Fluid Phase Equilibria 401 (2015) 110–126

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Multiphase equilibrium calculations using a reduction method

Martin Petitfrere [a,b], Dan Vladimir Nichita [a,*]

[a] CNRS UMR 5150, Laboratoire des Fluides Complexes et leurs Réservoirs, Université de Pau et des Pays de l'Adour, BP 1155, 64013 Pau, France
[b] Centre Scientifique et Technique Jean Feger, Total, Avenue Larribau, 64018 Pau Cedex, France

ARTICLE INFO

Article history:
Received 18 March 2015
Received in revised form 29 April 2015
Accepted 4 May 2015
Available online 8 May 2015

Keywords:
Multiphase flash calculations
Phase stability
Cubic equation of state
Binary interaction parameters
Convergence
Reduction method
Newton method

ABSTRACT

Phase equilibrium problems (phase stability testing and multiphase flash) have to be solved repeatedly, sometimes a very large number of times, in process simulators and in compositional reservoir simulation. The computational effort can be significant, particularly when a detailed description (with a large number of components nc) of the mixture is required. The reduction method represent an attractive technique in the attempt to reduce the computational time, by significantly reducing the dimensionality of the problem, from $nc \times (np-1)$ in the conventional methods to a maximum of $(2c+3)\times(np-1)$, where np is the number of equilibrium phases and c the number of components with non-zero binary interaction parameters (BIP). The number of independent variables does not depend on nc, but only on c, and the computation time increases linearly with nc. Traditionally, the reduction approaches use the reduction parameters and the phase mole fractions as independent variables. In this work, a recent improvement of two-phase reduced flash calculations (Nichita and Graciaa, Fluid Phase Equilib. 302, 2011, 226–233) is extended to multiphase equilibrium calculation with any number of phases. Two approaches are proposed: (i) a direct extension of the reduction method for two-phase flashes and (ii) a constrained minimization Gibbs free energy with respect to a specific set of variables and constraints (taking advantage of symmetry). The proposed algorithms are tested for several multiphase systems (with up to four phases and exhibiting complex phase envelopes) containing hydrocarbon components, carbon dioxide and hydrogen sulfide. Numerical experiments show that the reduction methods for multiphase flash calculations are robust and they become faster than the conventional methods when (i) the number of components increases, (ii) the number of equilibrium phases increases and (iii) the number of BIP families decreases. For mixtures with many components and few BIP families, the reduction method may be at least one order of magnitude faster than conventional methods.

1. Introduction

Phase equilibrium problems (phase stability testing and multiphase flash) have to be solved repeatedly, sometimes a very large number of times, in process simulators and in compositional petroleum reservoir simulation (more than two equilibrium phases can form – and play a major impact – in certain tertiary recovery processes, such as gas injection, surfactant injection, steam-injection, etc.). The computational effort can be significant, and it is increasing with the number of components in the mixture. Moreover, a single failure in thermodynamic calculations may cause significant error propagations leading to false solutions or failures of the simulation. Thus, it is imperative that phase equilibrium calculation algorithms are efficient and highly robust. Generally, pseudo-components grouping (lumping) several individual components or heavy fractions are generated to decrease the dimensionality of the system, leading to approximations of the original problem. The lumping affects phase distributions, bulk thermodynamic properties and the location of phase boundaries. In a multiphase context, the existence and position of tiny three- or four-phase regions on phase diagrams can be highly influenced by lumping [1]. The lumping is more severe in compositional reservoir simulations, the number of components being typically limited to a dozen.

The resolution of the multiphase split problem is based on the minimization of the Gibbs free energy [2]. Phase stability analysis, consisting in the minimization of the tangent plane distance (TPD) function [3] plays a key role in the initialization of multiphase flashes. While for two-phase flash calculation the stability is tested at most twice (Michelsen's two-side initialization [2]), in a multiphase context multiple initial guesses are required for phase stability [2,4,5]. If conventional variables are used (the minimum is sought in the compositional space) a nonlinear system of $nc \times (np-1)$ equations must be solved. Usually, phase mole

* Corresponding author. Tel.: +33 5 5940 7699; fax: +33 5 5940 7725.
E-mail addresses: dnichita@univ-pau.fr, dvnichita@hotmail.com (D.V. Nichita).

http://dx.doi.org/10.1016/j.fluid.2015.05.006
0378-3812/

Nomenclature

A EoS parameter
A_i Component EoS parameter
a Attractive parameter in the EoS
B EoS parameter, reduced variable
B_i Component EoS parameter
b Covolume in the EoS
C Reduction matrix
$\overline{\mathbf{C}}$ Matrix of elements $(1 - C_{ij})$
C_{ij} Binary interaction parameter between components i and j
c Number of components with non-zero BIPs
D Modified TPD function
e_α Error functions in the reduction method
f_{ik} Fugacity of component i in phase k
$\mathbf{f}$ RHS vector in Eq. (23)
G Gibbs free energy
$\mathbf{g}$ Gradient vector
h_α Coefficients in fugacity coefficients expression
$\overline{h}_\alpha$ Independent variables in reduction methods, Lagrange multipliers
$\mathbf{H}$ Hessian matrix
$\mathbf{J}$ Jacobian matrix
K_i Equilibrium constants
L Lagrangian function
M Number of reduction parameters
M Michelsen's objective function for solving the Rachford–Rice equations
m Number of nonzero eigenvalues (rank of $\overline{\mathbf{C}}$)
nc Number of components
np Number of phases
x_{ik} Mole numbers of component i in phase k
P Pressure
$\mathbf{Q}$ Vector of reduction parameters
Q_α Reduction parameters
$\overline{Q}$ Vector of modified reduction parameters
$\overline{Q}_\alpha$ Modified reduction parameters
$\mathbf{q}'$ Eigenvectors of $\overline{\mathbf{C}}$
$q'_{\alpha i}$ Elements of the eigenvectors of $\overline{\mathbf{C}}$
$q_{\alpha i}$ Elements of the reduction matrix
R Universal gas constant
S Euclidean norm of the error vector, proposed method
S_f Euclidean norm of the error vector based on fugacities
$\mathbf{S}$ Matrix of coefficients in Eqs. (23)
T Temperature
U_{ij} Elements of the matrix $\mathbf{U}$
$\mathbf{U}$ Matrix, ideal part of the Hessian
x_{ik} Mole fraction of component i in phase k
Y Formal mole numbers of component i in the trial phase
Y_T $\sum_{i=1}^{nc} Y_i$
z_i Feed composition
Z Compressibility factor

Greek letters
α_i $2\sqrt{Y_i}$, Michelsen's variables for stability testing
δ_1, δ_2 Parameter depending on EoS
δ_{ij} Kroneker delta
Δ $\delta_1 - \delta_2$
ε Tolerance for convergence
φ_{ik} Fugacity coefficient of component i in phase k
λ_α Eigenvalues of $\overline{\mathbf{C}}$
ω Acentric factor
ψ_i EoS coefficient
Ω_a, Ω_b Coefficients in the EoS
$\mathbf{\Phi}_{ij}$ Elements of the matrix $\mathbf{\Phi}$
$\mathbf{\Phi}$ Matrix, excess part of the Hessian
θ_k Phase mole fractions

Subscripts
E Excess part of G
F Feed
I Ideal part of G
c Critical
i,j Component index
k,p,m phase index
r Reduced
α,β,γ Reduction variable index

Superscripts
T Transposed
R (Matrix/vector) in reduction method

numbers [2] or the natural logarithm of equilibrium constants [6] are used as independent variables. A combination of successive substitution iterations (SSI) and Newton iteration is the most commonly used; trust-region methods [6–8] represent a robust alternative.

The so-called reduction methods [9] represent an attractive technique in the attempt to reduce the computational time, by significantly reducing the dimensionality of the problem, from $nc \times (np - 1)$ to maximum $(2c + 3) \times (np - 1)$, where np is the number of equilibrium phases and c is the number of components with non-zero binary interaction parameters (BIPs) in the equation of state (EoS) with the remaining components (for many mixtures of interest $c \ll nc$). The basic idea behind the reduction method is to express the fugacity coefficients in terms of a reduced number of variables, instead of expressing them as a function of compositions. The number of independent variables does not depend on nc, but only on c, and the computer time increases linearly with the number of components (in conventional methods this dependence is at least quadratic).

Starting with the first proposed reduction method (Michelsen's three-equation flash [10], applicable for all BIPs equal to zero) and the enunciation by Hendriks of the "reduction theorem" [9] (stating the circumstances under which the dimensionality of phase equilibrium problems can be reduced), many applications of the reduction method have been reported for two-phase flash calculations [11–24] and for phase stability analysis [25–29]. The application of the reduction method in phase equilibrium problems is restricted by the form of the mixing rules in the EoS, that is, reduction requires that the EoS parameters (presented in Appendix A) be linear forms (the case of the covolume B) or decomposable into linear forms (such as the energy term A). Several procedures to decompose the quadratic form A (Eq. (A3)) have been proposed: by spectral decomposition [12], by completing the square [11,15], by using linear transformations [16], or low-rank approximations [17], or by minimizing the approximation error of the parameter A [21], etc.

Recently, comparisons of conventional and reduction methods performance for two-phase equilibrium have been carried out by Michelsen et al. [8], Haugen and Beckner [30], Gorucu and Johns [31] and Petitfrere and Nichita [32]; the reference reduction method in all these papers was the reduced flash of Nichita and Graciaa [20]. A common conclusion is that the curves corresponding to the CPU time dependence on the numbers of components (linear for reduction methods, quadratic for conventional methods) are crossing each other at a certain value of nc (between 15 and 20); this suggests that