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APPLICATION OF CONTINUOUS THERMODYNAMICS TO THE STABILITY OF POLYMER SYSTEMS

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ABSTRACT

Continuous thermodynamics is a version of thermodynamics describing the composition of a mixture by a continuous distribution function instead of the mole fractions or weight fractions, etc. of individual components. In this way, continuous thermodynamics permits a simple treatment of phase equilibria in complex multicomponent systems containing a large number of similar species such as heavy petroleum fractions or polymer systems. In this paper, continuous thermodynamics is applied to the thermodynamic stability and the critical state of solutions and mixtures of polydisperse polymers. The traditional form of thermodynamic stability theory leading to the well-known determinant criteria is not applicable within the framework of continuous thermodynamics. The most convenient starting point proves to be determination of the sign of the second-order differential of the Gibbs free energy. The key quantity is the lowest value of this differential, which is obtainable by using Lagrangian multipliers. In this way, the spinodal and the critical point for the liquid-liquid equilibrium of solutions and mixtures of polydisperse polymers can be calculated. For polymer mixtures, these questions are important in studying polymer compatibility.

INTRODUCTION

Synthetic polymers show polydispersity with respect to the molecular weight M. Owing to the very large number of different species, characterization experiments lead only to continuous distribution functions. Rätzsch, Kehlen, and Bergmann [1-3], Salacuse and Stell [4], Gualtieri et al. [5], and Briano and Glandt [6] established a version of chemical thermodynamics based directly on such continuous distribution functions. It is called "continuous thermodynamics" and was applied by the present authors to calculate the liquid-liquid equilibrium of polymer solutions [7, 8], of copolymer solutions [9, 10], and of polymer mixtures (i.e., to calculate polymer compatibility) [11]. Superiority over the traditional pseudocomponent approach (based on splitting the continuous distribution arbitrarily into a number of discontinuous bars) could be shown, as has also been pointed out by Prausnitz and coworkers [12].

To complete the results on liquid-liquid equilibrium, it is interesting to calculate the spinodal and the critical point. These quantities can be obtained by applying the thermodynamic stability theory. To our knowledge, Stockmayer [13] was the first to present such results for polymer solutions. Applying a special expression for the real behavior, he obtained his results by a series expansion at the critical point. Later, his results were confirmed by Koningsveld and Staverman [14] by deriving closed expressions for a special case from the traditional stability determinant. The contents of the present paper consist in establishing a version of thermodynamic stability theory adapted to the description of a polydisperse polymer by a continuous distribution function.

THERMODYNAMIC BACKGROUND

In studying polymer systems, it is convenient to imagine all molecules to be divided into segments of equal size. Then, each molecular species possesses a characteristic segment number, and its relative amount may be specified by its segment fraction. Correspondingly, we choose as the key thermodynamic quantity the quotient $\overline{\overline{G}}$ of the Gibbs free energy and the total amount of segments in the phase considered.

To investigate thermodynamic stability of a phase with given composition, we consider variations of this composition as described by differentials of the composition variables. Then, the second order differential $\delta^2\overline{\overline{G}}$ (at constant temperature T and constant pressure P) corresponding to any given variation of the composition can be calculated. The sign of $\delta^2\overline{\overline{G}}$ provides information on the stability with respect to diffusion. According to the method dating back to Gibbs [15], the stability criterion reads:

$$\begin{array}{ll} \delta^2\bar{\bar{G}} > 0 & \text{for all variations: stable or metastable} \\ \delta^2\bar{\bar{G}} \geqq 0 & \text{for all variations where the case ``='' occurs: limit of instability (spinodal)} \\ \delta^2\bar{\bar{G}} < 0 & \text{for (at least) one variation: unstable} \end{array} \tag{1}$$

Of course, here (and in the following) only nonvanishing variations are to be considered.

In traditional thermodynamics, the composition of a phase is described by the mole fractions, or volume fractions, or segment fractions, etc. of individual components $i, = 1, \ldots, N$. Choosing the segment fraction ψ_i, the relation for the second-order differential $\delta^2\bar{\bar{G}}$ reads

$$\delta^2\bar{\bar{G}} = \sum_{i=1}^{N-1} \sum_{k=1}^{N-1} G_{ik}\delta\psi_i\delta\psi_k \tag{2}$$

with $G_{ik} = \partial^2\bar{\bar{G}}/\partial\psi_i\partial\psi_k$, where these and all following derivatives are to be formed at constant T and P. The set of the differentials $\delta\psi_1, \ldots, \delta\psi_{N-1}$ of the independent segment fractions describes the variation of the composition that is under consideration. According to Eq. (2), $\delta^2\bar{\bar{G}}$ is a quadratic form with respect to these differentials, and the contents of Eq. (1) may be expressed in the following way: The phase is stable or metastable if the quadratic form Eq. (2) is positive definite; the phase is unstable if the quadratic form is indefinite; if the phase lies on the limit of instability, then the quadratic form is positive semidefinite.

The following statement on the coefficients G_{ik} of the quadratic form may be obtained by algebra from Eqs. (1) and (2): "The homogeneous mixture is stable or metastable if the determinant

$$D = \begin{vmatrix} G_{11} & G_{12} & \cdots & G_{1,N-1} \\ G_{21} & G_{22} & \cdots & G_{2,N-1} \\ \vdots & \vdots & & \vdots \\ G_{N-1,1} & G_{N-1,2} & \cdots & G_{N-1,N-1} \end{vmatrix} \tag{3}$$

is positive with all principal minors." Principal minors are minors (determinants of lower order) resulting from D by neglecting rows and columns of equal numbers. As these conditions are not all independent, it is sufficient to require, for stability or metastability,

$$G_{11} > 0; G_{11}G_{22} - G_{12}^2 > 0; \ldots ; D > 0. \tag{4}$$

The condition for the limit of instability, the spinodal, is

$$D = 0. \tag{5}$$

The necessary relations describing the critical state may be expressed in a form similar to Eq. (1). They read:

$$\begin{array}{lll} \text{(a)}\ \delta^2\bar{\bar{G}} \geqq 0 & \multicolumn{2}{l}{\text{for all variations, where the case "=" occurs}} \\ \text{(b)}\ \delta^j\bar{\bar{G}} = 0 & j = 3, \ldots, p-1 & \multirow{2}{*}{$\left.\vphantom{\begin{array}{l}a\\b\end{array}}\right\}$ for all variations fulfilling $\delta^2\bar{\bar{G}} = 0$} \\ \phantom{\text{(b)}}\ \delta^p\bar{\bar{G}} > 0 & p = \text{even} & \end{array} \tag{6}$$

According to Condition (a), the critical state lies on the spinodal. Condition (b) results from the property of the critical state to be the fusion of two coexisting phases, and the inequality determines the critical state to be a stable one. Similarly to Eq. (5), the condition $\delta^3\bar{\bar{G}} = 0$ may also be expressed in the form of a determinant criterion [15].

When the system considered contains only a few components, Eqs. (4) and (5) and the corresponding relation for the critical state provide a fair method for studying stability and critical properties. But for large numbers N of components, such as in synthetic polymers, the calculation becomes very burdensome (with the exception of simple $\bar{\bar{G}}$ expressions).

Because the method of continuous thermodynamics, i.e., the direct application of continuous distribution functions in the framework of thermodynamics, proved to be very convenient for calculating phase equilibria for polymer systems, it is obvious that this method should also be applied for stability considerations. But there are no continuous determinants and also no other analogous mathematical quantities for the continuous case. Hence, the application of the criteria of Eqs. (1) and (6) with the help of determinants is not possible in the framework of continuous thermodynamics. Therefore, since the detailed calculation of the sign of the second-order differential $\delta^2\bar{\bar{G}}$ for all imaginable variations of the composition is not feasible, we need a practicable way to apply these criteria. Such a way may be found easily. By Eq. (1), the lowest value attainable by $\delta^2\bar{\bar{G}}$ proves to play the decisive role. Denoting that variation of the composition resulting in the minimum of $\delta^2\bar{\bar{G}}$ by $\delta\psi_0$ ($\neq 0$), the stability criterion may be written in the form [16]

$$\delta^2\bar{\bar{G}}(\delta\psi_0) \begin{cases} > 0, & \text{stable or metastable,} \\ = 0, & \text{limit of instability,} \\ < 0, & \text{unstable,} \end{cases} \tag{7}$$

and the necessary conditions for the critical state read (usually $p = 4$)

$$\begin{aligned} \delta^j\bar{\bar{G}}(\delta\psi_0) &= 0; \quad j = 2, \ldots, p-1, \\ \delta^p\bar{\bar{G}}(\delta\psi_0) &> 0; \quad p = \text{even}. \end{aligned} \tag{8}$$

As the variation minimizing $\delta^2\bar{\bar{G}}$ may also be obtained easily in the framework of continuous thermodynamics, these criteria provide a good way for performing stability considerations in polymer systems. This will be demonstrated for polymer solutions, for polymer mixtures, and for systems containing an arbitrary number of solvents and polymers.

POLYMER SOLUTIONS

Let us consider a Polymer B described by the distribution function $W_B(M)$ where M is the molecular weight. The distribution function is defined in such a way that $W_B(M)\,dM$ gives the segment fraction of all polymer species with molecular weights between M and $M + dM$. For treating a solution in Solvent A, the segment molar Gibbs free energy $\bar{\bar{G}}$ is given by [7, 8] (neglecting linear terms, which are immaterial in considering stability)

$$\bar{\bar{G}} = RT\frac{\psi_A}{r_A}\ln\psi_A + RT\int_M \frac{\psi_B W_B(M)}{r_B(M)}\ln\psi_B W_B(M)\,dM + \bar{\bar{G}}^E, \tag{9}$$

where r_A and $r_B(M)$ are the segment numbers of the solvent and of the different polymer species, while ψ_A and ψ_B are the segment fractions of the solvent and of the total polymer ensemble. The first two terms are the well-known Flory-Huggins expression (with $\chi = 0$) and the excess term $\bar{\bar{G}}^E$ describes the deviations with respect to such a mixture.

Comparison of Eq. (9) with the well-known corresponding expression in traditional thermodynamics shows the main differences between the discrete and continuous treatments [2]: 1) the discrete index i is replaced by a continuous variable (M in this case); 2) the segment fractions of discrete polymer species are replaced by a continuous distribution function; and 3) summation is replaced by integration. (The integration limits are the limits of the molecular weight range in question.)

Altogether, this means: In the discrete case, $\overline{\overline{G}}$ is a function of the individual segment fractions; in the continuous case, $\overline{\overline{G}}$ is a functional with respect to the distribution function. A function is a mapping of numbers to numbers, and a functional is a mapping of functions to numbers. In Eq. (9), a specific value of $\overline{\overline{G}}$ (at given temperature T, pressure P, and segment fractions ψ_A, ψ_B) is assigned to each function applied for $W_B(M)$.

The composition of the polymer solution is expressed by the segment fractions ψ_A and ψ_B and by the distribution function $W_B(M)$. These quantities obey the normalization conditions

$$\psi_A + \psi_B = 1; \quad \int_M W_B(M)\, dM = 1. \tag{10}$$

To study stability, a variation of the composition is to be considered which may be described by $\delta\psi_A = -\delta\psi_B$ and by the variation $\delta W_B(M)$ of the distribution function. But, according to the structure of Eq. (9), it is not convenient to operate with $\delta W_B(M)$ but with the expression $\delta[\psi_B W_B(M)] = W_B(M)\delta\psi_B + \psi_B \delta W_B(M)$ obeying the relation

$$\int_M \delta[\psi_B W_B(M)]\, dM = \delta\psi_B. \tag{11}$$

For stability considerations on the basis of Eqs. (7) and (8), the second-order differential and the higher-order differentials of $\overline{\overline{G}}$ are needed. In continuous thermodynamics, an expression for $\delta^2\overline{\overline{G}}$ analogous to Eq. (2) is obtained, where the second-order functional derivatives occur and the double sum is replaced by a double integral. But there exists a simpler and more direct way to calculate the higher-order differentials [16]:

$$\delta^k\overline{\overline{G}} = \left. \frac{\partial^k \overline{\overline{G}}(T,P,\psi_A + t\delta\psi_A; \psi_B W_B + t\delta[\psi_B W_B])}{\partial t^k} \right|_{t=0} \tag{12}$$

Hence, the following steps are necessary to obtain the kth order differential: 1) In the $\overline{\overline{G}}$-expression, ψ_A is replaced by $\psi_A + t\delta\psi_A$, and $\psi_B W_B(M)$ is replaced by $\psi_B W_B(M) + t\delta[\psi_B W_B(M)]$. 2) Then, this expression is differentiated k times with respect to t. 3) Finally, t is equated to zero. An analogous procedure is also possible in the framework of discontinued treatment.

Applying Eq. (12), we obtain Eqs. (13)-(15) by very simple calculations from Eq. (9):

$$\delta^2\overline{\overline{G}} = RT\frac{(\delta\psi_A)^2}{r_A\psi_A} + RT\int_M \frac{(\delta[\psi_B W_B(M)])^2}{r_B(M)\psi_B W_B(M)}\,dM + \frac{\partial^2\overline{\overline{G}}^E}{\partial\psi_A^2}(\delta\psi_A)^2, \tag{13}$$

$$\delta^3\overline{\overline{G}} = -RT\frac{(\delta\psi_A)^3}{r_A\psi_A^2} - RT\int_M \frac{(\delta[\psi_B W_B(M)])^3}{r_B(M)\psi_B^2 W_B^2(M)}\,dM + \frac{\partial^3\overline{\overline{G}}^E}{\partial\psi_A^3}(\delta\psi_A)^3, \tag{14}$$

$$\delta^4\overline{\overline{G}} = 2RT\frac{(\delta\psi_A)^4}{r_A\psi_A^3} + 2RT\int_M \frac{(\delta[\psi_B W_B(M)])^4}{r_B(M)\psi_B^3 W_B^3(M)}\,dM + \frac{\partial^4\overline{\overline{G}}^E}{\partial\psi_A^4}(\delta\psi_A)^4. \tag{15}$$

Here $\overline{\overline{G}}^E$ is assumed to be independent of the distribution function $W_B(M)$: $\overline{\overline{G}}^E = \overline{\overline{G}}^E(T,P,\psi_A)$. This simple assumption is often made when considering solutions of polymers and not of oligomers. It allows a comparison with results obtained in the traditional way.

To apply the criteria of Eqs. (7) and (8), the variation $\delta\psi_{A,0}$ and $\delta[\psi_B W_B(M)]_0$ is to be found that minimizes $\delta^2\overline{\overline{G}}$. Since we are only interested in the sign of $\delta^2\overline{\overline{G}}$ and since $\delta^2\overline{\overline{G}}$ is homogeneous (of the second degree) with respect to $\delta\psi_A$ and $\delta[\psi_B W_B(M)]$, in the minimizing quantities $\delta\psi_{A,0}$ and $\delta[\psi_B W_B(M)]_0$ a common factor remains undetermined. We may consider this factor to be equal to $\delta\psi_{A,0}$ and, hence, the task is to calculate the variation $\delta[\psi_B W_B(M)]_0$ minimizing $\delta^2\overline{\overline{G}}$ at a constant value of $\delta\psi_A = \delta\psi_{A,0}$.

According to Eq. (13), $\delta^2\overline{\overline{G}}$ is a functional with respect to $\delta[\psi_B W_B(M)]$. The minimum of a function is obtained by equating the derivative to zero and, analogously, the minimum of a functional is obtained by equating the functional derivative to zero. To distinguish it from ordinary derivatives, a functional derivative will be symbolized by $D\ldots/D\ldots$. In the case of a functional I of the simple form

$$I = \int_a^b F(f(x))\,dx,$$

the functional derivative $DI/Df(x)$ equals the ordinary derivative of the integrand $F(f(x))$ with respect to the function $f(x)$:

$$\frac{DI}{Df(x)} = \frac{dF}{df(x)},$$

for example:

$$I = \int_0^1 [f(x)]^n\,dx; \qquad \frac{DI}{Df(x)} = \frac{d[f(x)]^n}{df(x)} = n[f(x)]^{n-1}.$$

In minimizing $\delta^2\overline{\overline{G}}$, the condition of Eq. (11) must also be made. This may be done with the help of Lagrange's method of undetermined multipliers: The left-hand side of Eq. (11) is multiplied by a multiplier (we chose -2λ) and then added to $\delta^2\overline{\overline{G}}$. Then, the functional derivative of the resulting expression is formed and equated to zero:

$$\frac{D[\delta^2\overline{\overline{G}} - 2\lambda\int_M \delta\,[\psi_B W_B(M)]\,dM}{D\delta\,[\psi_B W_B(M)]} = \frac{D[\delta^2\overline{\overline{G}}]}{D\delta\,[\psi_B W_B(M)]} - 2\lambda = 0. \tag{16}$$

The result contains the multiplier which may be determined by insertion into Eq. (11).

In this way, we obtain from Eq. (13)

$$\delta\,[\psi_B W_B(M)]_0 = \delta\psi_B \frac{r_B(M)}{\bar{r}_B^{(1)}}\, W_B(M) \tag{17}$$

with

$$\bar{r}_B^{(n)} = \int_M [r_B(M)]^n W_B(M)\,dM \tag{18}$$

Hence, $\bar{r}_B^{(1)}$ denotes the mass (or weight) average of the segment number $r_B(M)$. By introducing Eq. (17) into Eq. (13), the stability condition Eq. (7) results in the criterion

$$\frac{RT}{r_A\psi_A}+\frac{RT}{\bar{r}_B^{(1)}\psi_B}+\frac{\partial^2\bar{\bar{G}}^E}{\partial\psi_A^2}\quad\begin{cases}>0, & \text{stable or metastable,}\\ =0, & \text{limit of instability,}\\ <0, & \text{unstable,}\end{cases}\tag{19}$$

When $\tilde{r}_B$ is the upper limit of r_B, $\tilde{r}_B$ is also the largest value attainable by $\bar{r}_B^{(1)}$, and the phase under consideration is stable for all distributions $W_B(M)$ if the relation

$$\frac{RT}{r_A\psi_A}+\frac{RT}{\tilde{r}_B\psi_B}+\frac{\partial^2\bar{\bar{G}}^E}{\partial\psi_A^2}\geqq 0\tag{20}$$

is valid for all ψ_A values. Metastability is also impossible in this case as it requires instability in other ranges of concentration. Since $\chi = 0$ implies $\bar{\bar{G}}^E \equiv 0$, Eq. (20) results in the well-known statement that a Flory-Huggins mixture with $\chi = 0$ is always stable.

By inserting Eq. (17) into Eqs. (14) and (15), the criterion for the critical-state Eq. (8) results in the following conditions (assuming $p = 4$):

$$\frac{RT}{r_A\psi_A}+\frac{RT}{\bar{r}_B^{(1)}\psi_B}+\frac{\partial^2\bar{\bar{G}}^E}{\partial\psi_A^2}=0\quad\text{(spinodal),}\tag{21}$$

$$-\frac{RT}{r_A\psi_A^2}+\frac{RT\bar{r}_B^{(2)}}{[\bar{r}_B^{(1)}]^3\psi_B^2}+\frac{\partial^3\bar{\bar{G}}^E}{\partial\psi_A^3}=0,\tag{22}$$

$$\frac{2RT}{r_A\psi_A^3}+\frac{2RT\bar{r}_B^{(3)}}{[\bar{r}_B^{(1)}]^4\psi_B^3}+\frac{\partial^4\bar{\bar{G}}^E}{\partial\psi_A^4}>0.\tag{23}$$

In the more general case (the number p is not restricted to 4), we obtain

$$(-1)^j RT\frac{(j-2)!}{r_A\psi_A^{j-1}}+RT\frac{(j-2)!\bar{r}_B^{(j-1)}}{[\bar{r}_B^{(1)}]^j\psi_B^{j-1}}+\frac{\partial^j\bar{\bar{G}}^E}{\partial\psi_A^j}=0;$$

$$j = 2, 3, \ldots, p-1,\tag{24}$$

$$RT\frac{(p-2)!}{r_A\psi_A^{p-1}}+RT\frac{(p-2)!\bar{r}_B^{(p-1)}}{[\bar{r}_B^{(1)}]^p\psi_B^{p-1}}+\frac{\partial^p\bar{\bar{G}}^E}{\partial\psi_A^p}>0;\quad p=\text{even}.\tag{25}$$

Equations (21) and (22) were presented earlier by Stockmayer [13] and by Koningsveld and Staverman [14] for special $\overline{\overline{G}}^E$ expressions. The agreement confirms the method applied here, which proves to be simpler and more general.

POLYMER MIXTURES

For a mixture of two polydisperse polymers, A and B, described by the distribution functions $W_A(M)$ and $W_B(M)$, the treatment becomes similar to that presented above. When ψ_A and ψ_B are the segment fractions of the total polymer ensembles A and B, respectively, the segment-molar Gibbs free energy $\overline{\overline{G}}$ reads [7] (again neglecting linear terms)

$$\overline{\overline{G}} = RT \int_M \frac{\psi_A W_A(M)}{r_A(M)} \ln \psi_A W_A(M)\, dM + RT \int_M \frac{\psi_B W_B(M)}{r_B(M)} \ln \psi_B W_B(M)\, dM + \overline{\overline{G}}^E. \tag{26}$$

Each polymer is treated as a continuous ensemble, but one polymer with respect to the other is treated in the well-known discontinuous manner.

The differentials may be obtained by a procedure analogous to Eq. (12). Assuming again $\overline{\overline{G}}^E$ to be independent of the distribution functions $W_A(M)$ and $W_B(M)$, i.e., $\overline{\overline{G}}^E = \overline{\overline{G}}^E(T,P,\psi_A)$, the differentials follow analogs of Eqs. (13)-(15) except that, in all cases, the first term has the same form as the second one (only replacing B by A).

To apply the criteria for stability and for the critical state, Eqs. (7) and (8), the variation $\delta[\psi_A W_A(M)]_0$, $\delta[\psi_B W_B(M)]_0$ has to be found that minimizes $\delta^2\overline{\overline{G}}$. Again a common factor remains undetermined, which we choose to be $\delta\psi_A = -\delta\psi_B$. In minimizing $\delta^2\overline{\overline{G}}$, two additional conditions have to be met: Eq. (11) and the corresponding relation for Polymer A. Hence, the minimizing variation (obtained from the functional derivatives with respect to $\delta[\psi_A W_A(M)]$ and to $\delta[\psi_B W_B(M)]$) is given by Eq. (17) and by the corresponding relation for Polymer A. Hence, the stability criterion Eq. (7) results in

$$\frac{RT}{\bar{r}_A{}^{(1)}\psi_A}+\frac{RT}{\bar{r}_B{}^{(1)}\psi_B}+\frac{\partial^2\bar{\bar{G}}^E}{\partial\psi_A{}^2}\ \begin{cases} >0, & \text{stable or metastable,}\\ =0, & \text{limit of instability,}\\ <0, & \text{unstable.}\end{cases} \tag{27}$$

Again, the additional statement follows that the phase under consideration is stable for all distributions $W_A(M)$ and $W_B(M)$ if the relation

$$\frac{RT}{\tilde{r}_A\psi_A}+\frac{RT}{\tilde{r}_B\psi_B}+\frac{\partial^2\bar{\bar{G}}^E}{\partial\psi_A{}^2}\geqq \tag{28}$$

is fulfilled for all ψ_A values. From Eq. (8), the following necessary criterion for the critical state is obtained for $p = 4$:

$$\frac{RT}{\bar{r}_A{}^{(1)}\psi_A}+\frac{RT}{\bar{r}_B{}^{(1)}\psi_B}+\frac{\partial^2\bar{\bar{G}}^E}{\partial\psi_A{}^2}=0 \quad \text{(spinodal),} \tag{29}$$

$$-\frac{RT\bar{r}_A{}^{(2)}}{[\bar{r}_A{}^{(1)}]^3\psi_A{}^2}+\frac{RT\bar{r}_B{}^{(2)}}{[\bar{r}_B{}^{(1)}]^3\psi_B{}^2}+\frac{\partial^3\bar{\bar{G}}^E}{\partial\psi_A{}^3}=0, \tag{30}$$

$$\frac{2RT\bar{r}_A{}^{(3)}}{[\bar{r}_A{}^{(1)}]^4\psi_A{}^3}+\frac{2RT\bar{r}_B{}^{(3)}}{[\bar{r}_B{}^{(1)}]^4\psi_B{}^3}+\frac{\partial^4\bar{\bar{G}}^E}{\partial\psi_A{}^4}>0. \tag{31}$$

Again, these relations may be obtained from the corresponding equations for polymer solutions, Eqs. (21)-(23), by assigning to the first term the same form as the second one. This statement is also valid in the more general case $p > 4$, i.e., the corresponding relations may be obtained by this procedure from Eqs. (24) and (25). Equations (29) and (30) were presented by Koningsveld and Kleintjens [17] in the framework of traditional thermodynamics.

MIXTURES CONTAINING SEVERAL SOLVENTS AND SEVERAL POLYMERS

Let $1, \dots, I$ be several solvents (individual components) and $I + 1, \dots, N$ be several polymers (ensembles) described by the distribution functions $W_{I+1}(M), \dots, W_N(M)$. Neglecting linear terms, the segment-molar Gibbs free energy $\bar{\bar{G}}$ reads [7]

$$\bar{\bar{G}} = RT\sum_{i=1}^{I} \frac{\psi_i}{r_i} \ln \psi_i + RT\sum_{i=I+1}^{N} \int_M \frac{\psi_i W_i(M)}{r_i(M)} \ln \psi_i W_i(M)\, dM + \bar{\bar{G}}^E. \tag{32}$$

Generalizing the procedure of Eq. (12), differentials of any order may be easily calculated. The assumption that $\bar{\bar{G}}^E$ does not depend on the distribution functions, i.e., $\bar{\bar{G}}^E = \bar{\bar{G}}^E(T,P,\psi_1, \ldots, \psi_I, \psi_{I+1}, \ldots, \psi_{N-1})$, leads to

$$\delta^2\bar{\bar{G}} = RT\sum_{i=1}^{I} \frac{(\delta\psi_i)^2}{r_i\psi_i} + RT\sum_{i=I+1}^{N} \int_M \frac{(\delta[\psi_i W_i(M)])^2}{r_i(M)\psi_i W_i(M)}\, dM + \sum_{i=1}^{N-1}\sum_{k=1}^{N-1} \frac{\partial^2 \bar{\bar{G}}^E}{\partial\psi_i \partial\psi_k} \delta\psi_i \delta\psi_k \tag{33}$$

$$\delta^3\bar{\bar{G}} = -RT\sum_{i=1}^{I} \frac{(\delta\psi_i)^3}{r_i\psi_i^2} - RT\sum_{i=I+1}^{N} \int_M \frac{(\delta[\psi_i W_i(M)])^3}{r_i(M)\psi_i^2 W_i^2(M)}\, dM + \sum_{i=1}^{N-1}\sum_{k=1}^{N-1}\sum_{m=1}^{N-1} \frac{\partial^3 \bar{\bar{G}}^E}{\partial\psi_i \partial\psi_k \partial\psi_m} \delta\psi_i \delta\psi_k \delta\psi_m \tag{34}$$

$$\delta^4\bar{\bar{G}} = RT\sum_{i=1}^{I} \frac{2(\delta\psi_i)^4}{r_i\psi_i^3} + RT\sum_{i=I+1}^{N} \int_M \frac{2(\delta[\psi_i W_i(M)])^4}{r_i(M)\psi_i^3 W_i^3(M)}\, dM + \sum_{i=1}^{N-1}\sum_{k=1}^{N-1}\sum_{m=1}^{N-1}\sum_{n=1}^{N-1} \frac{\partial^4 \bar{\bar{G}}^E}{\partial\psi_i \partial\psi_k \partial\psi_m \partial\psi_n} \delta\psi_i \delta\psi_k \delta\psi_m \delta\psi_n. \tag{35}$$

To obtain the criteria for stability and critical state, we have to look for the variation that minimizes $\delta^2\bar{\bar{G}}$. It proves convenient to perform this task in two steps: we first search for the variations $\delta[\psi_{I+1} W_{I+1}(M)]_0, \ldots, \delta[\psi_N W_N(M)]_0$ minimizing $\delta^2\bar{\bar{G}}$ at constant $\delta\psi_1, \ldots, \delta\psi_N$; and then we calculate the variations $\delta\psi_{2,0}, \ldots, \delta\psi_{N,0}$ minimizing $\delta^2\bar{\bar{G}}$ at a constant $\delta\psi_1 = \delta\psi_{1,0}$, which we choose to be the common undetermined multiplier.

In the first step, additional conditions of the type of Eq. (11) for $I + 1, \ldots, N$ have to be met, and the result reads, in complete analogy to Eq. (17),

$$\delta\,[\psi_i W_i(M)]_0 = \delta\psi_i \frac{r_i(M)}{\bar{r}_i^{(1)}}\, W_i(M); \qquad i = I+1, \dots, N. \tag{36}$$

To perform the second step, at first $\delta\psi_N$ is eliminated according to $\delta\psi_N = -(\delta\psi_1 + \cdots + \delta\psi_{N-1})$. In this way, we obtain from Eq. (33) and Eq. (36),

$$\delta^2\bar{\bar{G}} = \sum_{i=1}^{N-1}\sum_{k=1}^{N-1} G_{ik}\,\delta\psi_i\,\delta\psi_k \tag{37}$$

with

$$G_{ik} = \frac{RT\delta_{ik}}{\bar{r}_i^{(1)}\psi_i} + \frac{RT}{\bar{r}_N^{(1)}\psi_N} + \frac{\partial^2\bar{\bar{G}}^E}{\partial\psi_i\,\partial\psi_K}\,; \qquad i, k = 1, \dots, N-1, \tag{38}$$

where $\delta_{ik} = 1$ if $i = k$ and $\delta_{ik} = 0$ if $i \neq k$, and $\bar{r}_i^{(1)} = r_i$ for $i = 1, \dots, I$, i.e., if i is an individual component. The minimizing procedure leads to

$$\delta\psi_{i,0} = -\delta\psi_1 \frac{D_i'}{D'}\,; \qquad i = 2, \dots, N-1, \tag{39}$$

with an arbitrary value $\delta\psi_1 \neq 0$. The determinant D' is given by

$$D' = \begin{vmatrix} G_{22} & G_{23} & \cdots & G_{2,N-1} \\ G_{32} & G_{33} & \cdots & G_{3,N-1} \\ \vdots & \vdots & & \vdots \\ G_{N-1,2} & G_{N-1,3} & \cdots & G_{N-1,N-1} \end{vmatrix} \neq 0, \tag{40}$$

and the determinant D_i' results from D' by replacing the elements G_{ki} by G_{k1} $(k = 2, \dots, N-1)$.

From Eqs. (37) and (40), the stability criterion Eq. (7) results in the statement: "The homogeneous mixture is stable or metastable if the determinant

$$D = \begin{vmatrix} G_{11} & G_{12} & \cdots & G_{1,N-1} \\ G_{21} & G_{22} & \cdots & G_{2,N-1} \\ \vdots & \vdots & & \vdots \\ G_{N-1,1} & G_{N-1,2} & \cdots & G_{N-1,N-1} \end{vmatrix} \tag{41}$$

is positive with all principal minors." This is equivalent to the conditions

$$G_{11} > 0, \quad G_{11}G_{22} - G_{12}^2 > 0, \quad \ldots, \quad D > 0. \tag{42}$$

The criterion for the limit of instability (spinodal) reads

$$D = 0 \tag{43}$$

Equations (37) and (41)-(43) look very similar to Eqs. (2)-(5). But in Eqs. (2)-(5) the quantities G_{ik} are given by $G_{ik} = \partial^2\bar{\bar{G}}/\partial\psi_i\,\partial\psi_K = RT\delta_{ik}/r_i\psi_i + RT/r_N\psi_N + \partial^2\bar{\bar{G}}^E/\partial\psi_i\partial\psi_k$, where i and k indicate solvents or *discrete polymer species.* In contrast, in Eqs. (37) and (39)-(43), G_{ik} is defined by Eq. (38), i.e., the indices i and k refer to solvents or to *total polymer ensembles*; and for such ensembles, the mass average $\bar{r}_i^{(1)}$ of the total ensemble occurs in G_{ik}, instead of the segment number r_i of an individual species.

To discuss the critical state, we first apply Eq. (36) to Eqs. (34) and (35). Eliminating $\delta\psi_N$, the result reads

$$\delta^3\bar{\bar{G}} = \sum_{i=1}^{N-1}\sum_{k=1}^{N-1}\sum_{m=1}^{N-1} G_{ikm}\,\delta\psi_i\delta\psi_k\delta\psi_m, \tag{44}$$

$$\delta^4\bar{\bar{G}} = \sum_{i=1}^{N-1}\sum_{k=1}^{N-1}\sum_{m=1}^{N-1}\sum_{n=1}^{N-1} G_{ikmn}\,\delta\psi_i\delta\psi_k\delta\psi_m\delta\psi_n, \tag{45}$$

with

$$G_{ikm} = -\frac{RT\bar{r}_i^{(2)}\delta_{ik}\delta_{km}}{[\bar{r}_i^{(1)}]^3\psi_i^2} + \frac{RT\bar{r}_N^{(2)}}{[\bar{r}_N^{(1)}]^3\psi_N^2} + \frac{\partial^3\bar{\bar{G}}^E}{\partial\psi_i\partial\psi_k\partial\Psi_m};$$

$$i, k, m = 1, \ldots, N-1, \tag{46}$$

$$G_{ikmn} = \frac{2RT\bar{r}_i^{(3)}\delta_{ik}\delta_{km}\delta_{mn}}{[\bar{r}_i^{(1)}]^4\psi_i^3} + \frac{2RT\bar{r}_N^{(3)}}{[\bar{r}_N^{(1)}]^4\psi_N^3} + \frac{\partial^4\bar{\bar{G}}^E}{\partial\psi_i\partial\psi_k\partial\psi_m\partial\psi_n};$$

$$i, k, m, n = 1, \ldots, N-1, \tag{47}$$

where for $i = 1, \ldots, I$, i.e., for individual components, $\bar{r}_i^{(j)} = r_i^j$ leading to $\bar{r}_i^{(2)}/[\bar{r}_i^{(1)}]^3 = 1/r_i$ and to $\bar{r}_i^{(3)}/[\bar{r}_i^{(1)}]^4 = 1/r_i$. Applying Eq. (39) with the additional definition $D_1' = -D'$, the necessary criterion Eq. (8) for the critical state results in (assuming $p = 4$)

$$\sum_{i=1}^{N-1}\sum_{k=1}^{N-1} G_{ik}D_i'D_k' = 0, \tag{48}$$

$$\sum_{i=1}^{N-1}\sum_{k=1}^{N-1}\sum_{m=1}^{N-1} G_{ikm}D_i'D_k'D_m' = 0, \tag{49}$$

$$\sum_{i=1}^{N-1}\sum_{k=1}^{N-1}\sum_{m=1}^{N-1}\sum_{n=1}^{N-1} G_{ikmn}D_i'D_k'D_m'D_n' > 0. \tag{50}$$

Equation (48) is the relation for the spinodal and equivalent to Eq. (43). Also, Eq. (49) may be rewritten in the form of a determinant criterion:

$$\begin{vmatrix} D_1 & D_2 & \cdots & D_{N-1} \\ G_{21} & G_{22} & \cdots & G_{2,N-1} \\ \vdots & \vdots & & \vdots \\ G_{N-1,1} & G_{N-1,2} & \cdots & G_{N-1,N-1} \end{vmatrix} = 0 \tag{51}$$

This determinant results from the determinant D as defined by Eq. (41) by replacing the first line (or an arbitrary other line) by the quantities D_1, $\ldots, D_{N-1}$. These quantities are obtained from the determinant D by "extended" differentiation with respect to $\psi_1, \ldots, \psi_{N-1}$, respectively, accounting for the relation $\psi_N = 1 - (\psi_1 + \cdots + \psi_{N-1})$. The word "extended" means: When differentiating an element G_{ik} as defined by Eq. (38), in the first two terms, in addition to the differentiation with respect to ψ_i, the factors $1/\bar{r}_i^{(1)}$ and $1/\bar{r}_N^{(1)}$ are to be replaced by $\bar{r}_i^{(2)}/[\bar{r}_i^{(1)}]^3$ and $\bar{r}_N^{(2)}/[\bar{r}_N^{(1)}]^3$. Hence, "extended" differentiation of an element G_{ik} with respect to ψ_m yields G_{ikm} with $m = 1, \ldots, N-1$.

Of course, the "extension" is not relevant for individual components for which the discussed factors are identical. If only individual components are present, the "extension" becomes meaningless as then $D_i = \partial D/\partial\psi_i$; $i = 1, \ldots, N-1$ and Eq. (51) becomes identical with the well-known criterion dating back to Gibbs [15].

In a forthcoming paper the generalization of the treatment presented to more sophisticated $\overline{\overline{G}}^E$ expressions which depend additionally on the distribution function(s) will be discussed.

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