



# A stable algorithm for calculating phase equilibria with capillarity at specified moles, volume and temperature using a dynamic model<sup>☆</sup>



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## ARTICLE INFO

### Article history:

Received 1 May 2017

Received in revised form

18 September 2017

Accepted 20 September 2017

Available online 29 September 2017

### Keywords:

Phase equilibria

NVT flash

Phase stability

Capillarity

Thermodynamical modeling

Convex-concave splitting

## ABSTRACT

Capillary pressure can significantly affect the phase properties and flow of liquid-gas fluids in porous media, and thus, the phase equilibrium calculation incorporating capillary pressure is crucial to simulate such problems accurately. Recently, the phase equilibrium calculation at specified moles, volume and temperature (NVT-flash) becomes an attractive issue. In this paper, capillarity is incorporated into the phase equilibrium calculation at specified moles, volume and temperature. A dynamical model for such problem is developed for the first time by using the laws of thermodynamics and Onsager's reciprocal principle. This model consists of the evolutionary equations for moles and volume, and it can characterize the evolutionary process from a non-equilibrium state to an equilibrium state in the presence of capillarity effect at specified moles, volume and temperature. The phase equilibrium equations are naturally derived. To simulate the proposed dynamical model efficiently, we adopt the convex-concave splitting of the total Helmholtz energy, and propose a thermodynamically stable numerical algorithm, which is proved to preserve the second law of thermodynamics at the discrete level. Using the thermodynamical relations, we derive a phase stability condition with capillarity effect at specified moles, volume and temperature. Moreover, we propose a stable numerical algorithm for the phase stability testing, which can provide the feasible initial conditions. The performance of the proposed methods in predicting phase properties under capillarity effect is demonstrated on various cases of pure substance and mixture systems.

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## 1. Introduction

Capillarity plays a very important role in multiphase systems arising from a number of oil reservoir and chemical engineering problems. Typically, a gas-oil reservoir involves liquid phase, gas phase as well as water phase [3,6,16]. Capillary pressure is one of the most significant driving forces in multi-phase flow in porous media, especially in fractured media; in fact, capillarity is frequently deemed as the leading mechanism of oil production in fractured reservoirs [3,10]. A few important parameters of physical processes in a porous medium, including relative permeability and residual saturations, are also significantly influenced by capillary

pressure at a pore scale. In addition, capillarity is crucial for the counter-current flow [1], which is indeed driven by capillary pressure difference. Consequently, capillary pressure can substantially affect the flow and transport of the liquid and gas phases in a porous medium.

Phase equilibrium calculation is a key ingredient in modeling and simulation of multi-phase fluid systems. The physical properties of liquid and gas phases greatly impact the interfacial tension, which is one fundamental cause of capillarity. In the other hand, capillary pressure also significantly influences fluid behavior and phase equilibrium. In Ref. [36], it was shown that capillarity leads to significant changes in the phase densities and phase envelope of pure substances.

In the phase equilibrium calculation, the selection of specified thermodynamical variables largely depends on the practical problems to be solved. NPT-flash accounts for the condition at specified pressure, temperature, and chemical composition [17,18,20]. Another alternative phase equilibrium state is determined under

<sup>☆</sup> This work is supported by National Natural Science Foundation of China (No. 11301163). The authors cheerfully appreciate the generous support of the university research fund to the Computational Transport Phenomena Laboratory at KAUST.

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specified moles, volume, and temperature (the so-called NVT-flash). In Ref. [25], the volume-based thermodynamics was proposed to be used in equilibrium calculation; in Ref. [19], NVT-flash along with other specifications was discussed and formulated as minimization of a thermodynamic state function. The NVT-flash has been intensively studied recently [8,9,14,21,22,28].

Recently, capillary pressure is involved in the phase equilibrium at the NPT conditions [26,30,33,36,37] since capillarity can significantly change phase properties. However, there are very few contributions on the NVT-flash calculation incorporating capillarity effect. As shown in this work, capillarity has a great effect on fluid behaviors and phase equilibria at specified moles, volume and temperature. Moreover, the NVT-flash involving capillarity is beneficial to accurately model the motion of multi-phase fluids in porous media since capillarity effect is generally viewed as one of the most important Darcy-scale phenomena resulting from the liquid-gas interfaces at the pore scale, and consequently, it is evidently an interesting and important issue.

In this paper, we consider the phase equilibrium calculation incorporating capillarity at specified moles, volume and temperature (i.e. NVT conditions). A dynamical model for such problem is rigorously derived through the laws of thermodynamics: by using the first law of thermodynamics, we first derive an entropy variation equation, which involves the work done by the capillary pressure; subsequently, the evolutionary equations of moles and volumes are derived by applying the second law of thermodynamics and Onsager's reciprocal principle [7]. To the best of our knowledge, it is the first time to develop such model, which can characterize the dynamical process from a non-equilibrium state to an equilibrium state in presence of capillarity effect at the NVT conditions. Especially, the proposed model has a feature that it has a set of unified formulations for both pure-substance and multi-component systems.

Thermodynamically stable numerical algorithms are more appreciated for simulating dynamical problems based on a realistic equation of state in recent years [11–14,24,29] since such methods can preserve the thermodynamical features that are desired for these problems. The convex-concave splitting approach is extensively used in numerical simulation of various gradient flows, especially phase-field models, in the literature, for example, [4,32,38]. This approach splits a free energy function into a summation of a convex part and a concave part; subsequently, the convex part is treated by the implicit time schemes, while the concave part is updated explicitly; consequently, it leads to unconditionally energy-stable time schemes (that is, any time step size can be used theoretically). In this work, a thermodynamically stable numerical algorithm is introduced to simulate the proposed dynamical model. This algorithm is designed through using the convex-concave splitting of the total Helmholtz energy, and thus, it is proved to preserve the second law of thermodynamics (also called entropy stability).

The phase stability analysis is usually used to determine whether a fluid system remains in a single phase or splits into two phases at specified conditions. For NPT flash involving capillary pressure, the stability analysis for multicomponent mixtures was developed in Ref. [33]. For the NVT-flash without capillarity [22], has developed a phase stability testing approach, which is already employed to initialize the Newton's minimization method in Ref. [8]. The phase stability analysis is required to provide the appropriate initial conditions, including initial values of moles and volumes. If this system stays in a single phase, then capillarity never occurs; otherwise, capillarity may take effect so that the phase properties may be significantly changed. In this work, we develop the phase stability analysis with capillarity at specified moles, volume and temperature using the entropy principle. Moreover, a

stable numerical algorithm for the phase stability testing is developed through using the convex-concave splitting of the Helmholtz energy density.

The Kelvin equation, which reveals that the vapor pressure decreases with increasing interface curvature, has been applied for practical applications [6,37]. It is assumed in Kelvin's equation that the phase equilibria occur between an ideal gas and an incompressible liquid, but this assumption may be no longer valid at the small pore sizes [37]. In numerical tests, we will compare the simulation results with Kelvin's equation and demonstrate the validity of numerical results.

The paper is organized as follows. In Section 2, we derive a dynamical model for phase equilibria involving capillarity at specified moles, volume, and temperature. In Section 3, a thermodynamically stable numerical algorithm is proposed based on the convex-concave splitting of the total Helmholtz energy. In Section 4, we derive a phase stability condition involving capillarity at specified moles, volume, and temperature, and develop a stable numerical method for phase stability analysis. In Section 5, we apply the proposed numerical algorithms on various cases of pure substance and mixture systems. At last, we summarize the main results in Section 6.

## 2. Dynamical model for phase equilibria involving capillarity

In this section, we first formulate the total Helmholtz free energy and capillary pressure, and subsequently, through using the first and second laws of thermodynamics and Onsager's reciprocal principle, we derive a dynamical model for phase equilibria in the presence of capillarity effect at specified moles, volume and temperature.

### 2.1. Total Helmholtz free energy

For a mixture composed of  $M$  ( $M \geq 1$ ) components, we denote by  $n_i$  the molar density of component  $i$ , and further denote the molar density vector by  $\mathbf{n} = [n_1, n_2, \dots, n_M]^T$ . Let  $N_i$  represent the moles of component  $i$ , and then we denote the vector of moles by  $\mathbf{N} = [N_1, \dots, N_M]^T$ . The phase equilibria of the mixture is considered under the constant overall volume ( $V^t$ ), temperature ( $T$ ) and overall mole numbers ( $\mathbf{N}^t = [N_1^t, \dots, N_M^t]^T$ ). We denote by  $f(\mathbf{n})$  the Helmholtz free energy density of a homogeneous fluid, and its formulation can be found in Appendix A. For a two-phase system, we use  $V^G$  and  $V^L$  to represent the volumes of gas and liquid phases respectively, and we denote the moles of the gas phase by  $\mathbf{N}^G = [N_1^G, \dots, N_M^G]^T$  and moles of the liquid phase by  $\mathbf{N}^L = [N_1^L, \dots, N_M^L]^T$ . Since the overall volume and overall moles are fixed, the following volume and mole constraints shall be satisfied

$$\mathbf{N}^G + \mathbf{N}^L = \mathbf{N}^t, \quad V^G + V^L = V^t. \quad (2.1)$$

The total Helmholtz free energy, denoted by  $F$ , can be expressed as

$$F = f(\mathbf{n}^G)V^G + f(\mathbf{n}^L)V^L \quad (2.2)$$

where

$$\mathbf{n}^G = \frac{\mathbf{N}^G}{V^G}, \quad \mathbf{n}^L = \frac{\mathbf{N}^L}{V^L}.$$

On account of the mass and volume constraints (2.1),  $F$  can be reduced into a function of  $\mathbf{N}^G$  and  $V^G$  as  $F(\mathbf{N}^G, V^G)$ . The other choice of primal variables is also suggested in Refs. [8,9,35].

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