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Non-iterative phase stability calculations for process simulation using discriminating functions

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ABSTRACT

Phase stability calculations consume a significant part of a process or a compositional reservoir simulation CPU time as millions of two- or multi-phase equilibrium calculations on complex multicomponent mixtures need to be performed. The iterative nature of the solving methods involved in conjunction to the risk of false convergence render these computations as a hot research area. A new method is presented for generating discriminating functions of pressure, temperature and compositions which separate stable from unstable mixtures. These functions provide the same stability state predictions as the established minimum tangent plane distance since they exhibit exactly the same sign and zeroing points. Their simple explicit expressions allow for the rapid, non-iterative and robust evaluation of the stability state of the fluid under study. Being generated by using the fluid's Equation of State model they offer predictions which can be as accurate as the thermodynamic model itself. A set of examples demonstrates the accuracy of the proposed method as well as its very significant advantages with respect to computational speed.

1. Introduction

Phase equilibrium calculations have been attracting significant research interest particularly over the last decades due to the broad range of applications in which they are involved such as separation processes, pipeline flow, and compositional reservoir simulation. Prior of performing a phase behavior calculation, for a given feed composition and thermodynamic conditions, one needs to know the number and type of the coexisting equilibrium phases. Therefore, a phase stability test should be conducted first to be followed, whenever required, by a phase split calculation to provide the molar fraction and composition of each co-existing phase. The quality of the results bear direct impact on the accuracy of the simulation as they provide PVT and physical properties data input to the flow, mass and energy equations. Depending on the discretization of space and time, millions of such phase equilibrium calculations may need to be performed during a single run consuming a significant fraction of the total simulation CPU time [1]. As a result, both accuracy and computational speed are major factors affecting the performance of a simulation model.

Since the introduction of the minimum tangent plane distance criterion (*TPD*) by Michelsen [2], a large number of studies have been presented that address the phase stability issue as a problem of identifying the coexisting phases which minimize the *TPD*. The energy of the system is usually estimated by an Equation of State (EoS) model which introduces high non-linearities to the equations involved and multiple local minima to the energy surface, thus giving rise to two major challenges. The first one being accuracy and reliability while the second one is the speed of performing the calculations. Reliable methods focus at finding system's energy global minimum using a wide variety of approaches such as homotopy-continuation [3], Newton-interval optimization [4], dividing rectangles [5], tunneling [6], simulated annealing [7], and area methods [8]. Admittedly, all the above methods pay little or no attention to the speed of performing computations.

On the other hand, faster methods have been proposed for rapidly finding, in an iterative mode, a local minimum of the energy surface. Such methods depend on the quality of the initial estimations to ensure that the detected minimum happens to be the global one. The standard approach for speeding up computations is to lump the individual fluid components in a smaller number of pseudo-components [9] while preserving as much as possible the main characteristics of the energy surface. Reduction methods were initiated by Michelsen [10] who was the first one to link the number of non-linear equations that need to be solved in phase-split calculations to the rank of the binary interaction coefficients matrix (BIC) by showing that in the extreme case of zero BIC, the system equations are only three, on the condition that the Van der Waals mixing rules are utilized. Hendricks and Van Bergen [11] and Firoozabadi and Pan [12] extended this idea to phase stability

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calculations for fluids with non-zero BIC. By applying singular value decomposition to the BIC matrix and by maintaining only its dominant directions, the n original variables are replaced by a set of m new ones with $m \ll n$ thus significantly reducing the problem's dimensionality.

An alternative approach proposed by Rasmusen et al. [13] provides criteria for completely bypassing the stability test during a simulation run when the equilibrium conditions fall in certain regions of the phase diagram. They also proposed that any non-trivial values of the equilibrium coefficients obtained from the stability test which was performed at the precedent time step can be used as initial estimates to the subsequent one thus avoiding the utilization of the inaccurate Wilson's k-values. Nevertheless, special treatment is still required when the prevailing conditions at a discretization block meet either the phase envelope or the convergence pressure locus. Wang and Stenby [14] developed a phase split algorithm based on the linearization of the mass continuity and phase equilibrium equations which provides the number of moles of each component in each phase as the solution of a system of linear equations of order n^2. Stability is then determined by examining the sign of each phase's number of moles. Voskov and Tchelepi [15] proposed a parameterization of the compositional space which takes advantage of the linearity of the phase compositions along the tie-lines. By interpolating between preprocessed phase diagrams at several pressures and temperatures, phase compositions and mole fractions can be obtained also allowing for the solution of the stability problem. This approach has been extended to provide solutions at the supercritical region where tie-lines cannot be defined [16]. Schmitz et al. [17] proposed the use of neural networks for the treatment of ternary systems exhibiting a heterogeneous azeotrope. In their approach, each possible stability state is assigned to an integer that is non-iteratively predicted by the pretrained network. Evidently, stability calculations speed-up methods are required when repeated stability tests are performed for potential phases that can be described by a fixed EoS model, as it is the case with compositional full scale reservoir models, pipeline flow and separation process simulations.

In this work, a new approach for treating the phase stability problem in process simulation is proposed. A positive non-linear transformation of the established tangent plane distance exhibiting the same sign and the same zeroing points as the latter is used to provide a binary stable/unstable answer to the stability question. This appropriately designed discriminating function is an explicit function of composition, pressure and temperature, well defined anywhere in the operating space even outside the stability test limit locus [18]. Once generated, its explicit form allows stability state predictions to be obtained in a direct, non-iterative mode and with a computational effort which corresponds to a very small fraction of the CPU time required by conventional methods. By completely avoiding time consuming iterations and the requirement for suitable initial estimations, the number of operations required for any test point is constant even in the vicinity of the critical point, the stability test limit locus and the supercritical region.

The discriminating function can be generated quickly by a fully automated procedure using phase behavior data that is obtained by any reliable phase stability algorithm. Being generated against noise-free data, the proposed discriminating function provides the stability state as accurately as the EoS model utilized for its development. It is shown that the discriminating function can serve as a measure of any test point distance to the phase boundary thus allowing, whenever necessary, the utilization of conventional algorithms for the few ambiguous cases lying in the vicinity of the phase boundary. The method can be applied with any EoS model and with any set of mixing rules and it can be directly extended to stability calculations with an arbitrary number of phases.

This paper is organized as follows. Firstly, the equivalence between discriminating functions and the tangent plane distance is documented. Subsequently, the mathematical techniques utilized for generating and implementing the proposed discriminating function are presented. A set of representative examples demonstrates the value of the proposed method and a discussion on further enhancements precedes the conclusions.

2. Discriminating functions equivalence to the phase stability problem

According to the tangent plane distance criterion a mixture of given composition $\mathbf{z}$ at pressure p and temperature T will split into two or more phases if a composition $\mathbf{y}$ can be found which leads to a reduction of the mixture's Gibbs energy when an infinitesimal quantity of that composition forms a second phase. Let the reduced Gibbs energies of the original mixture and of the potential diphasic one be $g(\mathbf{z})$ and $g_{\text{mix}}(\mathbf{z}, \mathbf{y})$ respectively. Michelsen's criterion states that:

$$\text{Mixture is } \begin{cases} \text{unstable} & \text{if } TPD_{\min} < 0 \\ \text{stable} & \text{if } TPD_{\min} > 0 \\ \text{stable} & \text{if } TPD_{\min} = 0, \quad \mathbf{y}_{\min} = \mathbf{z} \\ \text{unstable} & \text{if } TPD_{\min} = 0, \quad \mathbf{y}_{\min} \neq \mathbf{z} \end{cases} \tag{1a}$$

where

$$TPD_{\min} = \Delta g_{\min} = g_{\text{mix}}(\mathbf{z}, \mathbf{y}_{\min}) - g(\mathbf{z}) \tag{1b}$$

$$\mathbf{y}_{\min} = arg \min_{y} \{g_{\text{mix}}(\mathbf{z}, \mathbf{y})\} \tag{1c}$$

The four branches in Eq. (1a) correspond to points lying in the interior of the pressure–temperature phase envelope, between the phase envelope and the stability test limit locus [18], outside the stability test limit locus and on the phase envelope (incipient equilibrium second phase) respectively. Due to the implicitness and non-linearity of Eq. (1c), the phase stability problem needs to be solved iteratively either by an optimization method or by utilizing function solving methods such as the Newton–Raphson or the Successive substitution ones for locating stationary points where the TPD derivative vanishes. An expression allowing for the direct evaluation of the minimum TPD and $\mathbf{y}_{\min}$ values would be highly beneficial as it would relax the need for iterative computations. In fact, according to Eq. (1), any function $d(\mathbf{z}, p, T)$ exhibiting the same sign with $TPD_{\min}$ over the full operating range would provide exactly the same stability predictions as the conventional criterion. More specifically, the conditions that function $d(\cdot)$ should satisfy are given by:

$$\begin{array}{ll} TPD_{\min}(\mathbf{z}, p, T) \neq 0 \Rightarrow TPD_{\min}(\mathbf{z}, p, T) \cdot d(\mathbf{z}, p, T) > 0 & \\ TPD_{\min}(\mathbf{z}, p, T) = 0, & \mathbf{y}_{\min} = \mathbf{z} \Rightarrow d(\mathbf{z}, p, T) > 0 \\ TPD_{\min}(\mathbf{z}, p, T) = 0, & \mathbf{y}_{\min} \neq \mathbf{z} \Rightarrow d(\mathbf{z}, p, T) = 0 \end{array} \tag{2}$$

Note that during a simulation run, the EoS model parameters are fixed to the values obtained from the tuning and, with their variance being equal to zero, they can be omitted from the functions arguments. By comparing Eqs. (1a) and (2) it can be readily seen that once a $d(\mathbf{z}, p, T)$ function has been derived satisfying the conditions above, the stability test rule can be described equivalently by:

$$\text{Mixture is } \begin{cases} \text{stable} & \text{if } d(\mathbf{z}, p, T) > 0 \\ \text{unstable} & \text{if } d(\mathbf{z}, p, T) < 0 \\ \text{unstable} & \text{if } d(\mathbf{z}, p, T) = 0 \end{cases} \tag{3}$$

where the third branch corresponds to an incipient equilibrium second phase. The "min" subscript from here and on will be omitted for the sake of simplicity.

In this work, the utilization of discriminating functions from the machine learning field [19] is proposed as suitable tools for generating explicit expressions of the $d(\cdot)$ function. Let a set of data