General algorithm for multiphase equilibria calculation at given volume, temperature, and moles

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ABSTRACT

We have developed a fast and robust algorithm for the general Π-phase equilibrium calculation at constant volume, temperature and moles, which is based on the direct minimization of the total Helmholtz energy of the mixture with respect to the mole- and volume-balance constraints. The algorithm uses the Newton–Raphson method with line-search and modified Cholesky decomposition of the Hessian matrix to produce a sequence of states with decreasing values of the total Helmholtz energy. To initialize the algorithm, an initial guess is constructed using the results of constant-volume stability testing. As the number of phases is not known a priori, the proposed strategy is based on repeated constant-volume stability testing and constant-volume phase-split calculation until a stable Π-phase state is found. The performance of the algorithm is shown on several examples of two-, three- and even four-phase equilibrium calculations of multicomponent mixtures under various conditions.

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1. Introduction

Studying multiphase equilibrium of multicomponent mixtures and development of robust and efficient algorithms for its computation play important roles in large-scale compositional hydrocarbon reservoir simulations. While there was a main focus on two-phase compositional modelling in the past, nowadays, there is an increasing interest in three and generally multi-phase compositional models which is motivated by CO_2 sequestration [12], processes related to CO_2 or steam enhanced oil recovery [1] or asphaltene precipitation from bitumens [14,15].

Injecting a pure component (e.g. CO_2) into a reservoir, it may dissolve in the reservoir fluid or it can mix and the mixture can split into two or more phases. Let us consider a closed system of total volume V containing a multicomponent mixture with mole numbers $N_1, \ldots, N_n$ at temperature T. To find out whether the system is under given conditions in single-phase or splits into two phases, the single-phase stability at constant volume, temperature, and moles (the so-called VT-stability) is solved. In case of phase-splitting, the two-phase split calculation at constant volume, temperature, and moles (the so-called VT-flash) is performed to establish amounts and compositions of both phases, and consequently the equilibrium pressure of the system is calculated from the equation of

state. In our previous work [22,23,9], these problems were formulated for two-phase systems and the algorithms were proposed and tested on a number of examples. In [10], the results were partially extended to three phases for CO_2–H_2O system and the performance of the algorithm was shown on several examples of two- and three-phase equilibrium calculations of CO_2–H_2O mixtures under geologic carbon storage conditions. In this work, we extend the method and propose a general strategy for Π-phase equilibrium computation at constant volume, temperature, and moles, where $\Pi \in N$ is the number of phases.

We use the formulations of phase stability and phase equilibrium computation which are based on VT variables (constant volume, temperature, and moles). This approach is alternative to the traditional formulation based on PT variables (constant pressure, temperature and chemical composition), which has been widely used in many applications including compositional reservoir simulation. Both the stability testing and the phase-split computation can be formulated either as local or global minimization problems, or as problems of direct solution of a nonlinear system of algebraic equations. Depending on the problem formulation and used variables, various methods have been developed to find the local minima and the global minimum of the tangent-plane-distant function in the stability testing [17,19,6], and the global minimum of either the Gibbs energy [18,6,16], or the Helmholtz energy [22,9] in computation of phase-equilibria. The reader is referred to [32] for a recent review of various global optimization methods for phase equilibrium calculations.

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Besides the *PT*-formulations, formulations involving other independent variables appear in the literature. The formulations in which temperature and concentrations are the independent variables were used by Nagarajan et al. in [26] for the investigation of phase stability and flash equilibrium calculation, and in [27] for the critical point calculation. Using volume as an independent variable in the *PT*-flash has also been shown advantageous by Pereira et al. in [29]. Although in these works the independent variables are temperature and concentrations or temperature, volume, and moles, respectively, the problem specification variables are still pressure, temperature, and composition. No matter how wide-spread the use of the *PT*-specification variables is, this approach has limitations which have already been noticed in the previous work. In the *PT*-variables specification, pressure is specified and volume is computed by inverting of the equation of state. In case of cubic equations of state (e.g. the Peng–Robinson EOS), the problem of multiple roots of the equation occurs; there may exist up to three different roots from which one is selected, usually the one with the lowest value of the Gibbs energy. In contrast, in the *VT*-approach volume of the cell is given and pressure can be directly computed from the equation of state without the need for inversion of the equation of state. In the *VT*-formulation, the problem of root selection is completely avoided. This is even more important when using non-cubic equation of state (e.g. the Cubic-Plus-Association EOS) for which the number of roots is not known a priori.

To illustrate another shortcoming of *PT* variables, let us consider pure CO_2 at temperature $T = 280\,K$ and saturation pressure $P_{sat}(T)$ corresponding to the temperature $T = 280\,K$. Using the *PT* variables, one cannot decide whether the system occurs in vapor or liquid state, or as a mixture of both, because all two-phase states and both saturated gas and saturated liquid occur at the same pressure $P_{sat}(T)$, temperature, and moles. Therefore, *PT*-stability and *PT*-flash cannot distinguish between these states, but *VT*-stability and *VT*-flash can, because these states have different volumes. This example shows that the *PT*-stability and *PT*-flash problems are not well posed since the volume of the system is not uniquely determined by specifying the pressure, temperature, and moles. On the other hand, if volume, temperature, and moles are specified, the equilibrium pressure is given uniquely by the equation of state. The ambiguity of volume is not limited to pure component. In [10] and in this work, we present non-trivial examples of multicomponent mixtures which exhibit in three- or even four-phase the same behaviour as the pure substances at saturation pressure.

The phase stability testing and phase equilibrium calculation are the integral part of the reservoir simulation. In compositional models the stability and flash formulations are based virtually exclusively on the *PT*-variables specification [4,8,21,24,25]. To the best of our knowledge, the only use of the *VT*-flash in compositional simulation has been reported in [30]. In [30] there is an example which the codes based on the *PT*-variables specification generally fail to compute because of the ambiguity in volume for given pressure, temperature, and overall composition. In the *VT*-flash formulation, the problem does not appear at all. This motivates our interest in the phase equilibrium calculation using the *VT*-variables specification that does not suffer from these issues.

To solve phase equilibria in other variables specifications (like *VT* in our case), Michelsen [20] proposed an approach based on nested iterations; the *PT*-flash algorithm is used in the inner loop while pressure is iterated in the outer loop until the correct pressure value is found for which the respective volume constraint is satisfied. This approach was used in [5] to find the conditions of thermodynamic equilibrium in systems subject to gravitational fields and in [3] to study segregation in centrifugal fields. This approach allows to reuse existing implementations of the *PT*-flash but is not computationally efficient since for a single computation of the *VT*-flash many computations of the *PT*-flash have to be performed before the

correct value of pressure is found. In [22] it has been shown that when the *VT*-flash problem is formulated directly using the minimization of the Helmholtz energy, the computational efficiency of the successive iteration method is about the same as for its *PT*-based counterpart. Moreover, as the nested loop approach uses the *PT*-flash in the inner loop, the method may not provide the correct phase volumes when the volume is ambiguous.

In [9] we have proposed a numerical algorithm for constant-volume two-phase split calculation which is based on the constrained minimization of the total Helmholtz energy of the mixture. The algorithm uses the Newton–Raphson method with line-search and the modified Cholesky decomposition of the Hessian matrix to produce a sequence of states with decreasing values of the total Helmholtz energy. Fast convergence towards the exact solution is ensured due to the Newton–Raphson method. Furthermore, as the method guarantees decrease of the total Helmholtz energy of the system in every iteration, it always converges to a state corresponding to at least a local minimum of the energy. To initialize the algorithm, the results of the constant-volume stability algorithm, which has been developed in [23], are used. In this work, we extend the method and propose a general strategy for Π-phase equilibrium computation at constant volume, temperature, and moles, where $\Pi \in N$ is the number of phases. As the number of phases is not necessarily known a priori, the proposed strategy is based on the repeated constant-volume stability testing and the constant-volume phase-split calculation until a stable Π-phase state is found. The performance of the algorithm is shown on several examples of two-, three- and even four-phase equilibrium calculations of multicomponent mixtures under various conditions. The basic approach adopted here is close to that of Cabral et al. [2] where the direct minimization of the Helmholtz energy is used to solve thermodynamic equilibrium in a system with various bulk and adsorbed phases. However, in [2] the authors claim that because pressure can be negative during the course of the iterations, their algorithm requires that a part of the computation be performed in the complex arithmetics. On the other hand, our algorithm uses formulation that can be performed in the real arithmetic. The use of complex numbers is thus avoided.

The paper is structured in the following way. In Section 2, we derive the equilibrium conditions in a multiphase system which is described using the Helmholtz energy. In Section 3, the constant-volume stability testing is applied on a multicomponent mixture in a Π-phase state and a method of introducing a new phase is described in the case that the Π-phase state is unstable and splits into $\Pi + 1$ phases. Finally, we propose a fast and robust numerical algorithm for the multiphase split calculation based on the direct minimization of the total Helmholtz energy of the Π-phase system. At the end of the section, we summarize essential steps of the algorithm and propose the general strategy for constant-volume phase-equilibria computation based on repeated stability testing and phase-split calculations. In Section 4, we present several numerical examples showing the performace, robustness and efficiency of the proposed strategy for multiphase equilibrium computation at constant volume, temperature, and moles. In Section 5, we discuss the results and draw some conclusions. In Appendix A, we provide details of the Peng–Robinson and Cubic-Plus-Association equations of state [28,13] that were used in this work. In Appendix B, we provide the details of the modified Cholesky factorization that is used in our method.

2. Multiphase equilibrium conditions for multicomponent system

Consider a closed system containing a mixture of *n* components with mole numbers $N_1, \ldots, N_n$ occupying total volume *V* at temperature *T*. The system is described using the Helmholtz energy