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APPLICATION OF CONTINUOUS THERMODYNAMICS TO THE STABILITY OF POLYMER SYSTEMS. III

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ABSTRACT

Based on the stability theory of continuous thermodynamics for polymer solutions, necessary and sufficient conditions for multiple critical points are derived assuming the segment-molar excess Gibbs free energy to be independent of the distribution function. Equations for calculating double and triple critical points are given. Higher order critical points may be obtained in a successive way. For polymers possessing a Schulz-Flory molecular weight distribution, general conditions for an m -fold critical point are presented.

INTRODUCTION

In synthetic polymers a large number of species differing by molecular weight occur. Due to this polydispersity, the thermodynamic treatment of the liquid-liquid equilibrium in polymer solutions becomes more complicated than in systems with a small number of components. The most useful way to overcome these difficulties is the method of continuous thermodynamics [3–6]. Continuous thermodynamics is based directly on the continuous molecular weight distribution instead of the amounts of individual polymer species.

Correspondingly, the thermodynamic stability theory was also converted into a continuous form not containing determinants whose elements refer to the individual polymer species [7]. On the basis of this continuous form of the stability theory, conditions for the occurrence of multiple critical points are presented in this paper.

The fundamental papers are multiple critical points date back to Korteweg [8], van der Waals [9, 10], and Schreinemakers [11]. More recent treatments were given by Griffiths [12] and Šolc [13–15].

MULTIPLE CRITICAL POINTS IN MULTICOMPONENT SYSTEMS

In a system consisting of $N + 1$ components $0, 1, 2, \dots, N$, the conditions for an m -fold critical point read

$$D_j = 0; \quad j = 0, 1, \dots, m \quad (1a)$$

$$D_{m+1} \neq 0 \quad (1b)$$

The determinant D_0 is given by

$$D_0 = \begin{vmatrix} \partial^2 G / \partial X_1^2 & \partial^2 G / \partial X_1 \partial X_2 & \cdots & \partial^2 G / \partial X_1 \partial X_N \\ \partial^2 G / \partial X_2 \partial X_1 & \partial^2 G / \partial X_2^2 & \cdots & \partial^2 G / \partial X_2 \partial X_N \\ \hline \partial^2 G / \partial X_N \partial X_1 & \partial^2 G / \partial X_N \partial X_2 & \cdots & \partial^2 G / \partial X_N^2 \end{vmatrix} \quad (2)$$

and the other determinants result successively from

$$D_n = \begin{vmatrix} \partial D_{n-1} / \partial X_1 & \partial D_{n-1} / \partial X_2 & \cdots & \partial D_{n-1} / \partial X_N \\ \partial^2 G / \partial X_2 \partial X_1 & \partial^2 G / \partial X_2^2 & \cdots & \partial^2 G / \partial X_2 \partial X_N \\ \hline \partial^2 G / \partial X_N \partial X_1 & \partial^2 G / \partial X_N \partial X_2 & \cdots & \partial^2 G / \partial X_N^2 \end{vmatrix}; \quad n = 1, 2, \dots \quad (3)$$

Here G is the molar Gibbs free energy, and X_1, X_2, \dots, X_N are the independent mole fractions of the system. For large values of N , the application of Eqs. (1) will be very expensive and, by using a computer, it may lead to senseless results due to rounding-off errors. Therefore, another method to obtain the conditions for an m -fold critical point will now be shown. This other method allows us to calculate D_1, D_2, \dots, D_{m+1} rapidly if D_0 is given by an analytic expression and, furthermore, it may easily be generalized to the continuous version of thermodynamics of

multicomponent systems. For simplicity, this other method will first be demonstrated for the case of a ternary system.

In ternary systems, G depends on two independent mole fractions, X_1 and X_2 . The spinodal obeys the condition

$$\text{Min } \delta^2 G = 0 \quad (4)$$

where the second-order differential $\delta^2 G$ according to $\partial^2 G / \partial X_2 \partial X_1 = \partial^2 G / \partial X_1 \partial X_2$ is given by

$$\delta^2 G = \frac{\partial^2 G}{\partial X_1^2} (\delta X_1)^2 + 2 \frac{\partial^2 G}{\partial X_1 \partial X_2} \delta X_1 \delta X_2 + \frac{\partial^2 G}{\partial X_2^2} (\delta X_2)^2 \quad (5)$$

Here δX_1 and δX_2 are arbitrary increases of X_1 and X_2 , respectively. According to Eq. (4), the first task is to determine that variation $\delta X_1, \delta X_2$ minimizes $\delta^2 G$. Since $\text{Min } \delta^2 G$ has to equal zero, a common factor in δX_1 and δX_2 remains undetermined. Choosing this factor to equal δX_1 , that value (δX_2^*) of δX_2 is to be calculated by minimizing $\delta^2 G$ at constant $\delta X_1 \neq 0$. For this purpose, on the basis of Eq. (5), the partial derivative of $\delta^2 G$ with respect to δX_2 is formed and equated to zero, resulting in

$$\delta X_2^* = - \left(\frac{\partial^2 G}{\partial X_1 \partial X_2} \bigg/ \frac{\partial^2 G}{\partial X_2^2} \right) \delta X_1 \quad (6)$$

assuming $\partial^2 G / \partial X_2^2 \neq 0$. Applying this variation $\delta X_1, \delta X_2^*$, Eq. (5) leads to

$$\text{Min } \delta^2 G = \left(D_0 \bigg/ \frac{\partial^2 G}{\partial X_2^2} \right) (\delta X_1)^2 \quad (7)$$

where D_0 is defined by

$$D_0 = \begin{vmatrix} \frac{\partial^2 G}{\partial X_1^2} & \frac{\partial^2 G}{\partial X_1 \partial X_2} \\ \frac{\partial^2 G}{\partial X_2 \partial X_1} & \frac{\partial^2 G}{\partial X_2^2} \end{vmatrix} \quad (8)$$

According to Eq. (4), the spinodal equation reads

$$D_0 = 0 \quad (9)$$

The first-order differential of D_0 is given by

$$\delta D_0 = \frac{\partial D_0}{\partial X_1} \delta X_1 + \frac{\partial D_0}{\partial X_2} \delta X_2 \quad (10)$$

Abbreviating $\delta D_0(\delta X_1, \delta X_2^*)$ by δD_0^* , the application of Eq. (6) results in

$$\delta D_0^* = \left(D_1 / \frac{\partial^2 G}{\partial X_2^2} \right) \delta X_1 \quad (11)$$

where D_1 is defined by

$$D_1 = \begin{vmatrix} \frac{\partial D_0}{\partial X_1} & \frac{\partial D_0}{\partial X_2} \\ \frac{\partial^2 G}{\partial X_2 \partial X_1} & \frac{\partial^2 G}{\partial X_2^2} \end{vmatrix} \quad (12)$$

Since the critical point may be considered as a double solution of the spinodal equation, the necessary conditions for a single critical point read

$$D_0 = 0; \quad D_1 = 0 \quad (13)$$

Equations (13) are equivalent to Eq. (4) and

$$\begin{aligned} \delta(\delta^2 G^*) = \delta^3 G^* = & \frac{\partial^3 G}{\partial X_1^3} (\delta X_1)^3 + 3 \frac{\partial^3 G}{\partial X_1^2 \partial X_2} (\delta X_1)^2 \delta X_2^* \\ & + 3 \frac{\partial^3 G}{\partial X_1 \partial X_2^2} \delta X_1 (\delta X_2^*)^2 + \frac{\partial^3 G}{\partial X_2^3} (\delta X_2^*)^3 = 0 \end{aligned} \quad (14)$$

where $\delta^2 G^* = \delta^2 G(\delta X_1, \delta X_2^*)$. Abbreviating analogously $\delta D_1(\delta X_1, \delta X_2^*)$ by δD_1^* ,

the application of Eq. (6) leads to

$$\delta D_1^* = \left(D_2 / \frac{\partial^2 G}{\partial X_2^2} \right) \delta X_1 \quad (15)$$

where D_2 is given by

$$D_2 = \begin{vmatrix} \frac{\partial D_1}{\partial X_1} & \frac{\partial D_1}{\partial X_2} \\ \frac{\partial^2 G}{\partial X_2 \partial X_1} & \frac{\partial^2 G}{\partial X_2^2} \end{vmatrix} \quad (16)$$

The double critical point as a double solution of $D_1 = 0$ has to satisfy the necessary conditions

$$D_0 = 0; \quad D_1 = 0; \quad D_2 = 0 \quad (17)$$

Generalizing this treatment, the necessary and sufficient conditions for an m -fold critical point read

$$D_j = 0, \quad j = 0, 1, 2, \dots, m \quad (18a)$$

$$D_{m+1} \neq 0 \quad (18b)$$

where D_0 is given by Eq. (8) and D_n ($n = 1, 2, \dots$) by

$$\delta D_{n-1}^* = \left(D_n / \frac{\partial^2 G}{\partial X_2^2} \right) \delta X_1 \quad (19a)$$

resulting in

$$D_n = \begin{vmatrix} \frac{\partial D_{n-1}}{\partial X_1} & \frac{\partial D_{n-1}}{\partial X_2} \\ \frac{\partial^2 G}{\partial X_2 \partial X_1} & \frac{\partial^2 G}{\partial X_2^2} \end{vmatrix}; \quad n = 1, 2, \dots \quad (19b)$$

Without additional difficulties, this treatment may be extended to an $N + 1$ component mixture [16]. Regarding the generalization to continuous thermodynamics, the most important result is Eq. (19a) which permits us to avoid the calculation of determinants, as will be shown in the next section.

MULTIPLE CRITICAL POINTS IN POLYDISPERSE POLYMER SOLUTIONS

Synthetic polymers always show a polydispersity, i.e., they consist of a large number of individual species differing in their molecular weight. To obtain multiple critical points, the generalization of the discontinuous procedure outlined above to multicomponent systems may be applied [16]. Another way is provided by a series expansion of the phase equilibrium conditions at the critical point [15]. The following treatment is based on the stability theory of continuous thermodynamics [1, 2, 7].

A polymer solution consisting of a Solvent A and a Homopolymer B is considered. Choosing a standard segment, the solvent and the different polymer species may be characterized by the segment numbers r_A and r , respectively. The overall concentration of all polymer species is given by the segment fraction ψ , i.e., the segment fraction of the solvent reads $1 - \psi$. To describe the composition of the polymer, the segment-molar distribution function $W(r)$ is introduced which equals the well-known mass distribution function, i.e.,

$$\int_{r'}^{r''} W(r) dr$$

is the relative segment fraction of all polymer species with segment numbers between r' and r'' . Here the term "relative" means "with respect to all polymer species." Therefore, the normalization condition

$$\int W(r) dr = 1; \quad \int = \int_{r_0}^{r^0} \quad (20)$$

has to be fulfilled. The quantities r_0 and r^0 signify the limits of the range of occurring segment numbers: $r_0 \leq r \leq r^0$.

For polymer solutions the nonlinear part $\Delta \bar{G}$ of Gibbs free energy per mole of segments may be written in the following form [1]:

$$\Delta \bar{G}/RT = \frac{1 - \psi}{r_A} \ln(1 - \psi) + \int \frac{\psi W(r)}{r} \ln \psi W(r) dr + \bar{G}^E/RT \quad (21)$$

Here R is the universal gas constant and T is the temperature. The quantity \bar{G}^E is called the segment-molar excess Gibbs free energy; it generalizes the classic χ -term, i.e., \bar{G}^E describes the deviations from a Flory-Huggins mixture [17, 18] with $\chi = 0$.

The second-order differential of $\Delta\bar{G}/RT$ reads [1]:

$$\delta^2(\Delta\bar{G}/RT) = \left[\frac{1}{r_A(1-\psi)} + \frac{\partial^2 \bar{G}^E/RT}{\partial \psi^2} \right] (\delta\psi)^2 + \int \frac{\delta[\psi W(r)]^2}{r\psi W(r)} dr \quad (22)$$

Here \bar{G}^E is assumed to be independent of the distribution function $W(r)$, i.e., \bar{G}^E depends only on T , P , and ψ . Excluding the case of oligomer solutions, this assumption is very often made. In calculating $\text{Min } \delta^2\bar{G}$ the condition

$$\int \delta[\psi W(r)] dr = \delta\psi \quad (23)$$

resulting from Eq. (20) has to be taken into account additionally [1]. By doing so, the application of Lagrange's method of undetermined multipliers results in the following variation:

$$\delta[\psi W(r)] * \frac{r}{\bar{r}^{(1)}} W(r) \delta\psi \quad (24)$$

to lead to the minimum of $\delta^2\bar{G}$ [1]. Here

$$\bar{r}^{(n)} = \int r^n W(r) dr \quad (25)$$

i.e., $\bar{r}^{(1)}$ is the weight-average segment number. Equations (22) and (24) may be considered to be generalizations of Eqs. (5) and (6), respectively. The application of $\delta[\psi W(r)] *$ to Eq. (22) results in

$$\text{Min } \delta^2(\Delta\bar{G}/RT) = L_0(\delta\psi)^2 \quad (26)$$

where L_0 is given by

$$L_0 = \frac{1}{r_A(1-\psi)} + \frac{1}{\bar{r}^{(1)}\psi} + \frac{\partial^2 \bar{G}^E/RT}{\partial \psi^2} \quad (27)$$

Equations (26) and (27) correspond to Eqs. (7) and (8), respectively, but here the quantity L_0 is not a determinant. In analogy to Eq. (9), the spinodal equation reads

$$L_0 = 0 \quad (28)$$

The first-order differential of L_0 is given by

$$\delta L_0 = \left[\frac{1}{r_A(1-\psi)^2} + \frac{\partial^3 \bar{G}^E/RT}{\partial \psi^3} \right] \delta \psi - \frac{1}{(\bar{r}^{(1)}\psi)^2} \int r \delta[\psi W(r)] dr \quad (29)$$

The different form of the last term results since $\bar{r}^{(1)}$ depends on the distribution function $W(r)$ due to Eq. (25). According to Eqs. (24), (25), and (29), $\delta L_0^* = \delta L_0(\delta[\psi W(r)]^*)$ reads

$$\delta L_0^* = L_1 \delta \psi \quad (30)$$

with

$$L_1 = \frac{1}{r_A(1-\psi)^2} - \frac{\bar{r}^{(2)}}{[\bar{r}^{(1)}]^3 \psi^2} + \frac{\partial^3 \bar{G}^E/RT}{\partial \psi^3} \quad (31)$$

By considering the critical point as a double solution of the spinodal equation, the necessary conditions for a single critical point read

$$L_0 = 0; \quad L_1 = 0 \quad (32)$$

This corresponds to $\delta^3 \bar{G}(\delta[\psi W(r)]^*) = 0$.

To find conditions for a double critical point, the differential

$$\delta L_1 = \left[\frac{2}{r_A(1-\psi)^3} + \frac{\partial^4 \bar{G}^E/RT}{\partial \psi^4} \right] \delta \psi - \frac{\int r^2 \delta[\psi W(r)] dr}{[\bar{r}^{(1)}]^3 \psi^3} + \frac{3\bar{r}^{(2)} \int r \delta[\psi W(r)] dr}{[\bar{r}^{(1)}]^4 \psi^3} \quad (33)$$

has to be considered. Applying Eq. (24), $\delta L_1^* = \delta L_1(\delta[\psi W(r)]^*)$ reads

$$\delta L_1^* = L_2 \delta \psi \quad (34)$$

with

$$L_2 = \frac{2}{r_A(1-\psi)^3} - \frac{\bar{r}^{(3)}}{[\bar{r}^{(1)}]^4 \psi^3} + \frac{3[\bar{r}^{(2)}]^2}{[\bar{r}^{(1)}]^5 \psi^3} + \frac{\partial^4 \bar{G}^E/RT}{\partial \psi^4} \quad (35)$$

Then the necessary conditions for a double critical point are

$$L_0 = 0; \quad L_1 = 0; \quad L_2 = 0 \quad (36)$$

Continuing this procedure, the necessary conditions for a triple critical point read

$$L_0 = 0; \quad L_1 = 0; \quad L_2 = 0; \quad L_3 = 0 \quad (37)$$

with

$$L_3 = \frac{6}{r_A(1-\psi)^4} - \frac{\bar{r}^{(4)}}{[\bar{r}^{(1)}]^5 \psi^4} + \frac{10\bar{r}^{(3)}\bar{r}^{(2)}}{[\bar{r}^{(1)}]^6 \psi^4} - \frac{15[\bar{r}^{(2)}]^3}{[\bar{r}^{(1)}]^7 \psi^4} + \frac{\partial^5 \bar{G}^E/RT}{\partial \psi^5} \quad (38)$$

These equations agree with the results of Šolc [15] based on a series expansion of the phase equilibrium conditions. By generalizing this treatment, the necessary

and sufficient conditions for an m -fold critical point read

$$L_j = 0 \text{ for } j = 0, 1, 2, \dots, m \quad (39a)$$

$$L_{m+1} \neq 0 \quad (39b)$$

The calculation of L_j may be performed successively based on the equation for L_{j-1} in each case. According to the presented treatment, L_j is calculated by

$$L_j = \delta L_{j-1}^* / \delta \psi \quad (40)$$

where δL_{j-1}^* is obtained by applying $\delta[\psi W(r)]^*$ according to Eq. (24) to δL_{j-1} .

The quantity L_j may also be expressed by

$$L_j = \frac{j!}{r_A(1-\psi)^{j+1}} + \frac{f_j(\bar{r}^{(1)}, \bar{r}^{(2)}, \dots, \bar{r}^{(j+1)})}{\psi^{j+1}} + \frac{\partial^{j+2} \bar{G}^E / RT}{\partial \psi^{j+2}} \quad (41)$$

where f_j has to be calculated successively from

$$f_0(\bar{r}^{(1)}) = 1/\bar{r}^{(1)} \quad (42a)$$

$$f_k(\bar{r}^{(1)}, \bar{r}^{(2)}, \dots, \bar{r}^{(k+1)}) = \sum_{i=1}^k \frac{\partial f_{k-1}(\bar{r}^{(1)}, \bar{r}^{(2)}, \dots, \bar{r}^{(k)})}{\partial \bar{r}^{(i)}} \frac{\bar{r}^{(i+1)}}{\bar{r}^{(1)}} \quad k = 1, 2, \dots \quad (42b)$$

GENERAL FORMULA FOR A SCHULZ-FLORY DISTRIBUTION

As shown in the preceding section, the calculation of the expressions L_j is to be performed successively. But for a (generalized) Schulz-Flory distribution, a direct formula may be easily obtained. The (generalized) Schulz-Flory distribution reads

$$W(r) = \frac{k^{k+1}}{\bar{r} \Gamma(k+1)} \left(\frac{r}{\bar{r}}\right)^k \exp(-kr/\bar{r}) \quad (43)$$

Here \bar{r} is the number-average segment number of all polymer species, k is the reciprocal of the non-uniformity (which is a measure for the breadth of the distribution), and Γ is the Gamma-function. In terms of the moments defined by Eq. (25) ($r_0 = 0$, $r^0 = \infty$), r and k read

$$\bar{r} = 1/\bar{r}^{(-1)} \quad (44a)$$

$$k = 1/(\bar{r}^{(-1)}\bar{r}^{(1)} - 1) \quad (44b)$$

Furthermore, Eqs. (25) and (43) yield

$$\bar{r}^{(n)} = \left(\frac{\bar{r}}{k}\right) \prod_{i=1}^n (k+i); \quad n = 1, 2, 3, \dots \quad (45)$$

To calculate the quantities of type L_j , the differentials $\delta\bar{r}$ and δk are needed. According to Eqs. (20), (23), (25), and (44a), $\delta\bar{r}$ is given by

$$\begin{aligned} \delta\bar{r} &= \frac{1}{[\bar{r}^{(-1)}]^2} \delta \frac{\int \frac{\psi W(r)}{r} dr}{\int \psi W(r) dr} \\ &= - \frac{1}{[\bar{r}^{(-1)}]^2 \psi} \left\{ \int \frac{\delta[\psi W(r)]}{r} dr - \bar{r}^{(-1)} d\psi \right\} \quad (46) \end{aligned}$$

With the aid of Eqs. (23), (24), (44a), and (45), δr^* becomes

$$\delta r^* = \frac{\bar{r}}{\psi(k+1)} \delta\psi \quad (47)$$

According to Eqs. (20), (23), (25), and (44b), δk is given by

$$\begin{aligned} \delta k &= - \frac{1}{[\bar{r}^{(-1)}\bar{r}^{(1)} - 1]^2} \delta \frac{\int \frac{\psi W(r)}{r} dr \int r \psi W(r) dr}{\left\{ \int \psi W(r) dr \right\}^2} \\ &= - \frac{1}{[\bar{r}^{(-1)}\bar{r}^{(1)} - 1]^2} \psi \left\{ \bar{r}^{(1)} \int \frac{\delta[\psi W(r)]}{r} dr \right. \\ &\quad \left. + \bar{r}^{(-1)} \int r \delta[\Psi W(r)] dr - 2\bar{r}^{(-1)}\bar{r}^{(1)} d\Psi \right\} \end{aligned} \quad (48)$$

Applying Eqs. (23)–(25), (44a), and (45), δk^* reads

$$\delta k^* = 0 \quad (49)$$

Equations (47) and (49) result in a simplification of the calculation of L_j according to Eq. (40), leading to

$$L_j = \frac{\partial L_{j-1}}{\partial \psi} + \frac{\partial L_{j-1}}{\partial \bar{r}} \frac{\bar{r}}{\psi(k+1)} \quad (50)$$

With the aid of Eqs. (27), (44a), and (44b), L_0 leads

$$L_0 = \frac{1}{r_A(1-\psi)} + \frac{1}{\bar{r}\psi} \frac{k}{k+1} + \frac{\partial^2 \bar{G}^E/RT}{\partial \psi^2} \quad (51)$$

Using Eqs. (50) and (51), L_1 is given by

$$L_1 = \frac{1}{r_A(1-\psi)^2} - \frac{1}{\bar{r}\psi^2} \frac{k}{k+1} \left(1 + \frac{1}{k+1}\right) + \frac{\partial^3 \bar{G}^E/RT}{\partial \psi^3} \quad (52)$$

Furthermore, L_2 reads

$$L_2 = \frac{2}{r_A(1-\psi)^3} + \frac{1}{\bar{r}\psi^3} \frac{k}{k+1} \left(1 + \frac{1}{k+1}\right) \left(2 + \frac{1}{k+1}\right) + \frac{\partial^4 \bar{G}^E/RT}{\partial \psi^4} \quad (53)$$

Generalizing this procedure, L_j is given by

$$L_j = \frac{j!}{r_A(1-\Psi)^{j+1}} + (-1)^j \frac{1}{\bar{r}\Psi^{j+1}} - \frac{k}{(k+1)^{j+1}} \prod_{i=1}^j$$

$$(ik + i + 1) + \frac{\partial^{j+2} \bar{G}^E / RT}{\partial \Psi^{j+2}} \quad (54)$$

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