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Efficient and reliable mixture critical points calculation by global optimization

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ABSTRACT

Multicomponent systems may exhibit several critical points or no critical point at all. Local methods can find only one critical point for a given initial guess. Recently, several global methods have been proposed for finding all the solutions of the problem. In the present work, we propose a gradient-based calculation method using global optimization, with temperature and molar volume as primary variables, and with analytical partial derivatives calculated from a two-parameter cubic equation of state. The Tunneling global optimization method is used for finding all the global minima. The implementation is based on a unique feature of the Tunneling method, which is able to find efficiently and reliably multiple minima at the same level. Several mixtures from binaries to petroleum reservoir fluids are used to test the proposed method. Numerical experiments proved the efficiency and reliability of the Tunneling method for finding all mixture critical points.

1. Introduction

Calculation of critical points is an important topic within the more general frame of phase equilibrium calculations, from both theoretical and practical points of view, with many applications in chemical and process engineering. Experimental determination of critical points is generally expensive, thus reliable calculation algorithms are valuable tools for system behavior assessment, from the calculation of critical loci of binary mixtures (and their classification according to van Konynenburg and Scott [1]), to practical problems such as recovery from hydrocarbon reservoirs.

Reid and Beegle [2] have shown that critical conditions can be derived using Legendre transforms. Various forms of the criticality conditions can be obtained depending on the choice of variables, their ordering and the order of the Legendre transform. Hicks and Young [3] calculated critical loci of binary mixtures by tracking sign changes in critical conditions; the method is not dependent on initialization but it can miss solutions. The first critical point calculation method for multicomponent systems based on rigorous thermodynamic criteria and a cubic equation of state (EoS) was proposed by Peng and Robinson [4]: crtical criteria are derived from the Gibbs free energy, and temperature and pressure are used as primary variables. Baker and Luks [5] proposed a method based on Helmholtz free energy with temperature and molar volume as primary variables. Both methods require the calculation of a large number of determinants, which make them computationally inefficient. Heidemann and Khalil [6] formulated the second criticality condition by setting to zero a cubic form; their formulation is the most widely used for critical points calculations. Later, Michelsen and Heidemann [7] expressed the problem as a general eigenvalue problem (this is maybe the most efficient local method). If all the binary interaction parameters (BIPs) are zero, the dimensionality in spinodal calculations is two. Billingsley and Lam [8] presented an interesting extension to non-zero BIPs. Nichita proposed two methods [9,10] to reduce the dimensionality of the problem from nc (number of components) to m, by using Hendriks' reduction theorem [11] and spectral decomposition [12] of the m-ranked matrix with elements $(1 - k_{ij})$. These methods are particularly efficient for mixtures with many components and relatively few non-zero BIPs, such as petroleum reservoir fluids. A computationally efficient method with pressure and temperature as primary variables was proposed by Michelsen [13]. Other formulations for critical point calculations have been presented by Nagarajan et al. [14], Quinones-Cisneros [15], Yermakova and Anikeev [16]. Critical points have also been calculated using various thermodynamic models, of higher complexity than cubic EoS [17–20], for semicontinuous mixtures, Rochocz et al. [21], and for polydisperse systems (Heidemann [22]). The problem of higher order critical points has also been addressed; for instance, Michelsen and Heidemann [23] proposed a method for tricritical points calculation.

Practically all critical point calculation methods consist in simultaneously solving a set of two equations. The first one is the spinodal equation obtained by setting to zero a determinant (or by solving an equivalent eigenvalue problem [24]) of nc or nc-1 order, containing

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second-order partial derivatives of thermodynamic potentials. The second equation locates the critical point on the spinodal, and it involves third-order partial derivatives of thermodynamic potentials.

Multicomponent systems may exhibit several critical points or no critical point at all. Local calculation methods can find only one critical point for a given initial guess. Recently, several global methods have been proposed for finding all the solutions of the problem. The first global method for critical points calculation was proposed by Stradi et al. [25], who used the Newton-Interval-General Bisection (NIGB) method which gives the mathematical guarantee that all solutions are eventually found. However, the NIGB method is computationally expensive, and their analysis was restricted to binary and ternary mixtures. Henderson et al. [26] formulated the problem as an optimization problem by defining an objective function whose global minima correspond to the critical points. They used the Simulated Annealing (SA) global optimization method and criticality criteria derived from a slightly modified tangent plane distance (TPD) function based on Gibbs free energy, and pressure and temperature as primary variables. Freitas et al. [27] applied the SA global optimization method to critical point calculations for various binary systems. The SA method was also used by Saĭnchez-Mares and Bonilla-Petriciolet [28], and by Justo-Garcia et al. [29]. The SA method can be computationally expensive and has a probability of convergence.

In this work, we use the gradient-based Tunneling global optimization method [30,31], which had previously proved its usefulness and efficiency for solving highly difficult optimization problems[32], including a variety of phase equilibrium problems [33–38]. The Tunneling method is able to find multiple minima at the same level [38]; this unique feature of the Tunneling method is exploited to find all global minima of an objective function with temperature and molar volume as independent variables. The formalism is developed for a general form of two-parameter cubic EoS, which includes the Soave–Redlich–Kwong [39] (SRK) EoS and the Peng–Robinson [40] (PR) EoS.

The paper is structured as follows: we first present the criticality criteria, then the objective function and the gradient vector (using analytical partial derivatives), and the Tunneling global optimization method. The proposed method is tested for a variety of numerical examples, with emphasis on mixtures with more than one critical point or with no critical point at all, and finally a discussion and concluding remarks are presented. The full analytical treatment of partial derivatives is detailed in Appendices A–C.

2. Criticality criteria

The spinodal (intrinsic limit of thermodynamic stability) separates intrinsically unstable from metastable states. According to Heidemann and Khalil [6], the spinodal equation is

$$Q\Delta n = 0 \tag{1}$$

where $\Delta n = (\Delta n_1, \Delta n_2, \ldots, \Delta n_{nc})^T$ with $\Delta n^T \Delta n = 1$, and the elements of symmetric matrix Q are

$$Q_{ij} = \left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_{T,V,n_{k\neq i},j} = RT\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{T,V,n_{k\neq j}} \quad ; \quad i,j = 1, \text{nc} \tag{2}$$

Using the spectral decomposition $Q = U\Lambda U^T$, where $\Lambda = \text{diag}(\lambda_i)$ and the matrix U contain as rows eigenvectors u_i corresponding to eigenvalues λ_i, and by taking $\Delta n = u_{\min}$ (eigenvector corresponding to minimum eigenvalue $\lambda_{\min}$), Eq. (1) can be written

$$Qu = \lambda_{\min} u \tag{3}$$

and the quadratic form

$$Q^* = \sum_{i=1}^{nc}\sum_{j=1}^{nc} Q_{ij}\Delta n_i \Delta n_j \tag{4}$$

is, due to orthogonality properties of eigenvectors [16,24],

$$Q^* = \lambda_{\min} \tag{5}$$

On the spinodal $Q^* = 0$; a negative value indicates a system intrinsically unstable, while positive values indicate stable or metastable states. The spinodal equation is

$$Q^*[T, v, \boldsymbol{\Delta n}(T, v)] = 0 \tag{6}$$

The quadratic form depends only on the primary variables T and v directly and by means of Δn.

Only the minimum eigenvalue and the corresponding eigenvector are required and can be efficiently calculated by inverse iteration (Wilkinson [41]).

The second criticality condition locates the critical point(s) on the spinodal:

$$C^* = \sum_{i=1}^{nc}\sum_{j=1}^{nc}\sum_{k=1}^{nc} C_{ijk}\Delta n_i \Delta n_j \Delta n_k = 0 \tag{7}$$

where

$$C_{ijk} = \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k}\right)_{T,V,n_{l\neq i,j,k}} = RT\left(\frac{\partial^2 f_i}{\partial n_j \partial n_k}\right)_{T,V,n_{l\neq j,k}} \tag{8}$$

The cubic form depends on T and v directly and by means of Δn; the second criticality condition is

$$C^*[T, v, \boldsymbol{\Delta n}(T, v)] = 0 \tag{9}$$

The expressions of C_{ijk} and of the cubic form C^* are given in Appendix B.

3. Critical points calculation as a global optimization problem

3.1. Objective function

In order to formulate the critical points (CPs) calculation problem as a global optimization problem, the key is to define a suitable objective function; the global minima of this function should correspond to the critical points, that is, both criticality conditions must be fulfilled at any and all of these minima. Such a formulation was first presented by Henderson et al. [26]. They defined an objective function with pressure and temperature as primary variables, using criticality criteria in terms of Gibbs free energy, and solved the optimization problem using the Simulated Annealing method.

In this work we use the criticality criteria in terms of Helmholtz free energy described in the previous section, and the independent variables are the temperature and the molar volume.

The objective function is

$$F(v, T) = Q^{*2}(v, T) + C^{*2}(v, T) \tag{10}$$

At any global minima with $F = 0$ (which means that $Q^* = 0$ and $C^* = 0$), the solution correspond to a CP.

The optimization problem is

$$\min F(v, T)$$

s.t.

$$T_{\min} < T < T_{\max} \text{ and } v_{\min} < v < v_{\max}$$

The bounds used by Henderson et al. [26,27] are problem dependent. Stradi et al. [25] perform the search within the box defined by $\kappa \in [1.1, 4.0]$ and $T(K)/200 \in [0.55, 4.00]$. In this work we