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# Homotopic Method for binodal curves computation in ternary liquid-liquid separation

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## Abstract

This paper analyses the intrinsic geometric structure of binodal curves of phase separation diagrams of ternary mixtures. A new computational method is presented, and the efficiency of the proposed approach is tested for the Flory-Huggins model identification of water – acetone – hexadecane mixture.

**Keywords:** liquid-liquid separation, bitangent plane, binodal curve, differential homotopy

## 1. Introduction

Controlling the phase separation in industrial processes requires detailed knowledge of thermodynamic diagrams of multi-component mixtures (Koningsveld et al., 2001). Many computational problems arise in this context: identification of model parameters from the experimental data, localization of phase separation envelopes, detection of multi-phase regions, etc. Despite the enormous progress in this domain in the past decades, there is still a real need for new fast and reliable algorithms, for instance, in industrial applications using bio-sourced mixtures or in polymer production.

This paper focuses on the analysis of liquid-liquid separation of ternary mixtures at constant temperature and pressure. The topological structure of phase separation diagrams is then defined by binodal and spinodal curves delimiting stable, metastable and unstable domains in the composition space. Knowing these domains is crucial for modeling the demixing process in a given mixture. The experimental detection of spinodals that delimits the material stability domain is a highly non-trivial task. Instead, the various techniques allows measuring the composition of coupled coexisting phases, which can be used to establish a reliable model, which can predict the spinodal location a-posteriori.

The standard method of numerical computation of binodal curves uses the Newton-Raphson-like iterative algorithm to solve a system of algebraic equations over the mesh covering the state space of the diagram, while the classical least square method is commonly used for model identification. Often this approach fails to meet at least one of the quality criteria characterizing the “good” model: the binodal curve shape and the bundle of tie-lines indicating the coupled phases composition. Inspired by the ideas of D.J. Korteweg (Levelt Sengers, 2002) applied to the topological analysis of the Gibbs free energy surface, in this paper, we propose a new numerical method for computing binodal curves by a kind of differential homotopy method. The key idea is to consider

binodals as the 2D projections of certain smooth curves in 4D configuration space formed by the pairs of points of the phase diagram. This geometrical definition leads to a set of ordinary differential equations (ODE) describing the 4D curve as an integral curve of a smooth vector field in 4D space. A conventional ODE solver can numerically compute this curve at desired precision.

In Section 3 of this paper, the developed approach is applied for the analysis of the water-acetone-hexadecane mixture, characterized by two non-miscibility binary gaps among its components. The Flory-Huggins model parameters, including the triple interaction term, were computed by solving a non-trivial minNLP problem associated with a criterion, which accounts for the intrinsic geometry of the binodal curve. The computations performed using Mathematica 9 software yield very promising results that meet both quality criteria cited above.

## 2. Binodal and spinodal curves: thermodynamics vs. geometry

### 2.1 Phase coexistence conditions in multi-component mixtures

The physicochemical properties of an  $N$ -component system can be described by the Gibbs free energy  $G(P, T, n)$ , where  $n = (n_1, \dots, n_N)$ ,  $n_i$  being the number of moles of  $i$ -th component,  $P$  the pressure and  $T$  the temperature of the system. Being a homogeneous function of 1-st order with respect to  $n_i$ ,  $G$  can be expressed in terms of chemical potentials  $\mu_i = \frac{\partial G}{\partial n_i}$  as  $G(P, T, n) = \sum_{i=1}^N n_i \mu_i(P, T, n)$ . The infinitesimal changes in the state of the system obey the fundamental Gibbs equation

$$dG = -S dT + V dP + \sum_{i=1}^N \mu_i dn_i \quad (1)$$

where  $S$  and  $V$  are the entropy and the volume of the system.

All expressions above rest valid for each phase of a closed system maintained at thermodynamic equilibrium with two coexisting phases. Numbering the phases by  $a$  and  $b$ , the equilibrium condition reads  $dG = dG^a + dG^b = 0$ . Since in a closed system  $n_i = n_i^a + n_i^b$  and  $n_{tot} = \sum_{i=1}^N n_i$  are constant, it follows that  $dn_i^a = -dn_i^b$ , and hence Eq. (1) implies that

$$T^a = T^b, \quad P^a = P^b, \quad \mu_i^a(P^a, T^a, n^a) = \mu_i^b(P^b, T^b, n^b), \quad i = 1, \dots, n \quad (2)$$

In principle, two different thermodynamic models can be used in expressions of the chemical potentials of phases  $a$  and  $b$ . In the rest of this paper, it is assumed that both phases can be described by the same model. In addition, only the isobaric isothermal conditions will be considered, so the first two of Eqs. (2) become trivial.

The physicochemical properties of real mixtures are usually expressed in terms of molar, volume or mass fractions. In particular, the Flory-Huggins model used in Section 3 to describe the mixture of a polymer with water and a solvent, employs the volume fractions. Assuming the total volume of the mixture to be equal to the sum of partial volumes of components, and denoting by  $x_i = v_i/V$  the volume fraction of  $i$ -th

component and by  $g(P, T, x) = G(P, T, n(x))/R V$  the free Gibbs energy of mixing per unit of volume, Eqs. (2) can be rewritten in the form

$$\begin{aligned} \frac{\partial g^a(x^a)}{\partial x_i^a} &= \frac{\partial g^b(x^b)}{\partial x_i^b}, \quad i = 1, \dots, N-1, \\ g^a(x^a) - g^b(x^b) - \sum_{i=1}^{N-1} \frac{\partial g^a(x^a)}{\partial x_i^a} (x_i^a - x_i^b) &= 0 \end{aligned} \quad (3)$$

In the binary case ( $N=2$ ) these conditions mean that the graph of function  $g(x)$  admits a bi-tangent line to it, as it is shown in Fig. 1a. Below the ternary case is analyzed in detail.

### 2.2 Ternary case: binodal curves and bitangent planes of the Gibbs free energy surface

To simplify notations, from now on  $g'_i$  stays for  $\frac{\partial g}{\partial x_i}$ , the symbols  $\nabla_x g$  and  $D_x^2 g$  are used for the gradient and for the Hessian of function  $g$ , and  $(\cdot | \cdot)$  for the scalar product in  $\mathbb{R}^2$ .

In case of ternary mixtures Eqs.(3) describe the specific properties of the surface, referred to as surface  $W$ , defined by equation  $z = g(x_1, x_2)$  in a 3D Cartesian space with coordinates  $x_1, x_2, z$ , as it is shown in Fig. 1b. The material stability condition implies that such a surface has a physical meaning only in the sub-domain of the volume fraction space where the function  $g(x)$  is convex:

$$\Omega = \{x = (x_1, x_2): x_1, x_2 \in [0,1], x_1 + x_2 \leq 1, D_x^2 g \text{ is weakly pos. definite} \}$$

The projection on the  $x$ -plane of the set of singular points of surface  $W$ , i.e. the points where  $D_x^2 g$  is singular, defines the spinodal curve of the phase diagram. The first two of Eqs.(3) guarantee the existence of a pair of points  $P_1$  and  $P_2$  on the surface  $W$  with collinear normals, whereas the latter of Eqs.(3) says that these points belong to the same plane tangent to  $W$ . The projection of the segment  $P_1 P_2$  on  $x$ -plane is called a tie-line. The one-parametric family of conodal points  $P_1, P_2$  define two directrices of a certain ruled surface in 3D space. Their projections on the  $x$ -plane correspond to the two branches of binodal curve on the phase diagram. These branches can meet each other at the critical point of the phase diagram. Since by definition the critical point also belongs to the spinodal, these are the only common point between the binodal and the spinodal curves, and the whole binodal curve lies on the same side with respect to the spinodal curve. Fig.1b. illustrates all these concepts for the mixture having one critical point.

### 2.3 Differential equations of binodal and spinodal curves

As it follows from the above analysis, the binodal curves are formed by the pairs of points. So it is natural to describe these curves in the 4D space  $\Sigma = \Omega \times \Omega$  defined as follows:

$$\Sigma = \{q = (q_1, q_2) \in \mathbb{R}^4 : q_1 = x^a \in \Omega, q_2 = x^b \in \Omega\}.$$

Consider now the three co-dimension one smooth sub-manifolds in  $\Sigma$  associated to the zero-levels of the functions

$$\begin{aligned} F_1(q) &= g'_1(q_1) - g'_1(q_2), & F_2(q) &= g'_2(q_1) - g'_2(q_2), \\ F_3(q) &= g(q_2) - g(q_1) + (\nabla_x g(q_1) | q_2 - q_1), & q &\in \Sigma \end{aligned} \quad (4)$$

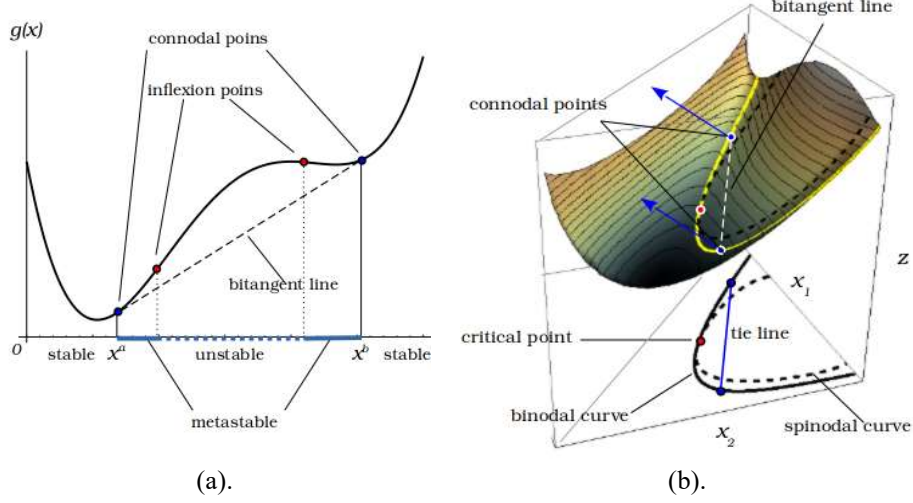


Fig.1. bi-tangent lines to the free Gibbs energy surface  $W$  in binary (a) and ternary (b) cases, and their projection on the composition space.

These sub-manifolds can intersect each other forming a one-dimensional sub-manifold  $\mathbf{B} = \{\mathbf{q} \in \Sigma : \mathbf{F}_i(\mathbf{q}) = \mathbf{0}, i = 1, 2, 3\}$ , whose orthogonal projections on two exemplars of  $\Omega$  define the two branches of the binodal curve. In what follows  $B$  will be referred to as the generalized binodal curve. This curve can be seen as the integral curve of the vector field  $\mathbf{q} \rightarrow \mathbf{V}(\mathbf{q}) \in T_{\mathbf{q}}\mathbf{B}$ . By definition,

$$\nabla_{\mathbf{q}} F_i(\mathbf{q}) \mathbf{V}(\mathbf{q}) = 0, \quad i = 1, 2, 3 \quad (5)$$

Define a pair of functions  $\Phi_i$  and  $\Psi_i$  such that  $(\Phi_i, \Psi_i)^T = \mathbf{D}_x^2 g(\mathbf{q}_i)(\mathbf{q}_1 - \mathbf{q}_2)$ , for  $i=1, 2$ . Then Eqs. (5) are equivalent to the following conditions:

$$\Phi_1 V_1 + \Psi_1 V_2 = 0 \quad \text{and} \quad \mathbf{D}_x^2 g(\mathbf{q}_1)(V_1, V_2) = \mathbf{D}_x^2 g(\mathbf{q}_2)(V_3, V_4) \quad (6)$$

The straightforward computation shows that  $\mathbf{V}(\mathbf{q})$  can be expressed as

$$\begin{aligned} V_1 &= \Psi_1 \det \mathbf{D}_x^2 g(\mathbf{q}_2), & V_2 &= -\Phi_1 \det \mathbf{D}_x^2 g(\mathbf{q}_2) \\ V_3 &= \Psi_2 \det \mathbf{D}_x^2 g(\mathbf{q}_1), & V_4 &= -\Phi_2 \det \mathbf{D}_x^2 g(\mathbf{q}_1). \end{aligned} \quad (7)$$

Clearly, the critical points of surface  $W$  correspond to the singular points of  $\mathbf{V}(\mathbf{q})$ .

**Remark.** The same argument can be used to define the spinodal curve as the integral curve of the vector field  $\nabla_x \mathbf{S}(\mathbf{x})^\perp$ , where  $\mathbf{S}(\mathbf{x}) = \det \mathbf{D}_x^2 g(\mathbf{x})$ .

The described construction is a geometrical interpretation of the differential homotopy method (Allgower and Georg, 2003) for computing implicitly defined smooth curves. Using Eq. (5) instead of Eqs. (3) it is possible to compute binodal curves by a conventional ODE solver without solving the set of algebraic Eqs. (3) or (2) by a Newton-Raphson type iterative algorithm, as it is usually done. The only iterative step concerns the computation of the starting point of the generalized binodal (or spinodal) curve, which

can be reduced to a 2D problem. An algorithm based on the same principles was described in detail in N. Shcherbakova et al. 2017 and O. Cots et al. 2021.

### 3. Case study: Flory-Huggins parameters of water-acetone-hexadecane

#### 3.1 The Flory-Huggins model with ternary interaction term

The classical Flory-Huggins model defines the excess free energy of mixing per unit of volume according to the expression

$$g = \varphi_1 \ln \varphi_1 + \frac{1}{N_2} \varphi_2 \ln \varphi_2 + \frac{1}{N_3} \varphi_3 \ln \varphi_3 + \sum_{i,j=1,i < j}^3 \chi_{ij} \varphi_i \varphi_j + \beta \varphi_1 \varphi_2 \varphi_3 \quad (8)$$

Here  $\varphi_i$ ,  $i=1,2,3$  are the volume fractions of water, the solvent and the polymer respectively,  $N_2$  and  $N_3$  are the number of segments in the molecules of the solvent and of the polymer referred to the water segment,  $\chi_{ij}$  and  $\beta$  are the binary and ternary interaction coefficients. In this paper  $N_2$ ,  $N_3$ ,  $\chi_{ij}$  and  $\beta$  are assumed to be constant. Notice that the cross term  $\beta \varphi_1 \varphi_2 \varphi_3$  contains several physical effects. Indeed, it is the simplest possible correction of the Flory-Huggins model that accounts for composition-dependent binary interaction parameters as well as for the failure of the total volume conservation hypothesis when mixing the components. Since the goal of present work is to propose a robust method for binodal identification, it is not necessary to investigate the real physical meaning of the cross term.

In further computations the volume fractions of acetone and of polymer are chosen as the independent variables so that  $x_1 = \varphi_2$ ,  $x_2 = \varphi_3$  and  $\varphi_1 = 1 - x_1 - x_2$ . Inserting Eq.(8) into Eqs. (4) yields three algebraic conditions to be verified along the binodal curve. Due to the particular form of Eq. (8), these conditions linearly depend on 6 scalar parameters  $\chi_{12}$ ,  $\chi_{13}$ ,  $\chi_{23}$ ,  $\beta$ ,  $r_1 = N_2^{-1}$ , and  $r_2 = N_3^{-1}$ .

#### 3.2 Case study: water-acetone-hexadecane

A further analysis is based on the experimental data obtained at  $P = 1 \text{ atm}$  and  $T=23 \text{ }^\circ\text{C}$  using Raman spectroscopy to measure each species fraction for a given sample. 14 measurements of coupled compositions were acquired defining tie-lines  $q^k \in \Sigma$  (black points in Fig. 2) and 17 non-coupled composition measurements  $x_m \in \Omega$  (white circles in Fig. 2) defining the phase-separation envelope. The latter series contains a pair of points defining the miscibility gap  $x^a$ ,  $x^b$  of the binary mixture acetone-hexadecane. Using Eqs.(3) for this binary mixture,  $\chi_{23}$  and  $N_2$  were computed in terms of  $x^a$ ,  $x^b$ . Analogously,  $\chi_{13}$  and  $N_3$  were found using the miscibility limits of water-hexadecane mixture reported in the literature. Due to the significant variation of these data in different sources, the term  $\chi_{13}$  in Eq. (8) was replaced by  $\chi_{13} + \delta$  in the next step of the computation. In this second step the remaining parameters  $\chi_{12}$ ,  $\beta$ ,  $\delta$  were found by solving the following non-linear optimization problem:

$$\min_{\chi_{12}, \beta, \delta} \sum_{k=1}^{14} \frac{F_1^2(q^k) + F_2^2(q^k)}{(1 - F_3^2(q^k))^2} \quad (9)$$

The particular form of criterion Eq.(9) push the minNLP solver toward the solutions which guaranties that each point  $q_k$  corresponds to a pair of points on  $W$  having collinear normal vectors, whereas the denominator term penalize those pairs of points that do not belong the same bi-tangent line.

The described method was implemented using Mathematica 9 package, the result is shown Fig. 2. Gray lines correspond to the measured tie-lines, and the dashed lines denote the computed tie-lines. The thick black curve corresponds to the computed binodal curve, which satisfies both of the quality criteria discussed above. The right part of Fig. 2 reproduces the vicinity of the acetone vertex in big resolution, showing an excellent coincidence between experimental and model identification results.

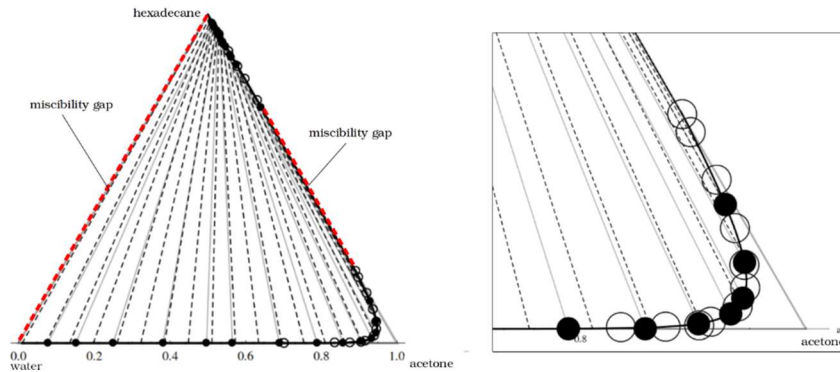


Fig.2

#### 4. Conclusion

The presented geometric viewpoint on binodal curves provides a deeper insight into their internal structure. Moreover, it allows for the reduction of the numerical computation of binodal and spinodal curves to a simple integration of ODE systems, gaining in execution time and accuracy. The proposed numerical method can be adapted to any thermodynamic model. We plan to implement the resulting differential homotopy algorithm in the next version of the SMITH code (Cots et al, 2021).

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