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SMITH: differential homotopy and automatic differentiation for computing thermodynamic diagrams of complex mixtures.

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Abstract

This paper presents SMITH, the working prototype of a new code which significantly improves the accuracy of thermodynamic diagrams thanks to the highly performant numerical technologies including differential homotopy and automatic differentiation.

1 Introduction

Extraction of singular compounds from multi-component mixtures through the separation process is the most commonly used technology in chemical, pharmaceutical and food-processing industries (Petlyuk, 2004). Analysis of the thermodynamic diagrams describing the fundamental physical properties of complex mixtures is a crucial step in the conceptual design of industrial process involving separation technologies. In very many cases the topology of these diagrams is non-trivial even for ternary mixtures. In particular, this concerns the computation of certain characteristic curves like univolatility curves, distillation profiles, the phase separation curves, the pinch-point curves, etc. Different types of diagrams are accessible via professional packages, but often they are incomplete or lack in precision, as in the example shown in Fig. 1 about univolatility curves used when designing extractive distillation process.

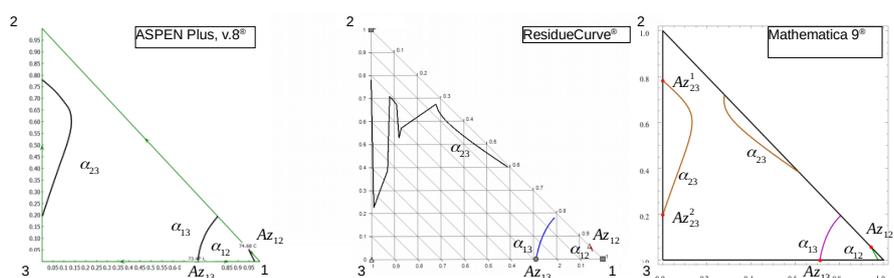


Figure 1: Hexane (1) - Benzene (2) - Hexafluorobenzene (3) at 1.2 atm (generalized NRTL). Univolatility curves computed by ASPEN Plus v.8[®], ResidueCurve[®], and Mathematica 9[®]. Here α_{ij} are the univolatility curves of i and j compounds, Az_{ij} are binary azeotropes. Both professional codes fail to identify the pair of binary azeotropes Az_{23} , ASPEN Plus[®] ignores the azeotrope-free branch of the curve α_{23} . ResidueCurve[®] lacks in precision.

The insufficiency of the professional softwares creates serious obstacles for the technological transfer from academic research to industrial implementation, so the search of new algorithmic solutions to improve computational efficiency are important for the process engineering community.

The major part of existing algorithms to compute characteristic curves of thermodynamic diagrams use the Newton-Raphson like procedures over the composition space. This implies an important computational effort to access the acceptable precision and requires an a-priori knowledge of the topology of the diagram in order to provide a good initial approximation. On the other hand, algorithms based on the differential homotopy principle provide a very promising alternative to the Newton-Raphson method for path following computations (Allgower and Georg, 2003; Caillau et al., 2012). In process engineering, this approach was proposed by several authors to compute distillation profiles, pinch point curves, univolatility curves (Poellmann and Blass, 1994; Feldbab, 2012; Skiborowski et al., 2016) and phase separation boundaries (Deiters, 2016). Although these codes showed excellent results in comparison with the Newton-Raphson based analogs, still they form a marginal branch in the process engineering computing. The main reason of this poor success is the access to the derivatives of the thermodynamic models required by these methods. Indeed, using analytical expressions of the model and its derivatives significantly increase precision and numerical stability of computations, but their implementation is technically difficult and may form an additional source of error.

In this paper we present SMITH (Separation of Mixtures In Thermodynamics by Homotopy) (SMITH, 2020), a working prototype of a new code allowing highly precise and efficient computation of different types of curves of ternary diagrams. In contrast with codes cited above SMITH realizes the differential homotopy algorithm in coupling with automatic differentiation of the thermodynamic models. Such a coupling allows to easily implement a large class of thermodynamic models, and access the high numerical performance with less computational effort. The current version of SMITH is limited to compute the univolatility curves of ternary mixtures, without an a-priori knowledge of the topological structure of the underlying VLE diagram and independently of the presence of azeotropes. The same computational approach can be developed for many other types of thermodynamic diagrams.

In Section 2 we briefly recall the geometric model of the univolatility curves introduced in Shcherbakova et al. (2017). Section 3 describes the main features of the SMITH code. The paper is concluded with a series of illustrating examples.

2 Geometrical model of univolatility curves

Univolatility curves α_{ij} are the sets of points on the ternary residue curve map (RCM) where the pair of compounds i and j have the same relative volatility. They are used as the feasibility indicators in the distillation process design. In extractive distillation, the placement and the terminal points of the univolatility curve on the composition triangle edges determine the order of the withdrawn products as well as the proper column configuration (Gerbaud and Rodriguez-Donis, 2014).

A ternary RCM may contain up to three families of univolatility curves according by their respective index, even in zeotropic case. The topology of univolatility curves is intrinsically related to the topology of the underlying RCM (Kiva et al., 2003; Shcherbakova et al., 2017). Indeed, three univolatility curves of different index intersect at ternary azeotropic points, and each binary azeotrope gives rise to a univolatility curve. Multiple binary and ternary azeotropy can occur. Note that the presence of azeotropes is sufficient but non necessary for the existence of the univolatility curves. A RCM may contain azeotrope-free curves and multiple curves of the same index may coexist. If the topological structure of the RCM is known, the computation of univolatility curves

starting at azeotropes is straightforward, while the detection of univolatility curves not associated with azeotropes is a more complicated and time-consuming process, especially in the case of zeotropic mixture.

Consider an open evaporation of a ternary mixture kept at thermodynamic equilibrium at constant pressure. Denote $x_i, y_i, i = 1, 2, 3$ the mole fractions in the liquid and in the vapor phases, and T the temperature of the system. In the absence of chemical reactions a two-phase ternary mixture has three independent state variables. By choosing x_1, x_2 and T , the complete state space of the system is $M = \{(\bar{x}, T) : T \in [T_{min}, T_{max}], \bar{x}_i \in \Omega, i = 1, 2\}$, where T_{min} and T_{max} are the minimum and maximum boiling temperatures of the mixture and $\Omega = \{\bar{x} = (x_1, x_2) : x_i \in [0, 1] \text{ with } x_1 + x_2 \leq 1, i = 1, 2\}$ is the composition space parameterized by the mole fractions of the first two compounds, while $x_3 = 1 - x_1 - x_2$. The distribution coefficients $K_i : M \rightarrow \mathbb{R}$ are the functions over M that describe the vapor-liquid equilibrium (VLE) in terms of molar fractions in the vapor and liquid phases: $y_i = K_i(\bar{x}, T)x_i$ for $i = 1, 2, 3$. Since $\sum_{i=1}^3 y_i = 1$, the following equilibrium condition holds:

$$\Phi(\bar{x}, T) = \sum_{i=1}^3 K_i(\bar{x}, T)x_i - 1 = 0. \quad (1)$$

In 3D state space M , Eq.(1) defines a smooth hyper-surface referred as the boiling temperature surface, namely W -surface. Along with W -surface, M contains three univolatility hypersurfaces defined by equations

$$\Psi_{ij}(\bar{x}, T) = K_i(\bar{x}, T) - K_j(\bar{x}, T) = 0. \quad (2)$$

Possible intersections of the W -surface with univolatility hypersurfaces are smooth curves $\Gamma_{ij} \in M$ called the generalized univolatility curves (Shcherbakova et al., 2017). Univolatility curves $\alpha_{ij} \in \Omega$ are the orthogonal projections of the curves $\Gamma_{ij} \in M$ to the composition space Ω . Since $\nabla\Phi$ and $\nabla\Psi_{ij}$ define the normal vector fields to the 2D surfaces defined by Eqs.(1, 2), the vector field $U^{ij} = \nabla\Phi \times \nabla\Psi_{ij}$ is tangent to the generalized univolatility curve Γ_{ij} . In other words, the curve Γ_{ij} is a solution to the following system of ordinary differential equations in M :

$$\dot{x}_1 = U_1^{ij}(x_1, x_2, T), \quad \dot{x}_2 = U_2^{ij}(x_1, x_2, T), \quad \dot{T} = U_3^{ij}(x_1, x_2, T). \quad (3)$$

In order to compute generalized univolatility curves it is enough to detect their end-points over the border of the composition triangle and use them as the initial points for the numerical integration of Eq.(3). This can be done solving Eqs.(1, 2) on the boundary of the composition triangle $\partial\Omega$ in the reduced 2D space. For the sake of completeness we remark, that in some cases α_{im} curve starts from the binary edge i, j of the triangle where m compound is missing (see for instance the α_{12} curve in Fig. 1). In this case, as it was proposed in (Kiva et al., 2003), the distribution coefficient K_m must be replaced by the distribution coefficient at infinite dilution, which can be obtained from the ternary distribution coefficient by setting $x_m = 0$:

$$K_m^{i,j,\infty} = \lim_{\substack{x_m \rightarrow 0 \\ m \neq i,j}} K_m(\bar{x}, T) \quad (4)$$

This generalization enables to compute complete univolatility diagrams independently of the presence of azeotropes.

3 SMITH algorithm

3.1 Differential homotopy method

The core of SMITH code uses the differential homotopy method with arc-length parameterization to solve the systems of algebraic equations. This approach is based on the following mathematical result (see in Allgower and Georg (2003) for more details).

Let $F : \mathbb{R}^{N+1} \rightarrow \mathbb{R}^N$, $F(q, \lambda)$, denote the homotopic function where λ denotes the homotopy parameter. Under certain regularity assumptions, the solution to the equation $F(q, \lambda) = 0$ forms a one-dimensional manifold. Indeed, if F is a continuously differentiable function such that

$$F(q_0, \lambda_0) = 0, \quad \text{rank} \frac{\partial F}{\partial \lambda}(q_0, \lambda_0) = N$$

for some q_0 and λ_0 , and if zero is a regular value of F , then a continuously differentiable curve starting from (q_0, λ_0) exists and it is either diffeomorphic to a circle or to the real line. The different branches of $F^{-1}(\{0\})$ form disjoint smooth curves.

As we showed in Section 2, the generalized univolatility curve Γ_{ij} is a "path of zeros" of the function $F_{ij} = (\Phi(q, \lambda), \Psi_{ij}(q, \lambda))$ with $q = (x_1, T)$ and $\lambda = x_2$. SMITH uses a predictor-corrector algorithm via the `nutopy` package with a high order step-size control Runge-Kutta scheme for the prediction, and with a classical simplified Newton method for the correction. The key point of success is the efficient computation of the Jacobian matrix of the homotopic function F_{ij} , which reduces to the computation of the derivatives of the distribution coefficients K_i , $i = 1, 2, 3$. In SMITH code these derivatives are computed via the automatic differentiation tool `tapenade` (Hasco and Pascual, 2012), which drastically simplifies numerical implementation of the homotopic method.

3.2 Initial points computation

To start the homotopy, the path-following method needs to be initialized at points (q_0, λ_0) verifying $F(q_0, \lambda_0) = 0$. Such points can be chosen on the border of the composition triangle Ω . In fact, according to the index i, j of the couple of compounds, each edge of $\partial\Omega$ may contain up to three types of extremity points verifying univolatility condition, moreover, several points of the same index may co-exist. Such points may be found by applying a standard Newton-Raphson procedure over the border of the composition triangle. SMITH realizes a much more efficient method, based on the following observation. Any edge I of the triangle $\partial\Omega$ can be parameterized by the mole fraction of one of the compounds $x_i = a \in [0, 1]$, $i \in 1, 2$. Denote $\phi(a, T) = \Phi(\bar{x}, T)|_{\bar{x} \in I}$, $\psi_{ij}(a, T) = \Phi_{ij}(\bar{x}, T)|_{\bar{x} \in I}$. Then initial points for the curve α_{ij} are zeros of the function $E_{ij} : \mathbb{R}^2 \rightarrow \mathbb{R}^2$ defined by $E_{ij}(a, T) = (\phi(a, T), \psi_{ij}(a, T))$. Due to the uniqueness of the boiling temperature T of a homogeneous mixture, equation $\phi(a, T) = 0$ defines a smooth graph in the 2D plan with coordinates a and T . According to the Implicit Function Theorem, it can be solved in order to express $T = T(a)$. Then the zeros of the function E_{ij} can be detected by finding zeros of the scalar function $\psi_{ij}(a, T(a))$.

SMITH implements the above idea as follows. In order to capture multiple solutions, each edge of $\partial\Omega$ is divided into K sub-intervals $[a_k, a_{k+1}]$, $k = 0, \dots, K - 1$ with $a_0 = 0$ and $a_K = 1$. $T(0)$ is computed by Brent's method in the interval $[T_{min}, T_{max}]$, and going further around the edge, $T(a_k)$ is computed via a standard Newton method using $T(a_{k-1})$ as the initial guess. The sign of $\psi_{ij}(a_k, T(a_k))$ is checked at each k . The change of the sign of ψ_{ij} at k -th step means the existence of a zero of this function in the interval $[a_{k-1}, a_k]$, which can be then found by a standard Newton-Raphson procedure. Realizing such a scheme along every edge of the triangle for all three families of equations (including the equations associated to the compound at infinite dilution) allows to build the complete set of initial points. Observe, that binary azeotropes can be detected a-posteriori by

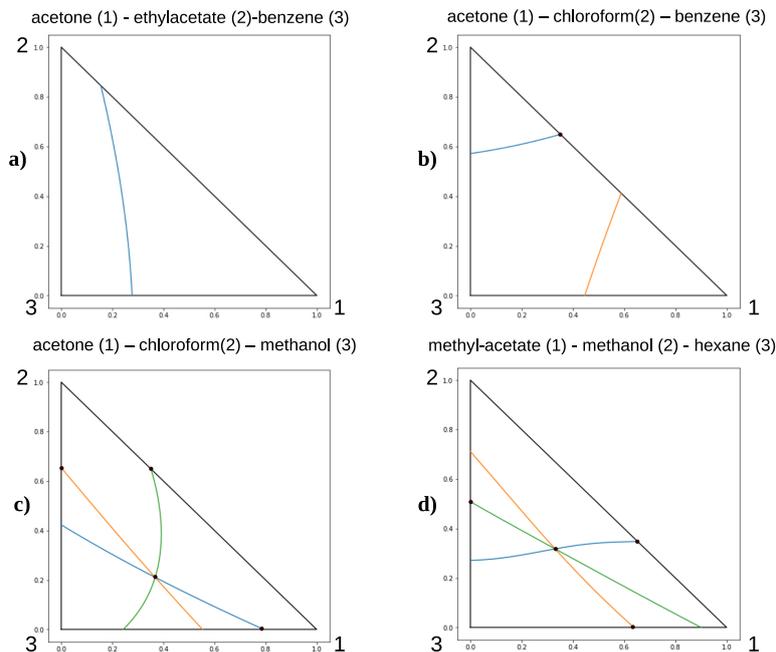


Figure 2: Univolatility diagrams of different Serafimov’s VLE topological classes computed by SMITH: a) 0.0-1; b) 1.0-2; c) 3.1-4; d) 3.1-2.

checking the condition $K_i = K_j = 1$ over the computed set of points. The binary bi-azeotropy can be easily detected.

3.3 Examples

The actual version of SMITH code allows computations using NRTL and UNIQUAC models for activity coefficients, and Antoine’s and DPPR equations for vapor pressure computations at various value of process pressure. Fig. 2 shows four examples of ternary univolatility diagrams of different topological classes (see in Kiva et al. (2003) for Serafimov’s ternary VLE classes). They were computed at standard atmospheric pressure using NRTL model for activity coefficients and Antoine’s equation for vapor pressure calculation. The black points indicate the position of azeotropes. Diagram a) provides an example of a purely zeotropic mixture (Serafimov class 0.0-1) which has one univolatility curve. Diagram b) contains two univolatility curves of different indexes, one of them is azeotrope-free. These two azeotrope-free univolatility curves cannot be detected by ASPEN Plus v.8[®]. Cases c) and d) provide examples of diagrams of three curves of different index, the essential difference is the type of ternary azeotrope: a saddle in c) and an unstable node in d) cases. The intersection points of the uni-volatility curves were used to find the ternary azeotropes.

4 Further perspectives

The current version of SMITH (SMITH, 2020) works on Unix systems. We are no working on the Windows version. Although the current version implements only the standard NRTL model,

other thermodynamical models are under development. Soon they will be available, as well as a more efficient method of initial points localization using homotopy. In a long term perspective, we plan to develop new applications to compute phase separation boundaries, pinch point curves, etc. The described mathematical and numerical approach can be easily adapted to these types of computation.

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