A unified presentation of phase stability analysis including all major specifications

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Abstract

The major specifications for phase equilibrium are: pressure and temperature (PT), volume, temperature and moles (VTN), pressure, enthalpy and moles (PHN), pressure, entropy and moles (PSN), internal energy, volume and moles (UVN) and entropy, volume and moles (SVN). For some of these specifications, stability testing is not well documented in the literature. It appears that derivations of stability criteria for PHN, PSN and SVN stability are presented here for the first time, as well as the possibility to solve the stability problem in their hyperspaces. Two general stability criteria are derived, which include all state functions and specifications. The general tangent plane distance (TPD) function degenerates to the TPD function corresponding to any desired specifications. The formalism is not model dependent. It is shown that stability testing for any specifications naturally reduces to either PT stability (when pressure is a specification, as in PHN and PSN stability) or VTN stability (when volume is a specification, as in UVN and SVN stability), by solving the appropriate nonlinear equation in temperature. In other words, there is no need (moreover, it is shown that there it is not even recommended) to minimize a specific TPD function in its hyperspace (defined by natural variables of the state function). This paper presents the first unified treatment of phase stability testing including all major specifications; beyond its theoretical importance, an important practical consequence is a unified calculation framework for phase stability testing, allowing a versatile numerical treatment and using existing highly robust and efficient procedures for PT, volume-based PT or VTN stability, whatever the specifications.

Keywords: phase stability, state functions, specifications, tangent plane distance, general phase stability criteria, Newton method, Hessian matrix

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1. Introduction

Phase stability testing is a key type of thermodynamic calculation. Phase stability assesses the state of a mixture at given conditions and it is crucial in multiphase flash initialization (for specifications other than pressure and temperature, stability testing is imperatively required even in the two-phase case); stability testing is also used to check the validity of a given phase split. Many applications, some of them important in the energy transition and environmental context (such as carbon dioxide capture and storage and geothermal energy) require phase equilibrium calculations at specifications other than pressure and temperature. Beyond the most widely encountered (and well documented in the literature) isothermal-isobaric (PT) case, the other major specifications for phase equilibrium are [1,2,3]: volume, temperature and moles (VTN), pressure, enthalpy and moles (PHN), pressure, entropy and moles (PSN), internal energy, volume and moles (UVN) and entropy, volume and moles (SVN). Note that throughout this paper, the abbreviation PT (not PTN) is used for pressure and temperature specifications, which are both intensive variables. For all other cases, at least one of the specifications is an extensive variable (volume or/and a state function) and the total number of moles must also be given (it is tacitly assumed that stability analysis is performed at given feed composition). The literature was extremely poor before the last decade, when a continuously increasing interest in such phase equilibrium calculations emerged. It appears that derivations of stability criteria and detailed analysis for PHN, PSN and SVN stability testing were not yet presented in the literature and are presented here for the first time. Moreover, up to date, to the best of our knowledge, a unified presentation of phase stability testing covering all major specifications and giving a general stability criterion is not available in the literature. The aim of this paper is to provide for the first time such a unified framework for phase stability testing.

Based on the early work of Gibbs [4], almost simultaneously Baker et al. [5] and Michelsen [6] presented two important papers on phase stability at pressure and temperature specifications. The former, more theoretical, includes several important theorems, while in the latter, beyond its theoretical importance, a practical solution was proposed for solving the phase stability problem as an unconstrained minimization problem. Michelsen's formulation is the most widely used since and became the standard in phase stability testing, along with his sequential stability-flash approach in multiphase equilibrium calculations [7].

The PT (isobaric-isothermal) phase equilibrium calculations are the most common and very well documented in the literature; at these specifications both flash and stability can be formulated as unconstrained minimization problems (Michelsen [6-7]).

For all other specifications, very few papers on phase equilibrium were available in the open literature (even fewer for phase stability testing) before the last decade, when an increasing interest for other specifications led to many papers on this subject. The interest in these topics is expected to grow, since in energy transition and environmental issues, more and more processes require phase equilibrium calculations at various specifications other than pressure and temperature.

VTN (isochoric-isothermal) phase equilibrium (consisting of the minimization of Helmholtz free energy at given volume, temperature and moles) [1,2] is basically applied to phase equilibrium in closed vessels at given temperature; some of its many applications are listed in Refs. [8,9]. Among all specifications other than PT, VTN phase equilibrium is the best documented in the literature [1,8-24]. Derivations of the TPD function for VTN stability were given by Mikyska and Firoozabadi [10] and Castier [11]. Phase stability testing at VTN condition was investigated by Nichita et al. [8], Mikyska and Firoozabadi [10], Castier [11], Nichita [12,13], Smejkal and Mikyška [14-16], Kou et al. [17], Kou and Sun [18], Jex and Mikyška [19]. A special topic, closely related to equilibrium at VTN specifications, consists of the so-called "volume-based" phase equilibrium calculations at PT specifications (Michelsen [1], Nagarajan et al. [25], Kunz et al. [26], Deiters and Kraska [27], Nichita [28], Paterson et al. [29], Sandoval et al. [30]). In volume-based methods, volume is an independent variable, thus the EoS is not solved for volume and the required partial derivatives have simpler expressions. Volume-based methods are slightly slower than conventional PT formulations (in terms of number of iterations) [28,34], but the cost of an iteration is smaller, especially when complex thermodynamic models are used. Volume-based phase stability testing at PT conditions was investigated by Nagarajan et al. [25], Michelsen [6], Nichita et al. [31], Pereira et al. [32,33], Nichita [34]. Another topic related to VTN stability is phase envelope construction in the VT (or molar density-temperature) plane [26,27,30,35].

PHN (isobaric isenthalpic) phase equilibrium (consisting of the maximization of entropy at given pressure, enthalpy and moles) [1-3, 36-48] has many practical applications, such as adiabatic expansions, throttling processes, compositional reservoir simulation of thermal recovery processes, etc. Phase stability testing at PHN conditions can be assessed using a classical PT stability testing, as correctly mentioned by Michelsen [36], Zhu and Okuno [39], Sun et al. [40]; however, no detailed analysis of phase stability testing was given for these very important specifications.

PSN (isobaric-isentropic) phase equilibrium (consisting of the minimization of enthalpy at given pressure, entropy and moles) [1-3, 49,50] is useful in the preliminary design of compressors and turbines under the assumption of adiabatic and reversible operation, in simulation of full bore rupture of pressurized pipelines, decompression of pipeline fluids, ideal adiabatic compressors, pumps, turbines, etc. As for PHN stability, no detailed analysis was provided in the literature.

UVN (isochoric-isoenergetic) phase equilibrium (consisting of the maximization of entropy at given internal energy, volume and moles) [1-3, 51-57] is applied in rigorous dynamic simulation of distillation columns; simulating two-phase pipe flow, filling tank, venting and leaks from pressure vessels, etc. A derivation of the TPD function at UVN conditions was apparently first given by Castier [52], who also showed that a PT stability testing can be carried out to assess UVN stability. Phase stability at UVN conditions was addressed by Castier [52], Smejkal and Mikyška [54,55], Bi et al. [56] and Nichita [13].

For the SVN (isochoric-isentropic) phase equilibrium (consisting of the minimization of internal energy at given entropy, volume and moles) [46-50], there are no known applications to date, but the

problem has a similar structure and fits the general pattern [46]. Phase stability is addressed here for the first time.

Michelsen [1] presented a unified approach to multiphase flash calculations for all major specification, showing that the phase split problem can be formulated as a minimization of a state function for all specifications. Michelsen's state functions and specifications are listed in **Table 1** [1]. He presented two solution approaches. In the first, which is extremely robust (and can be used as a backup for alternative methods), consists of a nested optimization in which a PT-flash is solved in an inner loop and temperature or/and pressure are corrected in an outer loop until the specifications are met. In a second one, modified objective functions with the Gibbs free energy as a "core function" are introduced and second-order Newton iterations are used to locate their saddle points. An alternative formulation based on the Helmholtz free energy is also given. Michelsen's Q-functions are listed in **Table 1**. Several recent papers [46-48], originating from the same research group at DTU, presented unified approaches including all major specifications, for various phase and chemical equilibrium problems using modified RAND methods.

A general stability criterion is given by Michelsen and Mollerup [2]. A unified presentation of phase stability and flash was presented by Smejkal and Mikyška [55], including only PT, VTN and UVN specifications. They presented a general criterion for phase stability and provided a comparison of phase equilibrium calculations at these specifications.

Up to date, to the best of our knowledge, a unified presentation of phase stability testing including all major specifications is not available in the literature. Moreover, derivations of stability criteria for certain specifications (PHN, PSN, SVN) are missing in the literature. This paper also shows that whatever the specifications other than PT or VTN, there is no need and it is not even recommended to minimize a specific TPD function in its hyperspace, since the same results can be obtained by solving a PT or VTN stability problem, at a temperature calculated from the specific nonlinear equation. Two different but equivalent general stability criteria are derived, both reducing to the TPD function corresponding to any desired specifications.

The paper is structured as follows. After a brief recall of PT stability, stability analysis at specifications other than pressure and temperature is presented in detail. A general formulation is presented, using two different methods; general stability criteria degenerate to any desired criterion for any major specification. PHN and UVN (except derivation of stability criterion) stability are presented in detail. For the remaining specifications, detailed presentations (derivation of stability criteria, convergence analysis and links with stability at other specifications) are given in Appendix A (PSN stability) and Appendix B (SVN stability).

This paper was prepared for a special issue of Fluid Phase Equilibria to honor the memory of Prof. Michael Locht Michelsen, his pioneering work and his outstanding contributions to computational thermodynamics.

2. TPD functions for PT stability

Michelsen's TPD function (1982) [7] at specified pressure and temperature is

$$D = \sum_{i=1}^{nc} x_i \left(\mu_i - \mu_{i0} \right) \tag{1}$$

A mixture is stable if D is nonnegative for all feasible compositions. Finding the stationary points of the TPD function consists of a constrained minimization (if all mole fractions are independent variables) [2], subject to

$$\sum_{i=1}^{nc} x_i = 1 \tag{2}$$

or an unconstrained one, if a mole fraction is dependent. The stationarity conditions of $D(\mathbf{x})$ are

$$\frac{\partial D}{\partial x_i} = \sum_{j=1}^{nc} \frac{\partial x_j}{\partial x_i} \left(\mu_j - \mu_{j0} \right) + \sum_{j=1}^{nc} x_j \frac{\partial \mu_j}{\partial x_i} = \mu_i - \mu_{i0} - \left(\mu_{nc} - \mu_{nc,0} \right) = 0; i = 1, nc-1 \tag{3}$$

where the dependent mole fraction is $x_{nc} = 1 - \sum_{i=1}^{nc-1} x_i$ and

$$\frac{\partial x_j}{\partial x_i} = \begin{cases} \delta_{ji}; i, j = 1, nc-1 \\ -1; i = 1, nc-1, \; j = nc \end{cases} \tag{4}$$

From Eq. (3)

$$\mu_i - \mu_{i0} = \mu_{nc} - \mu_{nc,0} = K; i = 1, nc-1 \tag{5}$$

or

$$\mu_i - \mu_{i0} = K; i = 1, nc \tag{6}$$

Taking into account that the chemical potentials are [2]

$$\mu_i \left(T, P, \mathbf{x} \right) = \mu_i^{ig} \left(T, P_{ref} \right) + RT \ln \frac{f_i \left(T, P, \mathbf{x} \right)}{P_{ref}} \tag{7}$$

and dividing Eq. (1) by RT, the dimensionless TPD function is

$$D_{PT}(\mathbf{x}) = \sum_{i=1}^{nc} x_i (\ln x_i + \ln \phi_i(\mathbf{x}) - \ln z_i - \ln \phi_i(\mathbf{z})) \tag{8}$$

Michelsen [7] also proposed an equivalent stability criterion based on a modified TPD function

$$D_{PT}^{*}(\mathbf{Y}) = (1 - \sum_{i=1}^{nc} Y_i) + \sum_{i=1}^{nc} Y_i \left(\ln Y_i + \ln \varphi_i(\mathbf{Y}) - \ln z_i - \ln \varphi_i(\mathbf{z}) \right) \tag{9}$$

or

$$D_{PT}^{*}(\mathbf{Y}) = f(\theta) + \theta D_{PT}(\mathbf{x}) \tag{10}$$

where $Y_i = x_i e^{-K}$, $\theta = \sum_{i=1}^{nc} Y_i$ and $f(\theta) = 1 - \theta + \theta \ln \theta$. The new variables Y_i are *formally* mole numbers, since $x_i = Y_i / \sum_{i=1}^{nc} Y_i$ (physically, mole numbers of an equilibrium phase are restricted by $0 \le n_i \le z_i$). However, throughout this paper, the notation n_i will be used instead of Y_i for all modified TPD functions.

Finding the stationary points of the modified TPD function requires an unconstrained minimization of D_{PT}^* with respect to mole numbers, with bounds on variables, $Y_i \ge 0$. The gradient vector is

$$g_i^{(PT)} = \frac{\partial D_{PT}^*}{\partial n_i} = \ln n_i + \ln \varphi_i(\mathbf{n}) - \ln z_i - \ln \varphi_i(\mathbf{z}) = \ln \theta + \ln f_i(\mathbf{n}) - \ln f_i(\mathbf{z}) \tag{11}$$

and the Hessian matrix is

$$H_{ij}^{(PT)} = \frac{\partial D_{PT}^*}{\partial n_i \partial n_j} = \frac{\delta_{ij}}{n_i} + \frac{\partial \ln \varphi_i}{\partial n_j} = \frac{1}{\theta} + \frac{\partial \ln f_i}{\partial n_j} \tag{12}$$

The Newton iteration equation is

$$\mathbf{H}^{(PT)} \Delta \mathbf{n} = -\mathbf{g}^{(PT)} \tag{13}$$

At the stationary points, the modified TPD function is

$$D_{PT}^*(P, T, \mathbf{n}) = 1 - \theta \tag{14}$$

The modified TPD function D_{PT}^* has the same stationary points and same sign as the TPD function D [2,7]. Michelsen's change of variables $\alpha_i = 2\sqrt{Y_i}$ [7] is most commonly used in the minimization of D_{PT}^*.

Highly robust and efficient methods were developed for PT stability testing, including volume-based methods and reduction methods.

3. Specifications other than P and T

In this section, phase stability analysis is addressed for all major specifications other than PT. PHN stability is presented in detail, including derivation of the stability criteria, convergence analysis and links with PT stability. For VTN stability, only equations required to analyze its links with UVN and SVN stability are presented. For UVN stability, a detailed analysis is provided (except stability criteria, which were previously established). PSN and SVN stability are only briefly presented and detailed analyses are given in Appendix A (PSN) and Appendix B (SVN). The TPD function for all major specifications are listed in **Table 2**.

3.1. PHN stability

Phase equilibrium calculations at given pressure, enthalpy and moles (PHN) consist of the maximization of entropy, or $min\left(-S\left(H,P,\mathbf{n}\right)\right)$ at the specifications $\left(H_0,P_0,\mathbf{n}_0\right)$. The stability criterion is given in Michelsen and Mollerup [2]. However, although it was correctly recognized that a PT stability at the temperature calculated at the specifications can assess PHN stability [36,39,40,41,43], a derivation of the TPD function and a detailed analysis of the PHN stability are not available in the literature for these very important specifications and are given for the first time in this work.

The total differential of enthalpy is [2]

$$dH = TdS + VdP + \sum_{i=1}^{nc} \mu_i dn_i \tag{15}$$

Solving Eq. (15) for dS, the total differential of entropy is

$$dS = \frac{1}{T} dH - \frac{V}{T} dP - \frac{1}{T} \sum_{i=1}^{nc} \mu_i dn_i \tag{16}$$

On the other hand

$$dS = \left(\frac{\partial S}{\partial H}\right)_{P,\mathbf{n}} dH + \left(\frac{\partial S}{\partial P}\right)_{H,\mathbf{n}} dP + \sum_{i=1}^{nc} \left(\frac{\partial S}{\partial n_i}\right)_{H,P,n_{j\neq i}} dn_i \tag{17}$$

From Eqs. (16) and (17), the partial derivatives are

$$\left(\frac{\partial S}{\partial H}\right)_{P,\mathbf{n}} = \frac{1}{T} \tag{18a}$$

$$\left(\frac{\partial S}{\partial P}\right)_{H,\mathbf{n}} = -\frac{V}{T} \tag{18b}$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{H,P,n_{j\neq i}} = -\frac{\mu_i}{T} \tag{18c}$$

Consider a mixture in an initial single-phase state of entropy $S_0 = S\left(H_0,P_0,\mathbf{n}_0\right)$ and a two-phase state, with a bulk phase (of composition $\mathbf{n}^*$) and an infinitesimal amount of incipient phase (of composition $\mathbf{n}'$), of entropy $S_1 = S^*\left(H^*,P^*,\mathbf{n}^*\right) + S'\left(H',P',\mathbf{n}'\right)$. The balance equations are

$$H^* + H' = H_0 \tag{19a}$$

$$n_i^* + n'_i = n_{i0}; i = 1, nc \tag{19b}$$

and the pressure is

$$P^* = P' = P_0 \tag{19c}$$

A Taylor series expansion around $S_0 = S\left(H_0,P_0,\mathbf{n}_0\right)$ gives (retaining only the first-order terms)

$$S^* = S_0\left(H_0, P_0, \mathbf{n}_0\right) + (H^* - H_0)\left(\frac{\partial S}{\partial H}\right)_{P_0,\mathbf{n}_0} - (P^* - P_0)\left(\frac{\partial S}{\partial P}\right)_{H_0,\mathbf{n}_0} + \sum_{i=1}^{nc}(n_i^* - n_{i0})\left(\frac{\partial S}{\partial n_i}\right)_{H_0,P_0,n_{0\,j\neq i}} \quad (20)$$

or, taking into account Eqs. (19),

$$S^* = S_0 - \frac{H'}{T_0} + \sum_{i=1}^{nc} n'_i \frac{\mu_{i0}}{T_0} \quad (21)$$

where $T_0 = T\left(H_0, P_0, \mathbf{n}_0\right)$ is calculated at the specifications from the nonlinear equation $H\left(T_0, P_0, \mathbf{n}_0\right) = H_0$ and $\mu_{i0} = \mu_i\left(P_0, T_0, \mathbf{n}_0\right)$.

The entropy of the incipient phase is

$$S' = \frac{H'}{T'} - \sum_{i=1}^{nc} n'_i \frac{\mu'_i}{T'} \quad (22)$$

where $T' = T'\left(H', P_0, \mathbf{n}'\right)$ and $\mu'_i = \mu_i\left(P_0, T', \mathbf{n}'\right)$.

The change in entropy between states 0 and 1 is

$$\Delta S = S_1 - S_0 = \left(S^* + S'\right) - S_0 \quad (23)$$

or, from Eqs. (20) to (23)

$$\Delta S = H'\left(\frac{1}{T'} - \frac{1}{T_0}\right) - \sum_{i=1}^{nc} n'_i \left(\frac{\mu'_i}{T'} - \frac{\mu_{i0}}{T_0}\right) \quad (24)$$

Dividing ΔS by the numbers of moles in the trial phase *n*, the TPD function in PHN stability is

$$D_{Ph} = \Delta s = \frac{\Delta S}{n} = h\left(\frac{1}{T} - \frac{1}{T_0}\right) - \sum_{i=1}^{nc} x_i \left(\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0}\right) \quad (25)$$

where $s = S/n$ and $h = H/n$ are the molar entropy and molar enthalpy, respectively.

A mixture is stable if the TPD function is negative or zero for all feasible **n** and *h* (or **n** and *T*); strictly positive values of the TPD function indicate instability. In other words, a phase is stable if any possible perturbation cannot increase its total entropy.

In the following, it is preferable to work in mole numbers rather than in mole fractions, to relate a modified TPD function for PHN stability to the modified TPD function in Eq. (9), which is effectively used in PT stability testing. The modified TPD function for PHN stability (similarly to PT [6], VTN [28] and UVN [13] stability) is

$$D_{PH}^* = -Rf(\theta) + \theta D_{Ph} \quad (26)$$

or

$$D_{PH}^* = -R\, f\left(\theta\right) - \sum_{i=1}^{nc} n_i \left(\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0}\right) + H\left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (27)$$

Since $f(\theta) \geq 0 \; \forall \theta > 0$, the first term is strictly negative; thus D_{Ph} is positive for any point where D^*_{PH} is positive and a positive D^*_{PH} indicates instability. Note that unlike D^*_{PT}, D^*_{PH} is not dimensionless (to avoid additional partial derivatives with respect to temperature).

The elements of the gradient of D^*_{PH} are (using the Gibbs-Duhem equation in the differentiation)

$$g_i = \left(\frac{\partial D^*_{PH}}{\partial n_i} \right)_{H,P,n_{j \neq i}} = -R \ln \theta - \left(\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0} \right); i = 1, nc \tag{28a}$$

and

$$g_{nc+1} = \left(\frac{\partial D^*_{PH}}{\partial H} \right)_{P,\mathbf{n}} = \frac{1}{T} - \frac{1}{T_0} \tag{28b}$$

Introducing the stationarity conditions into the expression of the TPD function, at the stationary points

$$D^*_{PH}(P,H,\mathbf{n}) = -R(1-\theta) \tag{29}$$

At the stationary points, $T = T_0$ from Eq. (28b); the elements of the gradient vectors in PHN and PT stability are related by

$$\left(\frac{\partial D^*_{PH}}{\partial n_i} \right)_{P,H,n_{j \neq i}} = -R \left(\frac{\partial D^*_{PT}}{\partial n_i} \right)_{P,T,n_{j \neq i}} \Bigg|_{T_0} = 0; i = 1, nc \tag{30}$$

and the TPD functions by

$$D^*_{PH}(P,H,\mathbf{n}) = -R \, D^*_{PT}(\mathbf{n},P,T_0)\big|_{T_0} \tag{31}$$

Thus, the modified TPD function in PHN stability, D^*_{PH}, has the same stationary points (from Eq. 29) as the modified TPD function in PT stability at T_0, D^*_{PT}, and opposite signs (from Eq. 31). This means that PHN stability (maximization of D^*_{PH}) can be replaced by a conventional PT stability (minimization of D^*_{PT}) at $T_0 = T(H_0, P_0, \mathbf{n}_0)$.

When the nonlinear equation $H(T_0, P_0, \mathbf{n}_0) = H_0$ is solved for temperature at the specifications, a special case arises if the EoS has multiple real roots; in this case a transition temperature *T** is calculated, where the system is known to be unstable and stability testing is optional (its results can be used to initialize PHN flash calculations]). Details can be found in Michelsen [36] and Sun et al. [41]. Note that solving a PT stability instead of a PHN stability also avoids a special treatment of the multiple roots case during iterations, the nonlinear equation being solved only once at the specifications.

Let us now analyze the maximization of the modified TPD function for PHN stability in its hyperspace (defined by *nc*+1 variables, mole numbers and enthalpy of the trial phase). The Newton iteration equation for PHN stability is

$$\mathbf{H}^{(PH)}\Delta\boldsymbol{\xi} = -\mathbf{g}^{(PH)} \tag{32}$$

where $\boldsymbol{\xi} = \left(n_1,...,n_{nc},H\right)^T$ is the vector of independent variables.

The elements of the Hessian matrix are

$$H_{ij} = \frac{\partial g_i}{\partial n_j} = -\frac{R}{\theta} - \left(\frac{\partial\left(\mu_i / T\right)}{\partial n_j}\right)_{P,H,n_{s\neq j}} \tag{33a}$$

$$H_{i,nc+1} = \frac{\partial g_i}{\partial H} = -\left(\frac{\partial\left(\mu_i / T\right)}{\partial H}\right)_{P,\mathbf{n}} = -\frac{1}{T^2}\left(\frac{\partial\mu_i}{\partial H}T - \mu_i\frac{\partial T}{\partial H}\right) \tag{33b}$$

$$H_{nc+1,j} = \frac{\partial g_{nc+1}}{\partial n_j} = \left(\frac{\partial\left(1/T\right)}{\partial n_j}\right)_{P,H,n_{s\neq j}} = -\frac{1}{T^2}\frac{\partial T}{\partial n_j} \tag{33c}$$

$$H_{nc+1,nc+1} = \frac{\partial g_{nc+1}}{\partial H} = \left(\frac{\partial\left(1/T\right)}{\partial H}\right)_{P,\mathbf{n}} = -\frac{1}{T^2}\frac{\partial T}{\partial H} \tag{33d}$$

Symmetry of second-order partial derivatives of entropy gives

$$-\left(\frac{\partial\left(\mu_i / T\right)}{\partial H}\right)_{P,\mathbf{n}} = \left(\frac{\partial T}{\partial n_j}\right)_{P,H,n_{s\neq j}} \tag{34}$$

where

$$\left(\frac{\partial T}{\partial n_j}\right)_{P,H,n_{s\neq j}} = -\frac{\left(\frac{\partial H}{\partial n_j}\right)_{P,T,n_{s\neq j}}}{\left(\frac{\partial H}{\partial T}\right)_{P,T,\mathbf{n}}} \tag{35}$$

The linear system Eq. (32) has a block structure and can be written as

$$\begin{pmatrix}\mathbf{A} & \mathbf{b}\\ \mathbf{b}^{\mathbf{T}} & c\end{pmatrix}\cdot\begin{pmatrix}\Delta\mathbf{n}\\ \Delta H\end{pmatrix} = -\begin{pmatrix}\mathbf{g}_n\\ g_H\end{pmatrix} \tag{36}$$

where **A** is an [*nc*×*nc*] matrix, with elements $A_{ij} = H_{ij}$, **b** is an [*nc*×1] vector, with elements $b_i = H_{i,nc+1}$, and $c = H_{nc+1,nc+1}$ is a scalar. The elements of the vector $\mathbf{g}_n$ are $g_{n,i} = g_i; i = 1, nc$ and $g_H = g_{nc+1}$. The system of equations in Eq. (36) is

$$\mathbf{A}\Delta\mathbf{n} + \mathbf{b}\Delta H = -\mathbf{g}_n \tag{37a}$$

$$\mathbf{b}^{\mathbf{T}}\Delta\mathbf{n} + \mathrm{c}\Delta H = -g_H \tag{37b}$$

Solving Eq. (37b) for ΔH gives

$$\Delta H = -c^{-1}\left(\mathbf{b}^{\mathbf{T}}\Delta\mathbf{n} + g_H\right) \tag{38}$$

which introduced in Eq. (37a) gives

$$\left(\mathbf{A} - c^{-1}\mathbf{b}\mathbf{b}^{\mathbf{T}}\right)\Delta\mathbf{n} = -\mathbf{g}_n + c^{-1}g_H\mathbf{b} \tag{39}$$

or, by putting/with the notation

$$\mathbf{M} = \mathbf{A} - c^{-1}\mathbf{b}\mathbf{b}^{\mathbf{T}} \tag{40}$$

and

$$\mathbf{r} = -\mathbf{g}_n + c^{-1}g_H\mathbf{b} \tag{41}$$

the linear system is

$$\mathbf{M}\Delta\mathbf{n} = \mathbf{r} \tag{42}$$

Solving the reduced system of equations (Eq. 42) for mole numbers and then updating enthalpy from Eq. (38) is equivalent to solve the original system (Eq. 32). The matrix **M** is the Schur complement of *c* in **H**, with elements

$$M_{ij} = \left(\frac{\partial\left(\mu_i / T\right)}{\partial n_j}\right)_{P,H,n_{s\neq j}} + \frac{1}{T^2}\left(\frac{\partial T}{\partial n_i}\right)_{P,H,n_{s\neq i}}\left(\frac{\partial T}{\partial n_j}\right)_{P,H,n_{s\neq j}}\left(\frac{\partial T}{\partial H}\right)^{-1}_{P,\mathbf{n}} \tag{43}$$

On the other hand, the partial derivative of chemical potentials with respect to mole numbers can be expressed as

$$\frac{1}{T}\left(\frac{\partial\mu_i}{\partial n_j}\right)_{P,T,n_{s\neq j}} = \left(\frac{\partial\left(\mu_i / T\right)}{\partial n_j}\right)_{P,T,n_{s\neq j}} = \left(\frac{\partial\left(\mu_i / T\right)}{\partial n_j}\right)_{P,H,n_{s\neq j}} + \left(\frac{\partial\left(\mu_i / T\right)}{\partial H}\right)_{P,\mathbf{n}}\left(\frac{\partial H}{\partial n_j}\right)_{P,T,n_{s\neq j}} \tag{44}$$

Combining Eq. (43) with Eqs. (44) and (35) and comparing with Eq. (12) gives

$$M_{ij}^{(PH)} = RH_{ij}^{(PT)}; i, j = 1, nc \tag{45}$$

The matrix **M** is formally the same as $\mathbf{H}^{(PT)}$, the elements of the two matrices being related by a factor of proportionality. Thus, solving the PHN stability in the $(\mathbf{n}, H)$ hyperspace is equivalent to performing a sequence of PT stability iterations at a series of temperatures converging to T_0, with a modified gradient containing some temperature information. It is clear that the Newton method in PHN stability will be inherently slower in terms of number of iterations, since both the Hessian and the gradient have lower levels of implicitness than in the PT stability (numerical evidences for closely related problems are given in Refs. [28,34]).

Other drawbacks of solving PHN stability are: i) the non-linear equation $H(T,P_0,\mathbf{n})=H$ must be solved for temperature at each iteration (a special treatment is required if the cubic EoS has three real roots, as described by Sun et al. [41] for PHN flash calculations); ii) the SSI method cannot be used [1], iii) the condition number of the Hessian matrix can be severely deteriorated by the bordering vectors **b** and convergence problems may occur without proper scaling (as shown for instance for volume-based PT stability [34] using mole numbers and volume as independent variables, and for other of phase equilibrium problems [28,58] which have a similar mathematical structure) and iv) the initial guess vectors must contain an estimation of *H* and the number of required initial guesses may be significantly increased.

Therefore, even though the PHN stability problem can be solved in its hyperspace, this is not recommended, since exactly the same results are obtained from a PT stability testing at T_0, using faster and more robust solvers.

3.2. PSN stability

Phase equilibrium calculations at given pressure entropy and moles consist of the minimization of the enthalpy, that is, $min\left(H(P,S,\mathbf{n})\right)$; the specifications are $(S_0,P_0,\mathbf{n}_0)$. As for PHN stability, the expression of the PSN stability criterion was given in Michelsen and Mollerup [2], but its derivation is given for the first time here (see Appendix A). The TPD function is

$$D_{Ps}=\sum_{i=1}^{nc}x_i\left(\mu_i-\mu_{i0}\right)+s\left(T-T_0\right) \tag{46}$$

where $T=T(S,P,\mathbf{n})$ is calculated by solving the non-linear equation $S=S(P_0,T,\mathbf{n})$.

A mixture is stable if the TPD function is non-negative for all feasible compositions and molar entropies. The modified TPD function is given in **Table 3**, the nonlinear equation to be solved for temperature is given in **Table 4** and the TPD function in terms of molar density in **Table 5**. A detailed analysis of PSN stability testing is also given in Appendix A.

3.3. VTN stability

Phase equilibrium calculations at VTN condition consist of the minimization of Helmholtz free energy, $min\left(A(V,T,\mathbf{n})\right)$, at specifications $(V_0,T_0,\mathbf{n}_0)$. Derivations of the stability criterion were given by Mikyška and Firoozabadi [10] and by Castier [11]. The TPD function is

$$D_{vT}(v,T,\mathbf{x}) = \sum_{i=1}^{nc} x_i \left(\mu_i - \mu_{i0}\right) - v\left(P - P_0\right) \tag{47}$$

where $v = V/n$, $\mu_i = \mu_i(v,T,\mathbf{x})$ and $P = P(v,T,\mathbf{x})$.

The modified TPD function presented by Nichita [34] for volume-based PT phase stability can be used for VTN stability

$$D_{VT}^* = RT\ f\left(\theta\right) + \sum_{i=1}^{nc} n_i \left(\mu_i - \mu_{i0}\right) - V\left(P - P_0\right) = RT\ f\left(\theta\right) + \theta D_{vT} \tag{48}$$

It was shown in Ref. [34] that D_{VT}^* has the same stationary points and the same sign as D_{PT}^*

In terms of component molar densities (the name and symbol used in Nagarajan et al. [25] are adopted), the TPD function is [10,11,25], at $T = T_0$

$$D_{dT}\left(\mathbf{d}\right) = \sum_{i=1}^{nc} d_i \left(\ln f_i\left(\mathbf{d}\right) - \ln f_i\left(\mathbf{d}_0\right)\right) - \frac{P\left(\mathbf{d}\right) - P\left(\mathbf{d}_0\right)}{RT} \tag{49}$$

where $d_i = n_i / V = x_i / v$, $\mu_i = \mu_i(T,\mathbf{d})$ and $P = P(T,\mathbf{d})$.

The TPD function must be minimized with respect to d_i, subject to the linear inequality constraint

$$\sum_{i=1}^{nc} b_i d_i - 1 < 0 \tag{50}$$

which is equivalent to $v > b$ and to bounds on variables ($d_i > 0$).

The minimization of D_{dT} appears to be used first by Nichita et al. [8] for VTN stability. The gradient is

$$g_i = \frac{\partial D_{dT}}{\partial d_i} = \ln f_i\left(\mathbf{d}\right) - \ln f_i\left(\mathbf{d_0}\right) = \ln d_i + \ln \Psi_i\left(\mathbf{d}\right) - h_i; i = 1, nc \tag{51}$$

where $\Psi_i\left(\mathbf{d}\right) = f_i\left(\mathbf{d}\right)/d_i$ is a density function (defined in such a way that molar densities are isolated in zero-gradient equation [12,18]) and $h_i = \ln d_{i0} + \ln \Psi_i\left(\mathbf{d_0}\right)$.

The Hessian matrix is

$$H_{ij} = \frac{\partial \ln f_i}{\partial d_j} = \frac{\delta_{ij}}{d_i} + \frac{\partial \ln \Psi_i}{\partial d_j}; i, j = 1, nc \tag{52}$$

and the Newton iteration equation is

$$\mathbf{H}^{(dT)} \Delta \mathbf{d} = -\mathbf{g}^{(dT)} \tag{53}$$

The required partial derivatives with respect to molar densities are related to partial derivatives with respect to mole numbers, based on homogeneity properties of the derivatives of the thermodynamic potentials, as described in Refs. [12,13,28].

3.4. UVN stability

Phase equilibrium at UVN consists of entropy maximization, or $min\left(-S\left(U,V,\mathbf{n}\right)\right)$. It appears that the expression of the TPD function for UVN stability was first derived by Castier [52]; derivations can be also found in Smejkal and Mikyška [54] and Bi et al. [56]. The UVN stability TPD function is

$$D_{uv} = -\sum_{i=1}^{nc} x_i \left(\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0} \right) + u\left(\frac{1}{T} - \frac{1}{T_0} \right) + v\left(\frac{P}{T} - \frac{P_0}{T_0} \right) \tag{54}$$

where the temperature $T = T\left(U,V,\mathbf{n}\right)$ is calculated by solving the nonlinear equation $U = U\left(T,V,\mathbf{n}\right)$, the pressure $P = P\left(V,T,\mathbf{n}\right)$ is calculated explicitly from the EoS and $\mu_i = \mu_i\left(V,T,\mathbf{n}\right)$.

A mixture is stable if the TPD function is non-positive for all feasible compositions, molar volumes and molar internal energies. The modified TPD function in terms of mole numbers for the UVN stability (Nichita [13]) is given in **Table 3**. In terms of molar densities, the TPD function is [52,54]

$$D_{u'd} = -\sum_{i=1}^{nc} d_i \left(\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0} \right) + u'\left(\frac{1}{T} - \frac{1}{T_0} \right) + \left(\frac{P}{T} - \frac{P_0}{T_0} \right) \tag{55}$$

where $u' = u / v = U / V$ is the internal energy density, the temperature is calculated from the nonlinear equation $u' = u'\left(T,\mathbf{d}\right)$, $\mu_i = \mu_i\left(V,T,\mathbf{n}\right) = \mu_i\left(T,\mathbf{d}\right)$ and $P = P\left(V,T,\mathbf{n}\right) = P\left(T,\mathbf{d}\right)$.

A mixture is stable if the TPD function is non-positive for all feasible **d** and *u'*; strictly positive values of the TPD function indicate instability.

The gradient of $D_{u'd}$ is [54]

$$\left(\frac{\partial D_{u'd}}{\partial d_i} \right)_{u',n_{j\neq i}} = -\left(\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0} \right); i = 1, nc \tag{56a}$$

$$\left(\frac{\partial D_{u'd}}{\partial u'} \right)_{\mathbf{d}} = \frac{1}{T} - \frac{1}{T_0} \tag{57b}$$

The function $D_{u'd}$ has the same stationary points as D_{dT} at $T = T_0$ and opposite signs (see Refs. [54,13] for details). This means that UVN stability (maximization of $D_{u'd}$) can be replaced by a VTN stability (minimization of D_{dT}) at $T_0 = T\left(u_0',\mathbf{d}_0\right)$, calculated by solving the nonlinear equation $U_0 = U_0\left(T_0,V_0,\mathbf{n}_0\right)$.

If the UVN stability problem is solved in its hyperspace (defined by *nc*+1 variables, component molar densities and internal energy density of the trial phase), like in Smejkal and Mikyška [54,55], that is as the maximization of $D_{u'd}$, the Newton iteration equation for UVN stability is

$$\mathbf{H}^{(u'd)} \Delta\boldsymbol{\xi} = -\mathbf{g}^{(u'd)} \tag{58}$$

with $\boldsymbol{\xi} = \left(d_1,...,d_{nc},u'\right)^T$ the vector of independent variables.

The linear system Eq. (58) has a block structure and can be written as:

$$\begin{pmatrix} \mathbf{A} & \mathbf{b} \\ \mathbf{b}^{\mathbf{T}} & c \end{pmatrix} \cdot \begin{pmatrix} \Delta\mathbf{d} \\ \Delta u' \end{pmatrix} = -\begin{pmatrix} \mathbf{g}_d \\ g_{u'} \end{pmatrix} \tag{59}$$

where

$$A_{ij} = H_{ij} = \frac{\partial^2 D_{u'd}}{\partial d_i \partial d_j} = \frac{\partial g_i}{\partial d_j} = -\left(\frac{\partial\left(\mu_i / T\right)}{\partial d_j}\right)_{u',d_{s\neq j}} = -\frac{1}{T^2}\left(\frac{\partial \mu_i}{\partial d_j}T - \mu_i \frac{\partial T}{\partial d_j}\right) \tag{60a}$$

$$b_i = H_{i,nc+1} = \frac{\partial g_i}{\partial u'} = -\left(\frac{\partial\left(\mu_i / T\right)}{\partial u'}\right)_{\mathbf{d}} = -\frac{1}{T^2}\left(\frac{\partial \mu_i}{\partial u'}T - \mu_i \frac{\partial T}{\partial u'}\right) \tag{60b}$$

$$b_j = H_{nc+1,j} = \frac{\partial g_{nc+1}}{\partial d_j} = -\left(\frac{\partial\left(1/T\right)}{\partial d_j}\right)_{u',d_{s\neq j}} = -\frac{1}{T^2}\frac{\partial T}{\partial d_j} \tag{60c}$$

$$c = H_{nc+1,nc+1} = \frac{\partial g_{nc+1}}{\partial u'} = \left(\frac{\partial\left(1/T\right)}{\partial u'}\right)_{\mathbf{d}} = -\frac{1}{T^2}\frac{\partial T}{\partial u'} \tag{60d}$$

Eq. (60b) corrects a misprint in Ref. [54]. Symmetry of second-order partial derivatives gives

$$\left(\frac{\partial\left(\mu_i / T\right)}{\partial d_j}\right)_{u',d_{s\neq j}} = \frac{1}{T^2}\frac{\partial T}{\partial d_j} \tag{61}$$

where

$$\left(\frac{\partial T}{\partial d_j}\right)_{u',d_{s\neq j}} = -\frac{\left(\frac{\partial u'}{\partial d_j}\right)_{T,d_{s\neq j}}}{\left(\frac{\partial u'}{\partial T}\right)_{\mathbf{d}}} \tag{62}$$

Proceeding as in the PHN case, the reduced linear system is

$$\mathbf{M}\Delta\mathbf{d} = \mathbf{r} \tag{63}$$

with

$$M_{ij} = -\left(\frac{\partial\left(\mu_i / T\right)}{\partial d_j}\right)_{u',d_{s\neq j}} + \left(\frac{\partial\left(\mu_i / T\right)}{\partial u'}\right)_{\mathbf{d}}\left(\frac{\partial T}{\partial d_j}\right)_{u',d_{s\neq j}}\left(\frac{\partial T}{\partial u'}\right)_{\mathbf{d}}^{-1} \tag{64}$$

and

$$\mathbf{r} = -\mathbf{g}_d + c^{-1} g_{u'}\mathbf{b} \tag{65}$$

Solving the original system (Eqs. 59) is equivalent to solve the reduced linear system for d_i and then update u' from $\Delta u' = -c^{-1}\left(\mathbf{b}^{\mathbf{T}}\Delta\mathbf{d} + g_{u'}\right)$. On the other hand, the partial derivative of chemical potentials with respect to molar densities can be written as

$$\frac{1}{T}\left(\frac{\partial \mu_i}{\partial d_j}\right)_{T,d_{s\neq j}} = \left(\frac{\partial (\mu_i / T)}{\partial d_j}\right)_{T,d_{s\neq j}} = \left(\frac{\partial (\mu_i / T)}{\partial d_j}\right)_{u',d_{s\neq j}} + \left(\frac{\partial (\mu_i / T)}{\partial u'}\right)_{\mathbf{d}} \left(\frac{\partial u'}{\partial d_j}\right)_{T,d_{s\neq j}} \quad (66)$$

Taking into account Eqs. (64), (66) and (62), the relation between matrices is

$$M_{ij}^{(du')} = \frac{1}{T} H_{ij}^{(dT)}; i, j = 1, nc \quad (67)$$

The matrix **M** is formally the same as $\mathbf{H}^{(u'd)}$ (they differ by a factor of proportionality). Solving the UVN stability in its hyperspace $(\mathbf{d}, u')$ is equivalent to performing a sequence of VTN stability iterations at a series of temperatures converging to T_0, with a modified gradient containing some temperature information (via *u*'); the Newton method in UVN stability will be inherently slower in terms of number of iterations than in VTN stability. Moreover, the nonlinear equation $u' = u'(T, \mathbf{d})$ must be solved for temperature at each iteration, the SSI method cannot be used, condition number of the Hessian may severely increase and a significantly higher number of initial guesses (incorporating estimations of u') are required. Smejkal and Mikyška [54] used 7(*nc*+2) initial guesses in the $(\mathbf{d}, u')$ hyperspace, while in the **d**-hyperspace only (*nc*+2) initial guesses were required; for vapor-liquid systems two to four initial guesses suffice [10,13,26]. Thus, it is not recommended to solve the UVN stability problem in its hyperspace, since exactly the same results are obtained from a VTN stability testing at T_0, using existing fast and robust solvers.

Castier [52] went one step further and showed that a PT stability can be performed at $T = T_0$ and $P = P_0$. However, using VTN stability has the advantage of handling negative pressures, where a mixture is clearly unstable, but stability testing is still required for initialization of flash calculations [52,54]. It can be shown that solving UVN stability in its hyperspace is equivalent to solving a reduced PT-like systems at each iteration, at a sequence of *T* and *P* converging to T_0 and P_0, respectively.

3.5. SVN stability

Phase equilibrium at SVN conditions consist of the minimization of internal energy, $min(U(S, V, \mathbf{n}))$ at the specifications $(S_0, V_0, \mathbf{n}_0)$. The expression of the TPD function was given in Michelsen and Mollerup [2], but a derivation is presented for the first time here (see Appendix B). The TPD function is

$$D_{sv} = \sum_{i=1}^{nc} x_i (\mu_i - \mu_{i0}) + s(T - T_0) - v(P - P_0) \quad (68)$$

where $T = T(S,V,\mathbf{n})$ is the solution of the nonlinear equation $S = S(T,V,\mathbf{n})$ and $T_0 = T(S_0,V_0,\mathbf{n}_0)$; at any temperature, the pressure is calculated explicitly from the EoS, $P = P(T,V,\mathbf{n})$.

A mixture is stable if the TPD function is non-negative for all feasible compositions, molar entropies and molar volumes. The modified TPD function for SVN stability is given in **Table 3**. As in VTN and UVN cases, it is more convenient to use molar densities instead of mole fractions. Dividing Eq. (68) by *v*, the TPD function in terms of molar densities is

$$D_{s'v} = \sum_{i=1}^{nc} d_i(\mu_i - \mu_{i0}) + s'(T - T_0) - (P - P_0) \tag{69}$$

whrere $s' = S/V = s/v$ is the entropy density.

An analysis of PSN stability testing is given in Appendix B.

4. General stability criteria

4.1. Derivation of a general stability criterion

Let us consider a state function $F(\boldsymbol{\xi})$ (can be any of the four thermodynamic potentials or entropy) and the vector of *nc*+2 variables is $\boldsymbol{\xi} = (\xi_1,...,\xi_{nc+2})^T = (n_1,...,n_{nc},\xi_{nc+1},\xi_{nc+2})^T$. Except *nc* mole numbers, the two additional variables can be either extensive (*V*, *H*, *S*, *U*), or intensive (*P*, *T*); let us note with *m* the number of extensive variables other than mole numbers.

Consider a mixture in an initial single-phase state with $F_0 = F(\boldsymbol{\xi}_0)$ and a possible two-phase state, with a bulk phase (described by ξ^*) and an infinitesimal amount of incipient phase (of variables ξ'), of state function

$$F_1 = F^*(\xi^*) + F'(\xi') \tag{70}$$

The balance equations for extensive specifications is

$$\xi_i^* + \xi_i' = \xi_{i0}; i = 1, nc + m \tag{71}$$

and for intensive specifications (*P* and/or *T*)

$$\xi_i^* = \xi_i' = \xi_{i0}; i = nc + m, nc + 2 \tag{72}$$

The total differential of a state function of variables ξ is

$$\mathrm{d}F = \sum_{i=1}^{nc+2} \frac{\partial F}{\partial \xi_i} d\xi_i \tag{73}$$

A state function is a homogeneous function of degree one in its extensive variables [2], thus according to Euler's theorem

$$F(\boldsymbol{\xi}) = \sum_{i=1}^{nc+m} \xi_i \frac{\partial F}{\partial \xi_i} \tag{74}$$

The expressions of total differentials and of partial derivatives of state functions are listed in **Table 6** for all major specifications.

A truncated Taylor series development of F around $\boldsymbol{\xi}_0$ gives

$$F^* = F_0(\boldsymbol{\xi}_0) + \sum_{i=1}^{nc+2} (\xi_i^* - \xi_{i0}) \frac{\partial F_0}{\partial \xi_{i0}} = F_0(\boldsymbol{\xi}_0) + \sum_{i=1}^{nc+m} (\xi_i^* - \xi_{i0}) \frac{\partial F_0}{\partial \xi_{i0}} \tag{75}$$

or, from the balance equations

$$F^* = F_0(\boldsymbol{\xi}_0) - \sum_{i=1}^{nc+m} \xi_i' \frac{\partial F_0}{\partial \xi_{i0}} \tag{76}$$

The state function of the incipient phase is

$$F'(\boldsymbol{\xi}') = \sum_{i=1}^{nc+m} \xi_i' \frac{\partial F'}{\partial \xi_i'} \tag{77}$$

The change in state function F between states 0 and 1 is

$$\Delta F = F_1 - F_0 = \left(F^* + F'\right) - F_0 \tag{78}$$

or

$$\Delta F(\boldsymbol{\xi}) = \sum_{i=1}^{nc+m} \xi_i \left(\frac{\partial F}{\partial \xi_i} - \frac{\partial F_0}{\partial \xi_{i0}} \right) \tag{79}$$

A general criterion for phase stability including all major specifications is obtained; $\Delta F(\boldsymbol{\xi})$ degenerates to the change of any state function between states 0 and 1 for the desired specifications, if the appropriate F and ξ are used. Dividing Eq. (79) by the number of moles in the incipient phase, the general expression of the TPD function is

$$D(\boldsymbol{\xi}^m) = \sum_{i=1}^{nc+m} \xi_i^m \left(\frac{\partial f}{\partial \xi_i^m} - \frac{\partial f_0}{\partial \xi_{i0}^m} \right) \tag{80}$$

where $\xi_i^m = \xi_i / n$ are the molar extensive specifications, $f = F / n$ are the molar state functions and $\boldsymbol{\xi}^m = \left(\xi_1^m, ..., \xi_{nc+m}^m\right)^T$, with $\xi_i^m = x_i; i = 1, nc$. The TPD functions for all specifications are collected in **Table 2**.

By adding and subtracting

$$F_0(\boldsymbol{\xi}_0) = \sum_{i=1}^{nc+m} \xi_{i0} \frac{\partial F_0}{\partial \xi_{i0}} \tag{81}$$

in Eq. (79) and taking into account Eq. (74), we obtain after rearrangement

$$\Delta F(\boldsymbol{\xi}) = \sum_{i=1}^{nc+m} \left(\xi_{i0} - \xi_i\right) \frac{\partial F_0}{\partial \xi_{i0}} + F - F_0 \tag{82}$$

which divided by the total number of moles in the trial phase *n* gives

$$D(\boldsymbol{\xi}) = \sum_{i=1}^{nc+m} \left(\xi_{i0}^m - \xi_i^m\right) \frac{\partial f_0}{\partial \xi_{i0}} + f - f_0 \tag{83}$$

which matches the expression given by Smejkal and Mikyška [55].

4.2. Legendre transformations from a core function

Given a function $y^{(0)} = f(x_1,...x_n)$ and its first-order partial derivatives, $\omega_i = \left(\partial y^{(0)} / \partial x_i\right)_{x_{j\neq i}}$, the k^{th} Legendre transformation of $y^{(0)}$ is [59,60,61]

$$y^{(k)}(\omega_1,...,\omega_k, x_{k+1},...x_n) = y^{(0)} - \sum_{i=1}^{k} \omega_i x_i \tag{84}$$

Usually, state functions are obtained as Legendre transformations starting from $U(S,V,\mathbf{n})$. Here state functions can be expressed as first-order (*A* and *H*) or second-order (*S* and *U*) Legendre transformations of a core function $M = M\left(P,T,n_1,...,n_{nc}\right)$. In some cases (PHN, UVN), it is more convenient to use the Planck function, $Y = G/T$ [62,63] (with P/T and $1/T$ as variables) instead of the Gibbs free energy. Thus, the core function is $M = M\left(v_1,v_2,n_1,...,n_{nc}\right)$ and the state functions are

$$F = M - \sum_{i=1}^{m} v_i \xi_i \tag{85}$$

where

$$\xi_i = \left(\frac{\partial M}{\partial v_i}\right)_{v_{j\neq i},\mathbf{n}} \tag{86}$$

The function *M* and the variables v_i and ξ_i $(i = 1,m)$ are given in **Table 7** for all major specifications.

4.3. Alternative derivation of a general stability criterion

As suggested by Michelsen [3], for a two-phase (say, without losing generality) vapor-liquid system the Gibbs free energy

$$G = G_L + G_V = \beta_L g_L + \beta_V g_V \tag{87}$$

can be expressed as (by adding and subtracting G_0 and after rearrangement)

$$G = G_0 + \beta_L D_L + \beta_V D_V \tag{88}$$

where G_0 is the Gibbs free energy of a hypothetical single-state phase with global composition. For strictly negative values of D, $G < G_0$, which means that the system splits into two or more phases.

The state function F for a two-phase system is

$$F = F_L + F_V = \beta_L f_L + \beta_V f_V \tag{89}$$

and a generalization of Eq. (88) gives

$$F = F_0 + \beta_L D_{F,L} + \beta_V D_{F,V} \tag{90}$$

where D_F is the TPD function corresponding to the state function F.

Adding and subtracting F_0 in Eq. (89) and taking into account Eq. (85), we obtain

$$F = F_0 + M_L + M_V - M_0 - \sum_{j=1}^{m} \left(\nu_{jL} \xi_{jL} + \nu_{jV} \xi_{jV} - \nu_{j0} \xi_{j0} \right) \tag{91}$$

The core function can be expressed as

$$M = \sum_{i=1}^{nc} n_i \left(\frac{\partial M}{\partial n_i} \right)_{\nu_1, \nu_2, n_{j \neq i}} = \sum_{i=1}^{nc} n_i \overline{M}_i \tag{92}$$

where

$$\overline{M}_i = \left(\frac{\partial M}{\partial n_i} \right)_{\nu_1, \nu_2, n_{j \neq i}} \tag{93}$$

are the partial molar core functions.

The balance equations are

$$n_{i0} = n_{iL} + n_{iV} = \beta_L x_i + \beta_V y_i : i = 1, nc \tag{94}$$

and

$$\xi_{i0} = \xi_{iL} + \xi_{iV} = \beta_L \xi_{iL}^m + \beta_V \xi_{iV}^m : i = 1, m \tag{95}$$

Combining Eq. (91) with Eqs. (94), (95) and (92) gives

$$F = F_0 + \beta_L \left[\sum_{i=1}^{nc} x_i \left(\overline{M}_{iL} - \overline{M}_{i0} \right) - \sum_{j=1}^{m} \xi_{jL}^m \left(\nu_{jL} - \nu_{j0} \right) \right] + \beta_V \left[\sum_{i=1}^{nc} y_i \left(\overline{M}_{iV} - \overline{M}_{i0} \right) - \sum_{j=1}^{m} \xi_{jV}^m \left(\nu_{jV} - \nu_{j0} \right) \right] \tag{96}$$

By identification from Eq. (90) and Eq. (96), the general TPD function is

$$D_F = \sum_{i=1}^{nc} x_i \left(\overline{M}_i - \overline{M}_{i0} \right) - \sum_{j=1}^{m} \xi_j^m \left(\nu_j - \nu_{j0} \right) \tag{97}$$

The procedure to obtain Eq. (97) is exactly a generalization of what Michelsen [3] did to obtain Eq. (88) for PT stability. Introducing in Eq. (97) the appropriate M, v_i and ξ_i from **Table 7**, the TPD functions in **Table 2** are obtained.

The two general stability criteria presented here are equivalent, both reducing to the TPD function corresponding to any desired specifications. The criterion in Eq. (80) contains the state function and its partial derivatives with respect to the natural variables and the criterion in Eq. (97) contains partial derivatives of a core function (Gibbs free energy (or the Planck function)) with respect to pressure and temperature. Regarding the second method, one can similarly use as a core function the Helmholtz free energy in its natural variables (*V*, *T*, **n**), or the Massieu potentials [62,64], $-A/T$, with natural variables (*V*, 1/*T*, **n**)). The TPD functions in terms of molar densities are listed in **Table 5** for all specifications.

4.4. Short final remarks

In Michelsen's [1] general formulation for flash calculations, in that of Smejkal and Mikyška [55], as well as in unified treatments of using RAND-type methods [46-48], a common Jacobian matrix is assembled, capable of handling all specifications. This is also possible for phase stability testing, but it would be rather a mathematical exercise, with no practical use, since minimization of TPD functions in their hyperspaces is not recommended for most specifications, as discussed throughout this paper; as shown earlier, phase stability testing for any major specifications can be reduced to either PT or VTN stability testing.

In the volume-based methods for PT stability [7,31,34] (which are useful particularly for complex thermodynamic models), the TPD function is formally the same as the TPD function in VTN stability and the same computational tools can be used. In VTN stability, the volume is specified and the pressure in Eq. (49) is calculated explicitly from the EoS; in volume-based PT stability, the pressure is specified and the volume is calculated by solving the EoS and selecting the root giving the minimum Gibbs free energy. Note that the volume-based formulation is natural if volume is a specification (i.e., VTN, UVN, SVN). In other cases, when pressure is a specification (i.e., PHN and PSN), a volume-based PT stability testing can be performed at $T = T_0$. Unlike for any other specifications other than PT, in VTN stability the SSI method can be formulated, but it is not robust; the explanation is given in Ref. [13], based on the earlier work of Michelsen [7] and Heidemann and Michelsen [65].

Our final recommendation is to solve a PT stability problem for PHN and PSN specifications and a VTN stability problem in molar densities for UVN and SVN specifications, after solving the corresponding nonlinear equation in temperature (nonlinear equations for each specifications are listed in **Table 3**).

Many robust and efficient computational methods are available for PT stability. A common practice is to use a combined SSI/Newton procedure, with SSI in the early iteration stages and a switch to the second-order Newton method when the solution is approached. A strong safety feature which makes the method extremely robust is to switch back to SSI whenever the Newton method fails to provide a descent direction; however, the method can be extremely slow in some cases [66,67]. Our favorite solvers [34,67] use either a modified Cholesky factorization [68,69] and a line-search procedure, or a Trust-region approach [70,71]. Reduction methods [72,73,66] are suitable for mixtures with many components and few binary interaction parameters in the cubic EoS; several formulations are available for phase stability testing [66, 73-76]. A promising research attempting to bridge phase stability and phase split (including the negative flash [77]) in a common framework was recently presented [78]. Further developments are expected in the light of this elegant approach. For VTN stability, the conventional SSI/Newton method is not robust; damped SSI [65] may be used with caution in the early iteration stages, as discussed in Ref. [13]. Robust implementations using Newton iterations with a modified Cholesky factorization and a two-stage line-search procedure were presented in Refs. [12,13,34].

5. Conclusions

This paper presents for the first time a formalism for phase stability analysis including all major specifications. Derivations of stability criteria and detailed analysis for PHN, PSN and SVN stability are presented here for the first time. It is shown that stability testing for any specifications naturally reduces to either PT stability (when pressure is a specification, as in PHN and PSN stability) or VTN stability (when volume is a specification, as in UVN and SVN stability), by solving the appropriate nonlinear equation in temperature.

Using the block structure of the Hessian matrix, it is shown that solving the phase stability problem in the hyperspace defined by the natural variables of the state function for any specifications other than PT and VTN will be inherently slower in terms of number of iterations and a number of additional drawbacks are discussed. Therefore, it is not recommended to minimize a specific TPD function for these specifications, since exactly the same results are obtained from PT or VTN stability testing using faster and more robust solvers.

Two general phase stability criteria (TPD functions) are proposed, which include all state functions and specifications. The first one contains the state function and its partial derivatives with respect to natural variables; in the second one, Legendre transformations of the Gibbs free energy (or the Planck function) taken as a core function are used and partial derivatives are with respect to pressure and temperature. Both general TPD functions degenerate to the TPD function corresponding to any given specifications.

Even though only a theoretical framework is presented here, an important practical consequence is that existing codes for PT stability (for which highly robust methods are available) or VTN stability and volume-based PT stability (for which important advances were made in the recent years) can be used whatever the specifications, by simply adding routines for solving the specific nonlinear equation in temperature. Such codes handling all major specifications would be valuable for compositional simulators addressing a variety of thermodynamic processes.

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Credit Author Statement

Dan Vladimir Nichita: Conceptualization, Methodology, Validation, Writing-Original Draft, Writing-review & editing.

Appendix A PSN stability

The total differential of the enthalpy is [2]

$$dH = TdS - VdP + \sum_{i=1}^{nc} \mu_i dn_i \tag{A1}$$

or

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,\mathbf{n}} dS + \left(\frac{\partial H}{\partial P}\right)_{S,\mathbf{n}} dP + \sum_{i=1}^{nc} \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} dn_i \tag{A2}$$

From Eqs. (A1) and (A2), the partial derivatives are

$$\left(\frac{\partial H}{\partial S}\right)_{P,\mathbf{n}} = T \tag{A3a}$$

$$\left(\frac{\partial H}{\partial P}\right)_{S,\mathbf{n}} = V \tag{A3b}$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \mu_i \tag{A3c}$$

Consider a mixture in an initial single-phase state of enthalpy $H_0 = H\left(S_0, P_0, \mathbf{n}_0\right)$ and a two-phase state, with a bulk phase (of composition $\mathbf{n}^*$) and an infinitesimal amount of incipient phase (of composition $\mathbf{n}'$), of enthalpy $H_1 = H^*\left(S^*, P^*, \mathbf{n}^*\right) + H'\left(S', P', \mathbf{n}'\right)$. The balance equations are

$$H^* + H' = H_0 \tag{A4a}$$

and

$$n_i^* + n'_i = n_{i0} \tag{A4b}$$

and the pressure is

$$P^* = P' = P_0 \tag{A4c}$$

A truncated Taylor series expansion around $H_0 = H\left(S_0, P_0, \mathbf{n}_0\right)$ gives

$$H^* = H\left(S_0, P_0, \mathbf{n}_0\right) + (S^* - S_0)\left(\frac{\partial H}{\partial S}\right)_{P_0,\mathbf{n}_0} - (P^* - P_0)\left(\frac{\partial H}{\partial P}\right)_{S_0,\mathbf{n}_0} + \sum_{i=1}^{nc} (n_i^* - n_{i0})\left(\frac{\partial H}{\partial n_i}\right)_{S_0,P_0,n_{0\,j\neq i}} \tag{A5}$$

or, taking into account the balance equations and $P^* = P_0$

$$H^* = H_0 - S'T_0 - \sum_{i=1}^{nc} n_i' \mu_{i0} \tag{A6}$$

The enthalpy of the incipient phase is

$$H' = S'T' + \sum_{i=1}^{nc} n_i' \mu'_i \tag{A7}$$

The change in enthalpy between states 0 and 1 is

$$\Delta H = H_1 - H_0 = \left(H^* + H'\right) - H_0 \tag{A8}$$

or, introducing Eq. (A6) and Eq. (A7) into Eq. (A8)

$$\Delta H = S'\left(T' - T_0\right) + \sum_{i=1}^{nc} n'_i \left(\mu'_i - \mu_{i0}\right) \tag{A9}$$

Dividing ΔH by the numbers of moles in the trial phase *n*, the TPD function in PSN stability is

$$D_{Ps} = \Delta h = \frac{\Delta H}{n} = s\left(T - T_0\right) + \sum_{i=1}^{nc} x_i \left(\mu_i - \mu_{i0}\right) \tag{A10}$$

where $s = S / n$ is the molar entropy.

A mixture is stable if the TPD function is non-negative for all feasible **n** and *s* (or **n** and *T*); strictly negative values of the TPD function indicate instability. The modified TPD function for PSN stability is

$$D^*_{PS} = -RT_0 f(\theta) + \theta D_{Ps} \tag{A11}$$

or

$$D^*_{PS} = RT_0 \, f\left(\theta\right) + \sum_{i=1}^{nc} n_i \left(\mu_i - \mu_{i0}\right) + S\left(T - T_0\right) = RT_0 \, f(\theta) + \theta D_{Ps} \tag{A12}$$

The gradient of D^*_{PS} is

$$\left(\frac{\partial D^*_{PS}}{\partial n_i}\right)_{S,P,n_{j\neq i}} = RT_0 \ln\theta + \left(\mu_i - \mu_{i0}\right) \tag{A13a}$$

$$\left(\frac{\partial D^*_{PS}}{\partial S}\right)_{P,\mathbf{n}} = T - T_0 \tag{A13b}$$

Introducing the stationarity conditions into TPD function gives

$$D^*_{PS}\left(P,H,\mathbf{n}\right) = RT_0\left(1-\theta\right) \tag{A14}$$

At the stationary points, $T = T_0$ from Eqs. (A13b). The elements of the gradient vectors in PSN and PT stability are related by

$$\left(\frac{\partial D^*_{PS}}{\partial n_i}\right)_{P,H,n_{j\neq i}} = RT_0 \left(\frac{\partial D^*_{PT}}{\partial n_i}\right)_{P,T,n_{j\neq i}} \Bigg|_{T_0} = 0; i = 1, nc \tag{A15}$$

and the TPD functions by

$$D^*_{PS}\left(P,H,\mathbf{n}\right) = RT_0 D^*_{PT}\left(\mathbf{n},P,T_0\right)\Big|_{T_0} \tag{A16}$$

The modified TPD function in PSN stability, D_{PS}^{*}, has the same stationary points as the modified TPD function in PT stability (from Eq. A15), D^{*} at T_0 and the same signs (from Eq. A16). Therefore, the PSN stability (minimization of D_{PS}^{*}) can be replaced by a conventional PT stability (minimization of D_{PT}^{*}) at $T_0 = T\left(S_0, P_0, \mathbf{n}_0\right)$.

If the PHN stability problem is solved by a minimization of the modified TPD function in its hyperspace (defined by *nc*+1 variables, mole numbers and entropy of the trial phase), the Newton iteration equation for PHN stability is

$$\mathbf{H}^{(PS)}\Delta\boldsymbol{\xi} = -\mathbf{g}^{(PS)} \tag{A17}$$

with $\boldsymbol{\xi} = \left(n_1, ..., n_{nc}, S\right)^T$

The linear system Eq. (A17) can be written as:

$$\begin{pmatrix} \mathbf{A} & \mathbf{n} \\ \mathbf{b}^{\mathbf{T}} & c \end{pmatrix} \cdot \begin{pmatrix} \Delta\mathbf{n} \\ \Delta S \end{pmatrix} = -\begin{pmatrix} \mathbf{g}_n \\ g_S \end{pmatrix} \tag{A18}$$

where the blocks of the Hessian matrix are

$$A_{ij} = H_{ij} = \frac{\partial^2 D_{PS}^{*}}{\partial n_i \partial n_j} = \frac{\partial g_i}{\partial n_j} = \frac{RT_0}{\theta} + \left(\frac{\partial \mu_i}{\partial n_j}\right)_{S, n_{s\neq j}} \tag{A19a}$$

$$b_i = H_{i,nc+1} = \frac{\partial g_i}{\partial S} = \left(\frac{\partial \mu_i}{\partial S}\right)_{\mathbf{n}} \tag{A19b}$$

$$b_j = H_{nc+1,j} = \frac{\partial g_{nc+1}}{\partial n_j} = -\left(\frac{\partial T}{\partial n_j}\right)_{S, n_{s\neq j}} \tag{A19c}$$

$$c = H_{nc+1,nc+1} = \frac{\partial g_{nc+1}}{\partial S} = \left(\frac{\partial T}{\partial S}\right)_{\mathbf{n}} \tag{A19d}$$

Symmetry of second-order partial derivatives of enthalpy gives

$$\left(\frac{\partial \mu_i}{\partial S}\right)_{\mathbf{n}} = -\left(\frac{\partial T}{\partial n_j}\right)_{S, n_{s\neq j}} \tag{A19e}$$

and

$$\left(\frac{\partial T}{\partial n_j}\right)_{P,S,n_{s\neq j}} = -\frac{\left(\frac{\partial S}{\partial n_j}\right)_{P,T,n_{s\neq j}}}{\left(\frac{\partial S}{\partial T}\right)_{P,T,\mathbf{n}}} \tag{A20}$$

Similar to PHN stability, it is equivalent to solve the original linear system in Eq. (A17) or a reduced linear system for mole numbers

$$\mathbf{M}\Delta\mathbf{n} = \mathbf{r} \tag{A21}$$

with $\mathbf{M}=\mathbf{A}-c^{-1}\mathbf{b}\mathbf{b}^{\mathbf{T}}$ and $\mathbf{r}=-\mathbf{g}_n+c^{-1}g_H\mathbf{b}$, then to update entropy from $\Delta S=-c^{-1}\left(\mathbf{b}^{\mathbf{T}}\Delta\mathbf{n}+g_S\right)$.

The elements of **M** are

$$M_{ij}=\left(\frac{\partial\mu_i}{\partial n_j}\right)_{P,S,n_{s\neq j}}+\left(\frac{\partial T}{\partial n_i}\right)_{P,S,n_{s\neq i}}\left(\frac{\partial T}{\partial n_j}\right)_{P,S,n_{s\neq j}}\left(\frac{\partial T}{\partial S}\right)^{-1}_{P,\mathbf{n}} \tag{A22}$$

The partial derivative of chemical potentials with respect to mole numbers can also be expresses as

$$\left(\frac{\partial\mu_i}{\partial n_j}\right)_{P,T,n_{s\neq j}}=\left(\frac{\partial\mu_i}{\partial n_j}\right)_{S,n_{s\neq j}}+\left(\frac{\partial\mu_i}{\partial S}\right)_{\mathbf{n}}\left(\frac{\partial S}{\partial n_j}\right)_{P,T,n_{s\neq j}} \tag{A23}$$

Comparing Eq. (A22) and (A23) and taking into account Eq. (A20)

$$M_{ij}^{(PS)}=RT_0H_{ij}^{(PT)};i,j=1,nc \tag{45}$$

The matrix **M** is formally the same as $\mathbf{H}^{(PT)}$, the elements of the two matrices being related by a factor of proportionality. From now on, all the points of the discussion on PHN stability (section 3.1.) hold for the PSN stability.

Appendix B SVN stability

The total differential of internal energy is

$$dU=TdS-PdV+\sum_{i=1}^{nc}\mu_i dn_i \tag{B1}$$

or

$$dU=\left(\frac{\partial U}{\partial S}\right)_{V,\mathbf{n}}dS+\left(\frac{\partial U}{\partial V}\right)_{S,\mathbf{n}}dV+\sum_{i=1}^{nc}\left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_{j\neq i}}dn_i \tag{B2}$$

From Eqs. (B1) and (B2), the partial derivatives are

$$\left(\frac{\partial U}{\partial S}\right)_{V,\mathbf{n}}=T \tag{B3a}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,\mathbf{n}}=-P \tag{B3b}$$

$$\left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_{j\neq i}}=\mu_i \tag{B3c}$$

Consider a mixture in an initial single-phase state of internal energy $U_0=U\left(S_0,V_0,\mathbf{n}_0\right)$ and a two-phase state, with a bulk phase (of composition $\mathbf{n}^*$) and an infinitesimal amount of incipient phase (of composition $\mathbf{n}'$), of internal energy $U_1=U^*\left(S^*,V^*,\mathbf{n}^*\right)+U'\left(S',V',\mathbf{n}'\right)$. The balance equations are

The balance equations are

$$S^* + S' = S_0 \tag{B4a}$$

$$V^* + V' = V_0 \tag{B4b}$$

$$n_i^* + n'_i = n_{i0} \tag{B4c}$$

A truncated Taylor series expansion of the internal energy around $U\left(S_0, V_0, \mathbf{n}_0\right)$ gives

$$U^* = U\left(S_0, V_0, \mathbf{n}_0\right) + (S^* - S_0)\left(\frac{\partial U}{\partial S}\right)_{V_0, \mathbf{n}_0} - (V^* - V_0)\left(\frac{\partial U}{\partial V}\right)_{S_0, \mathbf{n}_0} + \sum_{i=1}^{nc}(n_i^* - n_{i0})\left(\frac{\partial U}{\partial n_i}\right)_{V_0, S_0, n_{0\,j\neq i}} \tag{B5}$$

or

$$U^* = U_0 - S'T_0 + V'P_0 - \sum_{i=1}^{nc} n_i' \mu_{i0} \tag{B6}$$

The internal energy in the incipient phase is

$$U' = S'T' - V'P' + \sum_{i=1}^{nc} n_i' \mu_{i0} \tag{B7}$$

The change in the internal energy between states 0 and 1 is

$$\Delta U = U_1 - U_0 = \left(U^* + U'\right) - U_0 \tag{B8}$$

or

$$\Delta U = S(T - T_0) - V(P - P_0) + \sum_{i=1}^{nc} n_i (\mu_i - \mu_{i0}) \tag{B9}$$

Dividing ΔU by the numbers of moles in the trial phase *n*, the TPD function in SVN stability is

$$D_{sv} = \Delta u = \frac{\Delta U}{n} = \sum_{i=1}^{nc} x_i (\mu_i - \mu_{i0}) + s\left(T - T_0\right) - v\left(P - P_0\right) \tag{B10}$$

As in VTN and UVN cases, it is more convenient to express the TPD function in terms of molar densities, which is obtained by dividing Eq. (B10) by the molar volume

$$D_{s'd} = \sum_{i=1}^{nc} d_i \left[\mu_i - \mu_{i0}\right] + s'\left(T - T_0\right) - \left(P - P_0\right) \tag{B11}$$

where $s' = S/V = s/v$ is the entropy density.

The gradient is

$$\left(\frac{\partial D_{s'd}}{\partial d_i}\right)_{s', d_{j\neq i}} = \mu_i - \mu_{i0}; i = 1, nc \tag{B12a}$$

$$\left(\frac{\partial D_{s'd}}{\partial s'}\right)_{\mathbf{d}} = T - T_0 \tag{B12b}$$

It can be easily shown, similarly to the UVN case in Refs. [54,13], that the TPD functions $D_{s'd}$ and D_{dT} have the same stationary points and the same signs. This means that SVN stability (minimization

of $D_{s'd}$) can be replaced by a VTN stability (minimization of D_{dT}) at $T_0 = T\left(u_0', \mathbf{d}_0\right)$, calculated by solving the nonlinear equation $S_0 = S_0\left(T_0, V_0, \mathbf{n}_0\right)$.

If the SVN stability problem is solved in its hyperspace (defined by *nc*+1 variables, component molar densities and entropy density of the trial phase), that is, as the minimization of $D_{s'd}$, the Newton iteration equation for SVN stability is

$$\mathbf{H}^{(s'd)}\Delta\boldsymbol{\xi} = -\mathbf{g}^{(s'd)} \tag{B13}$$

with $\boldsymbol{\xi} = \left(d_1, ..., d_{nc}, s'\right)^T$

The linear system is

$$\begin{pmatrix} \mathbf{A} & \mathbf{b} \\ \mathbf{b}^{\mathbf{T}} & c \end{pmatrix} \cdot \begin{pmatrix} \Delta\mathbf{d} \\ \Delta s' \end{pmatrix} = -\begin{pmatrix} \mathbf{g}_d \\ g_{s'} \end{pmatrix} \tag{B14}$$

where the elements of the constitutive blocks of the Hessian matrix are

$$A_{ij} = H_{ij} = \frac{\partial^2 D_{s'v}}{\partial d_i \partial d_j} = \frac{\partial g_i}{\partial d_j} = \left(\frac{\partial \mu_i}{\partial d_j}\right)_{s', d_{s\neq j}} \tag{B15a}$$

$$b_i = H_{i,nc+1} = \frac{\partial g_i}{\partial s'} = \left(\frac{\partial \mu_i}{\partial s'}\right)_{\mathbf{d}} \tag{B15b}$$

$$b_j = H_{nc+1,j} = \frac{\partial g_{nc+1}}{\partial d_j} = \left(\frac{\partial T}{\partial d_j}\right)_{s', d_{s\neq j}} \tag{B15c}$$

$$c = H_{nc+1,nc+1} = \frac{\partial g_{nc+1}}{\partial s'} = \left(\frac{\partial T}{\partial s'}\right)_{\mathbf{d}} \tag{B15d}$$

and

$$\left(\frac{\partial \mu_i}{\partial s'}\right)_{\mathbf{d}} = \left(\frac{\partial T}{\partial d_j}\right)_{s', d_{s\neq j}} \tag{B16}$$

from the symmetry of second-order partial derivatives, where

$$\left(\frac{\partial T}{\partial d_j}\right)_{s', d_{s\neq j}} = -\frac{\left(\frac{\partial s'}{\partial d_j}\right)_{T, d_{s\neq j}}}{\left(\frac{\partial s'}{\partial T}\right)_{\mathbf{d}}} \tag{B17}$$

Solving the original system in Eq. (B13) is equivalent to solving a reduced linear system

$$\mathbf{M}\Delta\mathbf{d} = \mathbf{r} \tag{B18}$$

for d_i and then update s' from $\Delta s' = -c^{-1}\left(\mathbf{b}^{\mathbf{T}}\Delta\mathbf{d} + g_{s'}\right)$, where the elements of the matrix $\mathbf{M} = \mathbf{A} - c^{-1}\mathbf{b}\mathbf{b}^{\mathbf{T}}$ are

$$M_{ij} = \left(\frac{\partial \mu_i}{\partial d_j}\right)_{s',d_{s\neq j}} + \left(\frac{\partial \mu_i}{\partial s'}\right)_{\mathbf{d}} \left(\frac{\partial T}{\partial d_j}\right)_{s',d_{s\neq j}} \left(\frac{\partial T}{\partial s'}\right)_{\mathbf{d}}^{-1} \tag{B19}$$

and $\mathbf{r} = -\mathbf{g}_d + c^{-1} g_{s'} \mathbf{b}$.

On the other hand, the partial derivative of chemical potentials with respect to molar densities can be written as

$$\left(\frac{\partial \mu_i}{\partial d_j}\right)_{T,d_{s\neq j}} = \left(\frac{\partial \mu_i}{\partial d_j}\right)_{s',d_{s\neq j}} + \left(\frac{\partial \mu_i}{\partial s'}\right)_{\mathbf{d}} \left(\frac{\partial s'}{\partial d_j}\right)_{T,d_{s\neq j}} \tag{B20}$$

Taking into account Eqs. (B19), (B20) and B17), the relation between matrices is

$$M_{ij}^{(du')} = H_{ij}^{(dT)}; i, j = 1, nc \tag{67}$$

The matrix **M** is formally the same as $\mathbf{H}^{(dT)}$ in Eq. (53) for VTN stability. All the points of the discussion on UVN stability (section 3.4.) hold for the PSN stability.

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Table 1 State functions, specifications and *Q*-functions (Michelsen [1])

Specification	State function	*Q*-function	Q_V-function
PT	G	G	$A + P_{spec}V$
VTN	A	$G - PV_{spec}$	A
PHN	$-S$	$\left(G - H_{spec}\right)/T$	$\left(A + P_{spec}V - H_{spec}\right)/T$
PSN	H	$G + TS_{spec}$	$A + P_{spec}V + TS_{spec}$
UVN	$-S$	$\left(G - U_{spec} - PV_{spec}\right)/T$	$\left(A - U_{spec}\right)/T$
SVN	U	$G + TS_{spec} - PV_{spec}$	$A + TS_{spec}$

Table 2 TPD functions

Specification	TPD function	Variables
PT	$D = \sum_{i=1}^{nc} x_i \left[\mu_i - \mu_{i0}\right]$	$\mathbf{x}$
VTN	$D_{vT} = \sum_{i=1}^{nc} x_i \left[\mu_i - \mu_{i0}\right] - v\left(P - P_0\right)$	$\mathbf{x}$,$\boldsymbol{v}$
PHN	$D_{ph} = -\sum_{i=1}^{nc} x_i \left[\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0}\right] + h\left(\frac{1}{T} - \frac{1}{T_0}\right)$	$\mathbf{x}$,h
PSN	$D_{ps} = \sum_{i=1}^{nc} x_i \left[\mu_i - \mu_{i0}\right] + s\left(T - T_0\right)$	$\mathbf{x}$,s
UVN	$D_{uv} = -\sum_{i=1}^{nc} x_i \left[\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0}\right] + u\left(\frac{1}{T} - \frac{1}{T_0}\right) + v\left(\frac{P}{T} - \frac{P_0}{T_0}\right)$	$\mathbf{x}$,$\boldsymbol{v}$,u
SVN	$D_{sv} = \sum_{i=1}^{nc} x_i \left[\mu_i - \mu_{i0}\right] + s\left(T - T_0\right) - v\left(P - P_0\right)$	$\mathbf{x}$,$\boldsymbol{v}$,s

Table 3 Nonlinear equations for temperature and explicit pressure

Specification	Nonlinear equation	Pressure and/or temperature	
VTN		$T_0 = T_{spec}$	$P_0 = P\left(\mathbf{n}, V_{spec}, T_{spec}\right)$
PHN	$H_{spec} = H\left(\mathbf{n}_{spec}, T, P_{spec}\right)$	$T_0 = T\left(\mathbf{n}_{spec}, H_{spec}, P_{spec}\right)$	$P_0 = P_{spec}$
PSN	$S_{spec} = S\left(\mathbf{n}_{spec}, T, P_{spec}\right)$	$T_0 = T\left(\mathbf{n}_{spec}, S_{spec}, P_{spec}\right)$	$P_0 = P_{spec}$
UVN	$U_{spec} = U\left(\mathbf{n}_{spec}, T, V_{spec}\right)$	$T_0 = T\left(\mathbf{n}_{spec}, U_{spec}, V_{spec}\right)$	$P_0 = P\left(\mathbf{n}_{spec}, T_0, V_{spec}\right)$
SVN	$S_{spec} = S\left(\mathbf{n}_{spec}, T, V_{spec}\right)$	$T_0 = T\left(\mathbf{n}_{spec}, S_{spec}, V_{spec}\right)$	$P_0 = P\left(\mathbf{n}_{spec}, T_0, V_{spec}\right)$

Table 4 Modified TPD functions

Specification	TPD function	Variables
PT	$D^*_{PT} = RT_0\, f\left(\theta\right) + \sum_{i=1}^{nc} n_i \left[\mu_i - \mu_{i0}\right]$	$\mathbf{n}$
VTN	$D^*_{VT} = RT_0\, f\left(\theta\right) + \sum_{i=1}^{nc} n_i \left[\mu_i - \mu_{i0}\right] - V\left(P - P_0\right)$	$\mathbf{n}$, $\boldsymbol{V}$
PHN	$D^*_{PH} = -R\, f\left(\theta\right) - \sum_{i=1}^{nc} n_i \left[\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0}\right] + H\left(\frac{1}{T} - \frac{1}{T_0}\right)$	$\mathbf{n}$, H
PSN	$D^*_{PS} = RT_0\, f\left(\theta\right) + \sum_{i=1}^{nc} n_i \left[\mu_i - \mu_{i0}\right] + S\left(T - T_0\right)$	$\mathbf{n}$, S
UVN	$D^*_{UV} = -R\, f\left(\theta\right) - \sum_{i=1}^{nc} n_i \left[\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0}\right] + U\left(\frac{1}{T} - \frac{1}{T_0}\right) + V\left(\frac{P}{T} - \frac{P_0}{T_0}\right)$	$\mathbf{n}$, $\boldsymbol{V}$, U
SVN	$D^*_{SV} = RT_0\, f\left(\theta\right) + \sum_{i=1}^{nc} n_i \left[\mu_i - \mu_{i0}\right] + S\left(T - T_0\right) - V\left(P - P_0\right)$	$\mathbf{n}$, $\boldsymbol{V}$, S

Table 5 TPD functions in terms of molar densities

Specification	TPD function	Variables
PT	$D = \sum_{i=1}^{nc} d_i \left[\mu_i - \mu_{i0}\left(P_{spec}\right) \right] - \left(P - P_{spec}\right)$	**d**
VTN	$D_{vT} = \sum_{i=1}^{nc} d_i \left[\mu_i - \mu_{i0} \right] - \left(P - P_0\right)$	**d**
PHN	$D_{ph} = -\sum_{i=1}^{nc} d_i \left[\frac{\mu_i}{T} - \frac{\mu_{i0}\left(P_{spec}\right)}{T_0} \right] + h' \left(\frac{1}{T} - \frac{1}{T_0} \right) + \left(\frac{P}{T} - \frac{P_{spec}}{T_0} \right)$	**d**, h'
PSN	$D_{ps} = \sum_{i=1}^{nc} d_i \left[\mu_i - \mu_{i0}\left(P_{spec}\right) \right] + s'\left(T - T_0\right) - \left(P - P_{spec}\right)$	**d**, s'
UVN	$D_{uv} = -\sum_{i=1}^{nc} d_i \left[\frac{\mu_i}{T} - \frac{\mu_{i0}}{T_0} \right] + u' \left(\frac{1}{T} - \frac{1}{T_0} \right) + \left(\frac{P}{T} - \frac{P_0}{T_0} \right)$	**d**, u'
SVN	$D_{sv} = \sum_{i=1}^{nc} d_i \left[\mu_i - \mu_{i0} \right] + s'\left(T - T_0\right) - \left(P - P_0\right)$	**d**, s'

Table 6 Total differentials and partial derivatives of state functions

Spec.	Total differential [2]	Partial derivatives		
PT	$dG = -SdT + VdP + \sum_{i=1}^{nc} \mu_i dn_i$	$\left(\frac{\partial G}{\partial T}\right)_{P,\mathbf{n}} = -S$	$\left(\frac{\partial G}{\partial P}\right)_{T,\mathbf{n}} = V$	$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \mu_i$
PHN	$dS = \frac{1}{T}dH - \frac{V}{T}dP - \frac{1}{T}\sum_{i=1}^{nc} \mu_i dn_i$	$\left(\frac{\partial S}{\partial H}\right)_{P,\mathbf{n}} = \frac{1}{T}$	$\left(\frac{\partial S}{\partial P}\right)_{H,\mathbf{n}} = -\frac{V}{T}$	$\left(\frac{\partial S}{\partial n_i}\right)_{H,P,n_{j\neq i}} = -\frac{\mu_i}{T}$
PSN	$dH = TdS - VdP + \sum_{i=1}^{nc} \mu_i dn_i$	$\left(\frac{\partial H}{\partial S}\right)_{P,\mathbf{n}} = T$	$\left(\frac{\partial H}{\partial P}\right)_{S,\mathbf{n}} = V$	$\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \mu_i$
VTN	$dA = -SdT - PdV + \sum_{i=1}^{nc} \mu_i dn_i$	$\left(\frac{\partial A}{\partial T}\right)_{V,\mathbf{n}} = -S$	$\left(\frac{\partial A}{\partial V}\right)_{T,\mathbf{n}} = -P$	$\left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}} = \mu_i$
UVN	$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T}\sum_{i=1}^{nc} \mu_i dn_i$	$\left(\frac{\partial S}{\partial U}\right)_{V,\mathbf{n}} = \frac{1}{T}$	$\left(\frac{\partial S}{\partial V}\right)_{U,\mathbf{n}} = \frac{P}{T}$	$\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n_{j\neq i}} = -\frac{\mu_i}{T}$
SVN	$dU = TdS - PdV + \sum_{i=1}^{nc} \mu_i dn_i$	$\left(\frac{\partial U}{\partial S}\right)_{V,\mathbf{n}} = T$	$\left(\frac{\partial U}{\partial V}\right)_{S,\mathbf{n}} = -P$	$\left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_{j\neq i}} = \mu_i$

Table 7 State functions as Legendre transformations of Gibbs free energy or Plank function

F	Spec.	M	m	ν_1	ξ_1	ν_2	ξ_2	$F = M - \sum_{i=1}^{m} \nu_i \xi_i$
G	PTN	$G(P,T,\mathbf{n})$	0	-	-	-	-	G
S	PHN	$Y\left(P,\frac{1}{T},\mathbf{n}\right)$	1	$\frac{1}{T}$	$\left(\frac{\partial Y}{\partial(1/T)}\right)_{P,\mathbf{n}} = H$	-	-	$-S = \frac{G-H}{T}$
H	PSN	$G(P,T,\mathbf{n})$	1	T	$\left(\frac{\partial G}{\partial T}\right)_{P,\mathbf{n}} = -S$	-	-	$H = G + TS$
A	VTN	$G(P,T,\mathbf{n})$	1	P	$\left(\frac{\partial G}{\partial P}\right)_{T,\mathbf{n}} = V$	-	-	$A = G - PV$
S	UVN	$Y\left(\frac{P}{T},\frac{1}{T},\mathbf{n}\right)$	2	$\frac{P}{T}$	$\left(\frac{\partial Y}{\partial(P/T)}\right)_{T,\mathbf{n}} = V$	$\frac{1}{T}$	$\left(\frac{\partial Y}{\partial(1/T)}\right)_{\frac{P}{T},\mathbf{n}} = U$	$-S = \frac{G-PV-U}{T}$
U	SVN	$G(P,T,\mathbf{n})$	2	P	$\left(\frac{\partial G}{\partial P}\right)_{T,\mathbf{n}} = V$	T	$\left(\frac{\partial G}{\partial T}\right)_{P,\mathbf{n}} = -S$	$U = G - PV + TS$