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

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ABSTRACT

A determinant criterion for the critical state in solutions and mixtures of polydisperse polymers is established within the general framework of Gibbs theory. The treatment continues an earlier paper by considering more general Gibbs free energy relations: The function replacing the χ-term in the classic Flory-Huggins equation is permitted to depend on a finite number of moments of the polymer distribution(s) so as to embrace most Gibbs free energy relations of practical use. The new criterion leads to a very large reduction of computer time and of needed storage capacity compared to the traditional Gibbs determinant criterion. Some relations known from the literature are shown to be special cases of the established new criterion.

INTRODUCTION

In a preceding paper [1] the thermodynamic stability of solutions and mixtures of polymers was described by Gibbs free energy functions resulting from the classic Flory-Huggins expression [2, 3] by replacing the χ-term by a function $\bar{\bar{G}}^E$, which is assumed to depend on the temperature T, the pressure P, and the segment fractions ψ_i ($i = 1, \ldots, N$) of the N solvents and polymers ($\Sigma\, \psi_i = 1$; the symbol Σ without limits refers in this paper to from $i = 1$ to $i = N$). In many cases, however, a more detailed description of the thermodynamic behavior will be possible by permitting $\bar{\bar{G}}^E$ to depend additionally on the MW distribution(s) of the polymer(s) present in the system.

In practice, the consideration of some moments with respect to the segment numbers $r_i(M)$ is especially important. Hence, in this paper, the stability conditions are generalized to $\bar{\bar{G}}^E$ functions of the kind

$$\bar{\bar{G}}^E = \tilde{\Gamma}(T,P,\bar{r}_1{}^1, \ldots, \bar{r}_{n_1}{}^1, \ldots, \bar{r}_1{}^N, \ldots, \bar{r}_{n_N}{}^N)RT, \tag{1}$$

with

$$\bar{r}_a{}^i = \int [r_i(M)]^{k_{ia}} \psi_i W_i(M) dM \qquad (i = 1, \ldots, N; a = 1, \ldots, n_i). \tag{2}$$

The conditions are considered in the framework of continuous thermodynamics describing the composition of a polymer by a continuous distribution density function instead of the amounts of the individual species [4, 5]. In this paper a distribution density function $W_i(M)$ is applied that is defined by the statement that $W_i(M)dM$ gives the segment fraction of all i-species with MW between M and $M + dM$ within the polymer i. Hence, $\int W_i(M)dM = 1$. The integrals are always to be extended over the total M-range occurring for Polymer i, from $M_{0,i}$ up to $M^{0,i}$. If i does not designate a polymer but a solvent, then the relation $W_i(M) \equiv (M^{0,i} - M_{0,i})^{-1}$ is to be applied and, of course, $r_i(M) = r_i$ = constant. The quantities k_{ia} are real numbers including the number $k_{i1} = 0$ ($i = 1, \ldots, N$), resulting in $\bar{r}_1{}^i = \psi_i$, and R means the universal gas constant. The number of moments for the polymer i occurring in Eq. (1) is signified by n_i. If $n_i = 1$ ($i = 1, \ldots, N$), then Eq. (1) reduces to the case considered earlier [1]. The functions $r_i(M)$ are presumed to attain at least n_i different values; such segment number functions will be called "nondegenerate" (with respect to the $\bar{\bar{G}}^E$ relation Eq. 1).

According to $\Sigma \bar{r}_1{}^i = 1$, the quantity $\bar{r}_1{}^1 = \psi_1$ may be eliminated in Eq. (1), resulting in

$$\bar{\bar{G}}^E = \Gamma(T,P,\bar{r}_2{}^1, \ldots, \bar{r}_{n_1}{}^1, \ldots, \bar{r}_1{}^N, \ldots, \bar{r}_{n_N}{}^N)RT, \qquad n_1 > 1, \tag{3}$$

$$\bar{\bar{G}}^E = \Gamma(T,P,\bar{r}_1{}^2, \ldots, \bar{r}_{n_2}{}^2, \ldots, \bar{r}_1{}^N, \ldots, \bar{r}_{n_N}{}^N)RT, \qquad n_1 = 1. \tag{3'}$$

The functions Γ and $\tilde{\Gamma}$ are interrelated by

$$\Gamma(T,P,\bar{r}_2{}^1,\ldots,\bar{r}_{n_N}{}^N) = \tilde{\Gamma}(T,P,1-\sum_{i=2}^{N}\bar{r}_1{}^i,\bar{r}_2{}^1,\ldots,\bar{r}_{n_N}{}^N). \tag{4}$$

The Gibbs free energy per mole of segments, $\bar{\bar{G}}$, reads [4, 5]

$$\bar{\bar{G}} = RT\sum\int\frac{\psi_i W_i(M)}{r_i(M)}\ln\,[\psi_i W_i(M)]\,dM + \bar{\bar{G}}^E \tag{5}$$

neglecting terms depending linearly on $\psi_i W_i(M)$ since these terms are immaterial in considering stability. Also here, the transformation to the corresponding formula discussed earlier (Eq. 32 in Ref. 1) is immediately possible by considering the first I components $i = 1, \ldots, I$ as solvents and neglecting additional linear terms.

The following considerations for obtaining a critical state criterion are based on the necessary conditions established earlier [6]. If the thermodynamic system described by $(T,P;\psi W)$ and obeying Eqs. (1)-(5) is located on the limit of instability (spinodal), then

$$\delta^2\bar{\bar{G}}(T,P;\psi W,\delta(\psi W)) \geqslant 0 \qquad \text{for all variations } \delta(\psi W), \tag{6}$$

and there exist such variations $\delta(\psi W)_0 \not\equiv 0$ that

$$\delta^2\bar{\bar{G}}(T,P;\psi W,\delta(\psi W)_0) = 0. \tag{7}$$

If the system mentioned is in a critical state, then additionally

$$\delta^3\bar{\bar{G}}(T,P;\psi W,\delta(\psi W)_0) = 0. \tag{8}$$

Here ψW and $\delta(\psi W)$ designate the N-component vectors $(\psi_1 W_1, \ldots, \psi_N W_N)$ and $(\delta(\psi_1 W_1), \ldots, \delta(\psi_N W_N))$, respectively, where $\sum\int\delta(\psi_i W_i(M))dM = 0$. The variations $\delta^2\bar{\bar{G}}$ and $\delta^3\bar{\bar{G}}$ may be obtained from Eqs. (3)-(5) and read

$$\delta^2(\bar{\bar{G}}/RT) = \sum_{i=1}^{N}\int\frac{[\delta(\psi_i W_i(M))]^2}{r_i(M)\psi_i W_i(M)}\,dM + \sum_{i,j=1}^{N}\sum_{a=1+\delta_{1i}}^{n_i}\sum_{b=1+\delta_{1j}}^{n_j}\frac{\partial^2\Gamma}{\partial\bar{r}_a{}^i\partial\bar{r}_b{}^j}\,y_a{}^i y_b{}^j, \tag{9}$$

$$\delta^3(\bar{\bar{G}}/RT) = -\sum_{i=1}^{N} \int \frac{[\delta(\psi_i W_i(M))]^3}{r_i(M)[\psi_i W_i(M)]^2} dM +$$

$$\sum_{i,j,p=1}^{N} \sum_{a=1+\delta_{1i}}^{n_i} \sum_{b=1+\delta_{1j}}^{n_j} \sum_{c=1+\delta_{1p}}^{n_p} \frac{\partial^3 \Gamma}{\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j \partial \bar{r}_c{}^p} y_a{}^i y_b{}^j y_c{}^p, \tag{10}$$

$$y_a{}^i = \int [r_i(M)]^{k_{ia}} \delta(\psi_i W_i(M)) dM.$$

For $n_1 = 1$, the corresponding sums are omitted ($\delta_{ij} = 1$ if $i = j$ and zero otherwise).

In the next paragraph a determinant criterion for the limit of instability (spinodal equation) is given that is equivalent to Eqs. (6) and (7) but much simpler. This criterion will also be part of the critical state criterion to be stated and proved afterwards. Finally, several equations for the critical state as known from the literature will be shown to be special cases of the new critical state criterion.

STABILITY CRITERION

To formulate the stability criterion, some symbols will be introduced: $\bar{R}^i$ designates the $n_i \times n_i$ matrix with the elements

$$\bar{r}_{ab}{}^i = \int [r_i(M)]^{k_{ia}+k_{ib}+1} \psi_i W_i(M) dM \tag{11}$$

The elements of the matrix inverse to $\bar{R}^i$ are signified by $r_{ab}{}^i$. The symbol Q means a symmetric matrix with $n = \Sigma\, n_i - 1$ lines and columns and the following block structure:

$$Q = \begin{vmatrix} Q^{11} & Q^{12} & \dots & Q^{1N} \\ Q^{21} & Q^{22} & \dots & Q^{2N} \\ - & - & - & - \\ Q^{N1} & Q^{N2} & \dots & Q^{NN} \end{vmatrix} .$$

Here the quantities Q^{ij} are rectangular $(n_i - \delta_{1i}) \times (n_j - \delta_{1j})$ matrices with the elements

$$q_{ab}{}^{ij} = \frac{\partial^2 \Gamma}{\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j} + \delta_{ij}\hat{r}_{ab}{}^i + \delta_{a1}\delta_{1b}\hat{r}_{11}{}^1 - \delta_{1j}\delta_{a1}\hat{r}_{1b}{}^1 - \delta_{i1}\delta_{1b}\hat{r}_{a1}{}^1,$$
$$i, j = 1, \ldots, N; a = 1 + \delta_{1i}, \ldots, n_i; b = 1 + \delta_{1j}, \ldots, n_j. \tag{12}$$

For $n_1 = 1$, the first block line and the first block column of Q are omitted. Then, as shown earlier [7], the following theorem is valid.

Stability Criterion. If the functions $r_i(M)$ $(i = 1, \ldots, N)$ are nondegenerate, then Eqs. (6) and (7) are equivalent to

$$Q = \text{positive semidefinite}, \tag{6'}$$

$$|Q| = 0 \quad \text{(spinodal equation)}. \tag{7'}$$

Here $|Q|$ is the determinant of the matrix Q. Equation (7′) is equivalent to spinodal equations referring to the nonreduced problem as established by Eqs. (1), (2), and (5):

$$|\tilde{I} + \tilde{R}\tilde{C}| = 0 \quad \text{or} \quad |\tilde{R}^{-1} + \tilde{C}| = 0.$$

Here $\tilde{I}, \tilde{R}, \tilde{C}$ are $(n + 2) \times (n + 2)$ matrixes, where $\tilde{I}$ means the unit matrix and $\tilde{R}$ and $\tilde{C}$ are defined by

$$\tilde{R} = \begin{vmatrix} 1 & & & & \\ & \bar{R}^1 & & & 0 \\ & & \bar{R}^2 & & \\ 0 & & & \ddots & \\ & & & & \bar{R}^N \end{vmatrix}, \quad \tilde{C} = \begin{vmatrix} -1 & (\tilde{C}^1)^T & (\tilde{C}^2)^T & \ldots & (\tilde{C}^N)^T \\ \tilde{C}^1 & \tilde{C}^{11} & \tilde{C}^{12} & \ldots & \tilde{C}^{1N} \\ \tilde{C}^2 & \tilde{C}^{21} & \tilde{C}^{22} & \ldots & \tilde{C}^{2N} \\ - & - & - & - & - \\ \tilde{C}^N & \tilde{C}^{N1} & \tilde{C}^{N2} & \ldots & \tilde{C}^{NN} \end{vmatrix}.$$

The symbols $\tilde{C}^i$ and $\tilde{C}_{ab}{}^{ij}$ are given by $\tilde{C}^i = (1, 0, \ldots, 0)^T \in R^{n_i}$ and $\tilde{C}_{ab}{}^{ij} = \partial^2\tilde{\Gamma}/\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j$ $(a = 1, \ldots, n_i; b = 1, \ldots, n_j)$. It has to be pointed out that the condition of definity, Eq. (6′), is to be verified with respect to Q and not to $\tilde{Q} = \tilde{R}^{-1} + \tilde{C}$.

CRITICAL STATE CRITERION

Similarly as in the classic treatment dating back to Gibbs [8], a determinant $|Q_1|$ is introduced being derived from $|Q|$ according to $(n_1 > 2)$:

$$Q_1 = \begin{vmatrix} t^1 & t^2 & \cdots & t^N \\ Q_-^{11} & Q_-^{12} & \cdots & Q_-^{1N} \\ Q^{21} & Q^{22} & \cdots & Q^{2N} \\ - & - & - & - \\ Q^{N1} & Q^{N2} & \cdots & Q^{NN} \end{vmatrix} . \tag{13}$$

In this paper, matrices resulting from Q or Q^{ij} by neglecting the line a and the column b will be designated by $Q(a,b)$ or $Q^{ij}(a,b)$, respectively. Especially the abbreviation $Q_-^{ij} = Q^{ij}(1,-)$, $(j = 1, \ldots, N)$ is applied, The line vectors t^i are defined by

$$t^1 = \left(\frac{D|Q|}{D\bar{r}_2{}^1}, \ldots, \frac{D|Q|}{D\bar{r}_{n_1}{}^1}\right),$$

$$t^i = \left(\frac{D|Q|}{D\bar{r}_1{}^i}, \ldots, \frac{D|Q|}{D\bar{r}_{n_1}{}^i}\right) \quad (i = 2, \ldots, N).$$

The derivatives $D\ldots/D\ldots$ of a determinant obey the well-known rules for partial differentiation with the distinction that

$$\frac{Dq_{bc}{}^{jp}}{D\bar{r}_a{}^i} = \frac{\partial^3 \Gamma}{\partial\bar{r}_a{}^i \partial\bar{r}_b{}^j \partial\bar{r}_c{}^p} - \delta_{ij}\delta_{ip} \sum_{d,e,f=1}^{n_i} \bar{r}^i_{def}\hat{r}_{ad}{}^i\hat{r}_{be}{}^i\hat{r}_{cf}{}^j + (\delta_{1i}\delta_{1b}\delta_{1p}$$

$$+ \delta_{1i}\delta_{1j}\delta_{1c} + \delta_{1a}\delta_{1j}\delta_{1p} - \delta_{1i}\delta_{1b}\delta_{1c} - \delta_{1a}\delta_{1b}\delta_{1p} - \delta_{1a}\delta_{1j}\delta_{1c}$$

$$+ \delta_{1a}\delta_{1b}\delta_{1c}) \sum_{d,e,f=1}^{n_1} \bar{r}^1_{def}\hat{r}_{ad}{}^1\hat{r}_{be}{}^1\hat{r}_{cf}{}^1 \qquad (a = 1 + \delta_{1i}, \ldots, n_i;$$

$$b = 1 + \delta_{1j}, \ldots, n_j; c = 1 + \delta_{1p}, \ldots, n_p), \tag{14}$$

with

$$\bar{r}^i_{def} = \int [r_i(M)]^{k_{id}+k_{ie}+k_{if}+2}\, \psi_i W_i(M)dM.$$

Using these symbols, the following necessary condition for the critical state will be proved.

Critical State Criterion. If the functions $r_i(M)$ $(i = 1, \ldots, N)$ are nondegenerate and if $|Q(1,1)| \neq 0$, then Eqs. (6)-(8) are equivalent to Eqs. (6′)-(8′) with

$$|Q_1| = 0 \qquad \text{(critical state equation).} \tag{8′}$$

Proof. The significance of the regularity condition $|Q(1,1)| \neq 0$ is discussed in Refs. 9 and 10. Since, as mentioned in the preceding paragraph, the equivalence of Eqs. (6) and (7) and of Eqs. (6′) and (7′) has been shown earlier, the task is to prove, on this assumption, the equivalence of Eqs. (8) and (8′). To this end, the following matrix is introduced:

$$\tilde{Q}_1 = \begin{vmatrix} 0 & 1 & 0 & \ldots & 0 & \ldots & 1 & 0 & \ldots & 0 \\ 1 & \tilde{q}_{11}{}^{11} & \tilde{q}_{12}{}^{11} & \ldots & \tilde{q}^{11}_{1n_1} & \ldots & \tilde{q}_{11}{}^{1N} & \tilde{q}_{12}{}^{1N} & \ldots & \tilde{q}^{1N}_{1n_N} \\ 0 & \tilde{t}_1{}^1 & \tilde{t}_2{}^1 & \ldots & \tilde{t}_{n_1}{}^1 & \ldots & \tilde{t}_1{}^N & \tilde{t}_2{}^N & \ldots & \tilde{t}_{n_N}{}^N \\ 0 & \tilde{q}_{31}{}^{11} & \tilde{q}_{32}{}^{11} & \ldots & \tilde{q}^{11}_{3n_1} & \ldots & \tilde{q}_{31}{}^{1N} & \tilde{q}_{32}{}^{1N} & \ldots & \tilde{q}^{1N}_{3n_N} \\ & & \ldots & & & \ldots & & \ldots & & \\ 0 & \tilde{q}^{11}_{n_11} & \tilde{q}^{11}_{n_12} & \ldots & \tilde{q}^{11}_{n_1n_1} & \ldots & \tilde{q}^{1N}_{n_11} & \tilde{q}^{1N}_{n_12} & \ldots & \tilde{q}^{1N}_{n_1n_1} \\ \tilde{C}^2 & & \tilde{Q}^{21} & & \ldots & & & & \tilde{Q}^{2N} & \\ \ldots & & \ldots & & \ldots & & & & \ldots & \\ \tilde{C}^N & & \tilde{Q}^{N1} & & \ldots & & & & \tilde{Q}^{NN} & \end{vmatrix}. \tag{15}$$

The matrix $\widetilde{Q}_1$ is obtained from $\widetilde{Q}$ by replacing the elements $\widetilde{q}_{2b}{}^{1j}$ by $\widetilde{t}_b{}^j = D|\widetilde{Q}|/D\bar{r}_b{}^j$ ($j = 1, \ldots, N; b = 1, \ldots, n_j$) accounting, however, for the special relation to be applied here:

$$\frac{\partial \widetilde{q}_{bc}{}^{jp}}{\partial \bar{r}_a{}^i} = \widetilde{q}_{abc}^{ijp} = \frac{\partial^3 \widetilde{\Gamma}}{\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j \partial \bar{r}_c{}^p} - \delta_{ij}\delta_{ip} \sum_{d,e,f=1}^{n_i} \bar{r}^i_{def}\, \hat{r}_{ad}{}^i \hat{r}_{be}{}^i \hat{r}_{cf}{}^j. \tag{16}$$

By subtracting in $|\widetilde{Q}(3,3)|$, successively, the second column from the other $N - 1$ columns possessing the number 1 in the first line, and then the second line from the other $N - 1$ lines possessing the number 1 in the first column, it may easily be shown that $|Q(1,1)| = -|\widetilde{Q}(3,3)|$, resulting in $|\widetilde{Q}(3,3)| \neq 0$.

Now, the proof will be performed in two steps. Assuming the validity of Eqs. (6) and (7) or Eqs. (6′) and (7′), it will be shown 1) that Eq. (8) is equvalent to $|\widetilde{Q}_1| = 0$ and 2) that $|\widetilde{Q}_1| = 0$ is equivalent to $|Q_1| = 0$.

According to Eqs. (6) and (7), the variations $\delta(\psi W)_0$ fulfill the minimum condition

$$\min \delta^2 \bar{\bar{G}}(T,P;\psi W,\delta(\psi W)) = \delta^2 \bar{\bar{G}}(T,P;\psi W,\delta(\psi W)_0) = 0. \tag{17}$$

The minimum has to be taken over all variations obeying $\Sigma \int \delta(\psi_i W_i(M))dM = 0$. Applying Lagrange's method of undetermined multipliers, it was shown earlier [7] that $\delta(\psi W)_0$ fulfills Eq. (17) if and only if

$$\frac{\delta(\psi_i W_i)_0}{r_i W_i} = -\sum_{j=0}^{N} \sum_{a=1}^{n_i} \sum_{b=1}^{n_j} \frac{\partial^2 \widetilde{\Gamma}}{\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j} [r_i(M)]^{k_{ia}} \widetilde{y}_b{}^j. \tag{18}$$

Here $\widetilde{y} = (\widetilde{y}_1{}^0, \widetilde{y}_1{}^1, \ldots, \widetilde{y}_{n_1}{}^1, \ldots, \widetilde{y}_1{}^N, \ldots, \widetilde{y}_{n_N}{}^N)^T$ is the solution of the linear system of equations $\widetilde{Q}\widetilde{y} = 0$, and $n_0 = 1$. Due to the specific structure of the matrix $\widetilde{Q}$ (see preceding paragraph), Eq. (18) may be simplified to read

$$\frac{\delta(\psi_i W_i)_0}{r_i W_i} = \sum_{a=1}^{n_i} \sum_{b=1}^{n_i} \hat{r}_{ab}{}^i \widetilde{y}_b{}^i [r_i(M)]^{k_{ia}}.$$

In this way $\delta^3(\bar{\bar{G}}/RT)_0 = \delta^3 \bar{\bar{G}}(T,P;\psi W,\delta(\psi W)_0)/RT$ is written

$$\delta^3(\bar{\bar{G}}/RT)_0 = -\sum_{i=1}^{N} \sum_{a,b,c=1}^{n_i} \sum_{d,e,f=1}^{n_i} \bar{r}^i_{def} \hat{r}_{ad}{}^i \hat{r}_{be}{}^i \hat{r}_{cf}{}^i \tilde{y}_a{}^i \tilde{y}_b{}^i \tilde{y}_c{}^i +$$

$$\sum_{i,j,p=1}^{N} \sum_{a=1}^{n_i} \sum_{b=1}^{n_j} \sum_{c=1}^{n_p} \frac{\partial^3 \tilde{\Gamma}}{\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j \partial \bar{r}_c{}^p} \tilde{y}_a{}^i \tilde{y}_b{}^j \tilde{y}_c{}^p .$$

or, applying the symbol introduced by Eq. (16),

$$\delta^3(\bar{\bar{G}}/RT)_0 = \sum_{i,j,p=1}^{N} \sum_{a=1}^{n_i} \sum_{b=1}^{n_j} \sum_{c=1}^{n_p} \tilde{q}^{ijp}_{abc} \tilde{y}_a{}^i \tilde{y}_b{}^j \tilde{y}_c{}^p . \tag{19}$$

According to $|\tilde{Q}| = 0$ (spinodal equation in nonreduced form) and $|\tilde{Q}(3,3)| \neq 0$, the solutions of the system of linear equations $\tilde{Q}\tilde{y} = 0$ by using Cramer's rule becomes

$$\tilde{y}_a{}^i = -\tilde{y}_2{}^1 \frac{|\tilde{Q}_a{}^i(3,3)|}{|\tilde{Q}(3,3)|} \qquad (i = 1, \ldots, N; a = 1, \ldots, n_i). \tag{20}$$

Here $\tilde{Q}_a{}^i$ signifies a matrix obtained from $\tilde{Q}$ by replacing the column a in $\tilde{Q}^{ki}$ by the second column from $\tilde{Q}^{k1}$ ($k = 0, \ldots, N$) and applying $|\tilde{Q}_2{}^1(3,3)| = -|\tilde{Q}(3,3)|$. In Eq. (20), $\tilde{y}_2{}^1$ is an arbitrary real number. Combination of Eqs. (19) and (20) results in the statement: The relation $\delta^3(\bar{\bar{G}}/RT)_0 = 0$ is fulfilled if and only if

$$\sum_{i,j,p=1}^{N} \sum_{a=1}^{n_i} \sum_{b=1}^{n_j} \sum_{c=1}^{n_p} \tilde{q}^{ijp}_{abc} |\tilde{Q}_a{}^i(3,3)|\,|\tilde{Q}_b{}^j(3,3)|\,|\tilde{Q}_c{}^p(3,3)| = 0. \tag{21}$$

To conclude the first step of the proof, $|\tilde{Q}_1|$ is developed with respect to the third line according to Laplace's theorem

$$|\tilde{Q}_1| = -\sum_{i=1}^{N}\sum_{a=1}^{n_i} \frac{D|\tilde{Q}|}{D\bar{r}_a^{\,i}}\; |\tilde{Q}_a{}^i(3,3)|. \tag{22}$$

Introducing $n_{a\beta} = n_0 + n_1 + \cdots + n_{a-1} + \beta$, the relation

$$\frac{D|\tilde{Q}|}{D\bar{r}_a^{\,i}} = \sum_{j=1}^{N}\sum_{b=1}^{n_j}\sum_{p=1}^{N}\sum_{c=1}^{n_p} \frac{D\tilde{q}_{bc}{}^{jp}}{D\bar{r}_a^{\,i}}\; |\tilde{Q}(n_{pc}, n_{jb})|(-1)^{n_{pc}+n_{jb}} \tag{23}$$

is valid. Since, according to the assumptions, the third line of $\tilde{Q}$ is a linear combination of the others and since $\tilde{Q}$ is symmetric, there exist quantities $\tilde{\gamma}_d{}^\nu$ fulfilling the relation

$$\tilde{q}_{2a}{}^{1i} = \sum_{\substack{\nu=0 \\ |\nu-1|+|d-2|\neq 0}}^{N}\sum_{d=1}^{n_\nu} \tilde{\gamma}_d{}^\nu \tilde{q}_{ad}{}^{\nu i} = \sum_{\substack{\nu=0 \\ |\nu-1|+|d-2|\neq 0}}^{N}\sum_{d=1}^{n_\nu} \tilde{\gamma}_d{}^\nu \tilde{q}_{ad}{}^{i\nu} = \tilde{q}_{a2}{}^{i1}. \tag{24}$$

Replacing the elements $\tilde{q}_{2a}{}^{1i}$ in $|\tilde{Q}(n_{pc}, n_{jb})|(|p-1| + |c-2| \neq 0)$ according to Eq. (24), results in a sum of determinants which, for $|\nu - p| + |d - c| \neq 0$, equals zero since two equal lines occur. In the case $|\nu - p| + |d - c| = 0$, however, some lines and also some columns can be rearranged to yield

$$|\tilde{Q}(n_{pc}, n_{jb})| = \tilde{\gamma}_c{}^p(-1)^{n_{pc}+n_{jb}}|\tilde{Q}_b{}^j(3,3)|. \tag{25}$$

The formula is also valid for $|p - 1| + |c - 2| = 0$ if $\tilde{\gamma}_2{}^1 = -1$. Furthermore, according to Cramer's rule, Eq. (24) results in

$$\tilde{\gamma}_c{}^p = \frac{|\tilde{Q}_c{}^p(3,3)|}{|\tilde{Q}(3,3)|}. \tag{26}$$

Combination of Eqs. (22), (23), (25), and (26) leads to

$$|\tilde{Q}_1| = -\sum_{i,j,p=1}^{N}\sum_{a=1}^{n_i}\sum_{b=1}^{n_j}\sum_{c=1}^{n_p} \frac{D\tilde{q}_{bc}{}^{jp}}{D\bar{r}_a^{\,i}}\; \frac{|\tilde{Q}_a{}^i(3,3)|\,|\tilde{Q}_b{}^j(3,3)|\,|\tilde{Q}_c{}^p(3,3)|}{|\tilde{Q}(3,3)|}.$$

In combination with Eq. (21), this relation provides the desired statement: $\delta^3(\bar{\bar{G}}/RT)_0$ equals zero if and only if $|\widetilde{Q}_1| = 0$. In this way, a critical state equation for the nonreduced problem is established.

In the second step of the proof, the connection with $|Q_1|$ is provided. By analogous arguments leading to $|Q(1,1)| = -|\widetilde{Q}(3,3)|$, Eq. (15) results in

$$|\widetilde{Q}_1| = -\begin{vmatrix} \bar{t}^1 & \bar{t}^2 & \cdots & \bar{t}^N \\ \bar{Q}^{11} & \bar{Q}^{12} & \cdots & \bar{Q}^{1N} \\ - & - & - & - \\ \bar{Q}^{N1} & \bar{Q}^{N2} & \cdots & \bar{Q}^{NN} \end{vmatrix} \tag{27}$$

with

$$\bar{q}_{ab}{}^{ij} = \widetilde{q}_{ab}{}^{ij} + \delta_{a1}\delta_{1b}\widetilde{q}_{11}{}^{11} - \delta_{a1}\widetilde{q}_{1b}{}^{1j} - \delta_{1b}\widetilde{q}_{a1}{}^{i1}$$

$$\bar{t}_a{}^i = \widetilde{t}_a{}^i - \delta_{a1}\widetilde{t}_1{}^1 \qquad (i, j = 1, \ldots, N; a = 1 + 2\delta_{1i}, \ldots, n_i;$$

$$b = 1 + \delta_{1j}, \ldots, n_j).$$

According to Eq. (4), the relation

$$\frac{\partial^2\Gamma}{\partial\bar{r}_a{}^i\partial\bar{r}_b{}^j} = \frac{\partial^2\widetilde{\Gamma}}{\partial\bar{r}_a{}^i\partial\bar{r}_b{}^j} + \delta_{a1}\delta_{1b}\frac{\partial^2\widetilde{\Gamma}}{\partial\bar{r}_1{}^1\partial\bar{r}_1{}^1} - \delta_{a1}\frac{\partial^2\widetilde{\Gamma}}{\partial\bar{r}_1{}^1\partial\bar{r}_b{}^j} - \delta_{1b}\frac{\partial^2\widetilde{\Gamma}}{\partial\bar{r}_a{}^i\partial\bar{r}_1{}^1} \tag{28}$$

applies. Equation (28) and $\widetilde{q}_{ab}{}^{ij} = \partial^2\widetilde{\Gamma}/\partial\bar{r}_a{}^i\partial\bar{r}_b{}^j + \delta_{ij}r_{ab}{}^i$ result in

$$\bar{q}_{ab}{}^{ij} = \frac{\partial^2\widetilde{\Gamma}}{\partial\bar{r}_a{}^i\partial\bar{r}_b{}^j} + \delta_{ij}\hat{r}_{ab}{}^i + \delta_{a1}\delta_{b1}\hat{r}_{11}{}^1 - \delta_{1j}\delta_{a1}\hat{r}_{1b}{}^1 - \delta_{i1}\delta_{1b}\hat{r}_{a1}{}^1 = q_{ab}{}^{ij},$$

leading to $\bar{Q}^{ij} = Q^{ij}$ $(i \neq 1)$ and $\bar{Q}^{1j} = Q\_^{1j}$. Furthermore, Eqs. (23), (25), and (26) lead to

$$\tilde{t}_a{}^i = \frac{D|\tilde{Q}|}{D\bar{r}_a{}^i} = \sum_{j=1}^{N} \sum_{b=1+\delta_{1j}}^{n_j} \sum_{p=1}^{N} \sum_{c=1+\delta_{1p}}^{n_p} \frac{D\tilde{q}_{cb}{}^{pj}}{D\bar{r}_a{}^i} \frac{|\tilde{Q}_b{}^j(3,3)|\,|\tilde{Q}_c{}^p(3,3)|}{|\tilde{Q}(3,3)|}$$

$$+ \sum_{p=1}^{N} \sum_{c=1+\delta_{1p}}^{n_p} \frac{D\tilde{q}_{c1}{}^{p1}}{D\bar{r}_a{}^i} \frac{|\tilde{Q}_1{}^1(3,3)|\,|\tilde{Q}_c{}^p(3,3)|}{|\tilde{Q}(3,3)|} \tag{29}$$

$$+ \sum_{j=1}^{N} \sum_{b=1+\delta_{1j}}^{n_j} \frac{D\tilde{q}_{1b}{}^{1j}}{D\bar{r}_a{}^i} \frac{|\tilde{Q}_b{}^j(3,3)|\,|\tilde{Q}_1{}^1(3,3)|}{|\tilde{Q}(3,3)|} + \frac{D\tilde{q}_{11}{}^{11}}{D\bar{r}_a{}^i} \frac{|\tilde{Q}_1{}^1(3,3)|^2}{|\tilde{Q}(3,3)|}.$$

According to Eq. (20) and to $\Sigma \tilde{y}_1{}^i = 0$ (i.e., the first line of the system of of equations $\tilde{Q}\,\tilde{y} = 0$), the relation $\Sigma\, |\tilde{Q}_1{}^i(3,3)| = 0$ also is valid, resulting in the possibility to eliminate $|\tilde{Q}_1{}^1(3,3)|$ in Eq. (29). Furthermore, introducing the matrix $Q_c{}^p$ which is obtained from Q by replacing the elements $q_{bc}{}^{jp}$ by $q_{b2}{}^{j1}$ ($j = 1, \ldots, N; b = 1 + \delta_{1j}, \ldots, n_j$), the equality $|\tilde{Q}_c{}^p(3,3)| = -|Q_c{}^p(1,1)|$ applies. These considerations permit a reformulation of Eq. (29) leading to

$$\tilde{t}_a{}^i = \sum_{j=1}^{N} \sum_{b=1+\delta_{ij}}^{n_j} \sum_{p=1}^{N} \sum_{c=1+\delta_{1p}}^{n_p} \left(\frac{D\tilde{q}_{cb}{}^{pj}}{D\bar{r}_a{}^i} - \delta_{1b} \frac{D\tilde{q}_{c1}{}^{p1}}{D\bar{r}_a{}^i} - \delta_{1c} \frac{D\tilde{q}_{1b}{}^{1j}}{D\bar{r}_a{}^i} + \delta_{1b}\delta_{1c} \frac{D\tilde{q}_{11}{}^{11}}{D\bar{r}_a{}^i} \right) \cdot \frac{|\tilde{Q}_b{}^j(3,3)|\,|\tilde{Q}_c{}^p(3,3)|}{|\tilde{Q}(3,3)|}$$

$$= -\sum_{j=1}^{N} \sum_{b=1+\delta_{ij}}^{n_j} \sum_{p=1}^{N} \sum_{c=1+\delta_{1p}}^{n_p} \bar{q}\,{}^{ijp}_{abc} \frac{|Q_b{}^j(1,1)|\,|Q_c{}^p(1,1)|}{|Q(1,1)|}$$

with

$$\bar{q}\,{}^{ijp}_{abc} = \frac{\partial^3 \tilde{\Gamma}}{\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j \partial \bar{r}_c{}^p} - \delta_{ij}\delta_{ip} \sum_{d,e,f=1}^{n_i} \bar{r}^{\,i}_{def} \hat{r}_{ad}{}^i \hat{r}_{be}{}^i \hat{r}_{cf}{}^j$$

$$- \delta_{1b} \left(\frac{\partial^3 \tilde{\Gamma}}{\partial \bar{r}_a{}^i \partial \bar{r}_1{}^1 \partial \bar{r}_c{}^p} - \delta_{1i}\delta_{1p} \sum_{d,e,f=1}^{n_1} \bar{r}^{\,1}_{def} \hat{r}_{ad}{}^1 \hat{r}_{be}{}^1 \hat{r}_{cf}{}^1 \right)$$

$$- \delta_{1c} \left(\frac{\partial^3 \widetilde{\Gamma}}{\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j \partial \bar{r}_1{}^1} - \delta_{1i}\delta_{1j} \sum_{d,e,f=1}^{n_1} \bar{r}^1_{def} \hat{r}_{ad}{}^1 \hat{r}_{be}{}^1 \hat{r}_{cf}{}^1 \right)$$

$$+ \delta_{1b}\delta_{1c} \left(\frac{\partial^3 \widetilde{\Gamma}}{\partial \bar{r}_a{}^i \partial \bar{r}_1{}^1 \partial \bar{r}_1{}^1} - \delta_{1i} \sum_{d,e,f=1}^{n_1} \bar{r}^1_{def} \hat{r}_{ad}{}^1 \hat{r}_{be}{}^1 \hat{r}_{cf}{}^1 \right) .$$

Inserting this result into the formula for $\widetilde{t}_a{}^i - \delta_{a1} \widetilde{t}_1{}^1$ and considering Eqs. (4) and (14), the relation

$$\bar{t}_a{}^i = - \sum_{j=1}^{N} \sum_{b=1+\delta_{1j}}^{n_j} \sum_{p=1}^{N} \sum_{c=1+\delta_{1p}}^{n_p} \frac{Dq_{bc}{}^{jp}}{D\bar{r}_a{}^i} \frac{|Q_b{}^j(1,1)|\,|Q_c{}^p(1,1)|}{|Q(1,1)|} = -t_a{}^i .$$

$$(i = 1, \ldots, N; a = 1 + \delta_{1i}, \ldots, n_i)$$

is obtained. Therefore, the equality $|\widetilde{Q}_1| = |Q_1|$ applies and, hence, the proof is completed.

There are two additional remarks:

(1) The proof shows that, for all variations $\delta(\psi W)_0$ fulfilling Eq. (7), the relation $\delta^3 (\bar{\bar{G}}/RT)_0 = \alpha |Q_1| / |Q(1,1)|^2$ is valid where α is a real number.

(2) The theorem was proved assuming $n_1 > 2$. For $n_1 = 2$, the proof applies too; merely in Q_1 the line with $Q\_^{ij}$ ($j = 1, \ldots, N$) does not exist. For $n_1 = 1$ (e.g., if Substance 1 is a solvent) the matrix Q_1 exhibits further simplifications since then $i,j,p \neq 1$ and, therefore,

$$\frac{Dq_{bc}{}^{jp}}{D\bar{r}_a{}^i} = \frac{\partial^3 \widetilde{\Gamma}}{\partial \bar{r}_a{}^i \partial \bar{r}_b{}^j \partial \bar{r}_c{}^p} - \delta_{ij}\delta_{ip} \sum_{d,e,f=1}^{n_i} \bar{r}^i_{def} \hat{r}_{ad}{}^i \hat{r}_{be}{}^i \hat{r}_{cf}{}^i$$

$$+ \delta_{1a}\delta_{1b}\delta_{1c} \frac{\bar{r}^1_{111}}{(\bar{r}_{11}{}^1)^3} .$$

All special cases considered in the next section belong to this type. The corresponding critical-state equation reads ($Q\_^{2i} = Q^{2i}(1,-)$; $i = 2, \ldots, N$)

for $n_2 > 1$ $\qquad\qquad$ for $n_2 = 1$

$$|Q_1| = \begin{vmatrix} t^2 & \dots & t^N \\ Q^{22} & \dots & Q^{2N} \\ Q^{32} & \dots & Q^{3N} \\ - & - & - \\ Q^{N2} & \dots & Q^{NN} \end{vmatrix} = 0; \quad |Q_1| = \begin{vmatrix} t^2 & \dots & t^N \\ Q^{32} & \dots & Q^{3N} \\ Q^{42} & \dots & Q^{4N} \\ - & - & - \\ Q^{N2} & \dots & Q^{NN} \end{vmatrix} = 0$$

DISCUSSION

The application of the theorem proved in the preceding paragraph leads to a very large reduction of computer time and of needed storage capacity compared to the traditional Gibbs determinant criterion [8]. To illustrate this, a mixture consisting of three polymers, each with approximately 1000 molecular species, will be considered. Then, according to Gibbs, the stability determinant and the critical state determinant possess approximately the order 3000 X 3000. Just the partial differentiation of the stability determinant with respect to these 3000 variables would be enormously time-consuming. Assuming the $\bar{\bar{G}}^E$ function to depend on three moments of the (unnormalized) distribution density function for each polymer (i.e., the segment fraction, the number average, and the weight average), the proved theorem provides a reduction of Gibbs determinants to determinants ($|Q|, |Q_1|$) of the order 8 X 8.

The established critical-state theorem includes many cases known from the literature (the Gibbs criterion among them). This shall be verified for four examples. Examples 1 to 3 refer to cases treated in the framework of traditional (i.e., discrete) thermodynamics. In these cases the following manner of representation was chosen:

a) Statement of the nonlinear part of the segment-molar Gibbs free energy $\bar{\bar{G}}$ for the problem under consideration in traditional form.
b) Statement of the specifications needed to reduce the general problem treated in this paper to the example under consideration. In transforming from $\bar{\bar{G}}_{\text{discont}}$ to $\bar{\bar{G}}_{\text{cont}}$, additional linear terms can be neglected.
c) Application of these specifications to the general criterion (6′)-(8′), resulting in the special criterion desired.

For Example 4 that is formulated by continuous thermodynamics, these topics apply correspondingly. In Cases 1 and 2, a different numbering of the substances, starting with 0 instead of 1, has to be accounted for also.

1. Mixture of Discrete Species [8]

a) $$\frac{\bar{\bar{G}}}{RT} = \sum_{i=0}^{N} \frac{\psi_i \ln \psi_i}{m_i} + \Gamma(T,P,\psi_1,\ldots,\psi_N);\ \psi_0 = 1 - \sum \psi_i.$$

b) $n_i = 1;\ W_i(M) \equiv (M^{0,i} - M_{0,i})^{-1};\ r_i(M) \equiv m_i \quad (i = 0,\ldots,N).$

c) $\bar{r}_{11}{}^{i} = m_i\psi_i, \bar{r}^{i}_{111} = m_i{}^2\psi_i;\ Q = (q_{ij})^N_{i,j=1}.$

$$q_{ij} = \frac{\partial^2\Gamma}{\partial\psi_i\partial\psi_j} + \frac{\delta_{ij}}{m_i\psi_i} + \frac{1}{m_0\psi_0} = \frac{\partial(\bar{\bar{G}}/RT)}{\partial\psi_i\partial\psi_j}.$$

$$|Q_1| \equiv \begin{vmatrix} \frac{\partial|Q|}{\partial\psi_1} & \frac{\partial|Q|}{\partial\psi_2} & \cdots & \frac{\partial|Q|}{\partial\psi_N} \\ q_{21} & q_{22} & \cdots & q_{2N} \\ - & - & - & - \\ q_{N1} & q_{N2} & \cdots & q_{NN} \end{vmatrix} = 0.$$

In this case $a = b = c = 1$ always applies and, hence,

$$\frac{Dq_{bc}{}^{jp}}{D\bar{r}_a{}^{i}} = \frac{Dq_{11}{}^{jp}}{D\bar{r}_1{}^{i}} = \frac{\partial^3\Gamma}{\partial\psi_i\partial\psi_j\partial\psi_p} - \frac{\delta_{ij}\delta_{ip}}{m_i\psi_i{}^2} + \frac{1}{m_0\psi_0^2} = \frac{\partial q_{jp}}{\partial\psi_i}$$

$(i, j, p = 1, \ldots, N)$

On transforming to molar quantities, the well-known Gibbs criterion results.

2. Solution of a Polydisperse Polymer in a Solvent [11, 12]

Here the solvent and the polymer are identified by the indexes 0 and 1, respectively, and the different polymer species are identified by the additional index $j = 1, \ldots, P$.

a) $$\frac{\bar{\bar{G}}}{RT} = \psi_0 \ln \psi_0 + \sum_{j=1}^{P} \frac{\phi_j \ln \phi_j}{m_j} + \Gamma(T,P,M_{k_1}, \ldots, M_{k_n}),$$

$$M_{k_s} = \sum_{j=1}^{P} m_j^{k_s}\phi_j; k_1 = 0; M_0 = \sum_{j=1}^{P} \phi_j = \psi_1 = 1 - \psi_0.$$

b) The total interval from $M_{0,1}$ up to $M^{0,1}$ is divided into P disjunct partial intervals μ_j touching each other. The length of the jth partial interval is signified by $|\mu_j|$.

$n_0 = 1; n_1 = n; k_{1s} = k_s \quad (s = 1, \ldots, n),$

$W_0(M) \equiv (M_{0,0} - M^{0,0})^{-1}; r_0(M) \equiv 1,$

$W_1(M) = \phi_j/(\psi_1 |\mu_j|); r_1(M) = m_j \quad \text{if } M \in \mu_j.$

Hence, $\bar{r}_1{}^1 = \psi_1; \bar{r}_s{}^1 = M_{k_s}$.

c) $$\bar{r}_{11}{}^0 = \bar{r}^{\,0}_{111} = \psi_0; \bar{r}_{ab}{}^1 = \sum_{j=1}^{P} m_j^{k_a+k_b+1}\phi_j;$$

$$\bar{r}^{\,1}_{def} = \sum_{j=1}^{P} m_j^{k_d+k_e+k_f+2}\phi_j,$$

$$Q = (q_{ab}{}^{11})^n_{a,b=1}; q_{ab}{}^{11} = q_{ab} = \frac{\partial^2 \Gamma}{\partial M_{k_a} \partial M_{k_b}} + \hat{r}_{ab}{}^1 + \frac{\delta_{a1}\delta_{b1}}{\psi_0}.$$

The critical state equation reads [13]

$$|Q_1| \equiv \begin{vmatrix} \dfrac{D|Q|}{DM_{k_1}} & \cdots & \dfrac{D|Q|}{DM_{k_n}} \\ q_{21} & \cdots & q_{2n} \\ - & - & - \\ q_{n1} & \cdots & q_{nn} \end{vmatrix} = 0$$

where, according to $i = j = p = 1$,

$$\frac{Dq_{bc}{}^{jp}}{D\bar{r}_a{}^i} = \frac{Dq_{bc}}{DM_{k_a}} = \frac{\partial^3 \Gamma}{\partial M_{k_a} \partial M_{k_b} \partial M_{k_c}} - \sum_{d,e,f=1}^{n} \bar{r}^{1}_{def} \hat{r}_{ad}{}^1 \hat{r}_{be}{}^1 \hat{r}_{cf}{}^1$$

$$+ \frac{\delta_{1a}\delta_{1b}\delta_{1c}}{\psi_0{}^2} .$$

3. Mixture of Two Polydisperse Polymers [14]

a) $$\frac{\bar{\bar{G}}}{RT} = \sum_{j=1}^{P_1} \frac{\phi_{1,j} \ln \phi_{1,j}}{m_{1,j}} + \sum_{j=1}^{P_2} \frac{\phi_{2,j} \ln \phi_{2,j}}{m_{2,j}} + \Gamma(T, \psi_2).$$

$$\psi_I = \sum_{j=1}^{P_i} \phi_{i,j} \qquad (i = 1, 2);\ \psi_1 + \psi_2 = 1.$$

b) $N = 2;\ n_1 = n_2 = 1;\ \bar{r}_1{}^i = \psi_i$

$W_i(M) = \phi_{i,j}/(\psi_i |\mu_{i,j}|);\ r_i(M) = \mathrm{m}_{i,j} \qquad \text{if } M \in \mu_{i,j}$

$(i = 1, 2;\ j = 1, \ldots, P_i)$

c) $$\bar{r}_{11}{}^i = \psi_i m_{w,i},\ \bar{r}^i_{111} = \sum_{j=1}^{P_i} \phi_{i,j} m_{i,j}{}^2 = \psi_i m_{w,i} m_{z,i}$$

($m_{w,i}$ and $m_{z,i}$ are the weight-average and z-average for Polymer i). In this case, Q and Q_1 are 1×1 matrixes with

$$q_{11}{}^{22} = \frac{\partial^2 \Gamma}{\partial \psi_2{}^2} + \frac{1}{\psi_1 m_{w,1}} + \frac{1}{\psi_2 m_{w,2}} ,$$

$$q^{222}_{111} = \frac{Dq_{11}{}^{22}}{D\bar{r}_1{}^2} = \frac{\partial^3 \Gamma}{\partial \psi_2{}^3} - \frac{m_{z,2}}{\psi_2{}^2 m^2_{w,2}} + \frac{m_{z,1}}{\psi_1{}^2 m^2_{w,1}} .$$

4. Mixture Containing Several Solvents and Several Polydisperse Polymers Described by a Momentum-Independent Excess Part $\bar{\bar{G}}^E$ [1]

The I solvents are identified by the indexes $i = 1, \ldots, I < N$ and the N-I polymers by $i = I + 1, \ldots, N$.

$$\text{a)}\ \frac{\bar{\bar{G}}}{RT} = \sum_{i=1}^{I} \frac{\psi_i \ln \psi_i}{r_i} + \sum_{i=I+1}^{N} \int \frac{\psi_i W_i(M) \ln \psi_i W_i(M)}{r_i(M)}\, dM$$

$$+ \Gamma(T, P, \psi_2, \ldots, \psi_N).$$

b) $W_i(M) \equiv (M^{0,i} - M_{0,i})^{-1};\ r_i(M) = r_i = \text{constant} \qquad (i = 1, \ldots, I).$

$n_i = 1\ (i = 1, \ldots, N).$

c) $\bar{r}_{11}{}^i = \psi_i r_i;\ \bar{r}_{111}^{\,i} = \psi_i r_i^2 \qquad (i = 1, \ldots, I).$

$\bar{r}_{11}{}^i = \psi_i \int r_i(M) W_i(M) dM;\ \bar{r}_{111}^{\,i} = \psi_i \int [r_i(M)]^2 W_i(M) dM$

$(i = I + 1, \ldots, N).$

$$Q = (q_{ij})_{i,j=2}^{N};\ q_{ij} = \frac{\partial^2 \Gamma}{\partial \psi_i \partial \psi_j} + \frac{\delta_{ij}}{\bar{r}_{11}{}^i} + \frac{1}{\bar{r}_{11}{}^1} \qquad (i, j = 2, \ldots, N).$$

$$|Q_1| \equiv \begin{vmatrix} \dfrac{D|Q|}{D\psi_2} & \cdots & \dfrac{D|Q|}{D\psi_N} \\ q_{32} & \cdots & q_{3N} \\ - & - & - \\ q_{N2} & \cdots & q_{NN} \end{vmatrix} = 0.$$

Since $a = b = c = 1$ here also, the relation

$$\frac{Dq_{bc}{}^{jp}}{D\bar{r}_a{}^i} = \frac{Dq_{11}{}^{jp}}{D\bar{r}_1{}^i} = \frac{Dq_{jp}}{D\psi_i} = \frac{\partial^3 \Gamma}{\partial \psi_i \partial \psi_j \partial \psi_p} - \frac{\delta_{ij}\delta_{ip}\bar{r}_{111}^{\,i}}{(\bar{r}_{11}{}^i)^3} + \frac{\bar{r}_{111}^{\,1}}{(\bar{r}_{11}{}^1)^3}$$

applies for $i, j, p = 2, \ldots, N$. The difference with respect to Eq. (51) in Ref. 1 is due to the elimination of $\bar{r}_1{}^N = \psi_N$ in Ref. 1 but of $\bar{r}_1{}^1 = \psi_1$ in this paper (for the sake of uniformity).

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