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On the Riemannian structure of the residue curves maps

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A B S T R A C T

In this paper, we revise the structure of the residue curve maps (RCM) theory of simple evaporation from the point of view of Differential Geometry. RCM are broadly used for the qualitative analysis of distillation of multicomponent mixtures within the thermodynamic equilibrium model. Nevertheless, some of their basic properties are still a matter of discussion. For instance, this concerns the connection between RCM and the associated boiling temperature surface and the topological characterization of the distillation boundaries. In this paper we put in evidence the Riemannian metric hidden behind the thermodynamic equilibrium condition written in the form of the van der Waals–Storonkin equation, and we show that the differential equations of residue curves have formal gradient structure. We discuss the first non-trivial consequences of this fact for the RCM theory of ternary mixtures.

Keywords:

Residue curves

Gradient systems

Riemannian metric

1. Introduction

The preliminary design of distillation processes for the separation of multicomponent mixtures relies upon the analysis of residue curve maps (RCM). Typically RCM can be used for assessing the distillation column sequence in continuous operation or the step sequence in batch operation, the achievable product of each column or step, the composition and temperature trajectories in the product tanks and in the column.

Indeed, the topological properties of RCM enable to identify in the composition manifold some features like azeotropes and distillation boundaries, whose knowledge is of utmost importance for the choice of a suitable distillation process and its design. Other properties relevant for distillation processes are displayed in terms of temperature, unidistribution and univolatility manifolds. These properties have been surveyed in several works, in particular in the review paper by Kiva et al. (2003), which also provides a comprehensive history of RCM, and in Doherty and Malone (2001)

and Petlyuck books (2004). The usefulness of these properties for azeotropic distillation process design is described in Widagdo and Seider (1996) and Skiborowski et al. (2014) and for extractive distillation in Gerbaud and Rodriguez-Donis (2014).

In this paper, we focus on the simple isobaric distillation of homogeneous n -component mixtures under thermodynamic equilibrium. Residue curves describe the evolution of the liquid composition with respect to some parameter ξ , and can be computed by solving the system of ordinary differential equations

$$\frac{dx_i}{d\xi} = v_i(\mathbf{x}, T_b(x_1, \dots, x_{n-1})), \quad i = 1, \dots, n-1, \quad (1)$$

where $v_i = x_i - y_i$, $i = 1, \dots, n-1$ are components of the equilibrium vector field \mathbf{v} , T_b is the boiling temperature of the mixture of composition $\mathbf{x} = (x_1, \dots, x_{n-1})$, x_i , y_i being the molar concentrations of the i th component in the liquid and vapour phases correspondingly. Despite of their broad utilisation, some of the basic properties of residue curves are still a matter of

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discussion. Indeed, it turns out that the global intrinsic structure of RCM is not yet well established.

Several authors observed that many features of residue curves make think that they are integral curves of a gradient flow associated to the boiling temperature T_b . Indeed, the critical points of T_b are singular points of \mathbf{v} , which generically can be stable/unstable nodes or saddles. T_b is increasing along residue curves, moreover, T_b is a Lyapunov function for dynamical system (1). These are typical properties of gradient systems (Hirsch et al., 2004), but they are contradicted by the fact that in real mixtures \mathbf{v} is not orthogonal to the isotherm surfaces of T_b . For instance, the non-orthogonality was shown by van Dongen and Doherty (1984), who displayed the boiling temperature surface isotherms and the steepest descent lines along with the corresponding RCM for four azeotropic mixtures. They also proved that system (1) cannot be written as a gradient system of T_b . This result was later confirmed in Rev (1992). It is natural to ask what is then the true intrinsic structure of equations (1)?

The next question, closely related to the previous one, concerns the nature of the distillation boundaries of RCM. Recall that in the case of ternary mixtures, distillation boundaries are remarkable residue curves connecting nodes and saddles, which divide the distillation domain in distinct regions. By their nature, the boundaries cannot be crossed by other residue curves and they must start and end at the singular points of the RCM. Usually the distillation boundaries are computed numerically as separatrices of system (1) with some loss in precision due to the numerical integration. A different approach based on the variational viewpoint was recently proposed by Lucia and Taylor (2006, 2007). In the case of ternary mixtures, defining distillation boundaries as the concatenation of residue curves going from an unstable node to a stable node passing through a saddle, they showed that distillation boundaries maximize the length among all other residue curves joining the same points. In the case $n=4$ they claim that distillation boundaries are minimal surfaces (Bellows and Lucia, 2007). The interesting and still open question is whether distillation boundaries can be detected without numerical integration, for instance, by computing some scalar parameter that distinguishes them among other residue curves.

For many years it was a common belief that distillation boundaries are projections on the RCM plane of the flexures of the boiling temperature surface, the so-called ridge/valley curves. But it turns out that this picture contradicts with the experimental data, and numerical computations (Rev, 1992; van Dongen and Doherty, 1984), so that today most of the authors agree that the ridge/valley curves of the boiling temperature surface are not distillation boundaries since they can be crossed by some residue curves. In this context we want to stress out that there is no one commonly accepted definition of the ridge/valley curves of the boiling temperature (see in Kiva et al., 2003 and references therein). So, many of published results are based on rather wrong geometrical constructions, sometimes leading to paradoxical results, like the valleys presented in van Dongen and Doherty (1984) that do not even pass through azeotropes. However, the notion of a ridge or a valley on a surface has a clear mathematical meaning in Differential Geometry, and in particular in 3D Image Process domain (Bruce et al., 1996; Peikert and Sadlo, 2008). It seems important to analyze the consistency of this notion with the definition of distillation boundaries.

In this paper, we try to answer the following natural questions:

- Q1: What is the relation between isotherm hyper-surfaces and residue curves? More generally, what is the true intrinsic structure of equations (1)?
- Q2: How fast the boiling temperature grows along residue curves?
- Q3: What are the ridge/valley curves of the boiling temperature surface and is there any relation between them and the distillation boundaries?

The key tools of our analysis are the van der Waals–Storonkin equations of phase coexistence, which express the thermodynamic equilibrium condition $dG=0$ and generalize the classical van der Waals equations for binary mixtures to the multicomponent case (see in Storonkin, 1967; Zharov and Serafimov, 1975; Toikka and Jenkins, 2002). In the RCM theory these equations imply the remarkable relation between the boiling temperature gradient and the equilibrium vector field

$$\nabla T_b = \frac{1}{\Delta s} D_x^2 g^l \mathbf{v}, \quad (2)$$

which can be found, for instance, in Doherty and Malone (2001) and Doherty and Perkins (1978). Here Δs is some positive scalar function depending on the molar entropies and concentrations of each component in both phases, while g^l is the Gibbs free energy of the liquid phase. Already in 1970's, Filippov remarked that the Hessian of the Gibbs free energy appearing in the couple of van der Waals–Storonkin equations for both phases defines a metric in the mathematical sense (Filippov, 1977). He used this fact for the local analysis of the behavior of the residue curves in the vicinity of the internal azeotropes. Though in a different way, we come to a similar result and introduce a metric (different from the Filippov's one) associated to the Hessian of the Gibbs free energy of the liquid phase, which leads us to a rather far-going conclusion about the global gradient nature of RCM equations (1).

This paper is organized as follows. After a short review of some basic facts from Riemannian geometry in Section 2, in Section 3, using the van der Waals–Storonkin equation, we show that the RCM of open evaporation carries on a non-trivial Riemannian metric that we call *the Gibbs metric*. Recall that a metric in the space defines the way to compute scalar products, and hence norms and angles between vectors, as well as the length of curves and the gradients of functions. In general, the standard Euclidean metric used “by default” gives just the *local approximation* of the true geometrical structure of the space, like, for instance, the city plan that represents a small piece of the Earth globe. The presence of the non-trivial Gibbs metric allows us to prove that system (1) is a gradient system of T_b , where the gradient should be computed in the Riemannian sense. This fact explains the aforementioned qualitative properties of RCM, and in addition, it implies that residue curves are indeed orthogonal to the isotherm hyper-surfaces in the sense of the Gibbs metric. In Section 4 we analyze in greater detail the ternary mixtures case. In particular, we consider a rigorous mathematical definition of ridge/valley curves of the boiling temperature and show that there is no reason for these curves to coincide with distillation boundaries. We illustrate our computations for ternary mixtures combining

analytical and numerical computations using Mathematica 9 package.

2. Riemannian structures

In this paper, we consider the state space of a physical system as a *differential manifold* M , whose dimension is equal to the number of *degrees of freedom* of the system. The evolution of the system is usually measured with respect to some non-decreasing scalar parameter, for instance, time t . At a given moment of time the state of the system with n degrees of freedom is a point $\mathbf{x} \in M$, which can be described by the set of *local coordinates* $\mathbf{x} = (x_1, \dots, x_n)$, whose derivatives $\dot{\mathbf{x}} = (\dot{x}_1, \dots, \dot{x}_n)$ form a velocity vector $\dot{\mathbf{x}} \in T_{\mathbf{x}}M$ in the tangent space to M at \mathbf{x} . M is called a *Riemannian manifold* if its tangent bundle $TM = \bigcup_{\mathbf{x} \in M} T_{\mathbf{x}}M$ is endowed with a scalar product. In other words, there is a positive definite quadratic form called *metric*, which in local coordinates is described by a symmetric matrix $G(\mathbf{x}) = \{g_{ij}(\mathbf{x})\}$, so that for any two vectors $\mathbf{v}, \mathbf{w} \in T_{\mathbf{x}}M$

$$\langle \mathbf{v} | \mathbf{w} \rangle_G = \sum_{i,j=1}^n g_{ij}(\mathbf{x}) v_i w_j = \mathbf{v}^T G(\mathbf{x}) \mathbf{w}.$$

The metric defines a norm of vectors by $\|\mathbf{v}\|_G = \sqrt{\langle \mathbf{v} | \mathbf{v} \rangle_G}$, and hence the length of curves in M : given a curve γ joining points \mathbf{x}_0 and \mathbf{x}_1 in time τ , and such that $\dot{\gamma}(t) = \mathbf{v}$, the length of γ is given by $\ell(\gamma) = \int_0^\tau \|\mathbf{v}(\gamma(t))\|_G dt$.

The simplest example of a Riemannian manifold is the standard Euclidean space \mathbb{R}^n : the local coordinates are the usual Cartesian coordinates, and the scalar product is defined by the identity matrix $G(\mathbf{x}) = Id$. In particular, the distance between two points \mathbf{p} and \mathbf{q} is $d(\mathbf{q}, \mathbf{p}) = \sqrt{(q_1 - p_1)^2 + \dots + (q_n - p_n)^2}$, and more generally, the shortest path between two points is a straight line. These facts are no more true in Riemannian manifolds with non-trivial, i.e., non-Euclidean, metric structure. In fact, the shortest path between two points is the *geodesic curve* of the metric, i.e., the curve of minimal length, like for instance, the meridian circles on a sphere. Intrinsic topological properties of Riemannian manifolds can be characterized in terms of their curvature tensor, but we will not discuss it here. In what follows, in order to avoid any ambiguity, we use $\|\cdot\|_G$ and $\langle \cdot | \cdot \rangle_G$ to denote the scalar products and norms computed with respect to the Riemannian metric G , while $\|\cdot\|$ and $\langle \cdot | \cdot \rangle$ will denote their Euclidean equivalents.

We conclude this short review of Riemannian geometry by recalling the meaning of a gradient of a function (Dubrovin et al. (1991)). Let f be a smooth function in the Riemannian manifold M equipped with some metric G . Its differential $d_{\mathbf{x}}f = \sum_{i=1}^n \partial_{x_i} f(\mathbf{x}) dx_i$ is a linear operator in $T_{\mathbf{x}}M$, also called a differential 1-form.

Definition 1. A vector $\mathbf{w} \in T_{\mathbf{x}}M$ is called the *gradient* of the function f at a point $\mathbf{x} \in M$ if its scalar product with any other vector $\mathbf{v} \in T_{\mathbf{x}}M$ is equal to the directional derivative of f with respect to \mathbf{v} computed at \mathbf{x} :

$$\mathbf{v}f(\mathbf{x}) = d_{\mathbf{x}}f(\mathbf{v}) = \mathbf{v}^T \nabla f(\mathbf{x}) = \langle \mathbf{v} | \mathbf{w} \rangle_G.$$

In the rest of this paper $\nabla_G f(\mathbf{x})$ denotes the gradient of f in M defined in the sense of the metric G , i.e.,

$$\nabla f(\mathbf{x}) = \langle \mathbf{v} | \nabla_G f(\mathbf{x}) \rangle_G.$$

It is easy to verify that in local coordinates $\nabla_G f(\mathbf{x})$ is related to the usual Euclidean gradient $\nabla f(\mathbf{x})$ as follows:

$$\nabla_G f(\mathbf{x}) = G^{-1}(\mathbf{x}) \nabla f(\mathbf{x}). \quad (3)$$

3. Open evaporation of homogeneous multicomponent mixtures

Let us consider an open evaporation process of a n -component homogeneous mixture. We assume that the process is isobaric ($P = \text{const}$) and that the thermodynamic equilibrium between liquid and vapour phases is preserved.

3.1. The state space

For $i=1, \dots, n$ denote by x_i, y_i the partial mole fractions of the i th component in the liquid and vapour phases respectively. Since $\sum_{i=1}^n x_i = 1$, the $n-1$ independent mole fractions of the liquid phase $\mathbf{x} = (x_1, \dots, x_{n-1})$ belong to the *Gibbs simplex* $\Omega = \{x_i \in [0, 1] : \sum_{i=1}^{n-1} x_i \leq 1\}$. In what follows $\partial\Omega$ will denote the boundary of Ω . According to the Gibbs phase rule, the system under consideration has n degrees of freedom, and its thermodynamical state can be described in terms of $n-1$ independent mole fractions of the liquid phase \mathbf{x} and the temperature T . So, the state space of the system is the differential manifold $M = \{\mathbf{q} = (\mathbf{x}, T) : \mathbf{x} \in \Omega, T \in \mathbb{R}\}$.

3.2. Partial mass balance and boiling temperature

In the standard equilibrium model of open evaporation a multicomponent liquid mixture is vaporized in a still in such a way that the vapour is continuously evacuated from the contact with the liquid (Doherty and Perkins, 1978). The partial mass balance of such a system can be written in the form

$$\frac{dx_i}{d\xi} = x_i - y_i(\mathbf{x}, T) = v_i(\mathbf{x}, T), \quad i = 1, \dots, n-1. \quad (4)$$

Here $\xi \in [0, 1]$ is a non-decreasing parameter describing the change in the overall molar quantity of the liquid phase n^l in time t : $\xi = \ln(n^l(0)/n^l(t))$. Solutions to system of differential equations (4) are called *residue curves*, and their graphical representation in the simplex Ω forms the residue curve map (RCM). The right hand side of (4) defines a vector field $\mathbf{v} = (v_1, \dots, v_{n-1}) \in TM$ called the *equilibrium vector field*. Its singular points, i.e., the points $\mathbf{q} \in M$ such that $\mathbf{v}(\mathbf{q}) = 0$ describe the pure components and the azeotropes of a given mixture.

By definition of mole fractions,

$$\sum_{i=1}^n y_i(\mathbf{x}, T) = 1. \quad (5)$$

This constraint defines a hyper-surface W in the state space M , called the *boiling temperature surface*, which is invariant with respect to (4). Since in a homogeneous mixture each composition of the liquid phase \mathbf{x} is characterized by a unique value of T , in principle equation (5) can be solved in order to express $T = T_b(\mathbf{x})$, where the function T_b defines the *boiling temperature*

of a given mixture.¹ In other words, the boiling temperature surface can be represented as a graph of function T_b :

$$W = \{\mathbf{q} \in M : \mathbf{q} = (x_1, \dots, x_{n-1}, T_b(x_1, \dots, x_{n-1}))\}.$$

It is worth to underline that in practice, due to the high complexity of thermodynamical models of real mixtures, the function $T_b(\mathbf{x})$ cannot be written explicitly. Nevertheless, if the mole fractions $y_i(\mathbf{x}, T)$ are known, equations (4), (5) form a closed system of differential algebraic equations, which can be solved numerically. This is the standard chemical engineering approach for practical computations.

Despite its practical utility, the model made of equations (4) and (5) is not suitable for the qualitative analysis of RCM. In particular, it gives not answer to the questions posed in the Introduction. For this we have to look closer at the thermodynamic equilibrium condition.

3.3. The van der Waals–Storonkin equation

A different way to express the thermodynamic equilibrium is provided by the van der Waals–Storonkin equations of phase co-existence. Their rigorous mathematical derivation from the equilibrium condition $dG=0$, where G is the total Gibbs free energy of the system, can be found in [Storonkin \(1967\)](#), [Zharov and Serafimov \(1975\)](#) and in the review paper ([Toikka and Jenkins, 2002](#)). The equation for the liquid phase reads

$$\left(s^v - s^l + \sum_{i=1}^{n-1} (x_i - y_i) \frac{\partial s^l}{\partial x_i} \right) dT - \sum_{i,j=1}^{n-1} \frac{\partial^2 g^l}{\partial x_i \partial x_j} (x_i - y_i) dx_j = 0. \quad (6)$$

Here s^l and s^v are the entropies of the liquid and vapour phases, and g^l is the Gibbs free energy of the liquid phase. The terms containing dP are neglected in (6) since only isobaric processes are considered. An analogous equation can be also written for the vapour phase. In the case $n=1$ equation (6) implies the Clausius equation, whereas if $n=2$ it becomes the classical van der Waals equation.

Let us see under which condition the model (4), (5) based on the mass balance arguments is consistent with state equation (6).

3.4. The Gibbs metric

Consider the following differential 1-form in the state space M :

$$\sigma = \Delta s \, dT + \sum_{i,j=1}^{n-1} \frac{\partial^2 g^l}{\partial x_i \partial x_j} v_i dx_j,$$

where

$$\Delta s = s^v - s^l + \sum_{i=1}^{n-1} (x_i - y_i) \frac{\partial s^l}{\partial x_i} = \sum_{i=1}^n y_i (s_i^v - s_i^l),$$

s_i^l, s_i^v being the partial molar entropies of the i th component in each phase. In what follows we denote by $D_x^2 g^l = \{\partial_{x_i x_j}^2 g^l\}_{i,j=1}^{n-1}$ the Hessian matrix of g^l with respect to $x_i, i=1, \dots, n-1$. The material stability condition implies that $D_x^2 g^l$ defines a positive definite quadratic form, while $\Delta s > 0$ for all $(\mathbf{x}, T) \in M$, in particular, on the boiling temperature surface W .

Geometrically speaking, equation (6) means that if $\delta \mathbf{x}$ is a possible infinitesimal change in the system under thermodynamic equilibrium, then $\sigma(\delta \mathbf{x}) = 0$. All possible infinitesimal changes in the system under thermodynamic equilibrium form a vector distribution $\Sigma = \{\delta \mathbf{x} \in TM : \sigma(\delta \mathbf{x}) = 0\}$. Observe that the form σ places restrictions on the possible dynamics of the system rather than on its state at a given moment, while the boiling temperature surface $W \subset M$ represents all possible states of the system compatible with the thermodynamic equilibrium. Therefore $TW \subset \Sigma$. Since the tangent space to W is spanned by vectors of the form $\mathbf{r}_i = \partial_{x_i} + \partial_{x_i} T_b \partial_T$, we get $\sigma(\mathbf{r}_i) = 0$ for $i=1, \dots, n-1$, and hence

$$\nabla T_b(\mathbf{x}) = \frac{1}{\Delta s} D_x^2 g^l|_{T=T_b(\mathbf{x})} \mathbf{v}(\mathbf{x}), \quad \mathbf{x} \in \Omega. \quad (7)$$

The positive definiteness of $\frac{1}{\Delta s} D_x^2 g^l|_{T=T_b(\mathbf{x})}$ in Ω allows us to introduce a Riemannian metric in Ω associated to the symmetric matrix

$$\Gamma(\mathbf{x}) = \frac{1}{\Delta s} D_x^2 g^l|_{T=T_b(\mathbf{x})},$$

which we will call the *Gibbs metric*. Comparison of formulae (7) and (3) yields

$$\mathbf{v}(\mathbf{x}) = \nabla_{\Gamma} T_b(\mathbf{x}).$$

Calculating now the derivative of T_b along any residue curve $\mathbf{x}(\xi)$, we get

$$\frac{dT_b(\mathbf{x}(\xi))}{d\xi} = \mathbf{v}(\mathbf{x}(\xi))^T \Gamma(\mathbf{x}(\xi)) \mathbf{v}(\mathbf{x}(\xi)) = \|\mathbf{v}(\mathbf{x}(\xi))\|_{\Gamma}^2. \quad (8)$$

Remark. Although the 1-form σ is defined everywhere in M , some of the second derivatives $\partial_{x_i x_j}^2 g^l$ blow up at the pure components (vertices of Ω) and on the edges of Ω (see examples later). So, strictly speaking, the Gibbs metric Γ is a well defined Riemannian metric only in the interior points of Ω .

The above computations can be summarized as follows.

Theorem 1. *The open set $\text{int } \Omega = \{x_i \in (0, 1) : \sum_{i=1}^{n-1} x_i < 1\}$ of partial mole fractions endowed with the Gibbs metric Γ is a Riemannian manifold. Residue curves are solutions to the gradient system*

$$\frac{d\mathbf{x}}{d\xi} = \nabla_{\Gamma} T_b(\mathbf{x}), \quad \mathbf{x} \in \Omega, \quad (9)$$

where the boiling temperature T_b plays the role of the potential function. Moreover, along any residue curve $\mathbf{x}(\xi)$, the boiling temperature changes according to the equation

$$\frac{dT_b(\mathbf{x}(\xi))}{d\xi} = \|\mathbf{v}(\mathbf{x}(\xi))\|_{\Gamma}^2,$$

and thus it is a natural Lyapunov function for system (4).

Remark. Eqs. (8) and (9) provide the explicit answers to questions Q1 and Q2 formulated in Section 1. We also remark that Eqs. (8) and (7) are well known in the residue curves theory (see, for instance, in [Zharov and Serafimov, 1975](#), [Doherty and Perkins, 1978](#), [van Dongen and Doherty, 1984](#)), though their intrinsic gradient structure was denied ([van Dongen and Doherty, 1984](#); [Rev, 1992](#)).

Looking at residue curves through the optic of the Gibbs metric, one can derive all qualitative properties of RCM as the trivial consequence of the gradient form of system (4). Indeed,

¹ This fact follows from the Implicit function theorem.

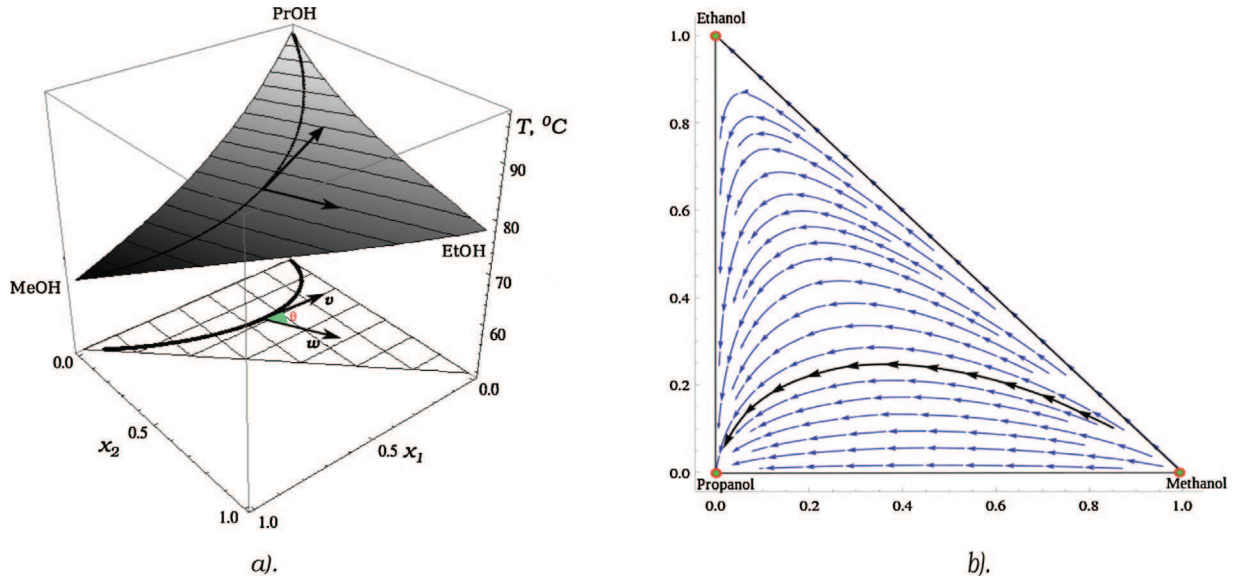


Fig. 1 – Ideal mixture: methanol (x_1), ethanol (x_2) and 1-propanol. (a) The boiling temperature surface and its isotherm level sets on it; (b) the residue curves map.

properties of Riemannian gradient systems are well known, and they are analogous to the properties of the classical gradient systems in the Euclidean space \mathbb{R}^n modulo the change of the metric (see for instance in [Hirsch et al. \(2004\)](#)). In particular:

- critical points of T_b are singular points of (4) in $\text{int } \Omega$;
- generically, they can be stable/unstable nodes or saddles;
- if c is a regular value of T_b , i.e., if $\nabla T_b|_{T_b^{-1}(c)} \neq 0$, then the vector field \mathbf{v} is orthogonal to the level set $T_b^{-1}(c)$ in the sense of the Gibbs metric Γ .

The first two properties are well known and widely used in the RCM analysis. The third one is true within the Riemannian viewpoint, but it is not if we use the Euclidean metric. This explains the debate about isotherms and residue curves orthogonality in the literature. However, the high non-triviality of the Gibbs metric Γ makes the topology of residue curves maps much more sophisticated than the one of a classical gradient flow.

One may ask what happens when a residue curve $\mathbf{x}(\xi)$ approaches the boundary $\partial\Omega$ of the Gibbs simplex Ω ? In this case the Gibbs metric blows up and $\|\cdot\|_\Gamma$ is not defined, while $\|\mathbf{v}\| \rightarrow 0$ and generically ${}^2 \nabla T_b|_{\partial\Omega} \neq 0$ and has bounded components. So, $\|\mathbf{v}\|_\Gamma = \sqrt{(\Gamma^{-1} \nabla T_b | \nabla T_b)}$ stays bounded on $\partial\Omega$, and hence as $\mathbf{x}(\xi)$ approaches a critical point $\mathbf{x}^* \in \partial\Omega$ (a pure component or an azeotrope of order $< n$), $\|\mathbf{v}(\mathbf{x}(\xi))\| \sim \|\mathbf{v}(\mathbf{x}(\xi))\|_\Gamma^2$ as $\mathbf{x}(\xi) \rightarrow \mathbf{x}^*$. Observe that the situation is different if $\mathbf{x}^* \in \text{int } \Omega$ is an azeotrope of order n , in this case $\|\mathbf{v}(\mathbf{x}(\xi))\| \sim \|\mathbf{v}(\mathbf{x}(\xi))\|_\Gamma$. So, the border and internal singularities of the residue curves maps in Ω are of different nature: while internal azeotropes are critical points of the boiling temperature, the singularities at pure components and at azeotropes of order $< n$ result from the blow up of the metric Γ . Moreover, since the boiling temperature is not decreasing along residue curves, those can be re-parametrized by taking T_b instead of ξ :

$$\frac{d\mathbf{x}}{dT_b} = \frac{\mathbf{v}(\mathbf{x})}{\|\mathbf{v}(\mathbf{x})\|_\Gamma^2}. \quad (10)$$

² i.e. if there is no tangential azeotropes.

This transformation can be used to regularize the whole RCM if it contains no internal azeotropes. In particular, this should simplify the numerical integration of residue curves since the new parameter is bounded: $T_b \in [T_b^{\min}, T_b^{\max}]$, while $\xi \in [0, +\infty)$.

4. Ternary mixtures: first results

The first non-trivial situation, where the Gibbs metric appears, concerns the simple evaporation of three-components mixtures. In addition, in this case we can easily visualize the concepts introduced above. The Riemannian viewpoint makes clear structural properties of the RCM, for instance, the relation between residue curves and isotherms, and between distillation boundaries and ridge/valley curves of the boiling temperature surface.

4.1. Residue curves and isotherms

We consider here only the generic situation of homogeneous ternary mixture without tangential azeotropes. Choosing two independent mole fractions x_1, x_2 , the boiling temperature surface W over Ω can be seen as a 2D surface in a 3D Euclidean space with coordinates x_1, x_2, T . On the \mathbf{x} -plane, along with the residue curves, we have another family of curves, the isotherms, defined as the projections of the level sets $T_b^{-1}(c)$ of the boiling temperature. At any point $\mathbf{x} \in \text{int } \Omega$, the tangent vector to the isotherm is given by $\mathbf{w} = (-\partial_{x_2} T_b(\mathbf{x}), \partial_{x_1} T_b(\mathbf{x})) = (\nabla T_b(\mathbf{x}))^\perp$. The Γ -orthogonality of vectors \mathbf{v} and \mathbf{w} can be verified directly:

$$\langle \mathbf{v} | \mathbf{w} \rangle_\Gamma = \langle \Gamma \mathbf{v} | \mathbf{w} \rangle = \langle \Gamma \Gamma^{-1} \nabla T_b | (\nabla T_b)^\perp \rangle = 0.$$

Moreover, away from ternary azeotropes the vectors $\mathbf{e}_v = \mathbf{v}/\|\mathbf{v}\|_\Gamma$ and $\mathbf{e}_w = \mathbf{w}/\|\mathbf{w}\|_\Gamma$ form a well defined Γ -orthonormal basis in $\text{int } \Omega$.

Example 1. The ideal mixture methanol (x_1)-ethanol (x_2)-1-propanol. Our computations are based on the 3-suffix Margules model for activity coefficients ([Prausnitz et al., 1998](#)). In [Fig. 1b](#), we show the RCM, while [Fig. 1a](#) shows the boiling temperature surface W where the thin curves correspond to the isotherm lines. Any curve $(\mathbf{x}(\xi), T(\mathbf{x}(\xi)))$ on W projects on the

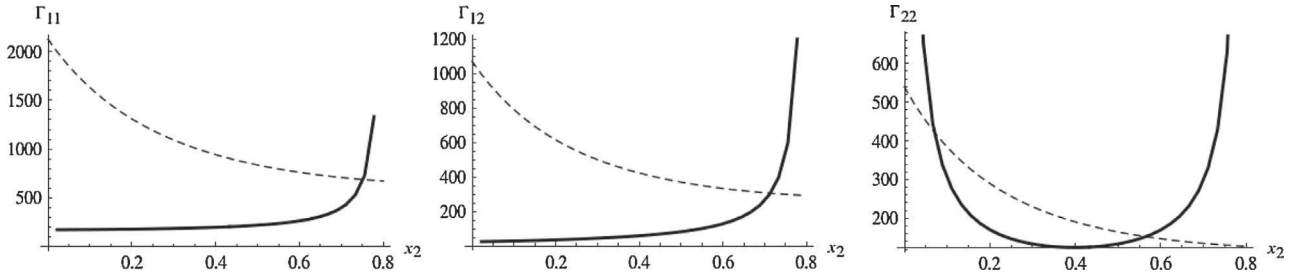


Fig. 2 – Components of Γ (thick curves) vs. components of $\tilde{\Gamma}$ (dashed curves).

residue curve $\mathbf{x}(\xi)$ (bold curve in Fig. 1b) on the plane (x_1, x_2) . The vectors \mathbf{v} and \mathbf{w} described above are not orthogonal along $\mathbf{x}(\xi)$, as shown in Fig. 1a. One may think that their prototypes on TW are orthogonal. To check this property we have to compute their scalar product, thus we need to choose a metric on W .

4.2. 3D geometry of the boiling temperature surface

Along with the Gibbs metric Γ , there is another metric on W , which describes the embedding of the graph of function T_b into the 3D Euclidean space with coordinates x_1, x_2, T . Indeed, assume that W is endowed with some Riemannian metric $\tilde{\Gamma}$. The length of any curve lying on W can be computed in two different ways: as a length with respect to the metric $\tilde{\Gamma}$ on W , or as a length of the same curve considered in the ambient 3D Euclidean space. There exists a unique choice of $\tilde{\Gamma}$ that assures that these two lengths coincide (Dubrovin et al., 1991).

Definition 2. The Riemannian metric on the boiling temperature surface $W = \{\mathbf{q} \in \mathbb{R}^3 : \mathbf{q} = (x_1, x_2, T_b(x_1, x_2))\}$ associated to the quadratic form with components

$$\tilde{\Gamma}_{11} = 1 + \left(\frac{\partial T_b}{\partial x_1}\right)^2, \quad \tilde{\Gamma}_{22} = 1 + \left(\frac{\partial T_b}{\partial x_2}\right)^2, \quad \tilde{\Gamma}_{12} = \frac{\partial T_b}{\partial x_1} \frac{\partial T_b}{\partial x_2}.$$

is called the *natural* Riemannian metric $\tilde{\Gamma}$.

In Differential Geometry the natural metric is also called the 1-st fundamental form of a surface. Roughly speaking, it describes the visible shape of the surface in 3D. Unlike the Gibbs metric Γ , the natural metric $\tilde{\Gamma}$ is well defined and finite everywhere in Ω , in particular, on its boundary. It is important to stress out that Γ and $\tilde{\Gamma}$ define two different geometries on W .

Example 1 (Continuation). In Fig. 2 we compare the components of the Gibbs metrics Γ with the components $\tilde{\Gamma}$ in the section $x_1 = 0.2$ for the ideal mixture of Fig. 1. Observe the blow up of the Gibbs metric (thick curves) in the neighborhood of the boundary of Ω . Let us now come back to the last question of the previous subsection. Denote by $\theta(\xi)$ the angle between the equilibrium vector \mathbf{v} and the tangent vector to isotherm \mathbf{w} along $\mathbf{x}(\xi)$. Remark that θ depends on the choice of the metric g since $\cos \theta = \frac{(\mathbf{v}|\mathbf{w})_g}{\|\mathbf{v}\|_g \|\mathbf{w}\|_g}$. Fig. 3 shows the variation of the $\cos \theta$ along the test curve $\mathbf{x}(\xi)$ of Fig. 1b according to three possible metrics: the Euclidean metric $g = Id$ (dashed curve), the natural metric $\tilde{\Gamma}$ (thick dashed curve), and the Gibbs metric Γ (thick curve). Only in the latter case $\cos \theta < 10^{-2}$, which means that \mathbf{v} and \mathbf{w} are Γ -orthogonal within the accuracy limits of the model.

4.3. Ridge/valleys curves of the boiling temperature

As we already mentioned, the relation between the distillation boundaries and ridge/valley curves on the boiling temperature surface W is still debated. Various definitions for ridge/valley curves were proposed in the literature (Kiva et al., 2003), but in our opinion none of them is satisfactory. Let us analyze the rigorous definition of this object used in Differential Geometry taking into account the non-trivial Riemannian metric Γ .

Consider a gradient dynamical system of form (9), and denote by C the isotherm corresponding to the level set $T_b = c$. A point \mathbf{x} on C belongs to a ridge or a valley of T_b if $\|\nabla_{\Gamma} T_b(\mathbf{x})\|_{\Gamma}^2 = \|\mathbf{v}(\mathbf{x})\|_{\Gamma}^2$ has a maximum or a minimum at this point (Boscaïn et al. (2013)). This leads to the following definition, which provides the answer to the first part of question Q3.

Definition 3. The ridge/valley curves of the boiling temperature are loci of points $\mathbf{x} \in \text{int } \Omega$ such that

$$\langle \nabla_{\Gamma} \|\mathbf{v}\|_{\Gamma}^2(\mathbf{x}) | \mathbf{w} \rangle_{\Gamma} = \mathbf{w} \|\mathbf{v}\|_{\Gamma}^2(\mathbf{x}) = 0. \quad (11)$$

where $\mathbf{w} \|\mathbf{v}\|_{\Gamma}^2$ denotes the directional derivative of $\|\mathbf{v}\|_{\Gamma}^2$ with respect to \mathbf{w} , \mathbf{w} being any tangent vector to the isotherm passing through \mathbf{x} .

According to Definition 3, the ridge/valley curves of the boiling temperature are intrinsically related to the Riemannian gradient of T_b . Eq. (11) implies that azeotropes and pure components belong to ridge/valley curves. Moreover, they are tangent to the eigenvectors of the Jacobian $D_{\mathbf{x}}\mathbf{v}$ at azeotropes and pure components. Observe also that knowing just the function $T_b(x_1, x_2)$ over Ω is not enough to compute the ridge/valley curves: in addition one needs to know the Gibbs metric Γ . For this reason the shape of the surface W in 3D cannot be used to define the distillation boundaries as the

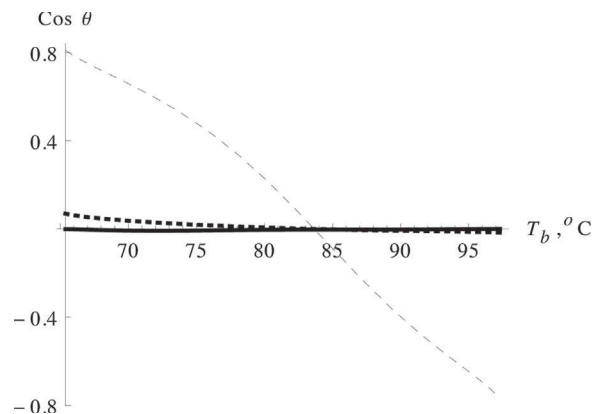


Fig. 3 – Orthogonality test along the bold curve of Fig. 1 in different metrics on Ω .

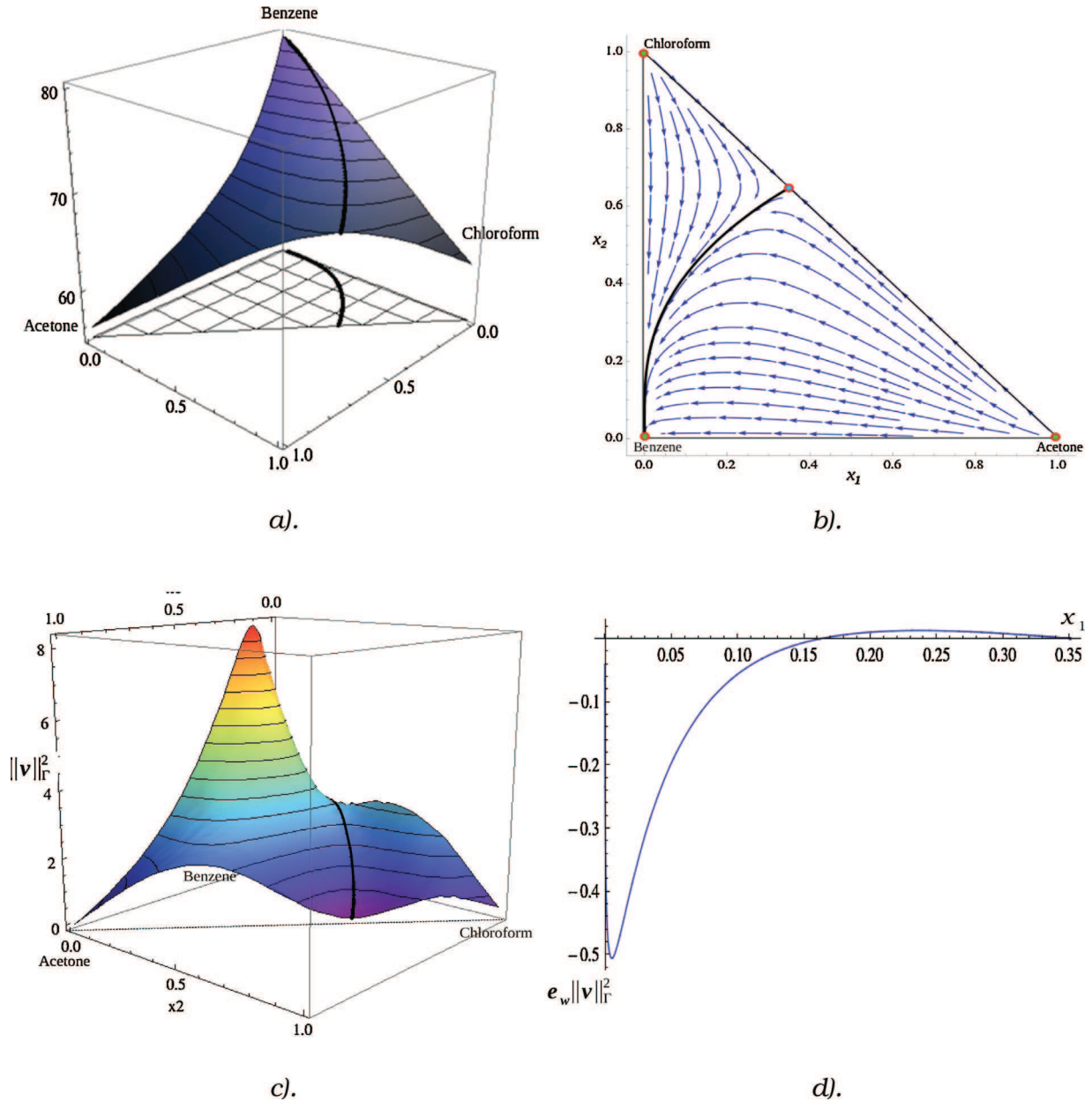


Fig. 4 – Non-ideal mixture: benzene, acetone (x_1), chloroform (x_2). (a) The boiling temperature surface and isotherm level sets; (b) the residue curves map; (c) the height surface of $\|\mathbf{v}\|_\Gamma^2$; (d) $e_w \|\mathbf{v}\|_\Gamma^2$ along the distillation boundary.

projections its flexures as some other authors did (van Dongen and Doherty, 1984, Rev, 1992 and other references in Kiva et al., 2003). In fact, it follows that in order to visualize the ridge/valley curves of the boiling temperature, we have to analyze the landscape of the height surface of $\|\mathbf{v}(\mathbf{x})\|_\Gamma^2$ rather than the W itself.

Remark. Observe that if both T_b and Γ (and hence \mathbf{v}) are known for all $\mathbf{x} \in \Omega$, the ridge/valley curves can be detected by finding zeros of the scalar test function $\mathbf{w}\|\mathbf{v}\|_\Gamma^2$ without solving any differential equation, which makes this notion particularly interesting from the computational point of view.

The next two examples illustrate our construction for ternary mixtures with distillation boundaries. In both cases we used the thermodynamic model based on the NRTL equations (Prausnitz et al., 1998).

Example 2. Benzene– acetone (x_1)–chloroform (x_2) (Serafimov’s topological class 1.0–2 according to Kiva et al., 2003).

The main features of this mixture are shown in Fig. 4: it has a binary azeotrope of saddle type at the point $\mathbf{x}^{az} \approx (0.351, 0.649)$, characterized by the boiling temperature $T_b^{az} \approx 65.11^\circ\text{C}$. The distillation boundary is the separatrix computed via numerical integration of system (4) on W . It is displayed by the thick black curve, which starts at \mathbf{x}^{az} and goes to the origin (benzene pure component, $T_b \approx 80.10^\circ\text{C}$). In Fig. 4c we show the height surface of $\|\mathbf{v}\|_\Gamma^2$: the thin curves are the isoclines, and the thick black curve shows the position of the distillation boundary on it. We see that the distillation boundary passes very close to the bottom of the valley of the height surface of $\|\mathbf{v}\|_\Gamma^2$. Nevertheless, the computation of the function $e_w \|\mathbf{v}\|_\Gamma^2$ along it (Fig. 4d) shows that it diverges from the valley’s bottom while approaching the point $\mathbf{x} = (0, 0)$ corresponding to the benzene pure component.

Example 3. Methanol–acetone (x_1)–chloroform (x_2) (Serafimov’s topological class 3.1-4 according to Kiva et al., 2003), Fig. 5. The shape of the boiling temperature surface W is

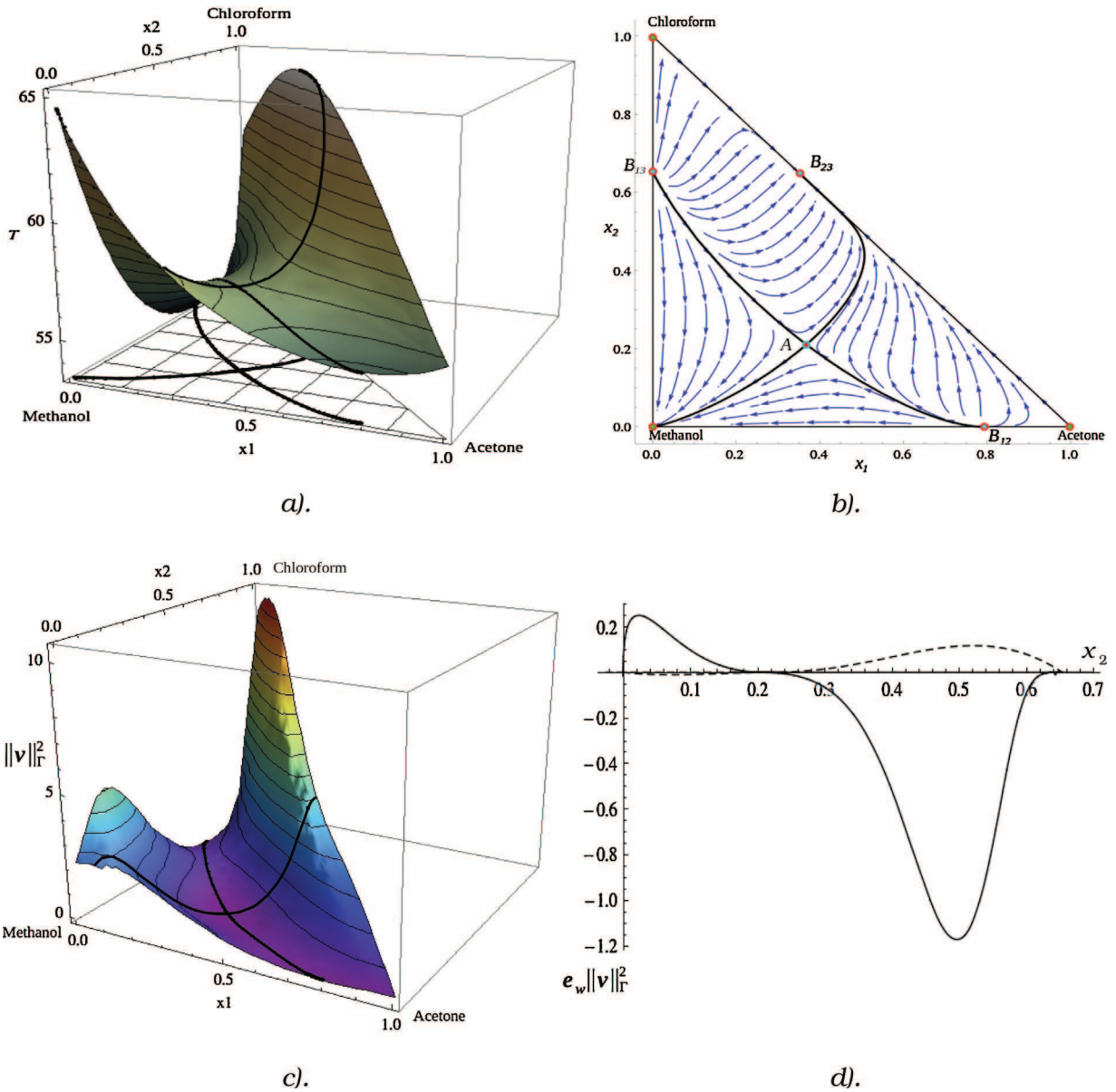


Fig. 5 – Non-ideal mixture: methanol, acetone (x_1), chloroform (x_2). (a) The boiling temperature surface and isotherm level sets; (b) the residue curves map; (c) the height surface of $\|\mathbf{v}\|_{\Gamma}^2$; (d) $e_w \|\mathbf{v}\|_{\Gamma}^2$ along the distillation boundaries.

shown in Fig. 5a. As we can see, the topological structure of the RCM (Fig. 5b) of this mixture is more complex. It has

- three binary azeotropes: 2 unstable nodes at the points $B_{12} \approx (0.7928, 0)$ and $B_{13} \approx (0, 0.6536)$, and one stable node at $B_{23} \approx (0.3511, 0.6489)$ with maximum boiling temperature $T_b^{23} \approx 65.11^\circ\text{C}$;
- one ternary azeotrope of saddle type at the point $A \approx (0.3676, 0.2107)$, characterized by the boiling temperature $T_b^{az} \approx 56.99^\circ\text{C}$.

Four separatrices (thick black curves) form the distillation boundaries, which divide the RCM into four distillation regions. As in the previous example, they were computed by numerical integration of system (4). Fig. 5.c shows the height surface of $\|\mathbf{v}\|_{\Gamma}^2$. As before, the thin curves are isoclines, and the thick black curves indicate the location of the distillation boundaries. While the distillation boundary connecting the points B_{12}, B_{13} seems to follow the bottom of the valley

of the height surface, the curve connecting B_{23} with $\mathbf{x}=(0, 0)$ (methanol pure component) diverges significantly from the ridge. In fact, this divergence become evident from the computation of the test function $e_w \|\mathbf{v}\|_{\Gamma}^2$ (Fig. 5.d): the thick curve corresponds to the curve connecting B_{23} with $(0, 0)$, the dashed curve corresponds to the curve connecting B_{12} with B_{13} . We conclude this example by showing the behavior of the components of Gibbs metric over the composition space Ω (Fig. 6). As stated in Section 3.4, they blow up along the boundary of Gibbs triangle Ω , but stay regular at the ternary azeotrope.

In both of the above examples we observed that distillation boundaries do not coincide with the ridge/valley curves of the boiling temperature. One may ask if the observed difference between the two types of curves is related to the accumulation of the numerical error, and Definition 3 is suitable to define distillation boundaries. As we will show in the next section with a simple academic example, the answer is negative: in general there is no reason for these two families of curves to coincide.

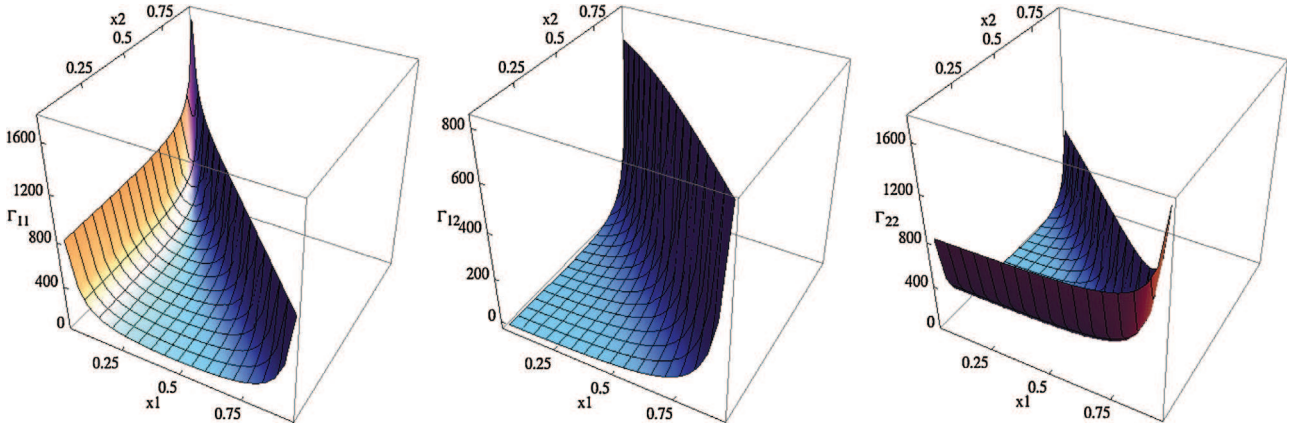


Fig. 6 – Level surfaces of the components of Gibbs metric for the mixture methanol - acetone - chloroform

4.4. Ridge/valleys and distillation boundaries

Let us now check if the notion of the ridge/valley curves introduced in Definition 3 is consistent with the notion of a distillation boundary. We precise that *distillation boundaries* are *separatrices* of RCM connecting stable/unstable nodes to saddles.³ In particular, if a curve $\gamma(\cdot) \in \Omega$ is a distillation boundary, then:

- it is a residue curve, i.e., it is an integral curve of system of differential equations (4), and hence it cannot be crossed by any other residue curve;
- it starts at an unstable node and finishes at a saddle, or starts at a saddle and finishes at a stable node;
- at its terminal points it is tangent to the eigenvectors of the Jacobian $D_x v$, or, equivalently (Zharov and Serafimov (1975)), of the Hessian $D_x^2 \Gamma_b$.

As we saw, properties (b) and (c) are also verified by ridge/valley curves defined by equation (11). This is why it seems natural to expect that the two definitions are equivalent. To conclude, one must test whether the ridge/valley curves verify property (a). Let us put this question in a more general mathematical context. On a plane (x_1, x_2) consider a gradient system associated to some potential function F , and assume that it has at least one node and one saddle. Is it true that the ridge/valley curve of F defined by equation (11) is an integral curve of the gradient system $\dot{x} = \nabla F(x)$ whatever is the metric of the plane? In general, the answer is negative, as it is shown by the following academic counterexample.

Example 4. For simplicity, we consider the Euclidean case where all the computations can be done explicitly. Let $F = x_1 - x_1^3 - (x_2 - x_1)^2$. The corresponding gradient system is

$$\dot{x}_1 = 1 - 3x_1^2 - 2(x_1 - x_2), \quad \dot{x}_2 = 2(x_1 - x_2), \quad (12)$$

it has a saddle type singularity at the point $A = (-1/\sqrt{3}, -1/\sqrt{3})$ and a stable node at $B = (1/\sqrt{3}, 1/\sqrt{3})$. Its phase portrait is shown in Fig. 7, where thick black curves represent the separatrices computed numerically. Equation (11) can be written in the form

$$4(-9x_1^4 - 4x_1 + 1) + 8(9x_1^3 + 6x_1^2 - 3x_1 + 2)x_2 - 48x_1x_2^2 = 0,$$

which yields two families of ridge/valley curves (red dashed curves in Fig. 7):

$$x_2 = \frac{9x_1^3 + 6x_1^2 \pm \sqrt{(3x_1^2 - 1)^2 (9x_1^2 + 4)} - 3x_1 + 2}{12x_1}.$$

As Fig. 7 shows, the dashed curves do not coincide with the black curves representing the separatrices. In order to avoid any doubt concerning the numerical error related to the integration of (12), observe that the point $x_0 = (0, -1/4)$ belongs to the ridge curve, which at this point is tangent to the vector (16, 13). On the other hand, $\nabla F(x_0) = (1/2, 1/2)$, so the ridge/valley curve passing through x_0 is not a solution to (12), and hence it can be crossed by integral curves of (12).

Now we are able to complete the answer to question Q3 posed in the Introduction: the ridge/valley curves of Definition 3 connect the singular points of RCM and are tangent to the distillation boundaries at these points, but in general, they are not residue curves, and thus they cannot be distillation boundaries. So, although we are using a different definition of

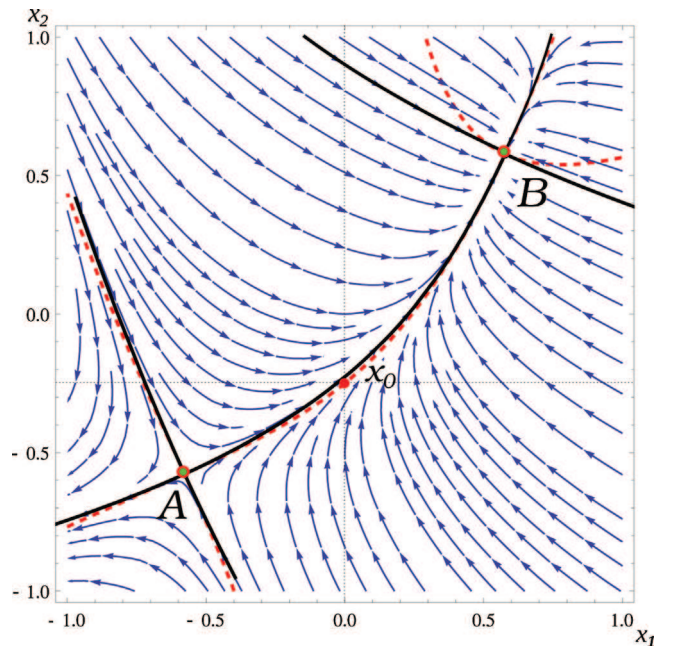


Fig. 7 – Phase portrait of the gradient flow of $F = x_1 - x_1^3 - (x_2 - x_1)^2$: separatrices (thick black curves) and ridge/valley curves (dashed curves).

³ In the theory of dynamical systems such curves are called *heteroclinic orbits* of system (4).

ridge/valley curves, we confirm the general conclusion made by van Dongen and Doherty (1984) and by other authors (Rev, 1992; Kiva et al., 2003).

5. Conclusion

The thermodynamical equilibrium condition, described by the van der Waals–Storonkin equation (6) endows RCM of open evaporation by a non-trivial Riemannian metric: the Gibbs metric Γ . Within this geometrical model, any RCM is the set of the integral curves of the Riemannian gradient flow associated to the boiling temperature T_b , which plays the role of a potential function for RCM. This key fact explains all well-known properties of the residue curves maps and of the role of T_b , and in addition, it implies that unlikely in the classical Euclidean case, the equilibrium vector field is Γ -orthogonal to the isotherm fronts away from azeotropes.

We explored the first non-trivial consequences of this geometric viewpoint in the case of ternary mixtures. In particular, we discussed the relation between distillation boundaries and the ridge/valley curves of the boiling temperature T_b and showed that they do not coincide in general since the T_b ridge/valley curves are not residue curves.

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