2)}} + A_{VM}\right)(\overline{M}\,\overline{M^2} - \overline{M^3})\delta V_m \tag{35}$$

where $\overline{M^3} = \sum_{i=1}^{K} x_i M_i^3$.

Combining eq.(30) with eqs.(31), (32), (33), (26) and (35), and eliminating all δV_ms, we obtain the critical-point criterion.

$$\begin{aligned} F_{cr} &= A_{VVV} RT - \mu_{(2)}(2A_{VM} A_{VVM} - A_{VVV} A_{MM} - A_{VV} A_{MMV}) \\ &- \frac{A_{VM}\mu_{(2)}}{RT + A_{MM}\mu_{(2)}}[2\overline{M}B - \mu_{(2)}(2A_{VM} A_{VMM} - A_{VVM} A_{MM} - A_{VV} A_{MMM}) + A_{VVM} RT] \\ &+ \left(\frac{A_{MM} A_{VV} \mu_{(2)}}{RT + A_{MM}\mu_{(2)}} - A_{VM}\right)(\overline{M}\,\overline{M^2} - \overline{M^3})\frac{B}{RT} = 0 \end{aligned} \tag{36}$$

After rearragement, eq.(36) transforms to

$$\mu_{(3)} = (RT)^2[-\frac{B_M}{B}\frac{A_{VV}^2}{B^2} + \frac{B_V}{B}\frac{A_{VV}}{B}\frac{A_{VM}}{B} + \frac{A_{VV}}{B}\frac{A_{VVM}}{B} - \frac{A_{VM}}{B}\frac{A_{VVV}}{B}] \tag{37}$$

where $\mu_{(3)}$ is the third-order central moment defined by

$$\mu_{(3)} = \sum_{i=1}^{K} x_i (M_i - \overline{M})^3 = \overline{M^3} - 3\overline{M^2}\,\overline{M} + 2\overline{M}^3 \tag{38}$$

$$B_M = \frac{\partial B}{\partial \overline{M}} \quad , \quad B_V = \frac{\partial B}{\partial V} \tag{39}$$

Again, eq.(37) is exactly the same as that derived by solving the corresponding determinant as shown earlier by Hu and Ying [15] by a lengthy derivation. It is also the same in form as that from Browarzik and Kehlen [14].

Numerical results were presented by Browarzik and Kehlen using a cubic equation of state.

IVa. POLYDISPERSE FLUID MIXTURES CONTAINING ONE HOMOLOGOUS SERIES AND ONE DISCRETE COMPONENT DESCRIBED BY A LATTICE MODEL

For a K-component polydisperse fluid mixture containing one homologous series and one discrete component designated by "o" (e.g. mixtures of a polydisperse polymer and a solvent), the molecular-thermodynamic model based on lattice theory by Hu, Ying, Wu and Prausnitz [13] can be written as:

$$\tilde{G}_V = \frac{\phi_o}{r_o}\ln\phi_o + \sum_{i=1}^{K-1}\frac{\phi_i}{r_i}\ln\phi_i + \phi_o\sum_{i=1}^{K-1}\phi_i g_i^{**} \tag{40}$$

where $\tilde{G}_V = \Delta_{mix}G / N_r kT$ is the reduced Gibbs function of mixing per site; N_r is the total number of sites in a lattice; ϕ_o, ϕ_i, r_o, r_i are volume fractions and chain lengths of the solvent o and the polydisperse solute i, respectively; g_i^{**} is the effective Flory parameter characterizing the interactions between the solvent o and the solute i.

Spinodal Criterion: For a lattice model [eq.(40)], the spinodal criterion, eq.(4), must be changed to $\delta^{(2)}\tilde{G}_V = 0$, which can be expressed by the variations of volume fractions:

$$\delta^{(2)}\tilde{G}_V = \sum_{i=1}^{K-1}\sum_{j=1}^{K-1}\tilde{G}_{ij}\delta\phi_i\delta\phi_j = 0 \tag{41}$$

where

$$\tilde{G}_{ii} = \left(\frac{\partial^2\tilde{G}_V}{\partial\phi_i^2}\right)_{T,p,\varphi[i]} = J + 2J_i + \lambda_i \tag{42}$$

$$\tilde{G}_{ij} = \left(\frac{\partial^2\tilde{G}_V}{\partial\phi_i\partial\phi_j}\right)_{T,p,\varphi[i,j]} = J + J_i + J_j \tag{43}$$

$$J = r_o^{-1}(1-\phi_s)^{-1} - 2\sum_{i=1}^{K-1}\phi_k g_k^{**'} + (1-\phi_s)\sum_{i=1}^{K-1}\phi_k g_k^{**''} \tag{44}$$

$$J_i = -g_i^{**} + (1-\phi_s)g_i^{**'} \tag{45}$$

$$\lambda_i = (r_i\phi_i)^{-1} \tag{46}$$

Here $\phi_s = \sum_i \phi_i$ is the total volume fraction of the solute; $g_i^{**'}, g_i^{**''}$ are the first-order and the second-order derivatives of g_i^{**} with respect to ϕ_s, respectively. Eq. (41) is then rewritten.

$$\delta^{(2)}\tilde{G}_V = J(\delta\phi_o)^2 + \sum_{i=1}^{K-1}\lambda_i(\delta\phi_i)^2 - 2\delta\phi_o\sum_{i=1}^{K-1}J_i\delta\phi_i \tag{47}$$

where the following constraint for the variations of volume fractions has been used:

$$\delta\phi_o = -\sum_{i=1}^{K-1}\delta\phi_i \tag{48}$$

Now we use the theorem. Eq.(7) vanishes. Eq.(8) should be changed to

$$\left(\frac{\partial(\delta^{(2)}\tilde{G}_V)}{\partial(\delta\phi_i)}\right)_{T,\delta\phi[i]} = 0 \tag{49}$$

Substituting eq.(47) into eq.(49) combined with the constraint eq.(48), we obtain the spinodal criterion by using the Lagrange method of undetermined multipliers.

$$F_{sp} = \sum_{i-1}^{K-1} \lambda_i^{-1}(J - \sum_{i-1}^{K-1} J_i^2 \lambda_i^{-1}) + (1 + \sum_{i-1}^{K-1} J_i \lambda_i^{-1})^2 \quad . \tag{50}$$

The derivation is shown in Appendix II. Eq.(50) is the same as that derived previously [13], the latter requires a much longer and more tedious derivation.

The critical-point criterion can also be derived using a method similar to that in section III. It is the same in form as that derived previously [13].

Numerical results for the spinodals and critical points were presented earlier [11,12,13].

IVb. POLYDISPERSE FLUID MIXTURES CONTAINING ONE HOMOLOGOUS SERIES AND ONE DISCRETE COMPONENT BASED ON AN EQUATION OF STATE

For a K-component polydisperse fluid mixture composed of one homologous series and one discrete component K (e.g. mixtures containing an oil and a solvent), the Helmholtz function is the same as that of eq.(9).

$$A_m = \sum_i^K x_i A_{m,i}^o + \sum_i^K x_i RT \ln x_i + A_m^r(T, V_m, a, b, c) = A_m^{id} + A_m^r \quad .$$

The total mole fraction of the homologous series is designated by x. The average molar mass of that series is

$$x\overline{M} = \sum_{i=1}^{K-1} x_i M_i \quad . \tag{51}$$

Parameters of the equation of state for the mixture are then functions of the temperature, the average molar mass of the homologous series and the total mole fraction of that series:

$$a = a(T, x\overline{M}, x) \quad , \quad b = b(T, x\overline{M}, x) \quad , \quad c = c(T, x\overline{M}, x) \quad . \tag{52}$$

Spinodal Criterion: On the spinodal surface at constant temperature, the second-order variation of A_m can be expressed by variations δx_i, $\delta x\overline{M}$, δx and δV_m.

$$\begin{aligned}
\delta^{(2)} A_m &= \sum_{i=1}^{K-1}\sum_{j=1}^{K-1} \frac{\partial^2 A_m^{id}}{\partial x_i \partial x_j} \delta x_i \delta x_j + A_{MM}[\delta(x\overline{M})]^2 + A_{xx}(\delta x)^2 + A_{VV}(\delta V_m)^2 \\
&\quad + 2A_{Mx}\delta(x\overline{M})\delta x + 2A_{VM}\delta(x\overline{M})\delta V_m + 2A_{Vx}\delta x \delta V_m \\
&= \sum_{i=1}^{K-1} j_i(\delta x_i)^2 + j_K(\delta x_K)^2 + A_{MM}[\delta(x\overline{M})]^2 + A_{xx}(\delta x)^2 + A_{VV}(\delta V_m)^2 \\
&\quad + 2A_{Mx}\delta(x\overline{M})\delta x + 2A_{VM}\delta(x\overline{M})\delta V_m + 2A_{Vx}\delta x \delta V_m = 0
\end{aligned} \tag{53}$$

where A_{MM}, A_{xx}, A_{Mx}, A_{VM}, A_{Vx} and A_{VV} are second-order partial derivatives of A_m^r with respect to the corresponding subscripts, i.e., $x\overline{M}$, x and V_m.

Variations of mole fractions and average molar mass are subject to two constraints.

$$\sum_{i=1}^{K} \delta x_i = 0 \qquad \text{or} \qquad \delta x_K = -\delta x = -\sum_{i=1}^{K-1} \delta x_i \tag{54}$$

$$\delta(x\overline{M}) = \sum_{i=1}^{K-1} M_i\, \delta x_i \quad . \tag{55}$$

Now we use our theorem. From eqs.(7) and (53), we have

$$A_{VM}\delta(x\overline{M}) + A_{Vx}\delta x + A_{VV}\delta V_m = 0 \quad . \tag{56}$$

From eqs.(8) and (53), we have

$$\begin{aligned} j_i\delta x_i - j_K\delta x_K + A_{MM}M_i\,\delta(x\overline{M}) + A_{xx}\delta x + A_{Mx}[M_i\delta x + \delta(x\overline{M})] \\ + A_{VM}M_i\,\delta V_m + A_{Vx}\delta V_m = 0 \end{aligned} \quad . \tag{57}$$

Combining eqs.(56) and (57) with the constraints, eqs.(54) and (55) to eliminate δx_i and δx_K, and to find relations between δx, $\delta(x\overline{M})$ and δV_m, we obtain the spinodal criterion.

$$F_{sp} = A_{VM}C + A_{Vx}D + A_{VV} = 0 \tag{58}$$

where

$$C = \frac{\delta(x\overline{M})}{\delta V_m}$$

$$= \frac{RTx(A_{VM}\overline{M^2} + A_{Vx}\overline{M}) + x^2\mu_{(2)}(j_K A_{VM} + A_{VM}A_{xx} - A_{Vx}A_{Mx})}{-(RT)^2 - RTx(j_K + A_{xx} + A_{MM}\overline{M^2} + 2A_{Mx}\overline{M}) + x^2\mu_{(2)}(A_{Mx}^2 - j_K A_{MM} - A_{xx}A_{MM})} \tag{59}$$

$$D = \frac{\delta x}{\delta V_m} = -\frac{x(A_{MM}\overline{M} + A_{Mx})C + x(A_{VM}\overline{M} + A_{Vx})}{RT + x(j_K + A_{xx} + A_{Mx}\overline{M})} \quad . \tag{60}$$

Here $\overline{M^2}$ is the average square molar mass of the homologous series defined by

$$x\overline{M^2} = \sum_{i=1}^{K-1} x_i M_i^2 \quad . \tag{61}$$

Critical-Point Criterion: For the critical-point criterion, similar to eq.(30), we write

$$\delta F_{sp} = \frac{\partial F_{sp}}{\partial V_m}\delta V_m + \frac{\partial F_{sp}}{\partial x}\delta x + \frac{\partial F_{sp}}{\partial(x\overline{M})}\delta(x\overline{M}) + \frac{\partial F_{sp}}{\partial(x\overline{M^2})}\delta(x\overline{M^2}) = 0 \tag{62}$$

where

$$\partial F_{sp} / \partial V_m = A_{VVM}C + A_{VM}C_V + A_{VVx}D + A_{Vx}D_V + A_{VVV} \tag{63}$$

$$\partial F_{sp} / \partial x = A_{VMx}C + A_{VM}C_x + A_{Vxx}D + A_{Vx}D_x + A_{VVx} \tag{64}$$

$$\partial F_{sp} / \partial(x\overline{M}) = A_{VMM}C + A_{VM}C_M + A_{VMx}D + A_{Vx}D_M + A_{VVM} \tag{65}$$

$$\partial F_{sp} / \partial(x\overline{M^2}) = A_{VM}C_{M^2} + A_{Vx}D_{M^2} \quad . \tag{66}$$

Here

$$C_V = \frac{\partial C}{\partial V_m} \;,\; C_x = \frac{\partial C}{\partial x} \;,\; C_M = \frac{\partial C}{\partial(x\overline{M})} \;,\; C_{M^2} = \frac{\partial C}{\partial(x\overline{M^2})} \tag{67}$$

$$D_V = \frac{\partial D}{\partial V_m} \;,\; D_x = \frac{\partial D}{\partial x} \;,\; D_M = \frac{\partial D}{\partial(x\overline{M})} \;,\; D_{M^2} = \frac{\partial D}{\partial(x\overline{M^2})} \quad . \tag{68}$$

To eliminate those variations, we need relations between them. The relations between δx, $\delta x\overline{M}$ and δV_m are given by eqs.(59) and (60). From eq.(61), we have

$$\delta(x\overline{M^2}) = \sum_{i=1}^{K-1} M_i^2 \delta x_i \quad . \tag{69}$$

Substitution of eqs.(57), (59) and (60) into eq.(69) yields the relation between $\delta x\overline{M^2}$ and δV_m:

$$E = \frac{\delta(x\overline{M^2})}{\delta V_m} = x[-(j_K\overline{M^2} + A_{xx}\overline{M^2} + A_{Mx}\overline{M^3})D \\ -(A_{MM}\overline{M^3} + A_{Mx}\overline{M^2})C - A_{VM}\overline{M^3} - A_{Vx}\overline{M^2}]/RT \quad . \tag{70}$$

Combining eq.(62) with (63), (64), (65), (66) and (59), (60), (70), and eliminating δV_m,, we obtain the critical-point criterion.

$$\begin{aligned} F_{cr} &= A_{VVM}C + A_{VM}C_V + A_{VVx}D + A_{Vx}D_V + A_{VVV} \\ &+ (A_{VMx}C + A_{VM}C_x + A_{Vxx}D + A_{Vx}D_x + A_{VVx})D \\ &+ (A_{VMM}C + A_{VM}C_M + A_{VMx}D + A_{Vx}D_M + A_{VVM})C \\ &+ (A_{VM}C_{M^2} + A_{Vx}D_{M^2})E = 0 \end{aligned} \quad . \tag{71}$$

V. POLYDISPERSE FLUID MIXTURES CONTAINING AN ARBITRARY NUMBER OF HOMOLOGOUS SERIES AND AN ARBITRARY NUMBER OF DISCRETE COMPONENTS BASED ON AN EQUATION OF STATE

We consider a K-component fluid mixture containing L homologous series and N discrete components. The ordinal numbers for the components in the series α are designated from $N_{\alpha-1}+1$ to N_α, $\alpha=1, 2,..., L$, where N_α is the cumulative total number of components from series 1 to series α. The ordinal numbers for the discrete components are designated from $K-N+1$ to K. For the homologous series α, the total mole fraction is x_α; the average molar mass $\overline{M_\alpha}$ is defined by

$$x_\alpha \overline{M_\alpha} = \sum_{i=N_{\alpha-1}+1}^{N_\alpha} x_i M_i \quad . \tag{72}$$

The Helmholtz function is the same as that of eq.(9).

$$A_m = \sum_i^K x_i A_{m,i}^{\circ} + \sum_i^K x_i RT \ln x_i + A_m^r(T, V_m, a, b, c) = A_m^{id} + A_m^r$$

Parameters of the equation of state for the mixture are functions of the temperature, the average molar masses and the total mole fractions of L series, and the mole fractions of N-1 discrete components:

$$a = a(T; x_1\overline{M_1}, x_2\overline{M_2}, \ldots, x_L\overline{M_L}; x_1, x_2, \ldots, x_L; x_{K-N+1}, \ldots, x_{K-2}, x_{K-1}) \tag{73}$$

$$b = b(T; x_1\overline{M_1}, x_2\overline{M_2}, \ldots, x_L\overline{M_L}; x_1, x_2, \ldots, x_L; x_{K-N+1}, \ldots, x_{K-2}, x_{K-1}) \tag{74}$$

$$c = c(T; x_1\overline{M_1}, x_2\overline{M_2}, \ldots, x_L\overline{M_L}; x_1, x_2, \ldots, x_L; x_{K-N+1}, \ldots, x_{K-2}, x_{K-1}) \tag{75}$$

Spinodal Criterion: On the spinodal surface at constant temperature, similar to eq.(53), the second-order variation of A_m can be expressed by variations δx_i for all components, $\delta x_\alpha \overline{M_\alpha}$ and δx_α for homologous series, δx_η for discrete components, and δV_m.

$$\begin{aligned}\delta^{(2)} A_m = & \sum_{i=1}^{K-1} j_i (\delta x_i)^2 + j_K (\delta x_K)^2 \\ & + \sum_{\alpha=1}^{L} \sum_{\beta=1}^{L} [A_{M_\alpha M_\beta} \delta(x_\alpha \overline{M_\alpha}) \delta(x_\beta \overline{M_\beta}) + A_{\alpha\beta} \delta x_\alpha \delta x_\beta + 2 A_{M_\alpha \beta} \delta(x_\alpha \overline{M_\alpha}) \delta x_\beta] \\ & + 2 \sum_{\alpha=1}^{L} \sum_{\eta=K-N+1}^{K-1} [A_{\alpha\eta} \delta x_\alpha \delta x_\eta + A_{M_\alpha \eta} \delta(x_\alpha \overline{M_\alpha}) \delta x_\eta] \\ & + \sum_{\eta=K-N+1}^{K-1} \sum_{\varsigma=K-N+1}^{K-1} A_{\eta\varsigma} \delta x_\eta \delta x_\varsigma + 2 \sum_{\alpha=1}^{L} [A_{V\alpha} \delta x_\alpha \delta V_m + A_{VM_\alpha} \delta(x_\alpha \overline{M_\alpha}) \delta V_m] \\ & + 2 \sum_{\eta=K-N+1}^{K-1} A_{V\eta} \delta x_\eta \delta V_m + A_{VV} (\delta V_m)^2 = 0\end{aligned} \tag{76}$$

where $A_{M_\alpha M_\beta}$, $A_{x_\alpha x_\beta}$, $A_{x_\eta x_\varsigma}$, A_{VV} and those with cross subscripts are second-order partial derivatives of residual Helmholtz function A_m^r with respect to corresponding subscripts, i.e., $x_\alpha \overline{M_\alpha}$, x_α, x_η and V_m.

Variations of mole fractions and average molar mass are subject to two kinds of constraints:

(1) mole fraction balance.

$$\sum_{i=N_{\alpha-1}+1}^{N_\alpha} \delta x_i = \delta x_\alpha \quad , \quad \alpha = 1,2,\ldots,L \tag{77}$$

$$\sum_{\alpha=1}^{L} \delta x_\alpha + \sum_{\eta=K-N+1}^{K-1} \delta x_\eta = -\delta x_K \tag{78}$$

(2) molar mass balance.

$$\sum_{i=N_{\alpha-1}+1}^{N_\alpha} M_i \delta x_i = \delta(x_\alpha \overline{M_\alpha}) \quad , \quad \alpha = 1,2,\ldots,L \tag{79}$$

Now we use our theorem. From eqs.(7) and (76), we have

$$\sum_{\alpha=1}^{L} [A_{VM_\alpha} \delta(x_\alpha \overline{M_\alpha}) + A_{V\alpha} \delta x_\alpha] + \sum_{\eta=K-N+1}^{K-1} A_{V\eta} \delta x_\eta + A_{VV} \delta V_m = 0 \tag{80}$$

From eqs.(8) and (76), we have

$$\begin{aligned} & j_i \delta x_i - j_K \delta x_K + \sum_{\beta=1}^{L} [A_{M_\alpha M_\beta} M_i \, \delta(x_\beta \overline{M_\beta}) + (A_{\alpha\beta} + A_{M_\alpha \beta} M_i) \delta x_\beta + A_{M_\beta \alpha} \delta(x_\beta \overline{M_\beta})] \\ & \quad + \sum_{\eta=K-N+1}^{K-1} (A_{M_\alpha \eta} M_i + A_{\alpha\eta}) \delta x_\eta + A_{VM_\alpha} M_i \, \delta V_m + A_{V\alpha} \delta V_m = 0 \\ & \quad i = N_{\alpha-1} + 1, \ldots, N_\alpha \quad , \quad \alpha = 1, \ldots, L \end{aligned} \tag{81}$$

$$j_\eta \delta x_\eta - j_K \delta x_K + \sum_{\varsigma=K-N+1}^{K-1} A_{\eta\varsigma}\delta x_\varsigma + \sum_{\alpha=1}^{L}[A_{M_\alpha\eta}\delta(x_\alpha \overline{M_\alpha}) + A_{\alpha\eta}\delta x_\alpha] + A_{V\eta}\delta V_m = 0 \tag{82}$$
$$\eta = K-N+1,\ldots,K-1$$

We now introduce two constraints, eqs.(77), (78) and (79). Substituting eq.(81) into eq.(77), we obtain for homologous series α,

$$\begin{aligned}\delta x_\alpha = \{ & j_K x_\alpha \delta x_K - x_\alpha \overline{M_\alpha} \sum_{\beta=1}^{L}[A_{M_\alpha M_\beta}\delta(x_\beta \overline{M_\beta}) + A_{M_\alpha\beta}\delta x_\beta] \\ & - x_\alpha \sum_{\beta=1}^{L}[A_{\alpha\beta}\delta x_\beta + A_{M_\beta\alpha}\delta(x_\beta \overline{M_\beta})] - x_\alpha \overline{M_\alpha} \sum_{\eta=K-N+1}^{K-1} A_{M_\alpha\eta}\delta x_\eta \\ & - x_\alpha \sum_{\eta=K-N+1}^{K-1} A_{\alpha\eta}\delta x_\eta - x_\alpha \overline{M_\alpha} A_{VM_\alpha}\delta V_M - x_\alpha A_{V\alpha}\delta V_m\} / RT \\ & \alpha = 1,\ldots,L\end{aligned} \tag{83}$$

For discrete component η from eq.(78),

$$\delta x_\eta = x_\eta \{ j_K \delta x_K - \sum_{\varsigma=K-N+1}^{K-1} A_{\eta\varsigma}\delta x_\varsigma - \sum_{\alpha=1}^{L}[A_{M_\alpha\eta}\delta(x_\alpha \overline{M_\alpha}) + A_{\alpha\eta}\delta x_\alpha] - A_{V\eta}\delta V_m\} / RT \tag{84}$$
$$\eta = K-N+1,\ldots,K-1$$

Substituting eq.(81) into eq.(79), we obtain for homologous series α,

$$\begin{aligned}\delta x_\alpha \overline{M_\alpha} = \{ & j_K x_\alpha \overline{M_\alpha}\delta x_K - x_\alpha \overline{M_\alpha^2} \sum_{\beta=1}^{L}[A_{M_\alpha M_\beta}\delta(x_\beta \overline{M_\beta}) + A_{M_\alpha\beta}\delta x_\beta] \\ & - x_\alpha \overline{M_\alpha} \sum_{\beta=1}^{L}[A_{\alpha\beta}\delta x_\beta + A_{M_\beta\alpha}\delta(x_\beta \overline{M_\beta})] - x_\alpha \overline{M_\alpha^2} \sum_{\eta=K-N+1}^{K-1} A_{M_\alpha\eta}\delta x_\eta \\ & - x_\alpha \overline{M_\alpha} \sum_{\eta=K-N+1}^{K-1} A_{\alpha\eta}\delta x_\eta - x_\alpha \overline{M_\alpha^2} A_{VM_\alpha}\delta V_M - x_\alpha \overline{M_\alpha} A_{V\alpha}\delta V_m\} / RT \\ & \alpha = 1,\ldots,L\end{aligned} \tag{85}$$

The number of equations in eqs.(83), (84) and (85) is $2L+N-1$. Eq.(78) has not yet been used. Therefore, altogether we have $2L+N$ linear equations. For homologous series, the number of variations δx_α is L; the number of variations $\delta(x_\alpha \overline{M_\alpha})$ is also L. For discrete components, the number of variations δx_η is N. Therefore, besides δV_m, altogether we have $2L+N$ unknown variations. Upon solving this set of linear equations, we can obtain relations between those variations and δV_m.

$$\delta(x_\alpha \overline{M_\alpha}) = C_\alpha \delta V_m \quad , \quad \alpha = 1,2,\ldots,L \tag{86}$$
$$\delta x_\alpha = D_\alpha \delta V_m \quad , \quad \alpha = 1,2,\ldots,L \tag{87}$$
$$\delta x_\eta = D_\eta \delta V_m \quad , \quad \eta = K-N+1,\ldots,K-1,K \tag{88}$$

Substituting eqs.(86), (87) and (88) into eq.(80), we obtain the spinodal criterion:

$$F_{sp} = \sum_{\alpha=1}^{L}(A_{VM_\alpha}C_\alpha + A_{V\alpha}D_\alpha) + \sum_{\eta=K-N+1}^{K-1} A_{V\eta}D_\eta + A_{VV} = 0 \tag{89}$$

A critical-point criterion can also be obtained using a procedure similar to that indicated by eqs.(62-71).

VI. DISCUSSION AND CONCLUSION

We have derived a relatively simple method for determining the stability of polydisperse fluid mixtures with very many components. In the classical method, we have to obtain analytical expressions for spinodal and critical-point criteria by solving determinants whose dimensions approach infinity. That procedure is not always successful. In this work, we retain the familiar, intuitive, discrete, multicomponent approach. With the use of a theorem that follows from the basic principle of stability thermodynamics, the tedious determinant with infinite dimension is reduced to solving a set of $2L+N$ linear equations. For example, if we have two homologous series and four discrete components, the number of linear equations is eight. This set of linear equations can easily be solved by standard methods such as the Cramer method. Concise analytical expressions can be easily obtained. However, if we solve the determinant, the computation is very large.

The essence of our new method is the theorem that tells us that, at constant temperature, on the spinodal surface, the partial derivatives of a second-order variation of the Helmholtz function with respect to variations of volume and mole fractions should be zero. This theorem is similar to the principle used in the functional approach. Although we have a verification for the theorem, it is essentially intuitive. On the spinodal surface, the second-order variation of the Helmholtz function is independent of the magnitude of the variations of volume and mole fractions, provided that the variations are sufficiently small to be considered as perturbations.

The method presented here can be used for both equation-of-state and lattice models. Although we derived the theorem using the Helmholtz function, the well-known thermodynamic relation

$$G_{ij} = \left(\frac{\partial^2 G_m}{\partial x_i \partial x_j}\right)_{T,p,x[i,j]} = A_{ij} - \frac{A_{iV} A_{Vi}}{A_{VV}} \tag{90}$$

enables us to transform the Helmholtz function to the Gibbs function. For lattice models where the Gibbs function is used, the theorem is simplified by neglecting the variation of volume. When we apply our theorem with the constraints in the lattice approach, the Lagrange method of undetermined multipliers should be used. However, when we use an equation of state, the Lagrange method of undetermined multipliers is not needed. Directly coupling the constraints with the theorem gives analytical results.

In this work we limited ourselves to cases where the parameters of the lattice model only depend on the chain length and the temperature, and the parameters of the equation of state only depend on the average molar mass for each homologous series as well as on the temperature and the volume. In these cases, the derivatives of the reduced Gibbs function of mixing for the former cases and the derivatives of the Helmholtz function for the latter cases needed in the calculations of spinodals and critical points can be obtained in analytical form straightforwardly. More complex cases, where the parameters depend on more then one property (e.g. aromaticity, degree of branching), the method discussed here can also be used to obtain a set of linear equations.

As shown in textbooks, binary fluid mixtures exhibit a variety of phase behavior and critical phenomena. For multicomponent systems, that variety increases. For mixtures with very many components, as found in nature, we expect to find an even wider, possibly highly surprising, variety of phase behavior. The method described here provides a tool for calculating such behavior.

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Appendix I. Verification of the theorem:

We start from the determinant in eq. (6). We multiply the first column by A_{Vj-1}/A_{VV}, then subtract that column from the jth column. For the spinodal surface, we obtain

$$\begin{vmatrix} A_{VV} & 0 & 0 & \cdots & 0 \\ A_{1V} & A_{11} - A_{1V}A_{V1}/A_{VV} & A_{12} - A_{1V}A_{V2}/A_{VV} & \cdots & A_{1,K-1} - A_{1V}A_{V,K-1}/A_{VV} \\ A_{2V} & A_{21} - A_{2V}A_{V1}/A_{VV} & A_{22} - A_{2V}A_{V2}/A_{VV} & \cdots & A_{2,K-1} - A_{2V}A_{V,K-1}/A_{VV} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ A_{K-1V} & A_{K-1,1} - A_{K-1V}A_{V1}/A_{VV} & A_{K-1,2} - A_{K-1V}A_{V2}/A_{VV} & \cdots & A_{K-1,K-1} - A_{K-1V}A_{V,K-1}/A_{VV} \end{vmatrix} = 0 \quad . \tag{I.1}$$

This determinant is equivalent to

$$\sum_{i=1}^{K-1}\sum_{j=1}^{K-1}(A_{ij} - A_{iV}A_{Vi}/A_{VV})\delta x_i \delta x_j = \sum_{i=1}^{K-1}\sum_{j=1}^{K-1}A_{ij}\delta x_i \delta x_j - (\sum_{i=1}^{K-1}A_{iV}\delta x_i)^2 / A_{VV} = 0 \quad . \tag{I.2}$$

Substitution of eq.(I.2) into eqs.(3) and (4) yields

$$\frac{1}{A_{VV}}\left((\sum_{i=1}^{K-1}A_{iV}\delta x_i)^2 + 2A_{VV}\sum_{i=1}^{K-1}A_{iV}\delta x_i \delta V_m + A_{VV}^2(\delta V_m)^2\right) = \frac{1}{A_{VV}}\left(\sum_{i=1}^{K-1}A_{iV}\delta x_i + A_{VV}\delta V_m\right)^2 = 0 \quad . \tag{I.3}$$

We then have

$$2\sum_{i=1}^{K-1}A_{iV}\delta x_i + 2A_{VV}\delta V_m = \left(\frac{\partial(\delta^{(2)}A_m)}{\partial(\delta V_m)}\right)_{T,\delta x} = 0 \quad . \tag{I.4}$$

Eq.(7) then follows when $\delta^{(2)}A_m=0$.

Further, by substituting eq.(I.4) into eqs.(3) and (4), we obtain

$$\sum_{i=1}^{K-1}\sum_{j=1}^{K-1}A_{ij}\delta x_i \delta x_j + \sum_{i=1}^{K-1}A_{iV}\delta x_i \delta V_m = \sum_{i=1}^{K-1}\left(\sum_{j=1}^{K-1}A_{ij}\delta x_j + A_{iV}\delta V_m\right)\delta x_i = 0 \quad . \tag{I.5}$$

Because all δx_is (i=1,...,K-1) are independent, the quantity inside the brackets is zero. We then have

$$2\sum_{j=1}^{K-1} A_{ij}\delta x_j + 2A_{iV}\delta V_m = \left(\frac{\partial(\delta^{(2)} A_m)}{\partial(\delta x_i)}\right)_{T,\delta x[i]} = 0 \qquad \text{(I.6)}$$

Eq.(8) then follows when $\delta^{(2)}A_m=0$.

Appendix II . Derivation of eq.(50):

Substituting eq.(47) into eq.(49), we obtain

$$\left(\frac{\partial(\delta^{(2)}\tilde{G}_V)}{\partial(\delta\phi_i)}\right)_{T,\delta\phi[i]} = -2J\delta\phi_o + 2\lambda_i\delta\phi_i + 2\sum_{i=1}^{K-1} J_i\delta\phi_i - 2J_i\delta\phi_o = 0 \qquad \text{(II.1)}$$

Now we use the Lagrange method of undetermined multipliers. We take the derivative of eq.(47) with respect to $\delta\phi_i$ with all other variations, including $\delta\phi_o$, kept constant. We obtain

$$\left(\frac{\partial(\delta^{(2)}\tilde{G}_V)}{\partial(\delta\phi_i)}\right)_{T,\delta\phi[i],\delta\phi_o} = 2\lambda_i\delta\phi_i - 2J_i\delta\phi_o \qquad \text{(II.2)}$$

We then take the derivative of the constraint eq.(48) with respect to $\delta\phi_i$ with all other variations, including $\delta\phi_o$, kept constant and multiply by an undetermined multiplier 2λ. We then add the obtained equation to eq.(II.2) and let the sum equal zero. We obtain

$$2\lambda_i\delta\phi_i - 2J_i\delta\phi_o - 2\lambda = 0 \qquad \text{(II.3)}$$

Substitution of this equation into eq.(48) yields

$$-\delta\phi_o = \lambda\sum_{i=1}^{K-1}\lambda_i^{-1} + \delta\phi_o\sum_{i=1}^{K-1} J_i\lambda_i^{-1} \qquad \text{(II.4)}$$

Upon eliminating λ from eqs.(II.3) and (II.4), we have

$$\delta\phi_i = \delta\phi_o\lambda_i^{-1}[J_i - (1+\sum_{i=1}^{K-1} J_i\lambda_i^{-1}) / \sum_{i=1}^{K-1}\lambda_i^{-1}] \qquad \text{(II.5)}$$

Substitution of this equation into eq.(II.1) yields eq.(50).

List of Symbols

A	Helmholtz function
A_V	first-order derivative of A with respect to V
A_{VM}	second -order derivative of A with respect to V and $\overline{M}$ or $x\overline{M}$
A_{vx}	second -order derivative of A with respect to V and x
A_{VMM}	third-order derivative of A with respect to V, $\overline{M}$ and $\overline{M}$ or $x\overline{M}$
B	$A_{VM}^2 - A_{VV}A_{MM}$
B_V	derivative of B with respect to V
B_M	derivative of B with respect to $\overline{M}$
a, b, c	model parameters
C	function defined by eq.(59)
C_V	derivative of C with respect to V
C_x	derivative of C with respect to x
C_M	derivative of C with respect to $x\overline{M}$

$C_{\overline{M^2}}$ derivative of C with respect to $x\overline{M^2}$
D function defined by eq.(60)
D_V derivative of D with respect to V
D_x derivative of D with respect to x
$D_{\overline{M}}$ derivative of D with respect to $x\overline{M}$
$D_{\overline{M^2}}$ derivative of D with respect to $x\overline{M^2}$
D_{sp} spinodal determinant
E function defined by eq.(70)
F_{cr} critical criterion
F_{sp} spinodal criterion
j_i RT/x_i
G Gibbs function
$\tilde{G}_V$ reduced Gibbs function of mixing per site
K total number of components
L number of homologues
M molar mass
M^+ M_i–M_K
$\overline{M}$ average molar mass
$\overline{M^2}$ average molar mass square
$\overline{M^3}$ average molar mass to the third
N number of discrete components
N_r total number of site in a lattice
r chain length
T temperature
x mole fraction

Greek letters

$\delta^{(k)}X$ k-th order variation of X
$\mu_{(n)}$ n-order central moment
ϕ volume fraction

superscript

° standard state
r residual properties

hat

¯ average

subscript

m molar
i component i

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