

# Investigation of mixture stability at given volume, temperature, and number of moles

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## ABSTRACT

We derive a criterion for phase stability under constant temperature, moles, and volume using the Helmholtz free energy. Using the volume-based formulation, we develop a numerical algorithm to investigate single-phase stability based on the Newton method. We demonstrate robustness and efficiency of the new method in a number of examples in single-phase stability testing.

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## 1. Introduction

Consider a mixture of  $n$  components with mole numbers  $N_1, \dots, N_n$  in a closed system of constant volume  $V$  at temperature  $T$ . We are interested to know whether the mixture is in single-phase or splits into two or more phases. This is the problem of phase stability under constant temperature, moles, and volume (VT-stability). The goal of the constant volume stability analysis is to determine whether a phase is stable at specified volume, temperature, and mole numbers. If the phase is unstable, this procedure may be followed by the equilibrium calculation at constant temperature and volume, in which the final pressure of the mixture in the cell is to be computed together with the compositions and amounts of the split-phases. The latter is the problem of the two-phase phase-split (also called flash) at constant temperature, moles, and volume (VT-flash). The problem has been formulated in a recent paper [1], where a simple iterative algorithm is developed to compute the two-phase equilibrium under constant temperature, volume and moles. VT-stability procedure can be developed to simplify the VT-flash calculation. As the VT-stability algorithm is simpler than VT-flash, it can be

performed first. If single-phase is stable, the VT-flash calculation is avoided. This paper is focused on the problem of testing VT-stability only. The application of the VT-stability to provide initial guesses for the VT-flash is an important problem which is currently under investigation.

The phase stability at constant pressure and temperature (PT-stability) is addressed in many references [2–5]. In this approach, pressure, temperature and overall chemical composition are given. Trial phases of various compositions are tested to find if there is a composition for which transfer of a small amount of the trial phase from the initial phase leads to a decrease of the Gibbs free energy. This is usually formulated using the so-called tangent plane distance function  $D$ . If a trial phase composition is found for which the function  $D$  is negative, the mixture is unstable and the trial phase composition can be used as an initial guess in the two-phase PT-flash [7]. If for all trial phase compositions the value  $D$  is non-negative, the mixture is in single-phase. For numerical efficiency, the search for the global minimum of function  $D$  [5] in the compositional space is replaced by local minimization using multiple initial guesses [2–4]. Many methods have been developed to locate the minima of function  $D$  in the literature cited above and in other papers.

The methods developed for PT-stability may not be corresponding to the VT-flash, in which the pressure is not known a-priori. Michelsen [3] suggested to use the PT-stability algorithm for investigation of the phase stability in other variables specifications ( $P, S$

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or  $P, H$ ). While these methods should provide the same results, in some special cases, as we will discuss later in the paper, they may not. They may be also differences in numerical efficiency. We have found out that the numerical implementation of the VT-stability using the PT-algorithm at the pressure given by the equation of state may fail to provide correct results. We will show two examples to illustrate this issue. An alternative to the PT-stability will also provide a new option. Therefore, we develop a new ‘volume-based’ formulation of the phase stability criterion and present a numerical algorithm for testing single-phase stability at constant temperature and volume. Although the VT-stability criterion can be found in Refs. [3,6,8], the working equations for phase stability at constant temperature and volume, to the best of our knowledge, have not appeared in the scientific literature.

The paper is structured as follows. In the first section, we derive conditions for single-phase stability at constant temperature and volume. Then, we reformulate this condition in terms of the volume functions that were introduced previously [1]. A numerical algorithm is suggested for testing VT-stability, and, finally, we present examples of phase stability testing based on the new formulation for a number of mixtures under different conditions.

## 2. Conditions for phase stability

Consider a mixture of  $n$  components with mole numbers  $N_1, \dots, N_n$  occupying volume  $V$  at temperature  $T$ . The question is whether the system stays in a single phase or splits into two phases. The Helmholtz free energy of a phase is given by

$$A = -PV + \sum_{i=1}^n N_i \mu_i, \quad (1)$$

where  $P = P(V, T, N_1, \dots, N_n)$  is the pressure given by a pressure-explicit equation of state, and  $\mu_i = \mu_i(V, T, N_1, \dots, N_n)$  is the chemical potential of the  $i$ -th component in the mixture. If the system is in single-phase, then the total Helmholtz free energy of the mixture reads as

$$A^I = A(V, T, N_1, \dots, N_n), \quad (2)$$

while in the two-phase

$$A^{II} = A(V', T, N'_1, \dots, N'_n) + A(V - V', T, N_1 - N'_1, \dots, N_n - N'_n). \quad (3)$$

In Eq. (3) the prime represents the variables of the trial phase. Note that the chemical composition of the trial phase can be quite different from that of the initial phase. Let us assume that if the single phase is unstable, then an arbitrarily small perturbation can turn the system into two-phase. Using the Taylor expansion of the second term of the right hand side of (3) around the point  $(V, T, N_1, \dots, N_n)$ , we derive

$$\begin{aligned} A(V - V', T, N_1 - N'_1, \dots, N_n - N'_n) &= A(V, T, N_1, \dots, N_n) \\ &- \frac{\partial A}{\partial V}(V, T, N_1, \dots, N_n)V' - \sum_{i=1}^n \frac{\partial A}{\partial N_i}(V, T, N_1, \dots, N_n)N'_i \\ &+ R_1(V', T, N'_1, \dots, N'_n), \end{aligned} \quad (4)$$

where  $R_1(V', T, N'_1, \dots, N'_n)$  denotes the remainder in the Taylor polynomial expansion after the first-order terms. Combining the last equation with (2), and using

$$\frac{\partial A}{\partial V} = -P, \quad \frac{\partial A}{\partial N_i} = \mu_i, \quad (5)$$

we rewrite the change of the Helmholtz free energy from the single-phase to the two-phase state as

$$\begin{aligned} \Delta A = A^{II} - A^I &= A(V', T, N'_1, \dots, N'_n) + P(V, T, N_1, \dots, N_n)V' \\ &- \sum_{i=1}^n \mu_i(V, T, N_1, \dots, N_n)N'_i + R_1(V', T, N'_1, \dots, N'_n). \end{aligned} \quad (6)$$

Using Eq. (1), the last equation can be rewritten as

$$\begin{aligned} \Delta A &= \sum_{i=1}^n [\mu_i(V', T, N'_1, \dots, N'_n) - \mu_i(V, T, N_1, \dots, N_n)]N'_i \\ &- [P(V', T, N'_1, \dots, N'_n) - P(V, T, N_1, \dots, N_n)]V' \\ &+ R_1(V', T, N'_1, \dots, N'_n). \end{aligned} \quad (7)$$

For sufficiently small perturbations  $(V', T, N'_1, \dots, N'_n)$  the remainder term cannot change the sign of  $\Delta A$ , which implies that the single phase is stable if (c.f. [6])

$$\begin{aligned} \sum_{i=1}^n [\mu_i(V', T, N'_1, \dots, N'_n) - \mu_i(V, T, N_1, \dots, N_n)]N'_i \\ - [P(V', T, N'_1, \dots, N'_n) - P(V, T, N_1, \dots, N_n)]V' \geq 0 \end{aligned} \quad (8)$$

for all admissible states  $(V', T, N'_1, \dots, N'_n)$ .

## 3. Different forms of the phase stability criterion

We will rewrite (8) into a more convenient form. Let us introduce the overall molar concentration  $c = N/V$ , the trial phase molar concentration  $c' = N'/V'$ , overall mole fractions  $z_i = N_i/N$ , and trial phase mole fractions  $x_i = N'_i/N'$ , where  $N = \sum_{i=1}^n N_i$  and  $N' = \sum_{i=1}^n N'_i$ . Dividing (8) by  $V'$  and using the fact that pressure and chemical potentials are homogeneous functions of degree zero in volume and moles, the single-phase is stable if and only if the tangent plane distance function  $D$  defined by

$$\begin{aligned} D(T, c'x_1, \dots, c'x_n) &= \sum_{i=1}^n [\mu_i(1, T, c'x_1, \dots, c'x_n) \\ &- \mu_i(1, T, cz_1, \dots, cz_n)]c'x_i \\ &- [P(1, T, c'x_1, \dots, c'x_n) \\ &- P(1, T, cz_1, \dots, cz_n)] \end{aligned} \quad (9)$$

is nonnegative for all admissible concentrations  $(c'x_1, \dots, c'x_n)$  at temperature  $T$ . To see whether a state with a negative value of  $D$  exists, it is sufficient to investigate the values of  $D$  in the minima. The stationary points of function  $D$  are given by

$$\frac{\partial D}{\partial (c'x_j)} = \mu'_j - \mu_j + \sum_{i=1}^n \frac{\partial \mu'_i}{\partial N'_j} c'x_i - \frac{\partial P'}{\partial N'_j} = 0, \quad j = 1, \dots, n. \quad (10)$$

In the equations above, the pressure and chemical potentials are understood as functions of independent variables  $V', T$ , and  $N'_1, \dots, N'_n$ ; therefore, the partial derivatives are denoted as  $\partial \mu'_i / \partial N'_j$ , and  $\partial P' / \partial N'_j$ , respectively. We use the convention that the primed pressure, chemical potentials and their derivatives are

evaluated at  $(1, T, c'x_1, \dots, c'x_n)$ , while the unprimed ones are evaluated at  $(1, T, cz_1, \dots, cz_n)$ . From the reciprocity relations

$$\frac{\partial \mu'_i}{\partial N'_j} = \frac{\partial \mu'_j}{\partial N'_i}, \quad \text{and} \quad \frac{\partial P'}{\partial N'_j} = -\frac{\partial \mu'_j}{\partial V'} \tag{11}$$

we obtain

$$\frac{\partial D}{\partial (c'x_j)} = \mu'_j - \mu_j + \sum_{i=1}^n \frac{\partial \mu'_j}{\partial N'_i} c'x_i + \frac{\partial \mu'_j}{\partial V'} = 0, \quad j = 1, \dots, n. \tag{12}$$

Note that the chemical potentials satisfy

$$\mu_i(\alpha V', T, \alpha N'_1, \dots, \alpha N'_n) = \mu_i(V', T, N'_1, \dots, N'_n) \tag{13}$$

for all admissible states  $(V', T, N'_1, \dots, N'_n)$  and  $\alpha > 0$  (i.e.  $\mu_i$  is a homogeneous function of degree zero in variables  $V'$  and  $N'_1, \dots, N'_n$ ). Therefore,

$$\sum_{i=1}^n \frac{\partial \mu'_j}{\partial N'_i} c'x_i + \frac{\partial \mu'_j}{\partial V'} = 0, \tag{14}$$

and the stationarity conditions (12) simplify to

$$\frac{\partial D}{\partial (c'x_j)} = \mu'_j - \mu_j = 0, \quad j = 1, \dots, n, \tag{15}$$

which means that in every stationary point of function  $D$ , the initial phase and the trial phase are in chemical equilibrium (the chemical potentials of each component in the trial phase and the initial phase are equal). Substituting (15) into (9), the value of  $D$  at the stationary point is equal to  $P - P$ . If the global minimum of function  $D$  is negative, the trial phase will be in chemical equilibrium with the initial phase, but not in mechanical equilibrium. When the trial phase will have higher pressure than the initial phase, the phase split will occur. If the global minimum of function  $D$  is zero (trivial solution has zero value of  $D$ , so the global minimum of  $D$  cannot have a positive value), then the mixture remains in single-phase.

In the development above, the stability criterion (8) was normalized to unit volume of the trial phase, however, it is interesting to mention that other reformulations are also possible. The criterion (8) can also be normalized to unit moles of the trial phase. In this case we define a modification of the  $D$  function by

$$D^*(T, c'x_1, \dots, c'x_n) = \frac{D(T, c'x_1, \dots, c'x_n)}{c'} \tag{16}$$

The condition for stationary points of the function  $D^*$  reads as

$$\frac{\partial D^*}{\partial (c'x_j)} = \frac{(\mu'_j - \mu_j)c' - D}{c'^2} = 0, \quad j = 1, \dots, n, \tag{17}$$

from which it follows that

$$\mu'_j - \mu_j = \frac{D}{c'} = K, \quad j = 1, \dots, n, \tag{18}$$

i.e. the difference between chemical potentials in the trial and initial phases has the same value  $K$  for all components. Combining (18) with (16) and (9), it can be shown readily that the  $D^*$  function in any stationary point is equal to the value  $K$  and that the pressures of the trial phase and the initial phase are equal.

As both functions  $D$  and  $D^*$  have the same signs in any point, the results of stability analysis have to be the same for both functions. However, the locations of minima for the  $D$  function are very different from those for  $D^*$ . The meaning of stationary point depends on which function is used for stability analysis. This indicates that any recommendation on using the global minimum of any of them as an initial guess for the flash calculation can be considered ad hoc.

#### 4. Limitations of the PT-stability analysis

The discussion above could lead us to the conclusion that to test the single phase stability of a mixture at constant  $V$  and  $T$ , it is sufficient to perform the conventional PT-stability testing of the mixture using the pressure given by the equation of state for the single phase. Although the conclusion, which has been mentioned in the literature [3], is theoretically correct, we have found out that the common numerical implementations of this approach may not provide correct results. To be specific, the mixtures from Examples 3 and 4 are not VT-stable at certain conditions (see Examples 3 and 4 below), but the PT-stability indicates stability. The reason is that the pressure computed from the equation of state is negative. When  $P$  is negative, one cannot use the Wilson correlation to obtain initial guess of  $K$  values. Even when we used other initial guesses by assuming various values of positive pressures in the Wilson correlation, the PT-stability predicted that the system is stable. Without good initial guesses, the PT-stability algorithm [2–4] can miss the global minimum of function  $D$  and indicate single-phase instead of two-phase. One may argue that if the pressure is negative, the system is unstable without performing flash calculations. Our algorithm would determine phase stability whether the pressure is positive or negative.

Another example when the conventional PT-stability analysis will fail is the situation in which the PT-stability testing is performed on a trivial mixture composed of a single component. In this situation, if the pressure  $P$  is higher than the saturation pressure  $P^{sat}(T)$  at a given temperature  $T$ , the 'mixture' is stable liquid. If pressure  $P$  is lower than  $P^{sat}(T)$ , the 'mixture' is stable gas. Only if  $P = P^{sat}(T)$ , the 'mixture' can be in two-phase but also in single-phase (saturated liquid or saturated gas). Note that all the latter states are indistinguishable in terms of  $P$  and  $T$  variables, but can be distinguished using the volume  $V$ . Although this issue is typical for pure components only, we would like to have a theory that will treat the real mixtures and the pure components in a unified way. These issues and desirability of an alternative approach to stability have lead us to develop a new 'volume-based' formulation of the phase stability that can address VT-stability directly.

#### 5. Numerical algorithm for testing phase stability

We will derive a numerical procedure for testing single-phase stability at constant temperature, volume, and moles based on the function  $D$ . Using the volume functions, which are introduced previously [1], the stationarity conditions (15) for function  $D$  can be rewritten as

$$\ln \frac{c'x_i}{cz_i} + \ln \Phi_i(\mathbf{cz}) - \ln \Phi_i(c'\mathbf{x}) = 0, \quad i = 1, \dots, n, \tag{19}$$

where  $\Phi_i$  is the volume function of the  $i$ -th component and  $\mathbf{cz}$  and  $c'\mathbf{x}$  denote vectors with components  $cz_1, \dots, cz_n$  and  $c'x_1, \dots, c'x_n$ , respectively.

It is tempting to solve the system (19) by the successive substitution method (SSI) defined by

$$c'x_i^{k+1} = cz_i \frac{\Phi_i(c'x^k)}{\Phi_i(\mathbf{cz})}, \tag{20}$$

where  $c'x^0$  is an initial guess. However, we have found that this approach does not work for the following reasons:

1. The sequence given by (20) does not converge in many cases. Frequently, after several iterations the iterate jumps out of the feasible region (i.e.  $c'x_i < 0$  for some  $i \in \{1, 2, \dots, n\}$  or  $\sum_{i=1}^n b_i c'x_i \geq 1$ , where  $b_i$  denotes the covolume parameter of the  $i$ -th component in the Peng–Robinson equation of state).

- Even if the sequence (20) converges to a limit, it is not guaranteed that the limit is the correct solution – the global minimum of function  $D$ . This is a common problem in local methods which is usually solved by proper initialization of the algorithm, but in case of the SSI method, this does not solve the problem (see the next point).
- We have seen the cases where the iterates diverge from the correct solution no matter how close the initial guess is to the correct solution. It thus happens that the correct solution is a fixed point of the iteration (20), but the iterates diverge from it rather than converge. In many cases, the algorithm converges to a saddle point of function  $D$  rather than (at least local) minimum.
- The convergence of SSI (if it is achieved) is typically slow. Unlike in PT-stability, the slow convergence is not compensated by the robustness of the method.
- It is not clear how to choose a stopping criterion. If the iterations are stopped whenever the norm of the increment  $\Delta c'x = c'x^{k+1} - c'x^k$  in an iteration is lower than a certain tolerance  $\varepsilon_{TOL} > 0$  or if the decrease of the value of  $D$  in an iteration is small, there is no guarantee that the error of approximation of  $c'x$  is small.

Therefore, the system of equations (19) is solved using the Newton–Raphson iterative method. Starting with an initial guess  $c'x^0$ , in each iteration we find a direction  $\Delta c'x^k$  by solving the system

$$\mathbf{J}(c'x^k)\Delta c'x^k = -\mathbf{F}(c'x^k), \quad (21)$$

where the vector  $\mathbf{F}$  has the elements

$$F_i(c'x) = \ln \frac{c'x_i}{cz_i} + \ln \Phi_i(\mathbf{c}z) - \ln \Phi_i(c'x), \quad i = 1, \dots, n, \quad (22)$$

and  $\mathbf{J}$  is the Jacobian matrix with elements

$$J_{i,j}(c'x) = \frac{\partial F_i}{\partial (c'x_j)}(c'x) = \frac{\delta_{i,j}}{c'x_j} - \frac{\partial \ln \Phi_i}{\partial (c'x_j)}(c'x), \quad i, j = 1, \dots, n, \quad (23)$$

where  $\delta_{i,j} = 1$  for  $i=j$  and  $\delta_{i,j} = 0$  for  $i \neq j$ . After solving for the direction  $\Delta c'x^k$ , the approximation is updated as

$$c'x^{k+1} = c'x^k + \lambda^k \Delta c'x^k, \quad (24)$$

where  $\lambda^k \in (0; 1)$  is a dumping factor. We set  $\lambda^k = 1$  for the first trial. If  $c'x^{k+1}$  is outside of the feasible domain,  $\lambda^k$  is halved until the new approximation stays in the feasible domain. This modification of the Newton method (the so-called line search) avoids overshooting and enables to achieve global convergence in the Newton method. This means that the approximations will converge to a stationary point of function  $D$  for any initial guess. It should be noted that the property of global convergence is different from the convergence to the global minimum of function  $D$ , which, of course, cannot be guaranteed neither by using Newton–Raphson, nor any other local minimization method. The approximations converge to a stationary point, including the local maxima or saddle points. We have observed in many cases that with poor initial guesses the approximations in the Newton–Raphson method converge to a saddle point. Unlike in SSI, the Newton–Raphson iterations always converge to a stationary point if the initial guess is close enough, i.e. there exist basins of attraction around all stationary points. To ensure convergence toward the global minimum of function  $D$ , proper initial guesses must be provided.

In PT-stability for vapor-liquid systems, Wilson's correlation [10] usually provides reasonable initial guesses. In VT-stability, this correlation cannot be used directly, because the initial pressure is unknown. One idea could be to use pressure given by equation of state for the initial phase. In some cases, this initial pressure can be negative. Therefore, we propose a robust method for initialization

of VT-stability algorithm based on the saturation pressure  $P_i^{sat}(T)$  of each component  $i$  at temperature  $T$ . We will discuss two situations depending on whether the initial phase is considered as liquid- or vapor-like. If the initial phase is liquid-like, then the vapor phase pressure  $P_{ini}$  is estimated as

$$P_{ini} = \sum_{i=1}^n P_i^{sat}(T)z_i, \quad (25)$$

and the trial (vapor) phase composition is estimated as

$$x_i^0 = \frac{P_i^{sat}}{P_{ini}}z_i, \quad i = 1, \dots, n. \quad (26)$$

If the initial phase is vapor-like, then we estimate the trial (liquid) phase composition as

$$x_i^0 = \frac{z_i \frac{P_i^{sat}}{P_j^{sat}}}{\sum_{j=1}^n z_j \frac{P_i^{sat}}{P_j^{sat}}}, \quad i = 1, \dots, n, \quad (27)$$

and the initial trial (liquid) phase pressure  $P_{ini}$  is given by

$$P_{ini} = \sum_{i=1}^n P_i^{sat}(T)x_i^0. \quad (28)$$

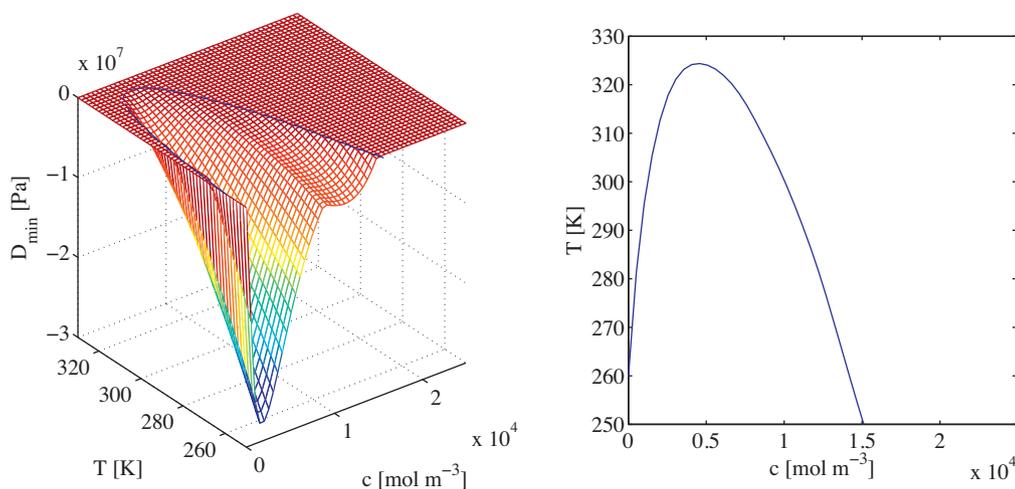
As we do not know a-priori whether the initial phase is vapor- or liquid-like, both possibilities are tested. The initial concentration  $c^0$  of the trial phase is evaluated from the equation of state using the estimated trial phase composition  $x_i^0 (i = 1, \dots, n)$  and initial pressure  $P_{ini}$ . For multiple roots in the equation of state, we obtain different initial guesses. In case of three different roots, only two of them are accepted and the middle one is disregarded. This way we obtain up to four initial guesses for the Newton method. We have tested this strategy on a number of mixtures (see the Examples) and we have not seen a case for which the global minimum of function  $D$  would be missed.

The iterations are stopped when the maximal number of iterations is achieved (500) or when the Euclidian norm of the direction vector is less than a prescribed limit. We use  $\|\Delta c'x^k\| < 10^{-7}$  as a stopping criterion in all examples below. For the Newton–Raphson method (and also for any other quadratically convergent method, see e.g. [11]), the norm of the error of  $c'x$  is approximately equal to the norm of increment  $\|\Delta c'x^k\|$  in the vicinity of the stationary point. This is not the case for SSI (and other methods that converge only linearly), in which the small increment does not generally imply a small error of approximation.

## 6. Numerical examples of VT-stability testing

We have tested the algorithm in several examples of VT-stability testing for binary and multi-component mixtures under different conditions. In all numerical experiments we investigate stability of an  $n$ -component mixture with prescribed chemical composition  $z_1, \dots, z_n$  as a function of temperature  $T$  and overall molar concentration  $c$ . The  $c, T$ -space is discretized by a grid with  $50 \times 50$  vertices. For each point  $(c, T)$  of the grid we perform the stability analysis. We provide plots of the value of the global minimum as a function of  $c$  and  $T$  which allows to detect two-phase stability boundaries. Parameters of the Peng–Robinson equation of state for all components used are presented in Table 1. In most examples we investigate VT-stability of mixtures whose phase-splitting at constant temperature, volume and moles has been investigated in our previous work [1].

**Example 1.** In the first example we investigate VT-stability for a binary mixture of methane ( $C_1$ ) and propane ( $C_3$ ) with mole fractions  $z_{C_1} = 0.547413$  and  $z_{C_3} = 0.452587$  for temperatures



**Fig. 1.** Global minimum of function  $D$  as a function of the overall molar density  $c$  and temperature  $T$  (left) and boundary between single-phase and two-phase regions in the  $c, T$ -space (right). **Example 1:** binary  $C_1$ – $C_3$  mixture.

$T \in (250 ; 330) \text{ K}$  and the whole range of feasible molar densities. The binary interaction coefficient  $\delta_{C_1-C_3} = 0.0365$ . The minima of function  $D$  for each point and the approximate boundaries of the two-phase region in the  $c, T$ -space are presented in Fig. 1.

**Example 2.** In the second example we investigate VT-stability for a binary mixture of methane ( $C_1$ ) and normal pentane ( $nC_5$ ) with mole fractions  $z_{C_1} = 0.547413$  and  $z_{nC_5} = 0.452587$  for temperatures  $T \in (320 ; 430) \text{ K}$  and the whole range of feasible molar densities. The binary interaction coefficient  $\delta_{C_1-nC_5} = 0.041$ . The minima of function  $D$  for each point and the approximate boundaries of the two-phase region in the  $c, T$ -space are presented in Fig. 2.

**Example 3.** In the third example we change the mole fractions in Example 2 and investigate VT-stability for a binary mixture of methane ( $C_1$ ) and normal pentane ( $nC_5$ ) with mole fractions  $z_{C_1} = 0.489575$  and  $z_{nC_5} = 0.510425$  for temperatures  $T \in (250 ; 450) \text{ K}$  and the whole range of feasible molar densities. The minima of function  $D$  for each point and the approximate boundaries of the two-phase region in the  $c, T$ -space are presented in Fig. 3.

Note that for  $c = 6135.3 \text{ mol m}^{-3}$  and  $T = 310.95 \text{ K}$ , the mixture is unstable, but the PT-stability analysis performed at the pressure provided by the equation of state ( $P = -9.93516 \text{ bar}$ ) with several initial guesses indicates single-phase. This is an example of one of the issues with the PT-stability analysis discussed above, which justifies the alternative formulation.

**Example 4.** In the fourth example we investigate VT-stability for a binary mixture of carbon dioxide ( $CO_2$ ) and normal decane ( $nC_{10}$ ) with mole fractions  $z_{CO_2} = 0.547413$  and  $z_{nC_{10}} = 0.452587$  for

temperatures  $T \in (250 ; 650) \text{ K}$  and the whole range of feasible molar densities. The binary interaction coefficient  $\delta_{CO_2-nC_{10}} = 0.15$ . The minima of function  $D$  for each point and the approximate boundaries of the two-phase region in the  $c, T$ -space are presented in Fig. 4. Note that for high molar densities  $c$  and low temperatures we can observe a second two-phase region which may correspond to a liquid–liquid two-phase region (provided that the solid phase does not form). As can be seen in Fig. 4, for  $c = 6307.21 \text{ mol m}^{-3}$  and  $T = 311 \text{ K}$ , the mixture is unstable. This is another example in which the PT-stability fails to provide correct answer because when performed at the pressure given by the equation state ( $P = -184.5 \text{ bar}$ ), it indicates single phase.

**Example 5.** In the fifth example we investigate VT-stability for a four-component mixture of nitrogen ( $N_2$ ), methane ( $C_1$ ), propane ( $C_3$ ), and normal decane ( $nC_{10}$ ) with mole fractions  $z_{N_2} = 0.2463$ ,  $z_{C_1} = 0.2208$ ,  $z_{C_3} = 0.2208$ , and  $z_{nC_{10}} = 0.3121$  for temperatures  $T \in (250 ; 650) \text{ K}$  and the whole range of feasible molar densities. The binary interaction coefficients are shown in Table 2. The minima of function  $D$  for each point and the approximate boundaries of the two-phase region in the  $c, T$ -space are presented in Fig. 5.

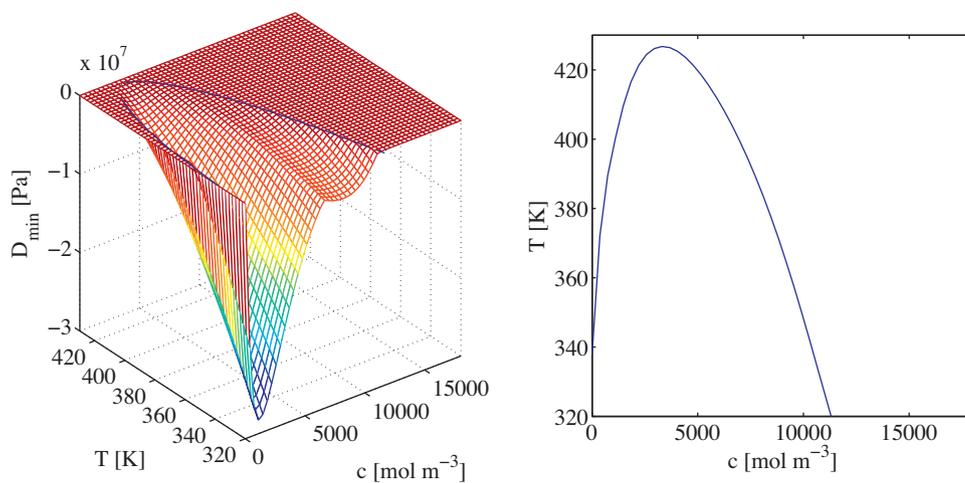
**Example 6.** In the sixth example we investigate VT-stability for a seven-component mixture of nitrogen ( $N_2$ ), carbon dioxide ( $CO_2$ ) with a multicomponent oil. The oil is modeled by seven (pseudo)components –  $N_2$ ,  $CO_2$ , methane ( $C_1$ ), and four hydrocarbon pseudo-components denoted as  $PC_1$  ( $H_2S + C_2 + C_3$ ),  $PC_2$  ( $C_4$ – $C_6$ ),  $PC_3$  ( $C_7$ – $C_{11}$ ), and  $C_{12+}$ . In this example oil is mixed with nitrogen to obtain a nitrogen-rich mixture with overall composition  $z_{N_2} = 0.466905$ ,  $z_{CO_2} = 0.007466$ ,  $z_{C_1} = 0.300435$ ,  $z_{PC_1} = 0.105051$ ,  $z_{PC_2} = 0.041061$ ,  $z_{PC_3} = 0.045060$ , and  $z_{C_{12+}} = 0.034021$ . We investigate VT-stability of this mixture for temperatures  $T \in (250 ; 650) \text{ K}$  and the whole range of feasible molar densities. The binary interaction coefficients are shown in Table 3. The minima of function  $D$  for each point and the approximate boundaries of the two-phase region in the  $c, T$ -space are presented in Fig. 6.

**Table 1**  
Parameters of the Peng–Robinson equation of state for all components used in all examples.  $PC_1$ – $PC_3$  are the pseudocomponents defined in Examples 6 and 7.

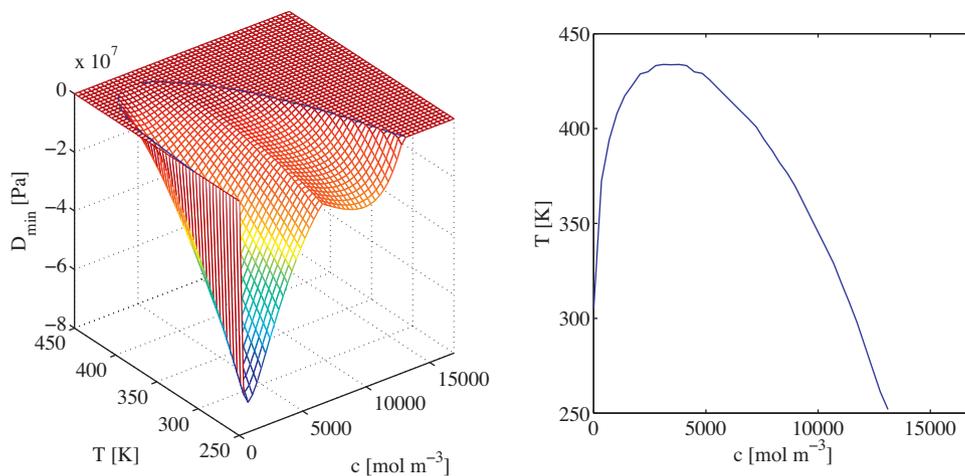
Component	$T_{i,crit}$ (K)	$P_{i,crit}$ (MPa)	$\omega_i$ (–)	$M_{w,i}$ (g mol <sup>-1</sup> )
CO <sub>2</sub>	304.14	7.375	0.2390	44
N <sub>2</sub>	126.21	3.390	0.039	28
C <sub>1</sub>	190.56	4.599	0.0110	16
C <sub>3</sub>	369.83	4.248	0.153	44.1
nC <sub>5</sub>	469.70	3.370	0.2510	72.2
nC <sub>10</sub>	617.70	2.110	0.489	142.28
PC <sub>1</sub>	333.91	5.329	0.1113	34.64
PC <sub>2</sub>	456.25	3.445	0.2344	69.52
PC <sub>3</sub>	590.76	2.376	0.4470	124.57
C <sub>12+</sub>	742.58	1.341	0.9125	248.30

**Table 2**  
Binary interaction coefficients for the four-component mixture used in Example 5.

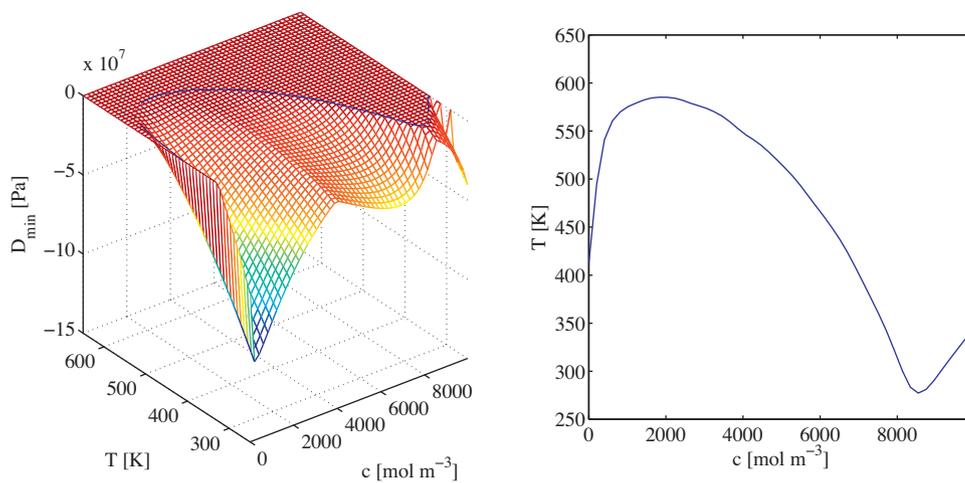
Component	N <sub>2</sub>	C <sub>1</sub>	C <sub>3</sub>	nC <sub>10</sub>
N <sub>2</sub>	0	0.1	0.1	0.1
C <sub>1</sub>	0.1	0	0.036	0.052
C <sub>3</sub>	0.1	0.036	0	0
nC <sub>10</sub>	0.1	0.052	0	0



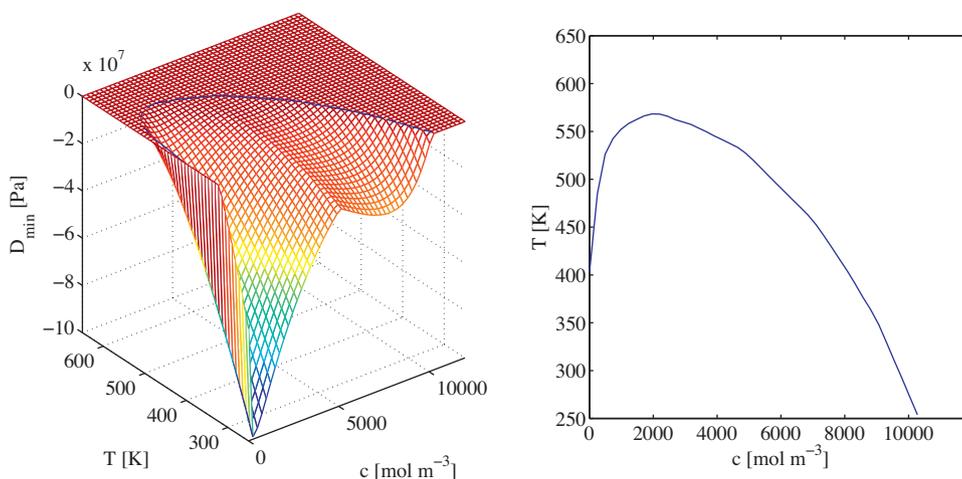
**Fig. 2.** Global minimum of function  $D$  as a function of the overall molar density  $c$  and temperature  $T$  (left) and boundary between single-phase and two-phase regions in the  $c$ ,  $T$ -space (right). **Example 2:** binary C<sub>1</sub>–nC<sub>5</sub> mixture (mole fractions in the text).



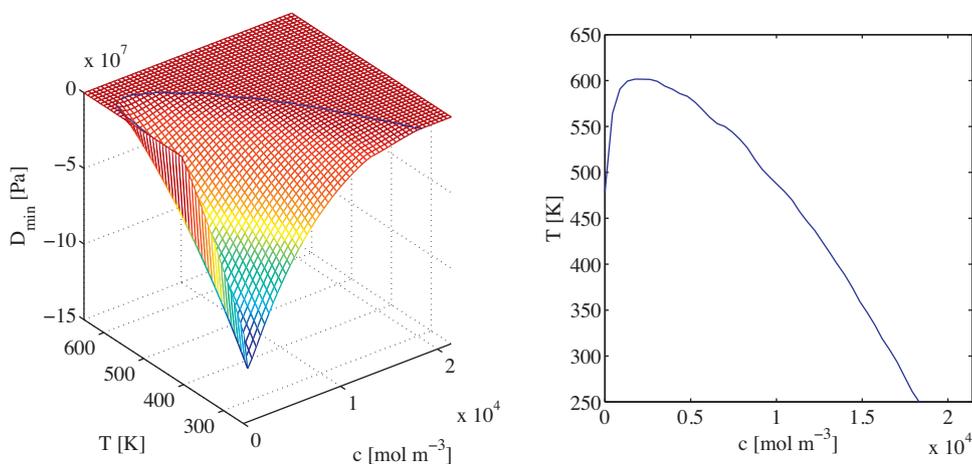
**Fig. 3.** Global minimum of function  $D$  as a function of the overall molar density  $c$  and temperature  $T$  (left) and boundary between single-phase and two-phase regions in the  $c$ ,  $T$ -space (right). **Example 3:** binary C<sub>1</sub>–nC<sub>5</sub> mixture (mole fractions in the text).



**Fig. 4.** Global minimum of function  $D$  as a function of the overall molar density  $c$  and temperature  $T$  (left) and boundary between single-phase and two-phase regions in the  $c$ ,  $T$ -space (right). **Example 4:** binary CO<sub>2</sub>–nC<sub>10</sub> mixture.



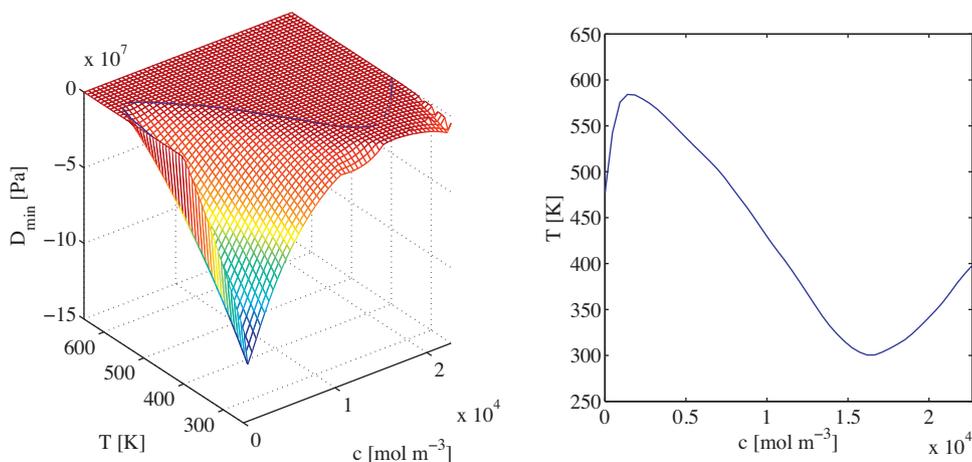
**Fig. 5.** Global minimum of function  $D$  as a function of the overall molar density  $c$  and temperature  $T$  (left) and boundary between single-phase and two-phase regions in the  $c$ ,  $T$ -space (right). **Example 5:** 4-component mixture of  $\text{N}_2$ - $\text{C}_1$ - $\text{C}_3$ - $n\text{C}_{10}$ .



**Fig. 6.** Global minimum of function  $D$  as a function of the overall molar density  $c$  and temperature  $T$  (left) and boundary between single-phase and two-phase regions in the  $c$ ,  $T$ -space (right). **Example 6:** 7-component mixture rich in  $\text{N}_2$ .

**Example 7.** In the last example we mix the oil from **Example 6** with  $\text{CO}_2$  so that we obtain a  $\text{CO}_2$ -rich seven-component mixture with overall composition  $z_{\text{N}_2} = 0.000131$ ,  $z_{\text{CO}_2} = 0.568185$ ,  $z_{\text{C}_1} = 0.246739$ ,  $z_{\text{PC}_1} = 0.086275$ ,  $z_{\text{PC}_2} = 0.033722$ ,  $z_{\text{PC}_3} = 0.037006$ , and

$z_{\text{C}_{12+}} = 0.027941$ . We investigate VT-stability of this mixture for temperatures  $T \in (250 ; 650)$  K and the whole range of feasible molar densities. The binary interaction coefficients are shown in **Table 3**. The minima of function  $D$  for each point and the approximate



**Fig. 7.** Global minimum of function  $D$  as a function of the overall molar density  $c$  and temperature  $T$  (left) and boundary between single-phase and two-phase regions in the  $c$ ,  $T$ -space (right). **Example 7:** 7-component mixture rich in  $\text{CO}_2$ .

**Table 3**  
Binary interaction coefficients for the reservoir fluids used in Examples 6 and 7.

Component	N <sub>2</sub>	CO <sub>2</sub>	C <sub>1</sub>	PC <sub>1</sub>	PC <sub>2</sub>	PC <sub>3</sub>	C <sub>12+</sub>
N <sub>2</sub>	0.000	0.000	0.100	0.100	0.100	0.100	0.100
CO <sub>2</sub>	0.000	0.000	0.150	0.150	0.150	0.150	0.150
C <sub>1</sub>	0.100	0.150	0.000	0.035	0.040	0.049	0.069
PC <sub>1</sub>	0.100	0.150	0.035	0.000	0.000	0.000	0.000
PC <sub>2</sub>	0.100	0.150	0.040	0.000	0.000	0.000	0.000
PC <sub>3</sub>	0.100	0.150	0.049	0.000	0.000	0.000	0.000
C <sub>12+</sub>	0.100	0.150	0.069	0.000	0.000	0.000	0.000

boundaries of the two-phase region in the  $c, T$ -space are presented in Fig. 7. We observe again an unstable region in the bottom right corner of Fig. 7 (right) which corresponds to a liquid–liquid two-phase state if the solid phase does not form.

## 7. Summary and conclusions

In this work we have formulated conditions for the phase stability at constant temperature, volume, and moles. This problem differs significantly from the common problem of stability at constant pressure, because the pressure is not known a-priori. Moreover, the pressures in the initial phase and in the trial phase are not generally the same. We have proposed a simple numerical algorithm for VT-stability testing, which is based on the Newton method with line search. This combination together with a special choice of initial guesses allows robust VT-stability testing. The algorithm has been tested on many mixtures under different conditions of different complexity. In most simulations, the algorithm converges in 10–20 iterations. In seven-components examples, the

$$A = \sum_{i=1}^n \sum_{j=1}^n N_i N_j a_{ij}, \quad a_{ij} = (1 - \delta_{i-j}) \sqrt{a_i a_j}, \quad a_i = 0.45724 \frac{R^2 T_{i,crit}^2}{P_{i,crit}} [1 + m_i (1 - \sqrt{T_r})]^2, \quad m_i = \begin{cases} 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2, & \text{for } \omega_i < 0.5, \\ 0.3796 + 1.485\omega_i - 0.1644\omega_i^2 + 0.01667\omega_i^3 & \text{for } \omega_i \geq 0.5 \end{cases}$$

typical number of Newton iterations is between 20 and 30. In most situations the line search is necessary in the first few iterations of the Newton method only. Once the iterates converge toward the true solution, we observe the quadratic convergence and the line search is not needed any more. In some cases the Newton method does not converge for some initial guesses, but these cases are very rare. If the Newton method does not converge for one initial guess, the other initial guesses converge rapidly. Therefore, we are able to obtain these results using at most four initial guesses for each VT-stability testing. This can not be achieved using the SSI method which breaks down frequently and does not allow to evaluate reliable phase boundaries in the  $c, T$ -space as it is for the Newton method.

### List of symbols

$A$	Helmholtz free energy
$b_i$	covolume parameter of the Peng–Robinson EOS
$c$	molar concentration
$D, D^*$	different forms of the tangent plane distance function
$\delta_{ij}$	Kronecker symbol
$\delta_{X-Y}$	binary interaction coefficient between components $X$ and $Y$
$\Phi_i$	volume function of the $i$ -th component
$i, j$	component indices
$k$	iteration index
$\mu_i$	chemical potential of the $i$ -th component
$M_{w,i}$	molar weight of the $i$ -th component
$n$	number of components
$N_i$	mole number of the $i$ -th component
$\omega_i$	acentric factor of the $i$ -th component
$P$	pressure

$P_{i,crit}$	critical pressure of the $i$ -th component
$P_i^{sat}$	saturation pressure of the $i$ -th component
$P_{ini}$	initial pressure
$R$	universal gas constant
$T$	absolute temperature
$T_{i,crit}$	critical temperature of the $i$ -th component
$V$	total volume of the system
$x_i$	mole fraction of the $i$ -th component in the trial phase
$z_i$	mole fraction of the $i$ -th component in the initial phase

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## Appendix A. Volume function coefficient for the Peng–Robinson equation of state

In this work we use the Peng–Robinson equation of state [9] in the form

$$P(V, T, N_1, \dots, N_n) = \frac{NRT}{V - B} - \frac{A}{V^2 + 2BV - B^2},$$

where  $R$  is the universal gas constant,  $N = \sum_{i=1}^n N_i$  is the total mole number, and coefficients  $A$  and  $B$  are given by

$$B = \sum_{i=1}^n N_i b_i, \quad b_i = 0.0778 \frac{RT_{i,crit}}{P_{i,crit}}$$

In these equations  $\delta_{i-j}$  denotes the binary interaction parameter between the components  $i$  and  $j$ ,  $T_{i,crit}$ ,  $P_{i,crit}$ , and  $\omega_i$  are the critical temperature, critical pressure, and acentric factor of the  $i$ -th component, respectively. Defining the molar densities of the  $i$ -th component by  $cx_i = N_i/V$ , the volume function coefficient for the Peng–Robinson equation of state can be written in terms of molar densities as (for details see [1])

$$\ln \Phi_i(T, cx_1, \dots, cx_n) = \ln(1 - \mathfrak{B}) - \frac{b_i c}{1 - \mathfrak{B}} + \frac{\mathfrak{A} b_i}{\mathfrak{B} RT} \frac{1}{1 + 2\mathfrak{B} - 2\mathfrak{B}^2} - \frac{1}{\sqrt{2}\mathfrak{B} RT} \left[ \frac{\mathfrak{A} b_i}{2\mathfrak{B}} - \sum_{j=1}^n cx_j a_{ij} \right] \ln \left| \frac{1 + (1 + \sqrt{2})\mathfrak{B}}{1 + (1 - \sqrt{2})\mathfrak{B}} \right|, \quad (29)$$

where

$$\mathfrak{A} = \frac{A}{V^2} = \sum_{i=1}^n \sum_{j=1}^n cx_i cx_j a_{ij}, \quad \mathfrak{B} = \frac{B}{V} = \sum_{i=1}^n cx_i b_i.$$

In the text the dependence of the volume function  $\Phi_i$  on temperature  $T$  is not written explicitly, because the temperature is assumed to be constant.

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