



Development of a thermodynamically consistent, robust and efficient phase equilibrium solver and its validations



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HIGHLIGHTS

- A robust and efficient equilibrium solver is developed.
- The solver is based on rigorous thermodynamics.
- Complex phase behaviors of multi-component mixtures are predicted.
- Liquid–liquid and vapor–liquid–liquid equilibria are predicted.
- Feasible region method is applied to accelerate three-phase flash.

ARTICLE INFO

Article history:

Received 3 May 2013

Received in revised form 25 June 2013

Accepted 25 June 2013

Available online 12 July 2013

Keywords:

Phase equilibrium

Phase stability

Phase splitting

Flash calculation

ABSTRACT

An applied phase-related equilibrium (APPLE) solver using only the Peng–Robinson equation of state is developed based on rigorous classical thermodynamics. The solver is theoretically and thermodynamically consistent with the stringent equilibrium criterion. It is mainly composed of phase stability and phase splitting calculations, which will be called routinely in the course of searching for the globally stable equilibrium state. It also makes use of various robust and efficient numerical methods. To demonstrate its performance, the solver is tested against various mixtures, such as oil and gas mixtures, hydrocarbon mixtures and hydrocarbon–nitrogen mixtures. Phase diagrams of these mixtures are constructed and verified with available experimental data or other researchers' calculations. Results show that the APPLE solver is reliable and fast to solve phase equilibrium problems, including three-phase equilibrium. Finally, its potential applications to droplet evaporation and computational fluid dynamics (CFD) calculations are discussed.

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1. Introduction

The phase transition/change process is an important physical process that occurs in many engineering applications, such as CO₂ injection and CO₂ storage in enhanced oil recovery, and liquid phase combustion upon evaporation. Considerations on the dynamics of phase transition, which requires analyses of non-equilibrium thermodynamics such as the nucleation process, are incomplete if the equilibrium state (“destination state”) is not known. Phase equilibrium, hence, is a starting point for further non-equilibrium analyses and it is of primary importance from the point view of classical thermodynamics. In reality, phase equilibrium thermodynamics-based calculations have been used in a wide range of industrial fields, such as for distillation columns,

and in reservoir simulation. An equation of state, as an important part of thermodynamics needed to quantify the state properties, is generally used to study non-ideal gas behaviors of mixtures.

From the fundamental thermodynamic postulate, the entropy is a continuous and monotonically increasing function of energy [1]. In terms of the Gibbs free energy G for a homogeneous and open system, the second law of thermodynamics limits the possible processes through:

$$dG = VdP - SdT + \sum \mu_i \cdot dn_i \leq 0 \quad (1)$$

Here, T is temperature; P is pressure; V is volume; S is entropy, μ is chemical potential; n is mole number and i is the species index. At the equilibrium state, the equality sign in the above equation holds. It is well known that the Gibbs free energy at the equilibrium state is the minimum in the phase space composed of T , P and \bar{n} . Mathematically, the problem now becomes to search for a global minimum point in multi-dimensional space. This problem is usually tackled by solving for the equality of the chemical potential, which is the partial molar Gibbs free energy. In actual calculations,

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fugacity equality is commonly used for identifying the equilibrium state by requiring, for a two-phase equilibrium,

$$f_i^1 = f_i^2, \quad i = 1, \dots, N_c \quad (2)$$

Here, j is the index of phase; f is the fugacity and N_c is the number of components. The advantage of this method is that fugacity coefficient can be relative easily calculated from various equations of state, such as the Peng–Robinson equation of state [2].

However, Eq. (2) is not a sufficient condition for phase equilibrium. Mathematically, the zero derivative location only indicates a local extreme but does not guarantee that it is also the global extreme. Hence, the equality of fugacity in Eq. (2), standing for a local stationary point in the phase space, is not necessarily the global minimum at the same time. In other words, solution of Eq. (2) could represent a “false” equilibrium state, which only corresponds to some local minima. As a result, fugacity equality is a necessary but not sufficient condition for phase equilibrium. While for simple mixtures, the local extreme could happen to be a global extreme, the situation quickly becomes complex when a multi-component mixture is considered since the phase dimension and the number of local extrema will increase. This is especially the case that occurs quite often at liquid–liquid and vapor–liquid–liquid equilibria [3]. All these noteworthy points are quantitatively illustrated in the work of Baker et al. [4], benefiting from the original work of Gibbs [5]. They suggested using Gibbs free energy directly for phase equilibrium to guarantee the “true” equilibrium state, rather than the traditional way with fugacity. They further proved that the necessary and sufficient condition for a system to be stable, for specified temperature, pressure and species, is that the tangent plane at the species feed composition to the Gibbs free energy surface should at no other point intersect (lie above) the Gibbs free energy, but only the tangent point.

This paper is organized as follows. The equation of state model is introduced first, since it is used for both phases throughout all the calculations. After this, the methodologies adopted for the current development of a robust and efficient applied phase equilibrium solver, named APPLE here, are presented in detail. We then evaluate the performance of the solver for various cases from the literature. Some potential applications of the solver to computational fluid dynamics (CFD) calculations are remarked upon. Summary and conclusions are then made.

2. Equation of state

The equation of State is a relationship between thermodynamic properties at a specified state. To consider the non-ideality of thermodynamic properties at high pressures, a proper equation of state other than the ideal gas law is needed. While there are no general guidelines for selecting a specific equation of state, the Peng–Robinson equation of state (PR EOS) [2] was chosen for all the calculations here for several reasons. First, it is a simple form of the cubic equation of state so it is easy to implement for engineering calculations. Second, it has better performance for the prediction of vapor–liquid phase equilibrium properties over other cubic equation of states. More importantly, it also has been widely used in the oil and gas industry with great successes.

Theoretically, using only one equation of state for both the liquid and gas phases would bring some numerical difficulties since more solutions of cubic equations are possible. However, it has the benefit of using one unified treatment for both phases and hence it is easier to handle and elegant to implement. In addition, the non-random mixing model, such as UNIFAC, is not used here because it is specially designed for handling the non-ideality of compressed liquids or solutions; and it is mainly used for sub-critical conditions where the molecular interactions are strong

and surface tension effects are important. An equation of state model, on the other hand, can be used for a wide range of conditions (from subcritical to supercritical). Besides, there is no need to specify the reference state for equation of state models since ideal gas limit is used exclusively. Finally, enthalpy and some other thermodynamic properties can be determined directly from an equation of state model in a consistent manner.

The PR EOS [2] is of the form:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (3)$$

Here, v is the molar volume. a and b are the two parameters determined from:

$$\begin{cases} a = 0.457235 \frac{R^2 T_c^2}{P_c} \cdot \alpha \\ b = 0.077796 \frac{RT_c}{P_c} \\ \alpha = [1 + \kappa(1 - \sqrt{T_r})]^2 \end{cases} \quad (4)$$

With

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5a)$$

Here, T_c , P_c and ω are the critical temperature, pressure and acentric factor, respectively. We also adopted a formula that is later expanded [6], which uses, when ω is greater than 0.5.

$$\kappa = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3 \quad (5b)$$

In the case of a mixture, the classical Van der Waals mixing rule is used:

$$\begin{cases} a = \sum_i \sum_j x_i x_j a_{ij} \\ b = \sum_i x_i b_i \\ a_{ij} = (1 - \delta_{ij}) \sqrt{a_i} \sqrt{a_j} \end{cases} \quad (6)$$

Here, x_i is the mole fraction of species i in the mixture. δ_{ij} is the binary interaction parameter between components i and j , and it is generally assumed to be independent of pressure or temperature for a mixture. Temperature-dependent interaction parameters can be used to improved vapor–liquid equilibrium predictions with the group contribution method discussed in Ref. [7,8]. This group contribution method is used in the petroleum industry to find interaction parameters for hydrocarbons (Avauller et al. [9]), but it is not pursued here. More advanced mixing rules are not pursued in the current work, either. Cubic equations generally have three roots at sub-critical conditions. In all the calculations here, when a compressibility root is to be solved, only the one with minimum Gibbs free energy is chosen.

3. Methodology

The equilibrium condition shown in Eq. (1) is written in terms of Gibbs free energy, which has been well applied to isothermal–isobaric flash (TPn) calculations. This kind of flash calculation has been investigated by many researchers and there are many well-developed theories and numerical methods. There is a growing recognition that robust and efficient phase equilibrium calculations should be composed of two essential parts: phase stability and phase splitting calculations [3,10,11].

3.1. Phase stability

The traditional two-phase flash calculation assumes that a two-phase solution exists. If no solution or trivial solution is found, a single phase is then believed to exist. This becomes more and more troublesome when the mixture approaches its thermodynamic

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