



# Multiphase equilibrium calculations using the semi-continuous thermodynamics of hydrocarbon mixtures



Martin Petitfrere<sup>a,b</sup>, Dan Vladimír Nichita<sup>a,\*</sup>, Francois Montel<sup>a,b</sup>

<sup>a</sup> CNRS UMR 5150, Laboratoire des Fluides Complexes, Université de Pau et des Pays de l'Adour, BP 1155, 64013 Pau Cedex, France

<sup>b</sup> Centre Scientifique et Technique Jean Feger, Total, avenue Larribau, 64018 Pau Cedex, France

## ARTICLE INFO

### Article history:

Received 15 July 2013

Received in revised form 28 October 2013

Accepted 30 October 2013

Available online 6 November 2013

### Keywords:

Semi-continuous thermodynamics

Distribution function

Quadrature

Orthogonal polynomial

Phase equilibrium

Delumping

## ABSTRACT

Natural hydrocarbon mixtures are composed of very many components. Usually, several components are lumped into pseudo-components to reduce the dimensionality of the equilibrium flash calculations. An interesting alternative to lumping is the use of semi-continuous thermodynamics, which enables a better characterization of mixture compositions. Traditionally, in the semi-continuous approach, the feed composition is approximated by a standard distribution function. Then, a Gaussian quadrature is used to find discrete carbon numbers representing the "pseudo-components", for which a discrete flash can be performed. However, the feed composition can be random and/or far from classical distributions. In the quadrature method of moments (QMoM), developed by Lage (Lage, *Comput. Chem. Eng.* 31 (2007) 782–799), an optimal quadrature rule is used, considering the feed composition distribution as the weight function. In this work, a hidden feature of QMoM is revealed, by identifying a distribution function used to approximate a newly considered dependence, which involves the feed composition and the component liquid mole numbers. This dependence is extremely smooth, and, the most important, the shape of the function remains identical for any composition, pressure and temperature. The smoothness of the distribution enables a really good accuracy in solving the quadrature. The calculation of the quadrature is based on a procedure which avoids problems due to the ill-conditioned nature of the problem, even for a larger number of pseudo-components (unlike the original QMoM formulation). An analytical delumping procedure can be used (with an extremely small computational effort) to recover detailed composition in each equilibrium phase. Comparisons between a full discrete flash and the semi-continuous description proved the QMoM to be highly accurate. Various test problems, including two-phase and multiphase flash calculations, showed that Lage's methodology is generally applicable, even in cases when no distribution function can model the feed composition, or several distribution functions are needed to model different portions of the mixture.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Several mixtures for interest in industry, such as naturally occurring hydrocarbon mixtures (crude oils and gas condensates), feeds encountered in chemical processing, polymer solutions, etc., contain a very large number of components. Because: (i) a very large number of components can make prohibitive phase equilibrium calculations (as for instance in petroleum reservoir compositional simulation) and (ii) it is impossible to identify all components by standard chemical analysis (the heavier fractions are difficult to characterize), pseudo-components (grouping several individual components or fractions) are used to decrease the dimensionality of the phase equilibrium problem.

Usually, a mixture is lumped into pseudo-components using certain proximity criteria to select which components belong to a given pseudo-component [1–3], then pseudo-component properties (critical pressure and temperature, acentric factor) and binary interaction parameters (BIPs) are assigned using appropriate averaging techniques. This approximation in fluid composition characterization may lead to significant errors in phase equilibrium calculations.

An elegant alternative to classical lumping procedures is the so-called continuous thermodynamics, which is based on the description of the composition of multicomponent mixtures by approximation with a continuous distribution function. In the semi-continuous thermodynamics, some of the individual components are treated discretely (usually light hydrocarbon components and non-hydrocarbon components: CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>O, etc.), while the remaining components (usually the heavy components) are included in the continuous part of the mixture. Continuous and semi-continuous thermodynamics were first developed by Rätzsch

\* Corresponding author. Tel.: +33 5 5940 7699; fax: +33 5 5940 7725.

E-mail addresses: [dnichita@univ-pau.fr](mailto:dnichita@univ-pau.fr), [dvnichita@hotmail.com](mailto:dvnichita@hotmail.com) (D.V. Nichita).

## Nomenclature

$a_i$	energy parameter in the EoS for component $i$ (in continuous gives $a(I)$ )
$b_i$	volume parameter in the EoS for component $i$ (in continuous gives $b(I)$ )
$D$	liquid to feed mole ratio (LFMR) distribution function
$I, J$	characterization variables
$K_i$	equilibrium constant
$k_{ij}$	BIPs
$L$	liquid mole fraction
$m$	number of components with non-zero BIPs
$n$	number of components
$n_C$	number of components in the continuous part of the mixture
$n_D$	number of discrete components
$N$	number of pseudo-components
$n_p$	number of equilibrium phases
$n_{iL}$	mole number of the component $i$ in the liquid phase
$P$	pressure
$p(x)$	orthogonal polynomial
$T$	temperature
$T_b$	true boiling point
$u, v$	generic elements of inner products
$V$	vapor mole fraction
$W$	weight function
$w_i$	discrete weights
$x$	variable in the quadrature problem
$x_i$	liquid mole fraction of the component $i$
$y_i$	vapor mole fraction of the component $i$
$z_i$	feed composition

### Greek letters

$\alpha_n$	parameter in the recurrence relation for orthogonal polynomials
$\beta_n$	parameter in the recurrence relation for orthogonal polynomials
$\gamma_{ki}$	reduction parameters

### Subscripts

$c$	critical
$i$	component index
$L$	liquid

### Superscripts

$C$	continuous
$D$	discrete
(df)	discrete feed
(del)	delumped feed
(sc)	semi-continuous feed

and Kehlen [4] and by Cotterman and Prausnitz [5], respectively. Soon thereafter in the 1980s, several authors worked on developing continuous or semi-continuous thermodynamic phase equilibrium calculation procedures: Cotterman et al. [6], Behrens and Sandler [7], Shibata et al. [8], Xillman and Teja [9,10], Rätzsch et al. [11]. Later on, semicontinuous thermodynamics has been applied to a variety of phase equilibrium problems: flash calculations at different specifications [12], phase stability analysis using the Gibbs tangent plane distance [13,14], critical point calculations [15], compositional gradients [16,17], liquid–solid equilibrium [18], asphaltene precipitation [19], vapor–liquid equilibrium using equations of state with group contributions [20], etc.

The most encountered method use the generalized Gauss–Laguerre quadrature to convert the continuous distribution of the mole (mass) concentration into a discrete one. More recently presented approaches are using specific techniques, such as a general Gauss–Stieltjes quadrature method able to calculate nodes and weights for any distribution function (Nichita et al. [21]), orthonormal polynomials (Liu and Wong [22]) or the quadrature method of moments (Lage [23]).

However, most of the approaches presented in the literature are based on standard distributions. If the feed composition cannot be modeled by a standard distribution functions, or if it is simply highly irregular, most methods would not work properly. The semi-continuous approach based on the quadrature method of moments developed by Lage [23] uses an optimal quadrature rule by taking the feed composition distribution as the weight function and it works with arbitrary compositions. However, in the original formulation of the QMoM the quadrature is solved using Gordon's product-difference algorithm (PDA) [24], which works well only for a small number of quadrature points. John and Thein [25] compared the performance of the QMoM using PDA with the long quotient-modified difference algorithm (LQMDA) (Sack and Donovan, [26]) and the Golub–Welsch algorithm [27]. They found that in certain situations the PDA failed (starting from eight quadrature nodes in their considered examples) whereas the two other examined methods were successful. Gautschi [28] showed that the problem is ill conditioned, and the condition number grows exponentially with the number of quadrature points.

In this work, the QMoM is applied to multiphase equilibrium calculations for actual oil mixtures using a cubic equation of state with non-zero BIPs. The calculation of the quadrature is based on the procedure proposed by Gautschi (ORTHPOL) [29], which avoids problems due to the ill-conditioned nature of the problem and is suitable for an undetermined number of quadrature points (unlike the QMoM with the PDA). In some applications, it is important to use a number of pseudo-components larger than seven (which seems to be the limit of applicability of the PDA).

The paper is structured as follows: first, a new distribution function is introduced; after a brief recall on Gaussian quadratures the semi-continuous description is presented. The general algorithm is given, then results for two- and three-phase flash calculations on a heavy oil mixed with carbon dioxide and water are presented before concluding. The calculation of the quadrature is detailed in two appendices.

## 2. A new distribution function

Usually, in semi-continuous thermodynamics, classical distribution functions are used to model the feed composition, such as the gamma [5,8,9,21,30], beta [31], exponential [7,21] distributions, etc., or even multivariate distributions [10]. In this work, a different way to define the distribution function and to use it within the Gaussian quadrature calculation is presented.

Let us consider the ratio of liquid mole numbers to feed composition

$$D_i = \frac{n_i^L}{z_i} = \frac{x_i L}{x_i L + y_i V} = \frac{1}{1 + (V/L)K_i} = \frac{1}{1 + (V/L)\exp(\ln K_i)} \quad (1)$$

where  $n_i^L$  are the component mole numbers in the liquid phase,  $L$  and  $V$  are the liquid and vapor phase mole fractions, respectively, and  $K_i = y_i/x_i$  are the equilibrium constants. From Eq. (1),  $D_i$  is a logistic function in terms of  $\ln K_i$ .

Download English Version:

<https://daneshyari.com/en/article/202903>

Download Persian Version:

<https://daneshyari.com/article/202903>

[Daneshyari.com](https://daneshyari.com)