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A duality-based optimisation approach for the reliable solution of (*P*, *T*) phase equilibrium in volume-composition space

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ABSTRACT

A reliable algorithm for the solution of fluid phase equilibrium at constant pressure and temperature (*P*, *T* flash) is presented. The approach is applicable to multi-component mixtures described with general equations of state and is based on a formulation of *P*, *T* phase equilibrium as a dual optimisation problem in volume-composition space, translated away from the Gibbs free energy to the Helmholtz free energy. This formulation facilitates the use of guaranteed solution algorithms, particularly in the case of sophisticated equations of state (EOSs) such as SAFT (statistical associating fluid theory), because such representations are higher-than-cubic functions in volume and are formulated in the Helmholtz free energy. With the proposed algorithm (which is based on a combination of local and global optimisation, where the number of subproblems to be solved globally is kept at a minimum) one is guaranteed to identify the number of stable phases present at equilibrium, along with their properties, without any need for initial guesses, or indeed any *a priori* knowledge about the behaviour of the system. The method is applicable to the calculation of any kind of fluid phase behaviour (e.g., vapour–liquid (VLE), liquid–liquid (LLE), vapour–liquid–liquid (VLLE), etc.). Several algorithmic options are investigated and their computational performance compared. A prototype implementation is used to determine the fluid phase equilibria of a number of binary and ternary systems, where the thermodynamic properties are calculated through a molecular-based EOS. Examples are shown for the VLE and VLLE for mixtures modelled with an augmented van der Waals EOS, a non-cubic EOS that incorporates the Carnahan and Starling representation of the repulsive interactions. Further examples are presented for VLE and VLLE in polymer systems, modelled with an EOS of the generic SAFT form. Fluid phase equilibrium calculations for polymer systems are notoriously difficult, and convergence problems are often encountered, even with good initial guesses. The proposed method is found to be reliable in all cases examined.

1. Introduction

The reliable determination of phase equilibrium is important in process and product design, as the appearance and disappearance of phases, and the composition of the stable phases, greatly affect process performance and product end-use properties. The phases at equilibrium depend on key design variables such as total composition, temperature and pressure. Within process modelling, the solution of phase equilibrium is the task to which the majority of CPU time is devoted. Even for binary mixtures, this problem can be challenging [1–3], due to the high degree of nonlinearity and the presence of discontinuities.

In many applications, the phase equilibrium problem at given pressure, temperature and total composition, the *P*–*T* flash, is of interest. This problem can be briefly described as follows: Given a multi-component mixture with specified total composition, pressure and temperature, how many stable equilibrium phases are present and what are their properties? The solution of phase equilibrium lies at the global minimum of the system's total Gibbs free energy [4]. This function is related to the intensive Gibbs free energy which has the natural variables $\underline{x}$, *P*, *T*, where $\underline{x}$ is a vector of component mole fractions, *P* is pressure and *T* is temperature. One particularly challenging aspect of the formulation is that the number of phases is generally unknown [5].

There is a large body of work on this subject, the most successful general concept to date being the alternating stability test/flash approach first introduced by Michelsen [6–8]. The development of reliable methods for the solution of phase equilibrium and stability remains an active area of research. A number of deterministic techniques have been proposed, in which analysis of or insight into the problem is used to increase the likelihood of finding the stable solution (e.g., [9–15]). A global analysis of the solution space is undertaken in several of these algorithms, e.g., ([11,15]), but without a formal guarantee of convergence. Such approaches are

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particularly valuable where computational speed is a prime consideration. The correct solution is identified in many cases, but not in some difficult instances as discussed in [16–20]. Several *guaranteed* deterministic techniques have also been developed, such as those discussed in [21–27], where the focus is placed on providing a mathematical guarantee of finite convergence to within a tolerance ϵ of the solution. Through the use of interval analysis, it is possible to extend the guarantee of correctness so that mathematical and computational convergence can be ensured, regardless of the round-off error, as shown in [18,28–31]. Finally, a number of stochastic algorithms have been developed that provide an infinite time guarantee of convergence [32–34]. Further references can be found in the reviews by Wakeham and Stateva [35] and by Segura et al. [36].

The use of guaranteed deterministic techniques comes at a computational cost, but they are particularly useful in difficult cases, or in cases where there are no external means of checking correctness, such as in parameter estimation [1]. In order to increase computational performance, a combination of local and global solvers is used to solve nonconvex subproblems in several guaranteed deterministic techniques, e.g., see [18,24,30]. The objective is to develop an algorithm for the solution of phase equilibrium, hereafter referred to as the PE algorithm, that guarantees convergence to the correct solution in finite time. The nonconvex subproblems are the tangent plane stability problem and the flash (or phase split) problem for a fixed number of phases. To guarantee that the correct solution of phase equilibrium has been found, it is necessary to use a deterministic global optimisation algorithm at least once during the PE algorithm, to solve the tangent plane stability test: if the proposed solution is found to be stable through this global test, the problem is solved and the PE algorithm can terminate. If it is found not to be stable, a flash problem must be solved for a fixed number of phases to generate a new solution, and a stability problem must eventually be solved to global optimality for a new potential phase configuration. The use of global optimisation for phase stability guarantees that when a final solution is reported by the PE algorithm, it is stable, i.e., the PE algorithm cannot converge to a wrong solution. This is not enough, however, to guarantee that the PE algorithm will find the stable solution in a finite time. For this, one must be able to guarantee that, for a given number of phases, the solution with the lowest Gibbs free energy is found. A local phase split algorithm is highly dependent on starting points and could converge repeatedly to a metastable solution, for example. In practice, this behaviour is often avoided by generating good initial points. Nevertheless, the only way to offer a theoretical guarantee of finite-time convergence is to ensure that global optimisation can be used to solve the flash problem; such an approach is implemented in GLOPEQ [24].

In the present work, we focus on the development of a guaranteed deterministic framework that can be applied to any equation of state (EOS), including those that are higher-than-cubic in volume such as the statistical associating fluid theory (SAFT) [37,38]. Higher-than-cubic EOSs are becoming increasingly popular due to their predictive capabilities for complex fluids, such as associating (i.e., hydrogen bonding) and polymer mixtures. When dealing with such approaches, which are typically formulated in the Helmholtz free energy $A(\underline{x}, V, T)$, where V is volume, the guaranteed solution of phase equilibrium is subject to additional difficulties. The Helmholtz free energy is the natural thermodynamic potential for developments within a statistical mechanical framework and has $\underline{x}$, V, T as natural variables, as opposed to $\underline{x}$, P, T for the Gibbs free energy. If the EOS is first-order in volume, then moving between the Helmholtz and Gibbs free energies is a trivial exercise. Unfortunately, this is only the case for the ideal gas EOS. For other EOSs, the evaluation of constant pressure properties requires a minimisation of the Gibbs free energy with respect to volume, with a constraint relating the volume to the pressure. This minimisation is often realised through the identification of all the volume roots of the EOS, and then the selection of the physically meaningful root (i.e., the most stable root, with the lowest Gibbs free energy). In the case of cubic equations of state, the volume roots of the EOS may be obtained analytically. For higher-than-cubic equations, calculations at a specified pressure and temperature are more time consuming, since the determination of $G(\underline{x}, P, T)$ at each point in composition requires the use of a nonlinear solver that can reliably identify the appropriate volume root for use in the calculation. In addition to increasing the cost of each Gibbs free energy evaluation, this inner minimisation can lead to complications when developing deterministic guaranteed approaches to fluid phase equilibrium. For instance, Xu et al. [30] have shown that the presence of an inner iteration can lead to large increases in the computational cost with a guaranteed deterministic algorithm. Though in the case of [30] the inner iteration is the system of equations arising from the association term of the SAFT approach [37,38], the solution of the pressure equation is also likely to lead to increases in computational cost: it is a low-dimensional but highly nonlinear problem. A promising avenue in this context is the formulation proposed by Nagarajan et al. [39,40], who developed a stability test and flash calculation method based on the Michelsen methodology, but using component molar densities as independent variables. This circumvents the need to solve for the volume roots of higher-than-cubic EOSs. It can also lead to enhanced robustness [19]. This formulation has been used successfully in an interval-based global optimisation algorithm to solve multi-component phase equilibria with a version of SAFT [30] and in a stochastic global optimisation algorithm [41].

Mitsos and Barton [27] have recently proposed an alternative approach to identifying a stable phase. They showed that the solutions of a dual formulation stemming from a single-phase Gibbs free energy minimisation problem, where mass balance constraints are imposed, are the stable equilibrium phases. This is an elegant new approach to the phase equilibrium problem, which requires no prior knowledge of the system being examined, neither in terms of the number of equilibrium phases present, nor in terms of the equilibrium phase compositions. At the solution of the dual problem, the composition of one of the stable equilibrium phases is obtained, as well as the equilibrium chemical potentials of all components. This information completely describes the common tangent plane connecting the equilibrium phases, and therefore may be used to find all other stable phases, which are in fact all the other (global) solutions of the dual problem. The dual approach has been applied to several case studies using the NRTL and UNIQUAC models and has been used in parameter estimation for a number of thermodynamic models [42,43]. Although the presence of a vapour phase is considered in [43], it is treated as ideal. In the solution algorithm proposed in [27] for the dual problem, one iterates between solving linear and nonconvex optimisation problems. The nonconvex problem has the same dimensionality as the tangent plane distance minimisation problem and a similar functional form. A feature of the dual approach is that it is not necessary to minimise the Gibbs free energy for different guesses of the number of phases. This approach has the potential to reduce the computational time required to solve the phase equilibrium problem provided that the number of iterations between the nonconvex and linear problems can be kept relatively low, and that, once a stable phase has been found, the remaining phases can be identified at low cost. This warrants further investigation and development for the case of general equations of state, particularly in the context of algorithms that identify all stable equilibrium phases.

In this paper, we develop a dual-based formulation of P, T phase equilibrium cast in the Helmholtz free energy and a guaranteed deterministic algorithm for its solution. The approach is general for any equation of state and any number of components. Instead of component molar densities [39], mole fractions and total molar