Efficient and robust stability analysis in the internal energy, volume, and moles (*UVN*) space

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ABSTRACT

Hydrodynamic simulation of fluids in vessels is often based on the internal energy (U), volume (V), and the number of moles of all components ($_{re}\boldsymbol{N} = N_1, N_2, ..., N_n$) as the working variables to determine the thermodynamic state by finding the global maximum of entropy. The procedure of finding the equilibrium state may be divided into two steps: stability analysis and phase-split computations. Stability analysis is performed first, and the phase-split computation proceeds if the system is unstable. Most of the past work on UVN space has been based on phase-split computations, while the stability analysis is barely investigated. Furthermore, previous studies for the stability analysis use only Newton's method to solve the non-linear algebraic equations. We present an efficient and robust approach for stability analysis where UVN is specified. The successive substitution iteration (SSI) is used to provide good initial guesses for Newton's method. The proposed approach results in a reduced number of unknowns and does not require a large number of iterations to achieve convergence in Newton's method. Our proposed formulation is compatible with different equations of state and is applicable to both pure component and multi-components. The robustness and efficiency of the algorithm for stability analysis are demonstrated in various examples.

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1. Introduction

Stability analysis is an essential element of compositional modeling in many applications such as compositional reservoir simulation [1–3], enhanced oil recovery processes [4,5], and precipitation problems [6]. For large-scale problems, such as compositional reservoir simulations, phase-behavior computations may be performed billions of times for a single simulation job. Finding the equilibrium state of a given system includes two parts: the stability analysis and phase-split computations. The stability analysis is carried out first to determine if there is a need to perform the phase-split computations. If the initial phase is stable, the phase-split computation is not required, and computational time is saved. Therefore, for phase-behavior computations, the stability analysis can have a significant influence on the efficiency of computations [1].

Consider a multicomponent mixture with specified internal energy (U), volume (V), and moles ($\boldsymbol{N} = N_1, N_2, ..., N_n$) of all components. We are interested in determining if the mixture is stable in a single-phase state. To solve this problem, one must find whether there is a multiphase state that has entropy higher than that of the given initial phase. The temperature, pressure, and composition of each phase that is consistent with the energy, volume, and total moles of components are computed in the process. Stability analysis determines the stability of the given phase and may and may not provide initial guesses for the subsequent phase-split computations depending on basic thermodynamic functions.

There are some ten published algorithms on the phase-behavior computations in the *UVN* space. Most approaches focus on the phase-split computations and use a Newton-based method to solve the highly non-linear algebraic system of equations. The authors do not report on the efficiency of the stability analysis. Castier [7] has proposed an approach that includes adding and removing phases during the phase equilibrium computations. The approach computes the temperature (T) and pressure (P) of the specified *UVN* space at the first step to allow the isothermal-isobaric stability analysis algorithm. This approach can correctly detect the stability

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or instability of the original single phase. However, the mole fractions of the trial phase obtained from the isothermal-isobaric stability analysis algorithm are not guaranteed to increase the entropy of the system. The algorithm requires a large number of iterations to achieve convergence. Coupling the stability analysis with phase-split computations can overcome the complexity of adding or removing phases in the latter if the former is robust.

To the best of our knowledge, only the work by Smejkal and Mikyška [8,9] covers the algorithm for stability analysis in the UVN space. The algorithm uses Newton's method. A damping parameter is applied for controlling the step size and a modified Cholesky decomposition for the Jacobian matrix to achieve convergence [8,9]. The work in Refs. [8,9] overcomes the convergence problems previously reported; however, it is not as computationally efficient as our algorithm, as will be demonstrated in this work. In Refs. [8,9] seven initial guesses of the temperature are required, which leads to $7(n + 2)$ initial guesses for a stability analysis computation in an n-component mixture instead of $n + 2$ in our algorithm. The authors do not provide a complete report on the efficiency of the stability analysis. Smejkal and Mikyška [8] report 124 iterations in one example and 71 iterations in another. We apply our algorithm to the same examples and compare the efficiency in Section 4 of this work. The efficiency of the stability analysis is also missing in another relevant publication by Smejkal and Mikyška [9].

Algorithms of stability analysis in the temperature, pressure, and moles (TPN) space are far more developed than they are in the UVN space. A large number of studies [1,3,6,10–13] have been published on the computations in the TPN space. Studies have initially focused on the use of Newton-based methods with various constraints. A progression of discoveries have driven the authors from relying entirely on Newton's method to adopting a two-technique approach (a combination of the SSI method and Newton's method). Although Newton's method can have quadratic convergence as opposed to the linear convergence of the SSI method, it requires good initial guesses and is computationally more expensive than the SSI method when the number of iterations is the same. The purpose of the SSI method is to provide initial guesses [6] for Newton's method.

This work presents a formulation of the stability analysis based on the SSI method to provide good initial guesses for Newton's method. The proposed algorithm improves the robustness of the computations and employs a dimensionality reduction. In addition, compared with the work by Smejkal and Mikyška [8,9], the proposed algorithm has advantages in computational efficiency. For both the SSI method and Newton's method, a general formulation is presented that is compatible with different equations of state. This work focuses on the stability analysis of the phase-behavior computation in UVN space.

The rest of the paper is structured as follows. Section 2 presents the formulation of stability analysis. Section 3 introduces the numerical details of SSI and Newton's methods. The efficiency of the proposed algorithm is demonstrated in Section 4 in problems with different degrees of complexity. A brief summary and concluding remarks are presented in Section 5. Following Smejkal and Mikyška [8], we use the well-known Peng-Robinson EOS [14] to model hydrocarbon fluids and non-hydrocarbons (e.g., hydrogen sulfide, carbon dioxide).

2. Formulation of the stability analysis

In this section, we introduce our approach for computing the stability of a single-phase system in the UVN space. Note that the stability in the context of phase equilibrium computations includes both absolute and metastability conditions. Also, note that the approach adopted in this work is related to fluid systems and will

not cover various crystallization processes.

Stability analysis determines if a given system is stable at a specified UVN condition. State I in Fig. 1 describes the given single-phase mixture which contains n components at fixed U^*, V^*, and N^*. State II shows a two-phase mixture by introducing a small amount of a second (trial) phase ($U'V'N'$). The total internal energy, volume, and moles of State II are U^*, V^*, and N^*; the same as in State I. Denote the total entropy of State I and State II as S_I and S_{II}, respectively. $\Delta S = S_{II} - S_I$ can be used to determine which state is more stable following the second law of thermodynamics. If any value of U', V', and N' leads to $\Delta S > 0$, the equilibrium state of the given system at U^*, V^*, and N^* is unstable and the system will split into two- or more phases. On the other hand, if $\Delta S < 0$ for all possible values of U', V', and N', the equilibrium state of the given mixture is stable and will remain in single-phase (State I).

Following Smejkal and Mikyška [8,9], and assuming the volume of the trial phase is fixed in a small scale, an expression of D which is a measure of entropy difference between the two can be derived:

$$D = \frac{S^{II} - S^I}{V'} = u'\left(\frac{1}{T'} - \frac{1}{T^*}\right) + \left(\frac{P'}{T'} - \frac{P^*}{T^*}\right)$$
$$- \sum_i^n c_i'\left(\frac{\mu_i'}{T'} - \frac{\mu_i^*}{T^*}\right) \quad (i = 1, 2, \ldots, n), \tag{1}$$

where u' is the energy density of the trial phase ($u' = U'/V'$) and c_i' is the concentration (molar density) of component i in the trial phase ($c_i' = N_i'/V'$). T', P', and μ_i' stand for the temperature, pressure, and chemical potential of component i of the trial phase, respectively. The superscripted quantities with a star (*) represent the original phase. We note that the temperature, pressure, and chemical potential of each component of a phase can be determined once the energy and molar density of each component are known. Therefore, all the quantities of the original phase in Eq. (1) can be computed using the specified U^*, V^*, and N^*. Like the original phase, T', P', and μ_i' can be computed by specifying u' and c_i'. The problem is then to investigate whether there exists a set of values for u' and c_i' such that $D > 0$.

The maximum of D can be computed by solving the following set of conditions

$$\left(\frac{\partial D}{\partial u'}\right)_{c'} = 0, \tag{2}$$
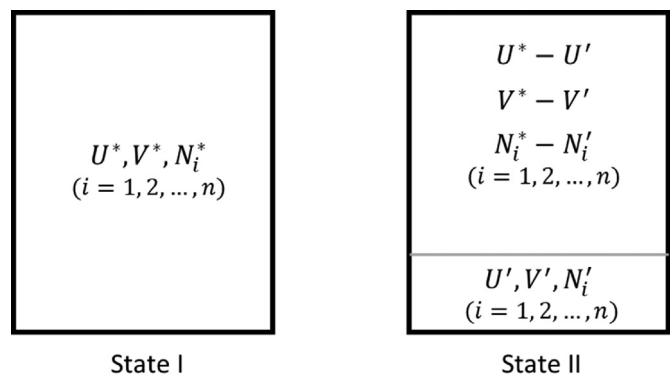

Fig. 1. Illustration of the two states considered in the stability analysis. The state with a higher total entropy S is thermodynamically more stable.

$$\left(\frac{\partial D}{\partial c_i'}\right)_{u', c_{j\neq i}'} = 0 \quad (i, j = 1, 2, ..., n), \tag{3}$$

where the subscript $c_{j\neq i}'$ indicates constant concentrations for all components except for i. Since all of the starred quantities are fixed, the derivatives of D in Eqs. (2) and (3) depend only on the quantities of the trial phase ('). This leads to the following equations:

$$\left(\frac{\partial D}{\partial u'}\right)_{c'} = \left(\frac{1}{T'} - \frac{1}{T^*}\right) - \frac{1}{T'}\left(\frac{\partial T'}{\partial u'}\right)_{c'}\left(\frac{u'}{T'} + \frac{P'}{T'} - \sum_{i=1}^{n} c_i'\frac{\mu_i'}{T'}\right)$$
$$+ \frac{1}{T'}\left[\left(\frac{\partial P'}{\partial u'}\right)_{c'} - \sum_{i=1}^{n} c_i'\left(\frac{\partial \mu_i'}{\partial u'}\right)_{c'}\right] = 0, \tag{4}$$

$$\left(\frac{\partial D}{\partial c_i'}\right)_{u', c_{j\neq i}'} = c_i'\left(\frac{\mu_i'}{T'} - \frac{\mu_i^*}{T^*}\right) = 0 \quad (i, j = 1, 2, ..., n). \tag{5}$$

We simplify the second and third terms in Eq. (4). From the expression $U = TS - PV + \sum_{i=1}^{n} N_i\mu_i$, one can obtain the expression for the entropy density by dividing by V' on the two sides of the equation. The entropy density of the trial phase ($s' = S'/V'$) can be expressed by

$$\left(\frac{u'}{T'} + \frac{P'}{T'} - \sum_{i=1}^{n} c_i'\frac{\mu_i'}{T'}\right) = s'. \tag{6}$$

Writing the Gibbs-Duhem relation

$$s'dT' - dP' + \sum_{i=1}^{n} c_i'd\mu_i' = 0. \tag{7}$$

From Eq. (7), we derive

$$\left[\left(\frac{\partial P'}{\partial u'}\right)_{c'} - \sum_{i=1}^{n} c_i'\left(\frac{\partial \mu_i'}{\partial u'}\right)_{c'}\right] = s'\left(\frac{\partial T'}{\partial u'}\right)_{c'}. \tag{8}$$

Substituting EEqs. (6) and (8) into Eq. (4) yields

$$\left(\frac{\partial D}{\partial u'}\right)_{c'} = \left(\frac{1}{T'} - \frac{1}{T^*}\right) = 0. \tag{9}$$

Eq. (9) states that $T' = T^*$, which implies the temperatures of the original phase (State I) and the trial phase in State II are identical at stationary points. Because T^* can be computed by the given U^*, V^*, and N^*, T' is also known. Since the energy density u' is a function of the temperature and concentration of the trial phase, the only unknown for finding a maximum of D becomes c'. The algorithm developed by Smejkal and Mikyška [8,9] requires to supply 7 initial guesses for T' (to compute u') to $n + 2$ initial guesses for c'. On this basis, the algorithm needs to examine $7(n + 2)$ initial guesses in stability analysis. Our algorithm does not need initial guesses for u' or T'. Thus, the number of initial guesses is $n + 2$ instead.

By taking the advantages of the simplifications, Eq. (5) leads to $\mu_i' = \mu_i^*$ for all i. Finding a maximum of D is equivalent to seeking a set of concentrations c' in the trial phase that satisfies

$$\mu_i'\left(u'\left(T^*, c_i'\right), c_i'\right) = \mu_i^* \quad (i = 1, 2, ..., n). \tag{10}$$

The chemical potentials can be expressed in terms of fugacity, f (2) as

$$\mu_i' - \mu_i^* = RT ln\left(\frac{f_i'(T^*, c')}{f_i^*(T^*, c^*)}\right) = 0 \quad (i = 1, 2, ..., n). \tag{11}$$

Let us define the fugacity coefficient, ϕ (2) of component i as

$$\phi_i = \frac{cf_i}{Pc_i} \quad (i = 1, 2, ..., n), \tag{12}$$

where $c = \sum_{i=1}^{n} c_i$ is the total molar density of the phase. Applying the natural logarithm on both sides and rearranging for the fugacity, we obtain

$$lnf_i = ln\phi_i + lnP + ln\frac{c_i}{c} \quad (i = 1, 2, ..., n). \tag{13}$$

Substituting Eq. (13) into Eq. (11), we obtain

$$ln\frac{\phi_i'(T^*, c')}{\phi_i^*(T^*, c^*)} + ln\frac{c_i'}{c_i^*} + ln\frac{P'}{P^*} - ln\frac{c'}{c^*} = 0 \quad (i = 1, 2, ..., n). \tag{14}$$

To solve Eq. (14) we propose to adopt the SSI method followed by Newton's method. The equation set for solving c' is given below.

$$lnc_i' = ln\frac{\phi_i^*(T^*, c^*)}{\phi_i'(T^*, c')} + lnc_i^* + ln\frac{P^*}{P'} - ln\frac{c^*}{c'} \quad (i = 1, 2, ..., n), \tag{15}$$

where $c' = \sum_{i=1}^{n} c_i'$ is the total molar density of the trial phase.

Quantities in the initial single-phase mixture (*) are fixed during the iterations, while the pressure and fugacity coefficients of the trial phase (') are functions of the concentrations c' that may vary with each iteration. As the solutions (c') change, P' and ϕ_i' are updated. In summary, the stability analysis contains n unknowns (the set of concentrations c') that will be determined by solving the n unknowns in Eq. (15).

3. Numerical algorithms

3.1. Initial guesses

As discussed in Section 2, we desire to compute the maximum of D defined in Eq. (1) in the c' space. If the maximum is negative, the initial single-phase mixture is stable. Otherwise, it will split into two or more phases. Since there might be several local maxima, we intend to investigate D using a few initial guesses of c'. In this work, we propose to follow the strategy in Smejkal and Mikyška [8]. The admissible set of concentrations of an n-component mixture form an n-simplex domain. We choose the barycenter of the simplex and the midpoints of the lines joining the barycenter with each of the $n + 1$ vertices as initial guesses of c' ($n + 2$ initial guesses for an n-component mixture). Fig. 2 presents an illustration of the initial
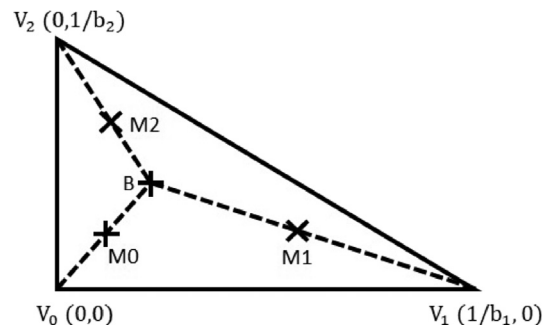
Fig. 2. Depiction of the initial guesses for c' in a binary mixture where the two components have molar volumes b_1 and b_2, respectively.

guesses of c' for a binary ($n = 2$) mixture. We can obtain four initial guesses which are marked with crosses (the barycenter B and the midpoints M0, M1, and M2). The barycenter has the coordinates $c' = (1/3b_1, 1/3b_2)$, and the coordinates of the midpoints are $(1/6b_1, 1/6b_2)$, $(2/3b_1, 1/6b_2)$, and $(1/6b_1, 2/3b_2)$ at M0, M1, and M2, respectively. We assume that this set of initial guesses is sufficient to explore the function D in the c' space.

3.2. SSI method

The SSI method is proposed to use the initial guesses of c' from the n-simplex method in the first iteration. Then, we perform the following steps to update c' by solving Eq. (15). The initial estimates of c' is tested sequentially. If any of the initial estimates leads to a positive D in eq. (1), the system is unstable. It is stable when D is negative for all the initial estimates.

1. Given U^*, V^*, and N^* of the original phase, $T^*(U^*, V^*, N^*)$ can be computed using Eq. (85) in Smejkal and Mikyška [8] by the bisection method. Following Smejkal and Mikyška [8], the reference state for computing the internal energy is $T_0 = 298.15\ K$ and $P_0 = 1\ bar$. The molar energy at the reference state is $u_0 = u(T_0, P_0) = -2478.96\ J/mol$. From an EOS (such as the Peng-Robinson EOS) one can find P^*, S^*, and fugacity coefficient ϕ^* of all components i. T' of the trial phase equals to T^*.
2. Determine the $n + 2$ initial guesses for the concentrations of the trial phase (c') from the n-simplex described above and perform the following steps for each of the guesses.
3. Let k denote the iteration count. At $k = 1$, $c'^{(k)}$ is set to one of the initial guesses we have chosen.
4. At each iteration, we aim to compute the right-side of Eq. (15). The quantities of the original phase ($*$) are already known from Step 1. The trial-phase quantities $\phi_i'^{(k)} = \phi_i'(T', c'^{(k)})$ and $P'^{(k)} = P'(T', c'^{(k)})$ are readily obtained from the EOS.
5. Update $c'^{(k)}$ by taking the exponential of the right-side of Eq. (15) to obtain $c'^{(k+1)}$.
6. Step 4 and 5 are repeated until a convergence criterion (switching tolerance) is met. Then we switch to the more efficient Newton's method.

3.3. Newton's method

We use the converged solution of c' in the SSI method as the concentrations c' for the first iteration in Newton's method. The concentrations c' in subsequent iterations are updated according to

$$c'^{(k+1)} = c'^{(k)} - J^{-1(k)} F^{(k)}. \tag{16}$$

The elements i, j of the Jacobian J, and F_i are given by

$$J_{ij}^{(k)} = \frac{\partial F_i^{(k)}}{\partial c_j'^{(k)}} = \frac{\delta_{ij}}{c_j'^{(k)}} + \frac{\partial}{\partial c_j'} \ln\varphi_i'^{(k)} + \frac{\partial}{\partial c_j'} \ln P'^{(k)} - \frac{1}{c'^{(k)}}, \tag{17}$$

$$F_i^{(k)} = \ln\frac{c_i'^{(k)}}{c_i^*} - \ln\frac{\varphi_i^*}{\varphi_i'^{(k)}} - \ln\frac{P^*}{P'^{(k)}} + \ln\frac{c^*}{c'^{(k)}} \qquad i = (1, 2, \ldots, n), \tag{18}$$

where δ_{ij} is the Kronecker delta.

Below is a brief outline of Newton's method algorithm that follows Step 6 in the SSI algorithm.

7. Let k denote the iteration count of Newton's method. At $k = 1$, $c'^{(k)}$ is the converged solution from the SSI method.
8. Solve Eq. (17) and Eq. (18) for $J_{ij}^{(k)}$ and $F_i^{(k)}$ and update $c'^{(k+1)}$ by Eq. (16).
9. Iteration is stopped once the convergence criterion is met.
10. Evaluate D defined in Eq. (1). If any of the initial guesses from Step 2 leads to a positive D, the original phase (State I in Fig. 1) is unstable, and the phase-split computations should be performed. Otherwise, the phase is stable.

4. Results

Following the procedure in Section 3, we have implemented the algorithm and performed the single-phase stability tests for examples in the literature. In this section, we report the stability analysis results of 8 problems in Castier [7] and Smejkal and Mikyška [8] that cover various degrees of complexity. Parameters of all components used in the computations in the EOS are presented in Table A1 in the Appendix. Correlation coefficients for the molar heat capacity of the ideal gases in internal energy and entropy computations are listed in Table A2 in the Appendix. In Refs. [7,8] the number of iterations in the stability analysis is not reported for problems 1–6. For problems 7 and 8, we compare the number of iterations in our algorithm with Smejkal and Mikyška [8]. We use the 2-norm (L2 norm) of the change in the concentrations from one iteration to the next to check the convergence in all the problems.

4.1. Binary mixtures of methane (C_1) and hydrogen sulfide (H_2S)

In the first four problems, we consider a binary mixture of methane (C_1) and hydrogen sulfide (H_2S) at four different specifications. Table 1 lists the specifications of the binary mixtures. According to Smejkal and Mikyška [8], Problem 1 has a solution at which large amounts of liquid and vapor phases are present. Problems 2 and 3 have the specifications that lead to solutions very close to the phase boundary (bubble-point and dew-point, respectively). The solution of Problem 4 gives a state close to the critical point of the mixture. The binary interaction parameter between C_1 and H_2S in the Peng—Robinson EOS is set equal to 0.083.

We report the concentration of all components, temperature, and pressure in the trial phase together with D and the number of iterations for convergence in Table 2. The stability analysis converges to a solution where D defined in Eq. (1) is positive. It indicates that the original mixtures are unstable. The T, P', and c_i' in the table represent one set of condition in the trial phase that makes the initial single-phase unstable and results the system to split into two or more phases subsequently.

The number of iterations depends on the tightness of the tolerance. Take Problem 2 as an example. Table 3 presents the number of iterations corresponding to various switching tolerance and final tolerance combinations. A tighter switching tolerance will lead to a higher number of iterations in the SSI method but fewer iterations in Newton's method. The number of iterations in Newton's method is rather small for the selected tightness of tolerances. The SSI method greatly facilies the convergence of Newton's

Table 1
Specifications of U, V, and N_i ; the internal energy, volume, and the total number of moles of component i, respectively: Problems 1–4.

Specifications	Problem 1	Problem 2	Problem 3	Problem 4
U (J)	-756500.8	-1511407.6	-331083.7	-636468
V (cm³)	52869	4268.1	80258.1	9926.71
N_{C_1} (mol)	10	0.95	15.1	10
N_{H_2S} (mol)	90	99.05	84.9	90

Table 2
Stability analysis provides. T, P', and c_i' (temperature, pressure, and the concentration of component i in the trial phase, respectively). Iterations contain two numbers, where the first one denotes the iterations required in the SSI to converge to within a switching tolerance of 10^{-5}, and the second number is in Newton's method to converge to within a final tolerance of 10^{-10}: Problems 1-4.

Stability analysis	Problem 1	Problem 2	Problem 3	Problem 4
T (K)	151.83	291.91	297.84	361.80
P' (MPa)	0.60	1.84	2.65	10.10
c'_{C_1} (mol /m^{-3})	104.12	146.18	13.22	1000.68
c'_{H_2S} (mol /m^{-3})	564.35	736.58	1413.64	8459.77
D(Pa /K)	875.5	26722.7	506.22	0.14
Iterations	27 + 2	17 + 2	478 + 11	3855 + 3

method. With the same initial guesses from the n-simplex method, we do not obtain a converged solution using Newton's method alone. The SSI method, which precedes Newton's method, improves the robustness of our approach. Even if we choose a large tolerance of 10^{-1} for the SSI, it is sufficient to achieve convergence.

The number of iterations of the SSI method is usually higher than those of Newton's method, because the convergence of the SSI algorithm is linear, while Newton's method is quadratic. However, for solving highly non-linear equations, the computation of the inverse of a Jacobian matrix in Newton's method can be costly when the system is complex, and it is typically the matrix inversion step which is computationally expensive. Our results in Table 2 show a small number of iterations in Newton's method in all the problems. Problems 3 and 4 require a large number of SSI iterations to converge to the switching criterion, but only a few Newton iterations to meet the convergence criterion. The SSI method requires a large number of iterations for the switching tolerance (10^{-5}) when the system of interest is close to the critical region. This number can be significantly reduced if we increase the value of switching tolerance. Tables 4 and 5 list the number of iterations based on a larger switching tolerance for Problems 3 and 4, respectively.

4.2. Liquefied petroleum gas (LPG) mixtures

Table 6 gives specifications of the 6-component LPG mixtures in Smejkal and Mikyška [8]. According to the authors, most of the fluid is in the liquid phase. The fluid system of Problem 6 is close to the critical point. Similar to Smejkal and Mikyška [8], all binary interaction coefficients are set equal to zero. The results of our computa − 16272506.4tion are summarized in Table 7.

We summarize the number of iterations in Problem 6 in Table 8. Similar to Problem 4, when the system is close to the critical point, the number of iterations in the SSI method noticeably increases, while Newton's method has a small number of iterations. Note that Newton's method converges in Problem 6 without implementing the SSI method. However, the number of iterations in Newton's method is large. It dramatically reduces by incorporating the SSI method even when the switching tolerance of the SSI is large.

4.3. Liquefied petroleum gas (LPG) mixture with water (H_2O)

In Problem 7, the LPG mixture in Problems 5 and 6 are mixed with water. The specification of the problem is presented in Table 9. All binary interaction coefficients are set to zero, the same as Smejkal and Mikyška [8]. According to the literature, Problem 7 leads to a three-phase vapor-liquid-liquid equilibrium. One liquid phase only consists of hydrocarbons, while the other liquid phase is almost pure water. The equilibrium state lies close to the phase boundary because the amount of the water-rich liquid phase is small. Our stability analysis (Table 10) finds that for an SSI switching tolerance of 10^{-5} and Newton's method stopping tolerance 10^{-10}, the number of iterations is 5 and 2, respectively. In comparison, Smejkal and Mikyška report that their algorithm, which relies on Newton's method only, requires 124 iterations to achieve convergence. Our method appears to be computationally more efficient.

Table 3
The number of iterations to reach convergence for various switching and final tolerance. The first number denotes the iterations required for the SSI, and the second number is for Newton's method: Problem 2.

SSI Switching Tolerance	Newton 10^{-2}	Newton 10^{-4}	Newton 10^{-6}	Newton 10^{-8}	Newton 10^{-10}
Newton only	failure	failure	failure	failure	failure
10^{-1}	10 + 2	10 + 2	10 + 2	10 + 3	10 + 3
10^{-3}		14 + 2	14 + 2	14 + 2	14 + 2
10^{-5}			17 + 2	17 + 2	17 + 2
10^{-7}				21 + 2	21 + 2
10^{-9}					25 + 2

Table 4
Number of iterations to reach convergence with switching tolerance of 10^{-5} and larger: Problem 3.

SSI Switching Tolerance	Newton 10^{-2}	Newton 10^{-4}	Newton 10^{-6}	Newton 10^{-8}	Newton 10^{-10}
10^{-1}	185 + 6	185 + 9	185 + 12	185 + 15	185 + 18
10^{-3}		331 + 6	331 + 9	331 + 11	331 + 16
10^{-5}			478 + 6	478 + 8	478 + 11

Table 5
Number of iterations to reach convergence with switching tolerance of 10^{-5} and larger: Problem 4.

SSI Switching Tolerance	Newton 10^{-2}	Newton 10^{-4}	Newton 10^{-6}	Newton 10^{-8}	Newton 10^{-10}
10^{-1}	820 + 4	820 + 4	820 + 4	820 + 5	820 + 5
10^{-3}		2316 + 3	2316 + 3	2316 + 3	2316 + 3
10^{-5}			3855 + 2	3855 + 3	3855 + 3

Table 6
Specifications of the system: Problems 5 and 6.

Specifications	Problem 5	Problem 6
U (J)		24858.2
V (cm^3)	479845	289380.3
N_{C_2} (mol)	10.8	10.8
$N_{C_3H_6}$ (mol)	360.8	360.8
N_{C_3} (mol)	146.5	146.5
N_{iC_4} (mol)	233	233
N_{nC_4} (mol)	233	233
N_{nC_5} (mol)	15.9	15.9

Table 7
Results of stability analysis. The SSI switching tolerance is 10^{-5}, and Newton's method stops when it converges to within a tolerance of 10^{-10}: Problems 5 and 6.

Stability analysis	Problem 5	Problem 6
T (K)	122.97	394.54
P' (MPa)	5.10×10^{-3}	4.22
c'_{C_2} (mol /m^{-3})	0.33	46.40
$c'_{C_3H_6}$ (mol /m^{-3})	3.10	1738.54
c'_{C_3} (mol /m^{-3})	0.91	718.80
c'_{iC_4} (mol /m^{-3})	0.39	1261.61
c'_{nC_4} (mol /m^{-3})	0.29	1304.72
c'_{nC_5} (mol /m^{-3})	0.0038	101.01
D(Pa /K)	35298.71	16.10
Iterations	5 + 2	478 + 2

Table 8
Number of iterations required to reach convergence as a function of the tolerance for the SSI method and Newton's method: Problem 6.

SSI Switching Tolerance	Newton 10^{-2}	Newton 10^{-4}	Newton 10^{-6}	Newton 10^{-8}	Newton 10^{-10}
Newton only	0 + 22	0 + 23	0 + 23	0 + 23	0 + 23
10^{-1}	294 + 2	294 + 3	294 + 3	294 + 4	294 + 4
10^{-3}		386 + 2	386 + 2	386 + 3	386 + 3
10^{-5}			478 + 2	478 + 2	478 + 2
10^{-7}				569 + 2	569 + 2
10^{-9}					661 + 2

Table 9
Specifications of the system: Problem 7.

Specifications	Problem 7
U (J)	− 17008802.6
V (cm^3)	401916.6
N_{C_2} (mol)	10.8
$N_{C_3H_6}$ (mol)	360.8
N_{C_3} (mol)	146.5
N_{iC_4} (mol)	233
N_{nC_4} (mol)	233
N_{nC_5} (mol)	15.9
N_{H_2O} (mol)	14

4.4. A single-component fluid (CO_2)

Problem 8 covers pure carbon dioxide (CO_2) with specified $UV\boldsymbol{N}$ in Table 11. Our algorithm computes the stability analysis (Table 12) using 40 SSI iterations to converge to within a switching tolerance of 10^{-5}, and 2 additional Newton's method iterations to the stopping tolerance of 10^{-10}. In comparison, Smejkal and Mikyška [8] state that their algorithm requires 71 iterations for Newton's method to achieve convergence.

Table 10
Results of the stability analysis. The SSI switching tolerance is 10^{-5}, and Newton's method stops when it converges to within a tolerance of 10^{-10}: Problem 7.

Stability analysis	Problem 7
T (K)	130.29
P' (MPa)	4.05×10^{-3}
c'_{C_2} (mol /m^{-3})	0.27
$c'_{C_3H_6}$ (mol /m^{-3})	2.31
c'_{C_3} (mol /m^{-3})	0.66
c'_{iC_4} (mol /m^{-3})	0.25
c'_{nC_4} (mol /m^{-3})	0.18
c'_{nC_5} (mol /m^{-3})	0.0021
c'_{H_2O} (mol /m^{-3})	0.080
D(Pa /K)	47342.63
Iterations	5 + 2

Table 11
Specification of the system: Problem 8.

Specifications	Problem 8
U (J)	− 87211375.74
V (cm^3)	1×10^6
N_{CO_2} (mol)	1×10^4

Table 12
Results of the stability analysis. The tolerances of 10^{-5} and 10^{-10} are used in the SSI and Newton's method, respectively: Problem 8.

Stability analysis	Problem 8
T (K)	280.00
P' (MPa)	4.16
c'_{CO_2} (mol /m^{-3})	2790.06
D(Pa /K)	4069.49
Iterations	40 + 2

We have also examined a number of other examples which the stable state is in three-phases. In some of those example stability finds a single phase to be stable with temperature to be negative. We interpret the negative temperature as indication that the single phase is unstable.

5. Conclusions

An efficient algorithm is presented for single-phase stability analysis in fluid systems with specified internal energy U, volume V, and moles $\boldsymbol{N}$ of all components. The our proposed algorithm has various merits over the method in the literature. We take advantage of the fact that the trial phase temperature is the same as the temperature of the original single-phase mixture, to reduces the dimension of the search space. This results in fewer initial guesses compared to the method in the literature. In the proposed algorithm, the successive substitution interactions (SSI) method is coupled with Newton's method. The robustness of the algorithm is demonstrated in problems with different degrees of complexity.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Ran Bi: Writing - original draft, Writing - review & editing. **Ali Zidane:** Conceptualization. **Abbas Firoozabadi:** Conceptualization, Investigation, Supervision.

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Appendix

Table A1
Parameters of various components. T_{crit}, P_{crit}, and ω represent the critical temperature, critical pressure, and acentric factor, respectively: Problems 1−8.

Component	T_{crit} (K)	P_{crit} (bar)	ω
C_1	190.4	46.0	0.011
H_2S	373.2	89.4	0.081
C_2	305.4	48.8	0.099
C_3H_6	364.9	46.0	0.144
C_3	369.8	42.5	0.153
iC_4	408.2	36.5	0.183
nC_4	425.2	38.0	0.199
nC_5	469.7	33.7	0.251
H_2O	647.3	221.2	0.344
CO_2	304.14	73.75	0.239

Table A2
Correlation coefficients $(\alpha_0, \alpha_1, \alpha_2, \alpha_3)$ from Smejkal and Mikyška [8] for computing the heat capacity of the ideal gases $-1.160 \times 10^{-4} c_{p,i}^{ig}(T) = \sum\limits_{k=0}^{3} \alpha_{ik}T^k$: Problems 1−8.

Component	α_0	α_1	α_2	α_3
C_1	19.25	5.213×10^{-2}	1.197×10^{-5}	-1.132×10^{-8}
H_2S	31.94	1.463×10^{-3}	2.432×10^{-5}	-1.176×10^{-8}
C_2	5.409	1.781×10^{-1}	-6.938×10^{-5}	8.713×10^{-9}
C_3H_6	3.710	2.345×10^{-1}		2.205×10^{-8}
C_3	-4.224	3.063×10^{-1}	-1.586×10^{-4}	3.215×10^{-8}
iC_4	-1.390	3.847×10^{-1}	-1.846×10^{-4}	2.895×10^{-8}
nC_4	9.487	3.313×10^{-1}	-1.108×10^{-4}	-2.822×10^{-9}
nC_5	-3.626	4.873×10^{-1}	-2.580×10^{-4}	5.305×10^{-8}
H_2O	32.24	1.924×10^{-3}	1.055×10^{-5}	-3.596×10^{-9}
CO_2	19.80	7.344×10^{-2}	-5.602×10^{-5}	-1.715×10^{-8}

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