Degenerate Critical States for Polydisperse Polymer Solutions

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ABSTRACT

If, in a spinodal point, the rank of the stability matrix is less than the order of this matrix minus one, then Gibbs' determinant criterion for the critical state loses its importance since it is fulfilled automatically by the spinodal condition. In this paper a generalized critical state criterion is established for such degenerate cases in polydisperse polymer solutions.

INTRODUCTION

To calculate critical states for multicomponent systems, more than a hundred years ago Gibbs [1] established the well-known necessary criterion

$$D = \text{positive semidefinite}; \quad |D| = \det D = 0; \quad |D_1| = 0. \tag{1}$$

In Eq. (1), D is the matrix of the second-order partial derivatives of the molar Gibbs free energy G with respect to the independent mole fractions X_i

$(i = 1, \ldots, N)$ of the $(N + 1)$-component system under consideration. The matrix D_1 is obtained from D by substituting $\partial |D|/\partial X_i$ for the elements of the first, or of an arbitrary other, row.

But only as recently as 1985 Solc and Koningsveld [2] pointed out that Eq. (1) has to be completed by the requirement that only those rows of the matrix D that possess at least one element with a cofactor different from zero are used for the substitution. This requirement immediately leads to the question of which critical state criterion has to be applied if no row of the matrix D has the mentioned property, i.e., if together with $|D|$ also all of its $(N - 1)$-rowed minors equal zero.

In an earlier paper [3] the present authors treated a more general problem resulting in the statement: If, besides $|D|$, also all of its $(N - i)$-rowed minors $(i = 0, \ldots, m - 1 < N)$ equal zero and if at least one of its $(N - m)$-rowed minors differs from zero (i.e., if rank $D = N - m$), then in a (stable) critical state all determinants D_{ijp} $(0 \leqslant i \leqslant j \leqslant p \leqslant m)$ equal zero. These determinants D_{ijp} possess $N - m + 1$ rows and are calculated as described in the cited paper [3]. If $m = 1$, then this statement is equal to the classical Gibbs criterion in the refined version of Solc and Koningsveld [2].

A critical state with rank $D < N - 1$ shall be named "degenerate." With increasing number $(N + 1)$ of components the order of the determinants becomes larger and the calculation of degenerate critical states $(T_c, X_{1c}, \ldots, X_{NC})$ becomes much more difficult. (For polydisperse polymer solutions, N may equal 1000 or 2000.) The problem is that, in such a degenerate critical point, all $(N - i)$-rowed minors $(i = 0, \ldots, m - 1)$ of $|D|$ and all D_{ijp} $(0 \leqslant i \leqslant j \leqslant p \leqslant m)$ equal zero simultaneously, whereas the computer calculates values different from zero due to its limited number of digits, and the problem gets worse with increasing N.

Therefore, the question is treated in this paper whether it is possible to derive simpler criteria for degenerate critical states by assuming the moment-dependent Gibbs free energy relation for polydisperse polymer solutions considered by Irvine and Gordon [4]. This relation generalizes the original Flory-Huggins function so as to embrace most functions of practical use in polymer thermodynamics. On the assumption of this relation, criteria for regular (i.e., nondegenerate) critical states are known [4, 5].

The development will be performed by applying the concept of continuous thermodynamics [6. 7]. For the results obtained, the transition to traditional notation is immediately possible by writing all occurring moments as finite sums.

PROBLEM

Considering a polydisperse polymer solution the nonlinear part $\Delta \bar{\bar{G}}$ of the Gibbs free energy per mole of segments depends on the segment fraction $\bar{\bar{X}}_A$ of the solvent A, the overall segment fraction $\bar{\bar{X}}_B$ of the polydisperse polymer B and on its (normalized) segment-molar distribution density function $\bar{\bar{W}}_B(M)$:

$$\frac{\Delta \bar{\bar{G}}}{RT} = \frac{\bar{\bar{X}}_A \ln \bar{\bar{X}}_A}{r_A} + \int \frac{\bar{\bar{X}}_B \bar{\bar{W}}_B(M) \ln \bar{\bar{X}}_B \bar{\bar{W}}_B(M)}{r_B(M)} \, dM + \Gamma. \tag{2}$$

Here $\bar{\bar{X}}_A + \bar{\bar{X}}_B = 1$; $\int \bar{\bar{W}}_B(M) \, dM = 1$. The quantities $r_A > 0$, $r_B(M) > 0$ are the segment numbers of the solvent molecules and of the polymer species identified by the molecular weight M with $M_0 \leqslant M \leqslant M^0$. The integrals are generally to be taken from M_0 to M^0. Equation (2) generalizes the classical Flory-Huggins expression [8, 9], assuming Γ to depend on some moments $\bar{r}_B{}^i = \int [r_B(M)]^{k_i} \bar{\bar{X}}_B \bar{\bar{W}}_B(M) \, dM$: $\Gamma = \Gamma(T, P, \bar{r}_B{}^1, \ldots, \bar{r}_B{}^0)$. These moments also include the zeroth moment, i.e., the number $k_s = 0$ is also among the different real numbers k_i $(i = 1, \ldots, n)$.

The necessary conditions for the spinodal and for the critical state can be expressed in the framework of continuous thermodynamics as follows [10]:

If the system is located on the spinodal, then

$$\delta^2 (\Delta \bar{\bar{G}}/RT) \geqslant 0 \text{ for all variations } \delta(\bar{\bar{X}}_B \bar{\bar{W}}_B) \tag{3a}$$

and

there exists a variation $\delta(\bar{\bar{X}}_B \bar{\bar{W}}_B)_0 \neq 0$ leading to $\delta^2(\Delta \bar{\bar{G}}/RT)_0 = 0$ (3b)

If the system is in a (stable) critical state, then Eqs. (3a,b) are valid, and

$$\delta^3 (\Delta \bar{\bar{G}}/RT)_0 = 0 \text{ for all variations } \delta(\bar{\bar{X}}_B \bar{\bar{W}}_B)_0 \text{ obeying Eq. (3b).} \tag{4}$$

Here $\delta^k(\Delta \bar{\bar{G}}/RT)$ is the kth variation of $\Delta \bar{\bar{G}}/RT$:

$$\delta^k(\Delta \bar{\bar{G}}/RT) = \frac{1}{RT} \, \delta^k \Delta \bar{\bar{G}}(T, P; \bar{\bar{X}}_B \bar{\bar{W}}_B, \delta(\bar{\bar{X}}_B \bar{\bar{W}}_B))$$

$$= \frac{d^k \Delta \bar{\bar{G}}(T, P; \bar{\bar{X}}_B \bar{\bar{W}}_B + t\delta(\bar{\bar{X}}_B \bar{\bar{W}}_B))}{RT dt^k} \Bigg|_{t=0}, \tag{5}$$

and $\delta(\bar{\bar{X}}_B \bar{\bar{W}}_B)$ is a random variation of the nonnormalized distribution density function $\bar{X}_B \bar{W}_B(M)$. The index 0 at $\delta^k(\Delta\bar{G}/RT)$ indicates that this variation in Eq. (5) obeys Eq. (3b). Furthermore, in Eq. (5) $\bar{X}_A = 1 - \bar{\bar{X}}_B = 1 - \bar{r}_B{}^s$ was used. Equations (2) and (5) result in

$$\delta^2\left(\frac{\Delta\bar{\bar{G}}}{RT}\right) = \int \frac{[\delta(\bar{\bar{X}}_B \bar{\bar{W}}_B(M))]^2}{r_B(M)\bar{\bar{X}}_B \bar{\bar{W}}_B(M)}\, dM + \sum_{i,j=1}^{n} c_{ij} y_i y_j, \tag{6}$$

$$\delta^3\left(\frac{\Delta\bar{\bar{G}}}{RT}\right) = -\int \frac{[\delta(\bar{\bar{X}}_B \bar{\bar{W}}_B(M))]^3}{r_B(M)[\bar{\bar{X}}_B \bar{\bar{W}}_B(M)]^2}\, dM + \sum_{i,j,p=1}^{n} c_{ijp} y_i y_j y_p, \tag{7}$$

with

$$y_i = \int [r_B(M)]^{k_i}\delta(\bar{\bar{X}}_B \bar{\bar{W}}_B(M)) dM, \tag{8}$$

and

$$c_{ij} = \frac{\partial^2 \Gamma}{\partial\bar{r}_B{}^i \partial\bar{r}_B{}^j} + \frac{\delta_{is}\,\delta_{js}}{r_A \bar{\bar{X}}_A}, \qquad c_{ijp} = \frac{\partial^3 \Gamma}{\partial\bar{r}_B{}^i \partial\bar{r}_B{}^j \partial\bar{r}_B{}^p} + \frac{\delta_{is}\delta_{js}\delta_{ps}}{r_A \bar{\bar{X}}_A{}^2}. \tag{8a}$$

Introducing the abbreviations

$$r_{ij} = \int [r_B(M)]^{k_i+k_j+1}\, \bar{\bar{X}}_B \bar{\bar{W}}_B(M) dM;$$

$$r_{ijp} = \int [r_B(M)]^{k_i+k_j+k_p+2}\, \bar{\bar{X}}_B \bar{\bar{W}}_B(M) dM, \tag{8b}$$

the matrices $\bar{R}$ with elements r_{ij}, C with elements c_{ij}, and Q with elements $q_{ij} = \hat{r}_{ij} + c_{ij}$ ($\hat{r}_{ij}$ are the elements of the matrix $\bar{R}^{-1}$ inverse to $\bar{R}$), and a generalized differentiation $D../D..$ by

$$\frac{Dq_{ij}}{D\bar{r}_B{}^p} = -\sum_{a,\beta,\gamma=1}^{n} r_{a\beta\gamma}\hat{r}_{ai}\hat{r}_{\beta j}\hat{r}_{\gamma p} + c_{ijp} = q_{ijp}. \tag{9}$$

it was shown earlier [11]: If $r_B(M)$ possesses at least n different values and if rank $Q = n - 1$ for the thermodynamic state considered, which is identified by $(T,P;\bar{\bar{X}}_B \bar{\bar{W}}_B)$, then the statements of Eqs. (3a), (3b), and (4) are equivalent to

$$Q = \text{positive semidefinite}; \quad |Q| = 0; \quad |Q_1| = 0. \tag{10}$$

Here Q_1 is the matrix obtained from Q by substituting $D|Q|/D\bar{r}_B^i$ for an appropriate row, i.e., a row possessing at least one element with a cofactor different from zero.

Thus, the problem becomes: Which conditions have to be substituted for Eq. (10) to make this statement valid also for rank $Q = n - m$ with $1 < m \leqq n$?

In this case a rearrangement of the variables of $\Delta \tilde{\tilde{G}}$ is always possible such that the $(n - m)$-rowed determinant $\tilde{Q}$ formed by the elements of the lower right-hand-side corner of Q can be assumed to be different from zero without restricting the generality:

$$\tilde{Q} = \begin{vmatrix} q_{m+1,m+1} & \cdots & q_{mn} \\ -----&-----&- \\ q_{n,m+1} & \cdots & q_{nn} \end{vmatrix} \neq 0 \quad (m < n). \tag{11}$$

GENERALIZED CRITERION FOR CRITICAL STATES

For a concise formulation, the symbols $Q_{\tau\zeta}$ and $Q_{\tau\zeta\eta}$ are introduced to designate the following determinants derived from Q:

$$Q_{\tau\zeta} = \begin{vmatrix} q_{\tau\zeta} & q_{\tau,m+1} & \cdots & q_{\tau n} \\ q_{m+1,\zeta} & q_{m+1,m+1} & \cdots & q_{m+1,n} \\ -&-&-&- \\ q_{n\zeta} & q_{n,m+1} & \cdots & q_{nn} \end{vmatrix} ,$$

$$Q_{\tau\zeta\eta} = \begin{vmatrix} u_{\tau\zeta\eta} & u_{\tau\zeta,m+1} & \cdots & u_{\tau\zeta n} \\ q_{m+1,\eta} & q_{m+1,m+1} & \cdots & q_{m+1,n} \\ -&-&-&- \\ q_{n\eta} & q_{n,m+1} & \cdots & q_{nn} \end{vmatrix} .$$

with $u_{\tau\zeta\rho} = DQ_{\tau\zeta}/D\bar{r}_B^p$ $(\tau, \zeta, \eta = 1, \ldots, m; p = 1, \ldots, n)$. Then the following criterion holds:

If $r_B(M)$ possesses at least n different values, then for a thermodynamic state identified by $(T,P;\bar{\bar{X}}_B \bar{W}_B)$, the statements of Eqs. (3a), (3b), and (4) are equivalent to:

$$Q = \text{positive semidefinite.} \tag{12}$$

There exists such a natural number m $(1 \leqslant m \leqslant n)$ that

$$\text{rank } Q = n - m, \tag{13}$$

$$Q_{ijp} = 0 \text{ for all } 1 \leqslant i \leqslant j \leqslant p \leqslant m. \tag{14}$$

As pointed out earlier [11], Eqs. (12) and (13) are equivalent to Eqs. (3a) and (3b). Hence, only the equivalence with respect to Eq. (4) has to be shown in this paper. Assuming Eq. (3a), the variation $\delta(\bar{\bar{X}}_B \bar{W}_B)_0$ fulfills Eq. (3b) if and only if

$$\delta(\bar{\bar{X}}_B \bar{W}_B)_0 = -r_B(M)\bar{\bar{X}}_B \bar{W}_B(M) \sum_{i,j=1}^{n} [r_B(M)]^{k_i} y_j, \tag{15}$$

where the vector $y = (y_1, \ldots, y_n)^T$ obeys the relation $Qy = 0$. Introduction of Eq. (15) into Eq. (7) leads to

$$\delta^3 (\Delta\bar{\bar{G}}/RT)_0 = \sum_{i,j,p=1}^{n} d_{ijp} y_i y_j y_p, \tag{16}$$

with

$$d_{ijp} = c_{ijp} + \sum_{a,\beta,\gamma=1}^{n} r_{a\beta\gamma} c_{ia} c_{j\beta} c_{p\gamma}. \tag{17}$$

The second term on the right-hand side of Eq. (17) may be reformulated:

$$\sum_{i,j,p=1}^{n} \sum_{a,\beta,\gamma=1}^{n} r_{a\beta\gamma} c_{ia} c_{j\beta} c_{p\gamma} y_i y_j y_p$$

$$= \sum_{a,\beta,\gamma=1}^{n} r_{a\beta\gamma} \sum_{i=1}^{n} c_{ia}y_i \sum_{j=1}^{n} c_{j\beta}y_j \sum_{p=1}^{n} c_{p\gamma}y_p$$

$$= - \sum_{i,j,p=1}^{n} \sum_{a,\beta,\gamma=1}^{n} r_{a\beta\gamma}\hat{r}_{ia}\hat{r}_{j\beta}\hat{r}_{p\gamma}y_iy_jy_p.$$

The last equality results from $Qy = 0$, i.e., for all $\alpha = 1, \ldots, n$, the relation

$$0 = \sum_{i=1}^{n} q_{ai}y_i = \sum_{i=1}^{n} q_{ia}y_i = \sum_{i=1}^{n} (c_{ia} + r_{ia})y_i$$

applies. Thus, Eq. (16) may be rewritten to read

$$\delta^3(\Delta\bar{\bar{G}}/RT)_0 = \sum_{i,j,p=1}^{n} q_{ijp}y_iy_jy_p, \tag{18}$$

in which

$$q_{ijp} = c_{ijp} - \sum_{a,\beta,\gamma=1}^{n} r_{\epsilon\beta\gamma}\hat{r}_{ia}\hat{r}_{j\beta}\hat{r}_{p\gamma}$$

is symmetrical with respect to all indices.

Since $\tilde{Q} \neq 0$, the vector y is the solution of the equation $Qy = 0$ if and only if

$$y_i = -\frac{1}{\tilde{Q}} \sum_{\tau=1}^{m} \begin{vmatrix} q_{m+1,m+1} & \cdots & q_{m+1,\tau} & \cdots & q_{m+1,n} \\ \text{---------------} \\ q_{n,m+1} & \cdots & q_{n\tau} & \cdots & q_{nn} \end{vmatrix} y_\tau = -\sum_{\tau=1}^{m} \frac{Q_i^{\tau}}{Q} y_{\tau i}$$

$$\tag{19}$$

for $i = m + 1, \ldots, n$. In the determinants Q_i^{τ}, the elements $q_{j\tau}$ are substituted for the elements q_{ji} $(j = m + 1, \ldots, n)$. The quantities y_τ $(\tau = 1, \ldots, m)$ are freely choosable (permitting, in this way, the specification of m linearly independent spinodal directions). Equation (19) may be written more concisely:

$$y_i = -\sum_{\tau=1}^{m} \lambda_i{}^\tau y_\tau; \quad i = 1, \ldots, n, \tag{20}$$

with

$$\lambda_i{}^\tau = \begin{cases} -\delta_{i\tau}, & i = 1, \ldots, m \\ Q_i{}^\tau/\tilde{Q}, & i = m+1, \ldots, n \end{cases} \quad ; \tau = 1, \ldots, m. \tag{21}$$

Equations (18), (20), and (21) result in

$$\delta^3(\Delta\bar{\bar{G}}/RT)_0 = -\sum_{\tau,\varsigma,\eta=1}^{m} \left(\sum_{i,j,p=1}^{n} q_{ijp}\lambda_i{}^\tau\lambda_j{}^\varsigma\lambda_p{}^\eta \right) y_\tau y_\varsigma y_\eta.$$

This expression equals zero for arbitrary y_τ $(\tau = 1, \ldots, m)$ if and only if

$$\sum_{i,j,p=1}^{n} q_{ijp}\lambda_i{}^\tau\lambda_j{}^\varsigma\lambda_p{}^\eta = 0 \text{ for all } \tau, \varsigma, \eta = 1, \ldots, m. \tag{22}$$

The development of $Q_{\tau\varsigma\eta}$ with respect to the first line results in

$$Q_{\tau\varsigma\eta} = u_{\tau\varsigma\eta}\tilde{Q} - \sum_{p=m+1}^{n} u_{\tau\varsigma p}Q_p{}^\eta = -\tilde{Q}\sum_{p=1}^{n} u_{\tau\varsigma p}\lambda_p{}^\eta.$$

After some reformulations, the differentiation rules for determinants lead to

$$u_{\tau\varsigma p} = \tilde{Q}\sum_{i,j=1}^{n} q_{ijp}\lambda_i{}^\tau\lambda_j{}^\varsigma$$

and hence,

$$Q_{\tau\varsigma\eta} = -\tilde{Q}^2\sum_{i,j,p=1}^{n} q_{ijp}\lambda_i{}^\tau\lambda_j{}^\varsigma\lambda_p{}^\eta.$$

Therefore, Eq. (22) is fulfilled if and only if $Q_{\tau\zeta\eta} = 0$ for all $\tau, \zeta, \eta = 1, \ldots, m$. Since $Q_{\tau\zeta\eta}$ is symmetrical with respect to all indices, Eq. (22) and, hence, Eq. (4) are fulfilled if, and only if, Eq. (14) is valid.

DISCUSSION

At first sight there seems to be no essential difference between the criterion stated by Eqs. (12)-(14) and that presented earlier [3]. Also here, $m(m + 1)$ $(m + 2)/6$ additional equations (of the type of Eq. 14) occur, and Eqs. (12)-(14) result in Eq. (10) if $m = 1$. However, the difference is indeed enormous. According to the criterion presented earlier [3], the additional equations contain determinants whose order for polydisperse polymer solutions equals approximately 1000 or 2000. In contrast to this, the determinants occurring in Eqs. (14) are of order one or two since the excess part Γ in Eq. (2)—according to Gibbs free energy relations—may be presumed to contain no more than three moments (usually the zeroth, the minus first, and the first moment corresponding to the overall segment fraction $\bar{\bar{X}}_B$, the number-average and the weight-average segment number). Therefore, the new criterion permits the numerical calculation of degenerate critical states with much lower computational burden and with much higher precision or, in favorable cases, even an analytical evaluation.

A further result of the new criterion is the statement that for a moment-dependent excess part Γ of the Gibbs free energy relation, the number of linearly independent spinodal directions (i.e., of those $\delta(\bar{\bar{X}}_B \bar{W}_B)_0$ resulting in $\delta^2 \Delta\bar{\bar{G}}/RT) = 0$) in a critical point cannot be larger than the number of moments occurring in the Γ-relation.

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