On the classification of generic phenomena in one-parameter families of thermodynamic binary mixtures

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Even binary mixtures exhibit surprisingly complex phase equilibria behavior. Understanding their relationships is of primary industrial importance. A tool is the global phase diagram (GPD) *i.e.* the partition of the space of the external (model) parameters into regions where points represent system such that the corresponding pT diagrams have the same topological type. The boundaries of these regions are hypersurfaces (of codimension 1) in the space of parameters. We present here a complete classification of the local phenomena corresponding to codimension 3 singularities in the pT phase diagrams of *proper* binary mixtures (*i.e.* the molar fraction x of one of the species satisfies $0 < x < 1$) when a parameter varies so that such a hypersurface is intersected. This work represents a complement to the classification by Nezbeda *et al.* (I. Nezbeda, J. Kolafa and W. R. Smith, *J. Chem. Soc., Faraday Trans.*, 1997, **93**(17), 3073). Following Varchenko's approach, (A. N. Varchenko, *J. Sov. Math.*, 1990, **52**(4), 3305) generic phenomena encountered in binary mixtures when the pressure p and the temperature T change, correspond to singularities of the convex envelope (with respect to the x variable) of the "front" (a multifunction of the variable x) representing the Gibbs potential $G[p,T](x)$. Pressure p and temperature T play the role of external parameters like λ. A total amount of 26 singularities is found (at least 6 of them were not previously described in the literature), and 56 scenarios of evolution of the pT diagram are obtained. As far as possible, we have quoted examples of modeled or real binary mixtures where these singularities appear.

1 Introduction

Codimension 2 singularities of pT-diagrams of binary mixtures were classified in ref. 1. In this paper, we consider codimension 3 singularities (*i.e.* the case when the system depends on a parameter). The physical nature of this external parameter λ is left unspecified. For example λ can be a parameter in the equation of state of the mixture. The theory does not apply directly to ternary mixtures, since a molar fraction is not an external parameter (the Gibbs potential has to be convexified with respect to this variable, see below).

All mathematical ideas used below are explained in ref. 1. We will use below the notation of this paper. Recall some facts about the two parameter case (the pressure and the temperature are considered as two external parameters):

Denote by $G[p,T](x)$ the Gibbs potential considered as a *multivalued* function (with singularities) of the variable x (where x denotes the molar fraction of the second component), with p and T fixed. A point (p,T) will be called *generic* if the convexification of $G[p,T]$ with respect to x is generic. For such a generic (p,T), the number of singularities in the convexification of $G[p,T]$ is even, say $2n$, and these singularities subdivide the interval [0,1] (where x lives) into n disjoint segments which correspond to heterogeneous equilibria and $n+1$ segments which correspond to homogeneous equilibria. A generic (p,T) point is thus labeled by an odd integer $(2n+1)$ which indicates the total number of phases of the system as x varies when (p,T) is constant. The generic phenomena encountered in binary mixtures when p and T vary are met when the point (p,T) is such that the convexification of $G[p,T]$ has degenerate (*i.e.* non-generic) singularities. The set of such points (p,T) is made of some curves which separate regions were the potential is generic. Codimension one singularities correspond to *critical points, azeotropies or triple points*. The codimension two singularities are isolated points in the (p,T)-plane. It was proved in ref. 1 that there are 5 different codimension 2 singularities, not considering those of pure components (arriving at $x = 0$ or $x = 1$), and the transverse intersections of two codimension one singularities (points (p,T) where the convexification of the potential contains two distinct non-generic events of codimension one).

Let's consider now the addition of some external parameters λ. The Gibbs potential will be denoted by $G[p,T,\lambda]$. In thermodynamics, binary mixture models depending on several external parameters are studied. The codimension one singularities in the space of external parameters correspond to codimension 3 singularities of convex envelopes of $G[p,T,\lambda]$. The space of proper parameters (called *global phase space* or GPD) is subdivided by an hypersurface into regions where the (p,T)-diagram is generic. These regions correspond to the set of λs such that for all (p,T), the convexification of $G[p,T,\lambda]$ shows singularities of codimension at most 2.

We describe below what happens when a path crosses transversely the hypersurface which separates these regions. Our goal is to list all possible ways to pass from a generic (p,T)-diagram to another generic (p,T)-diagram by a generic one-parameter family of (p,T)-diagrams.

To do this, we consider the three-dimensional parameter space (p,T,λ). At each point of this space there corresponds a particular $G[p,T,\lambda]$, defined over the [0,1] interval of the x vari-

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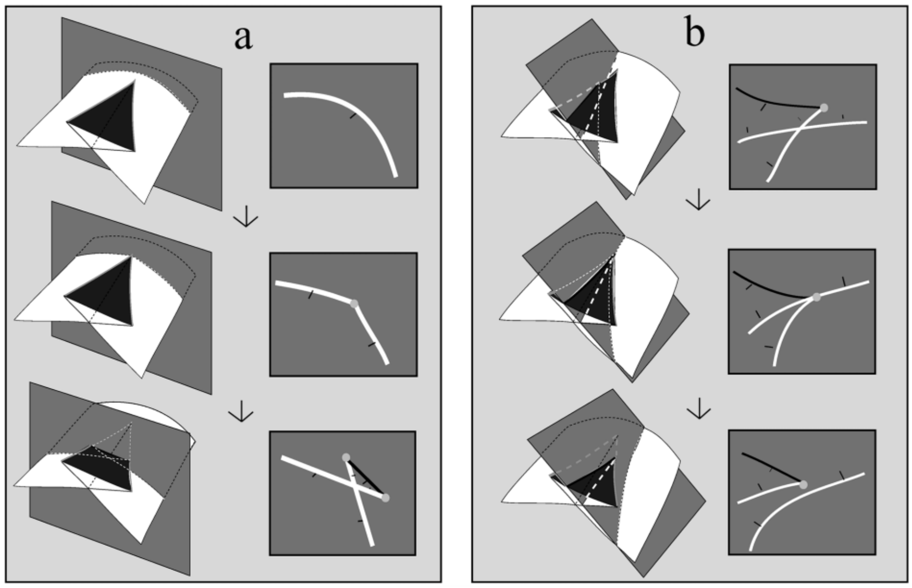

Fig. 1 Generic (a) and non-generic (b) scenarios obtained as sections of Σ near the (1,6) singularity.

able. This space is thus subdivided into regions containing the (p,T,λ) for which the convexification of $G[p,T,\lambda]$ is generic. Denote by Σ the complement of these regions. Σ is a singular surface. The singularities of Σ are located on some curves lying on this surface. These curves meet at some isolated points which corresponds to more complicated singularities. Codimension 1 singularities of the convexification of $G[p,T,\lambda]$ (which correspond to critical points, azeotropies and triple points) occur when (p,T,λ) lies on the smooth part of Σ. Codimension 2 singularities occur when (p,T,λ) lies on the singular curves of Σ. Codimension 3 singularities occur when (p,T,λ) is one of the isolated singular points of Σ.

The smooth parts of Σ receive a natural coorientation by the following procedure: A smooth component of Σ separates two regions where the potential is generic. Such a region can be labeled by its number of phases. The coorientation (shown by a small stroke in our pictures) indicates the region where the number of phases is higher.

The local features of Σ in a neighborhood of a singularity are described by a mathematical model of the singularity in an abstract 3-dimensional space. The true physical singularity, in the (p,T,λ) space, is diffeomorphic to this abstract model.

Therefore, having the model of Σ in the neighborhood of a singular point, the (p,T) diagram corresponding to the non-generic value of λ (denoted by λ^*) is the section of Σ at $\lambda = \lambda^*$. The scenario of the variation of the (p,T) diagram is given by the film of the successive sections of Σ when λ varies in $(\lambda^* - \varepsilon, \lambda^* + \varepsilon)$. This scenario depends on the relative position of Σ with respect to the λ axis. So, for a given singularity, there are different scenarios for the variation of the (p,T) diagram. There are 13 possible singularities of codimension 3 for Σ, and 20 generic scenarios.

Example. Fig. 1a contains a generic scenario obtained by generic sections of Σ near a singular isolated point (which is called a *tricritical point*, see Section 3.1). This singularity separates regions II and IV (using the terminology of ref. 7) in GPD. A non-generic scenario, obtained by a non-generic section of Σ at the singular point, is shown in Fig. 1b. In fact this non-generic scenario appears when one moves from class II to class III in GPD (see Fig. 7 in ref . 4, where the singular point is called a symmetrical tricritical point).

Still another type of codimension 3 singularity in the (p,T) diagram appears when the (p,T) plane is non-transverse (*i.e.* tangent) to a curve of codimension 2 singularities of Σ. By analyzing the non-generic (codimension 1) intersections of the models of Σ for the 5 codimension 2 singularities, we obtain 15 additional scenarios.

Eventually, another way to obtain codimension 3 singularities in the (p,T) plane (and hence new scenarios): When the smooth part of Σ is tangent to a (p,T) plane λ = constant. The smooth parts of Σ can be labeled by the 3 types of codimension 1 singularities of convexification. There should be 3 possible scenarios for each of the 3 types. However, we doubt that all these scenarios effectively appear in binary mixtures (we found only two of these scenarios in the literature concerning binary mixtures).

This paper is organized as follows: In Section 2, we explain the notations used throughout this paper. In Section 3, the list of all models of possible isolated singularities of Σ is given, with the corresponding generic scenarios. In Section 4, we list all possible scenarios corresponding to the case when the (p,T) plane is tangent to a curve of singularities of Σ. In Section 5, we list all possible scenarios corresponding to the case when the (p,T) plane is tangent to a smooth component of Σ. Examples we are aware of, where these scenarios occur in modeled and real binary mixtures are indicated in each section. In Section 6, we discuss another type of local codimension 3 phenomenon in (p,T) diagrams. In the Appendix the diagram of adjacencies of the singularities is briefly described.

2 About the notation

We list here the mathematical notation for the singularities used in this paper. Our notation is somewhat complementary to that given in ref. 2. The latter is more phenomenological, the former is based on the mathematical features of the singularities. At a generic point, the graph of the convexification of $G[p,T,\lambda]$ has a contact of order 2 with its tangent line. Such a generic point is denoted by (1,2). Codimension 1 singularities of the convexification of $G[p,T,\lambda]$ (corresponding to the smooth part of Σ), are denoted as follows:

(i) (1,4) (critical point),

(ii) (2,2) (azeotropy),

(iii) (1,2)(1,2)(1,2), also denoted by $(1,2)^3$ (triple point).

The meaning of this notation is the following: each parenthesized sequence of numbers denotes a point x above which different pieces of the (multivalued) graph of $G[p,T,\lambda]$ are tangent. The first integer denotes the number m of such tangent pieces; the second number after a comma (or a sequence of

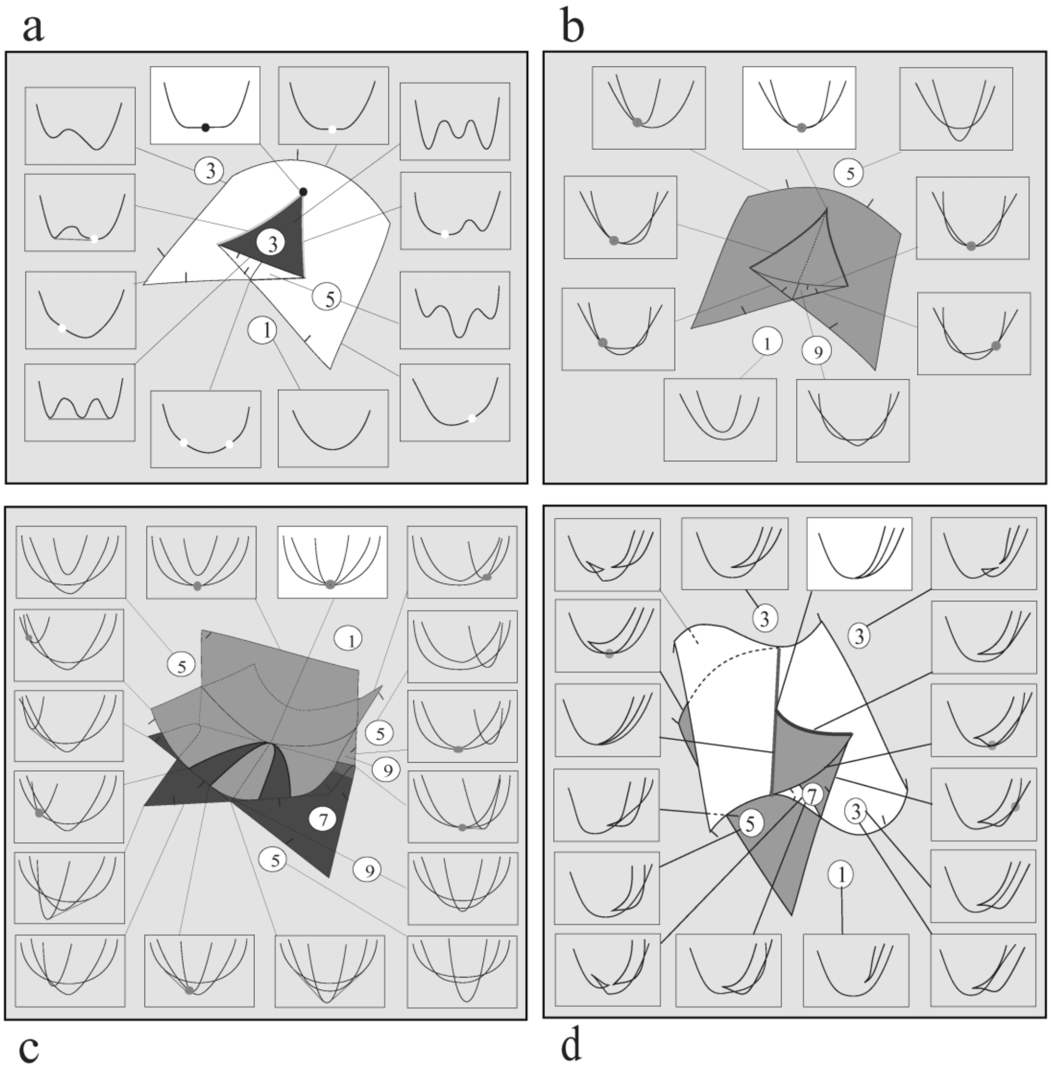

Fig. 2 The Σ surface near (a) the (1,6), (b) the (2,2,4), (c) the (3,2), (d) the (3,2,7/2) singularities.

numbers separated by a line) denotes the different orders of contact of the m pieces with the tangent line. A third number after a comma (if present), denotes the order of contact between two pieces, in the case when it is different from 2. If this last number is half-integer, it means that the two corresponding branches form a cusp point. A series of parenthesized sequences denotes the coexistence of several such points of tangency having a common tangent line.

Codimension 2 singularities of the convexification of $G[p,T,\lambda]$ are denoted as follows:

(i) (1,4)(1,2) (*Split pleat tail*, also known as *critical end point* in ref. 9),

(ii) (2,2)(1,2) (*Dove*, a.k.a. *azeotropic end point* in ref. 9)

(iii) (3,2,5/2) (*Wings*, missing in ref. 14, a.k.a. *critical azeotropic point* in ref. 9)

(iv) $(1,2)^4$ (*Quadruple point* in ref. 9)

(v) (2,2,3) (*Double pleat*, missing in ref. 9, a.k.a. *critical cusp* in ref. 2)

Our notations for codimension 3 singularities will be in accordance with the above.

3 The thirteen generic isolated singularities of Σ

3.1 The (1,6) singularity

This singularity occurs when the graph of the convexified potential $G[p,T,\lambda](x)$ has a contact of order six with its tangent line at some point x.

The local picture of Σ near such a point (see Fig. 2a) contains a surface of (1,4) singularities (white) with a self-intersection starting at the (1,6) isolated point. This line represents an example of transverse intersection: in the potential there are two distinct (1,4) singularities. The edge of this surface is the line of (1,4)(1,2) *split-pleat tails* (light grey), which contains a cusp point at the (1,6) singularity and borders the surface of triple points (dark grey).

Generic sections of Σ representing the evolution of the (p,T)-diagrams, avoid the tangent line to the self-intersection line at the (1,6) point. The smooth critical line becomes non-smooth at the singular point and afterwards a self-intersection point appears together with two split-pleat tails (Fig. 3a).

Remark. This singularity is called *tricritical point* in ref. 9.

Examples. The (1,6) singularity separates II and IV classes of GPD, (using the notation of ref. 7) in global diagrams (see also Fig. 3 in ref. 4 and Fig. 4 in ref. 12).

3.2 The (2,2,4) singularity

It occurs when two branches of $G[p,T,\lambda]$ have a contact of order four.

In the neighborhood of this point (see Fig. 2b) the two branches of the potential, which remain convex, have up to four intersection points. The convexified graph has up to four added segments (*i.e.* nine different phases). At the (2,2,4)-singularity the azeotropy surface (2,2) (grey) has a swallowtail. Its cusp edge is the double pleat line (2,2,3) (dark grey). At

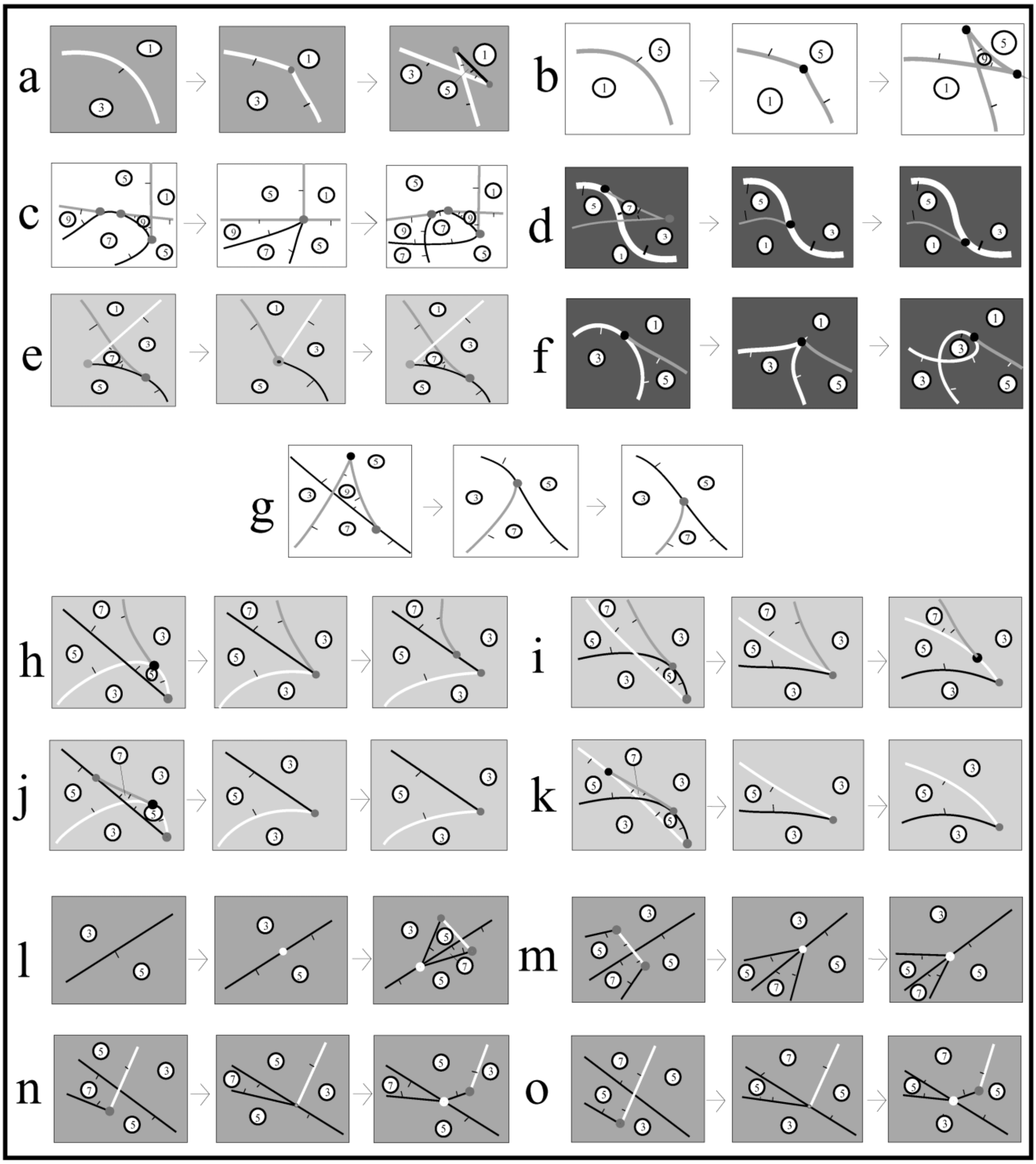

Fig. 3 Scenarios, table I.

the singular point it has a spatial cusp. The transverse self-intersection of the azeotrope surface represents the coexistence of two azeotropes.

Generic sections of Σ at such a point, representing the evolution of the (p,T)-diagram as the parameter λ varies, avoid the tangent line to the self-intersection line at the (2,2,4) point. Such (p,T)-diagrams are shown in Fig. 3b.

Remark. This singularity is not mentioned in ref. 9.

3.3 The (3,2) singularity

This corresponds to the case when three branches of the potential $G[p,T,\lambda]$ are mutually tangent in a point.

At this singular point (see Fig. 2c), three dove lines (2,2)(1,2) (black) are mutually tangent. The triple-points surface $(1,2)^3$ (dark grey) has a Whitney umbrella at the (3,2) point. Σ contains the following multiple singularities (transverse intersections): self-intersection of the triple points surface and intersections of two branches of the azeotropy surface (coexistence of two azeotropes).

A generic section of Σ containing the singular point avoids the common tangent line to the dove lines and the tangent to the self-intersection line of the triple points surface. The evolution of the (p,T)-diagram crossing the singularity is shown in Fig. 3c.

Remark. This singular point is called a *double azeotrope* in ref. 9. Double azeotropy means coexistence of two azeotropes, at different concentrations,[5] which appear at a double pleat singularity,[1] see also Fig. 4d. At the (3,2) singularity three azeotropes meet, together with two triple points.

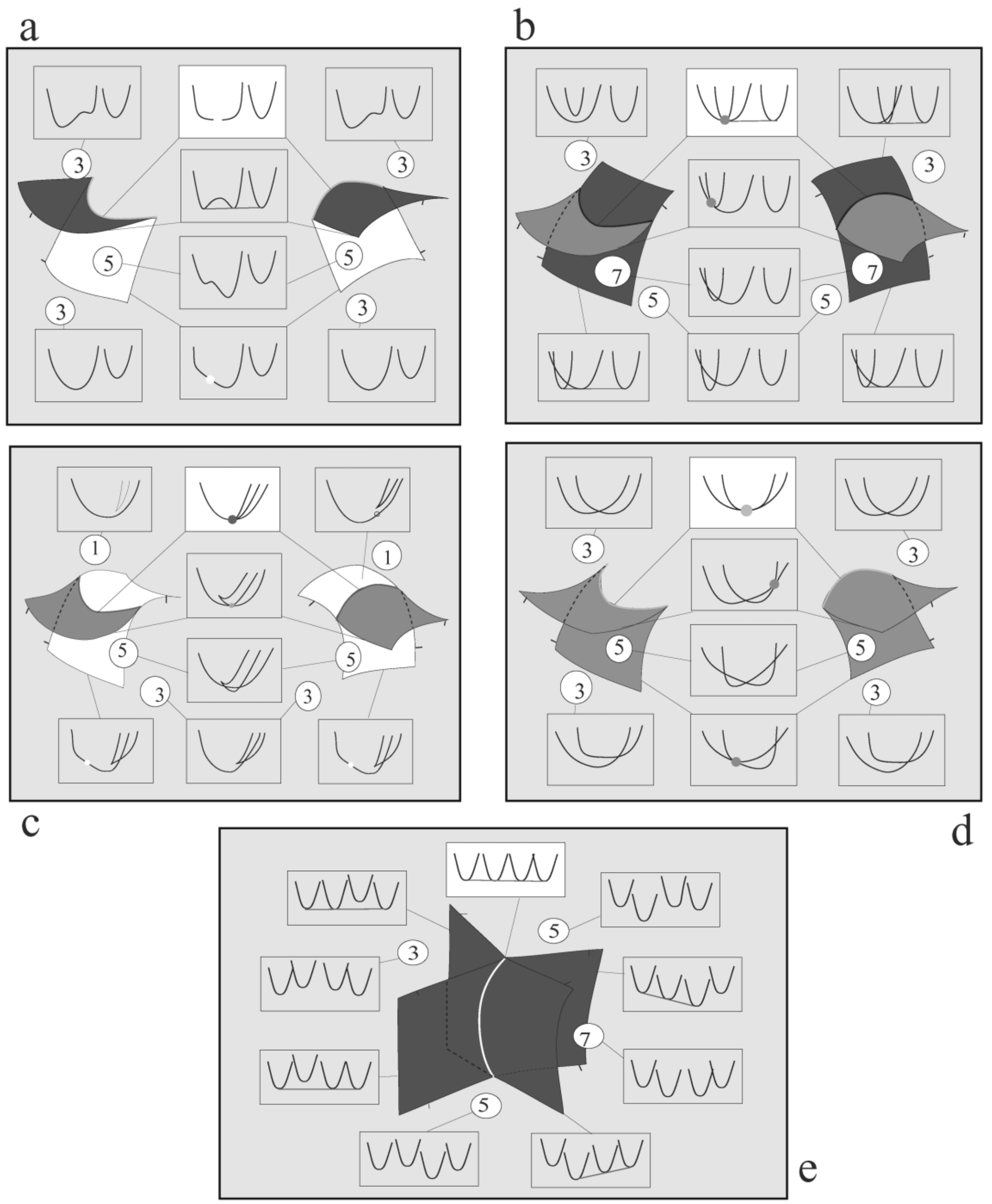

Fig. 4 The Σ surface near (a) the (1,4)(1,2), (b) the (2,2)(1,2), (c) the (3,2,5/2), (d) the (2,2,3), (e) the $(1,2)^4$ singularities.

3.4 The (3,2,7/2) singularity

This occurs when a smooth branch of the graph of $G[p,T,\lambda]$ becomes tangent to a cusp point of type 7/2.

At such a point (see Fig. 2d), an azeotrope surface (grey) with a cusp edge (dark grey) of double pleat points, ends tangentially to the critical points surface (white) along the wings line (grey). Note that the (transverse) intersection of the critical points surface and the azeotrope surface ends on this singularity, tangentially to the wings line.

The generic sections of Σ at the singular points do not contain the common tangent to the wings and the double pleat lines. In the (p,T)-plane the double pleat point disappears and the azeotrope line ends on the opposite side of the critical points line (see Fig. 3d).

Remark. This singularity is not mentioned in ref. 9.

3.5 The (2,4–2) singularity

It occurs when the potential $G[p,T,\lambda]$ has at the same time a branch which experiences an (1,4) singularity (contact of order four with the tangent line) and another branch which is tangent to it at the same point.

At such a point (see Fig. 5a), a split-pleat tail line (light grey) is tangent to a dove line (black) and to the intersection line of the critical points surface (white) with the azeotropy surface (grey). This intersection line is a transverse intersection.

A generic section does not contain the common tangent line to the dove and split-pleat tail lines. The (p,T)-diagrams before and after the singular event are similar (see Fig. 3e).

Remark. This singularity is called *double critical/azeotropic end-point* in ref. 9.

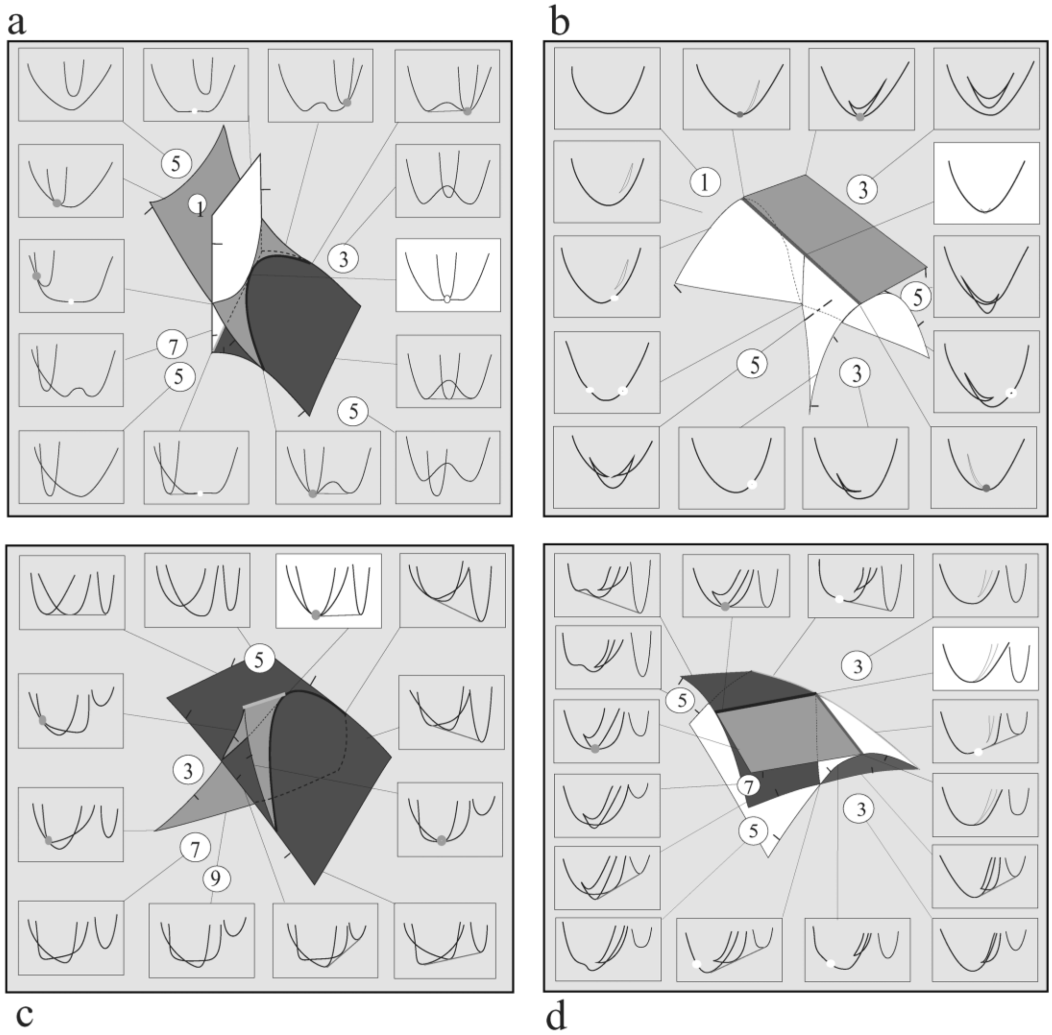

Fig. 5 The Σ surface near (a) the (2,4–2), (b) the (1,8/3), (c) the (2,2,3)(1,2), (d) the (3,2,5/2)(1,2) singularities.

Examples. An example of this singularity is given in ref. 10, Fig. 8.

3.6 The (1,8/3) singularity

This singularity is a special point of the wings line, where the lips having a cusp point tangent to another branch of the potential vanish, and reappear with the opposite cusp tangent to the same branch.

In Fig. 5b, the surface of critical points forms a Whitney umbrella (white). The azeotrope surface (grey) is tangent to this umbrella along the wings line (dark grey). The selfintersection of the critical points surface is transverse and represents potentials with two different (1,4) singularities.

A generic section of Σ at the singularity does not contain the tangent to the wings line and the tangent to the self-intersection line of the umbrella. The (p,T)-diagrams before and after the singular event are similar in the neighborhood of the wings; at the singular point the critical points line has a cusp (see Fig. 3f).

Remark. This singularity is not mentioned in ref. 9.

Examples. An example of this singularity is given in ref. 7, Fig. 5. The azeotrope line meets the critical line at its cusp point.

3.7 The (2,2,3)(1,2) singularity

This occurs when the tangent line to the graph of $G[p,T,\lambda]$ at a double pleat point (2,2,3) is tangent to the graph of the potential at another point.

At such a point (see Fig. 5c), an azeotrope surface (grey) with a cusp edge (light grey) of double pleat points, ends tangentially to the triple points surface (dark grey) along the dove line (black). Note that the (transverse) intersection of the triple points surface and the azeotrope surface ends on this singularity.

The generic sections of Σ at the singular points do not contain the common tangent to the dove and the double pleat lines. In the (p,T)-plane the double pleat point disappears and the azeotrope line ends on the opposite side of the triple points line (see Fig. 3g).

Remark. This singularity is not mentioned in ref. 9.

3.8 The (3,2,5/2)(1,2) singularity

It occurs when at a wings point of $G[p,T,\lambda]$, the tangent line is tangent to the graph of the potential at another point.

At such a point (see Fig. 5d), a dove line (black) and a wings line (dark grey) end together and meet transversely on a split pleat tail line. Moreover, at the singular point, a transverse intersection between the triple points surface (grey) and the critical point surface (white) is ending.

There are four generic sections of Σ at the singular point: the corresponding evolutions of the (p,T)-diagram are shown in Fig. 3h, i, j and k.

Remark. This singularity is called a *critical azeotropic endpoint* in ref. 9.

Examples. This singularity (section of type (c)) separates the J and K domains in Fig. 4a of Nezbeda *et al.*[9]

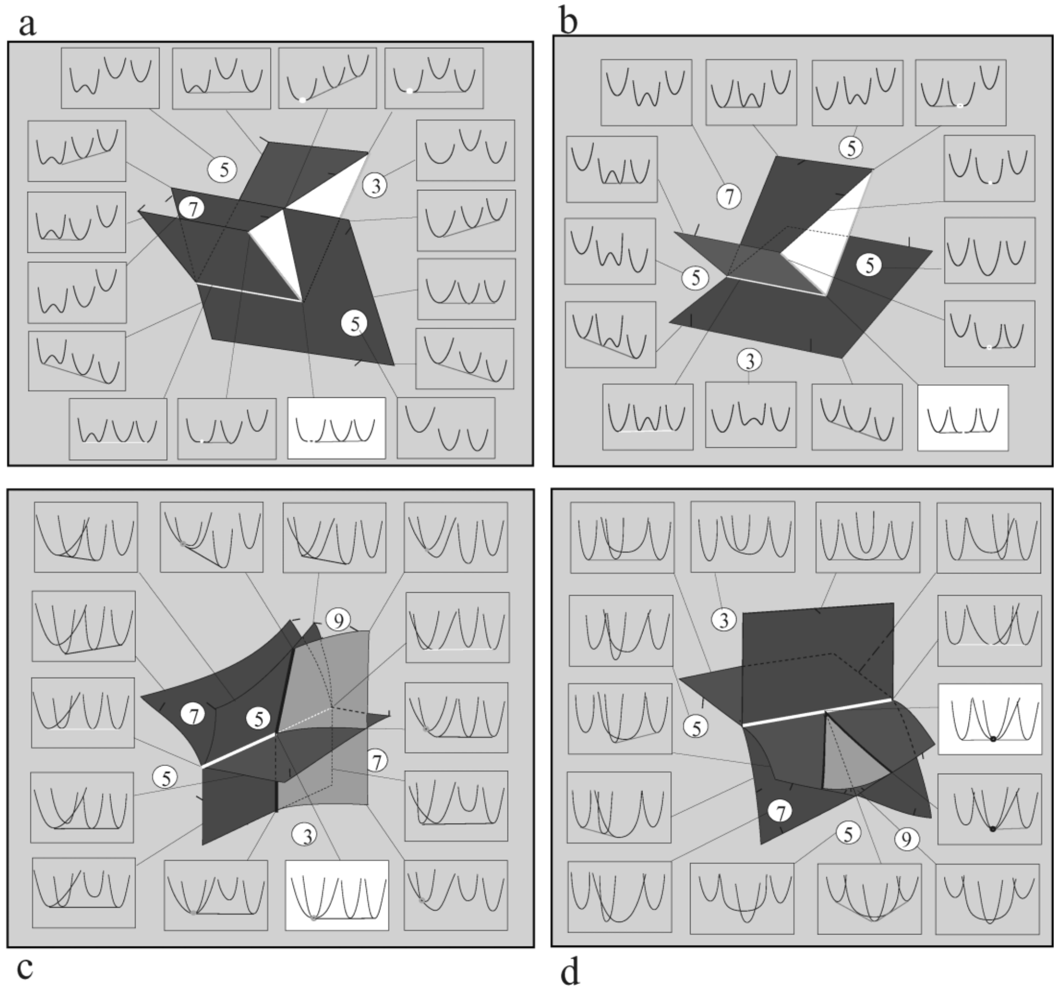

Fig. 6 The Σ surface near (a) the (1,4)(1,2)(1,2), (b) the (1,2)(1,4)(1,2), (c) the (2,2)(1,2)(1,2), (d) the (1,2)(2,2)(1,2) singularities.

3.9 The (1,4)(1,2)(1,2) singularity

It occurs when three branches of the potential have a common tangent line: the first one has a contact of order four, the other ones have a contact of order two with the line.

At such a point (see Fig. 6a), a quadruple points line (white) ends where it meets the end-points of two split-pleat tail lines (light grey). These split-pleat tail lines border a critical point surface (white) which intersects transversely one of the triple points surfaces (dark grey).

There are 4 types of generic sections of Σ containing this singular point (see Fig. 3l, m, n and o).

Remark. This singularity is called *quadruple critical end-point* in ref. 9 and *critical–normal–normal point* in ref. 2.

3.10 The (1,2)(1,4)(1,2) singularity

It occurs when three branches of the potential have a common tangent line: the middle one has a contact of order four, the other ones of order two with the tangent.

At such a point (see Fig. 6b), a quadruple points line (white) ends where it meets the end-points of two split-pleat tail lines (light grey). These split-pleat tail lines border a critical point surface (white).

There are three types of generic sections of Σ containing this singular point (see Fig. 7a, b and c).

Remark. In ref. 9, this singularity has the same name as (1,4)(1,2)(1,2): *quadruple critical end-point*, whereas it is called a *normal–critical–normal point* in ref. 2.

Examples. This singularity (section of type (c)) separates the domains IV* and IV_4 of Fig. 12 in ref. 4 (see also, in Fig. 14 of ref. 4 the (p,T)-diagrams in these two domains).

3.11 The (2,2)(1,2)(1,2) singularity

It occurs when four branches of the potential have a common tangent line such that the points of tangency of the first two branches with this line coincide.

At such a point (see Fig. 6c), a quadruple points line (white) is intersected by a dove line (black) at the singular point. At that point the dove line is not smooth: along this line the azeotrope surface (grey) is tangent to two different triple points surfaces (dark grey). Moreover, a transverse intersection between the azeotrope surface and a third triple points surface ends tangentially on the quadruple point line (white).

There are three non-equivalent sections of Σ containing this singular point (see Fig. 7d, e, and f).

Remark. This singularity is called *quadruple azeotropic end-point* in ref. 9 and *azeotropic–normal–normal* inref. 6.

3.12 The (1,2)(2,2)(1,2) singularity

It occurs when four branches of the potential have a common tangent line such that the points of tangency of the two central branches coincide.

At such a point (see Fig. 6d), two dove lines (black) end on a quadruple points line (white) at the singular point. The dove lines border the same azeotrope surface (grey), but belong to two different triple points surfaces (dark grey), which intersect transversely along a line which ends at the singular point, tangentially to the azeotrope surface.

A generic section of Σ containing the singular point avoids the tangent to the quadruple point line and the tangent to the self-intersection line. There are two types of generic sections (see Fig. 7g and h).

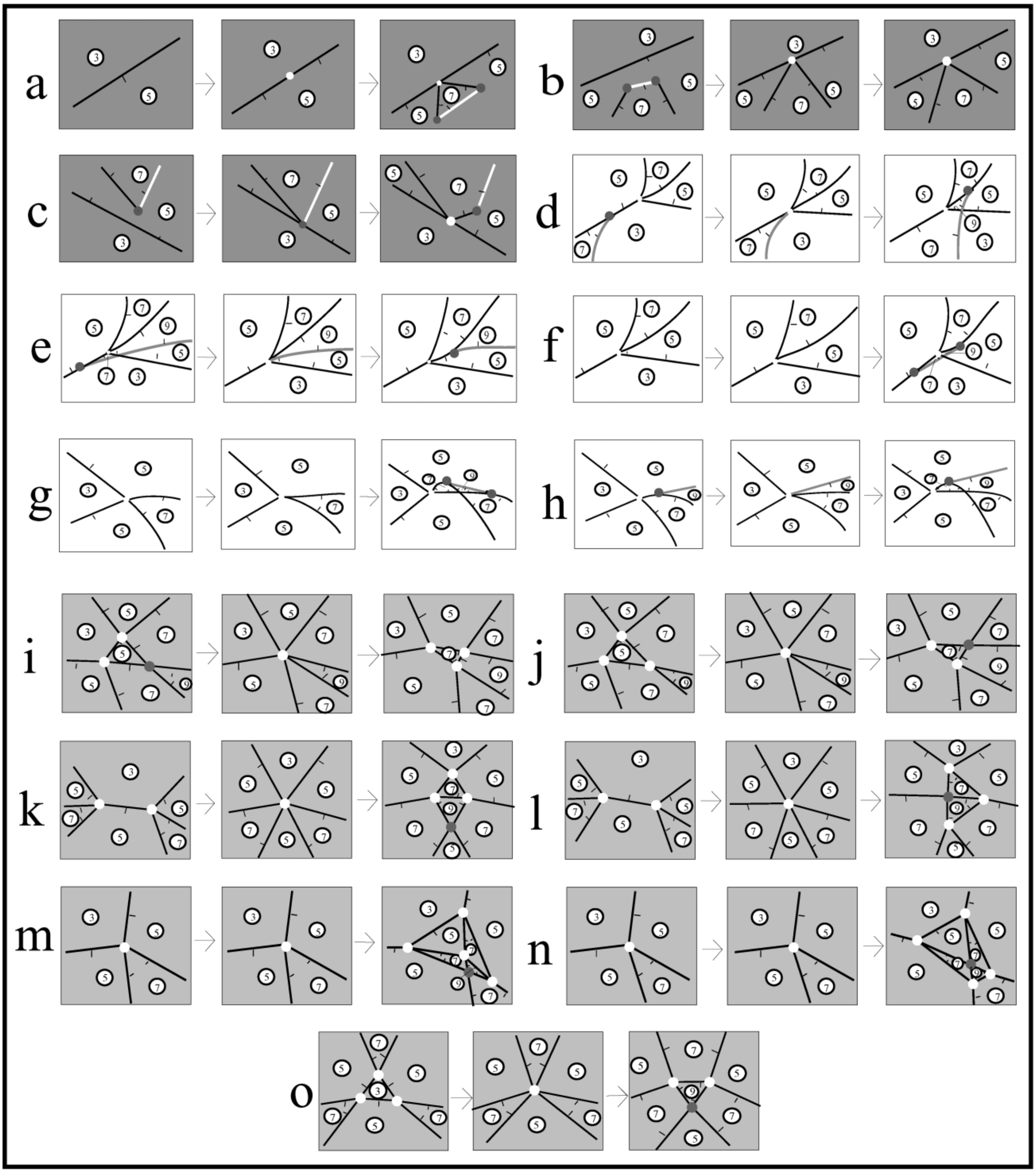

Fig. 7 Scenarios table II.

Remark. This singularity is called *normal–azeotropic–normal* in ref. 6. The (2,2)(1,2)(1,2) and (1,2)(2,2)(1,2) singularities are not distinguished in ref. 9.

3.13 The $(1,2)^5$ singularity

It occurs when five different generic points of the graph of the potential have a common tangent line.

Such a point (see Fig. 8) is the meeting point of five lines of quadruple points (white) and of ten surfaces of triple points (dark grey). Two of such triple points surfaces intersect each other transversely (along the light grey line). The surfaces are cooriented. Around the quintuple point there are eight regions (generic domains) where the number of phases varies from three to nine.

There are seven non-equivalent sections of Σ. In Fig. 7, the scenarios i and j (resp. k and l; resp. m and n) are distinguished only by the position of the double triple point.

Remark. This singularity is called a *quintuple point* in ref. 9.

4. The five cases of tangency between the (p,T) plane and the singular curves on Σ

4.1 Tangential section of the split-pleat tail line

At such a point (see Fig. 4a), the surface of triple points $(1,2)^3$ (dark grey) and the surface of critical points (1,4) (white) meet together and form an angle along the split-pleat tail line (light grey).

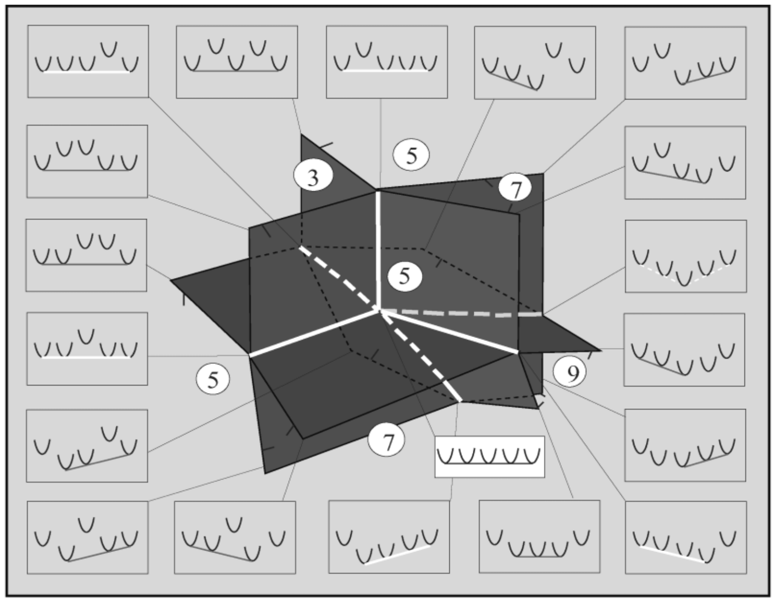

Fig. 8 The Σ surface near the $(1,2)^5$ singularity.

Near to the points of tangency of the singular line with the (p,T) plane, Σ can be of two types (both depicted in Fig. 4a), depending on the local shape of the singular curve. A section of Σ tangent to the split-pleat tail curve may lie generically in 2 different positions, giving rise to 4 generic scenarios in the (p,T)-plane (see Fig. 9a–c and d). They all feature the birth or the death of a pair of split pleat tails.

Remark. These scenarios in the (p,T)-plane are those shown in ref. 9, Fig. 6(a) and 6(b), where the singular point is called *double critical end-point*.

Examples. An example of this singularity (scenario a) is given in Nezbeda *et al.*,[11] Fig. 7 and 8.

This singularity (scenario a) separates the domains II and VI of Fig. 4 in van Pelt *et al.*,[12] whereas domains IV and VII are separated by the scenario c.

Also, Fig. 4 of Deiters and Pegg,[4] is an example of scenario a.

4.2 Tangential section of the dove line

At such a point (see Fig. 4b), the surface of azeotropy (2,2) (grey) ends along the dove line (black) on the triple points surface $(1,2)^3$ (dark grey).

Near the points of tangency of the singular line with the (p,T) plane, Σ can be of two types (both depicted in Fig. 4b), depending on the local shape of the singular curve. Hence one obtains two generic scenarios which feature the birth or the death of a pair of doves (see Fig. 9e and f).

Examples. These scenarios are those shown in ref. 9, Fig. 10a and 10b (where the singular point is called a *double azeotropic end-point*).

4.3 Tangential section of the wings line

At such a point (see Fig. 4c), the surface of azeotropy (2,2)(grey) ends tangentially on the critical points surface (1,4) (white) along the wings line (light grey).

Near to the points of tangency of the singular line with the (p,T) plane, Σ can be of two types (both depicted in Fig. 4c), depending on the local shape of the singular curve. Hence here are two generic scenarios, which feature the birth or death of a pair of wings (see Fig. 9g and h).

Remark. In ref. 9, this singular point is called *double critical azeotropic point*.

4.4 Tangential section of the double pleat line

At such a point (see Fig. 4d), the surface of azeotropy (2,2)(grey) has a cusp-edge along the double pleat line (2,2,3) (light grey). Near to the points of tangency of the singular line with the (p,T) plane, Σ can be of two types (both depicted in Fig. 4d), depending on the local shape of the singular curve. Hence there are two generic scenarios, which feature the birth or the death of two double pleats (see Fig. 9i and j).

Remark. This singularity is not mentioned in ref. 9.

4.5 Tangential section of the quadruple points line

At such a point (see Fig. 4e), four surfaces of triple points $(1,2)^3$ (dark grey) meet along the quadruple points line (white). There are five generic scenarios, depending on the mutual position of the (p,T) plane, Σ, and the quadruple point line in Σ. All these scenarios feature the birth or death of a pair of quadruple points in the (p,T) plane (see Fig. 9k, l, m, n and o).

Remark. In ref. 9, this singular point is called *double quadruple end point*.

5 The six cases of tangency between the (p,T) plane and the smooth part of Σ

5.1 Tangential section by the (p,T) plane of the critical points surface

5.1.1 Hyperbolic case. The point of tangency of the surface with the (p,T) plane is a generic hyperbolic point of the critical points surface (white) (see Fig. 10a). In the corresponding scenario, two smooth components of the critical line meet at the singular point (a double point of the critical line), which is successively transformed into a different pair of smooth components.

Examples. This phenomenon separates classes V^h and VIII of the global phase diagram in ref. 12, Fig. 14.

5.1.2 Locally convex case. The point of tangency of the surface with the (p,T) plane belongs to a generic locally convex part of the the critical points surface (white) (see Fig. 10b). The corresponding scenario features the birth or death of a smooth closed component of the critical line in the p,T plane.

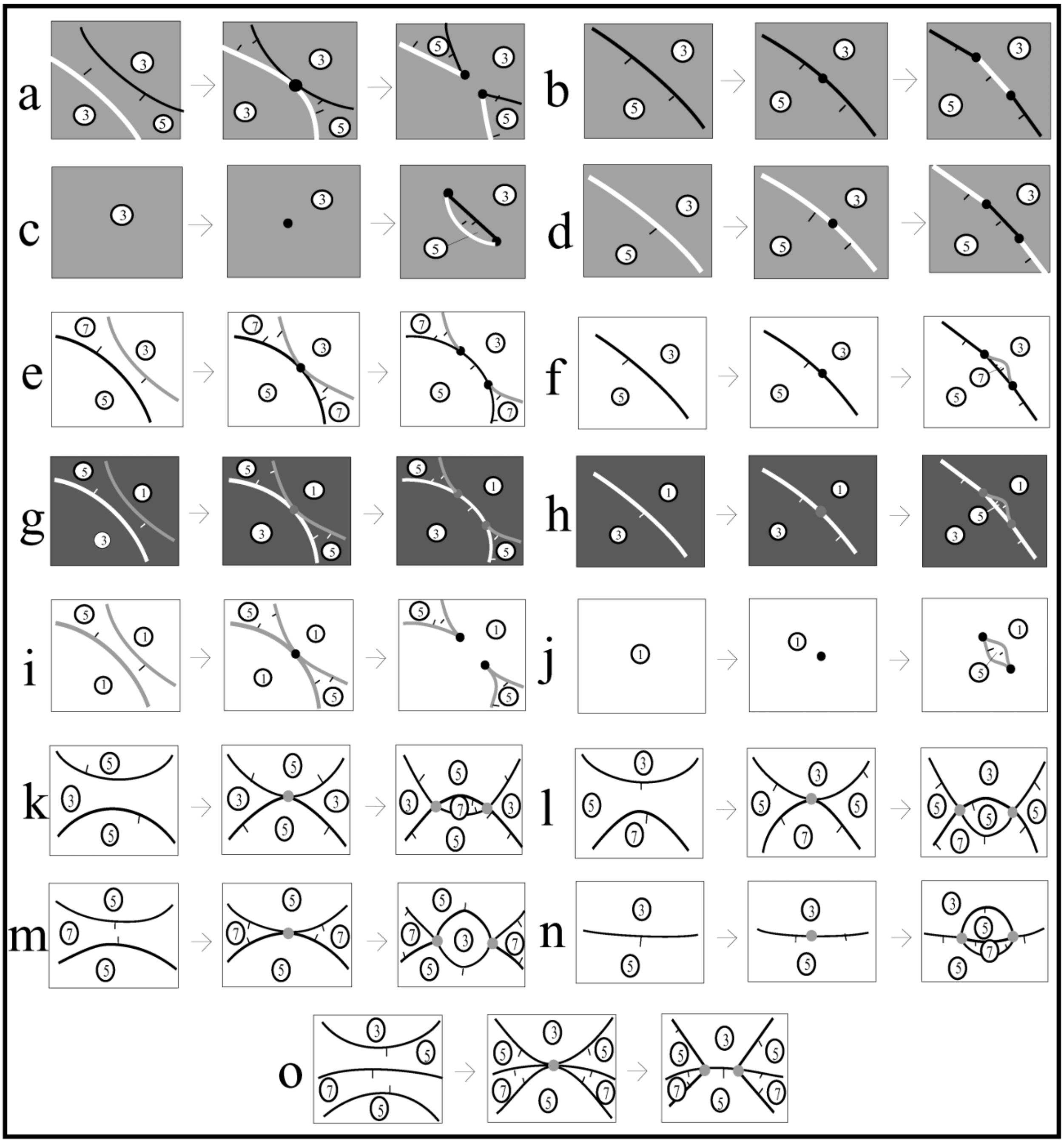

Fig. 9 Scenarios table III.

Notice that in this case there are two scenarios, depending of the coorientation of Σ (see Fig. 10b).

Examples. This phenomenon is pointed out by Boshkov[3] (see also Schneider[13]).

5.2 Tangential section by the (p,T) plane of the triple points and azeotropy surfaces

Our theoretical model applies in a similar way to the smooth part of Σ containing triple points and azeotropies. In ref. 6 there is an *azeotropic saddle point* described which corresponds to the hyperbolic case of tangential section of the azeotropy surface. We do not know evidences of the existence of the other corresponding phenomena. It would be interesting to investigate whether there are some physical reasons of the non-occurrence of such scenarios.

6 Yet another local variation of the (p,T)-diagram

For the sake of completeness, we mention another *local* phenomenon which may arise in the (p,T) diagram as an external parameter varies. It is the birth or death of a pair of an upper and a lower critical point in a critical line. This phenomenon is not included in the previous classification because the topology of the (p,T) diagram does not change. However, the topology of the (x,T) diagrams does change, *i.e.* the system experiences new behavior. For this reason this phenomenon separates different regions in the GPD.

In the (p,T) diagram the critical line has an inflection point with horizontal tangent. When the external parameter (λ) varies in one direction, a minimum and a maximum appear in the critical curve (expressed as $p = p(T)$). In terms of Σ, this point is a pleat of the projection of Σ on a plane p = constant (see Fig. 11).

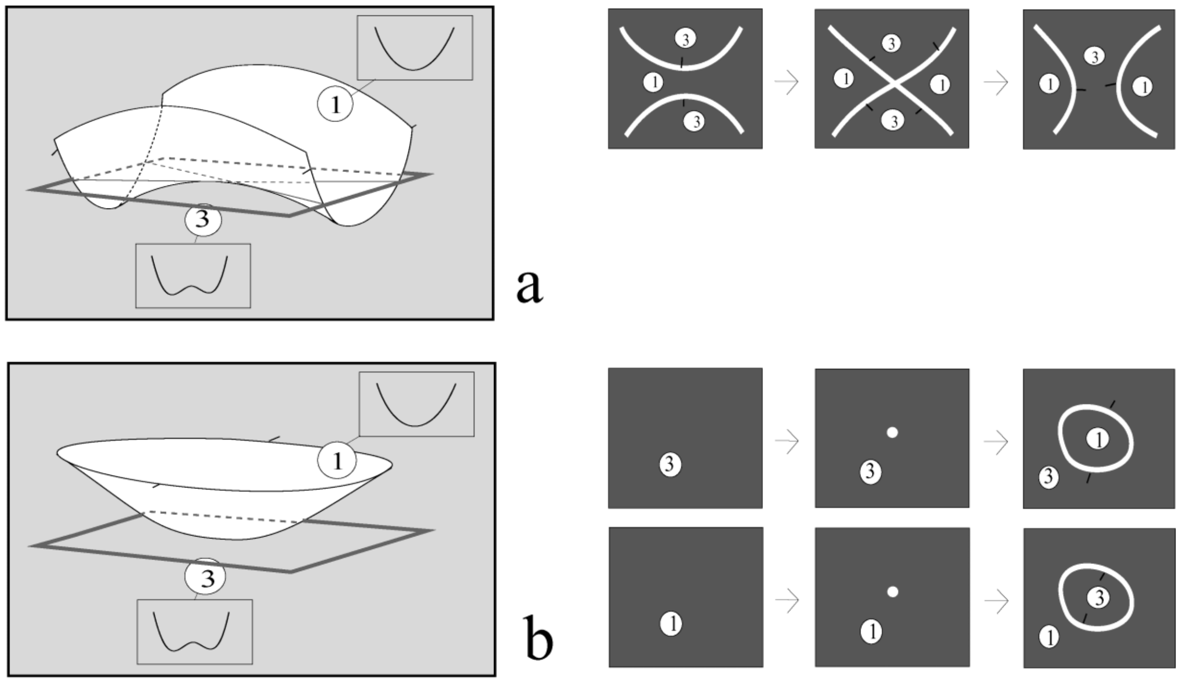

Fig. 10 Left: (p,T) plane tangent to (a) a locally hyperbolic surface, (b) a locally convex surface of critical points; right: corresponding scenarios.

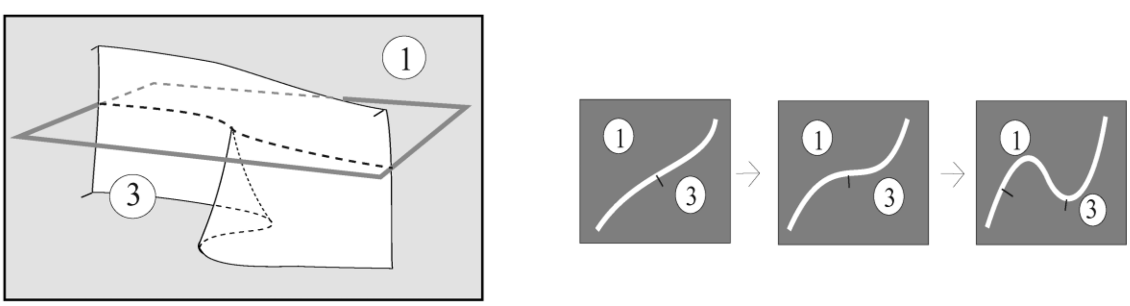

Fig. 11 Pleat of the projection of the critical points surface of Σ along the p direction and the corresponding scenario.

Of course, we could consider theoretically other similar (non-topological) variations of the (p,T) diagram implying a change, for example, in the (x,p) diagrams (*i.e.* when an inflection point of a codimension 1 line in the (p,T) diagram has a vertical tangent). We do not know, however, any example of this type.

Examples. This phenomenon separates regions III and III_m of the GPD in ref. 7 and 8. See also ref. 3.

Remark. An analogous phenomenon concerning the azeotropy surface is described in ref. 6, where it is called a *double azeotropic cusp*. A similar point for triple lines likely does not exist.

7 Conclusions

In this paper, we made a few steps into the systematic application of the methods of singularity theory to the local study of GPD. Here the GPD was the one-dimensional space of a parameter λ, which may have many different physical meanings: a parameter in a model (including the case when this parameter is the "time" in a contact transformation), a (smoothed) number of carbons in an homologous series, *etc*.

Several issues for which a similar approach should be relevant were not considered here. A natural sequel to this work would be to examine what happens in the neighborhood of the pure states $x = 0$ and $x = 1$. Furthermore, some non-local phenomena may occur when some singularity arrives from infi-

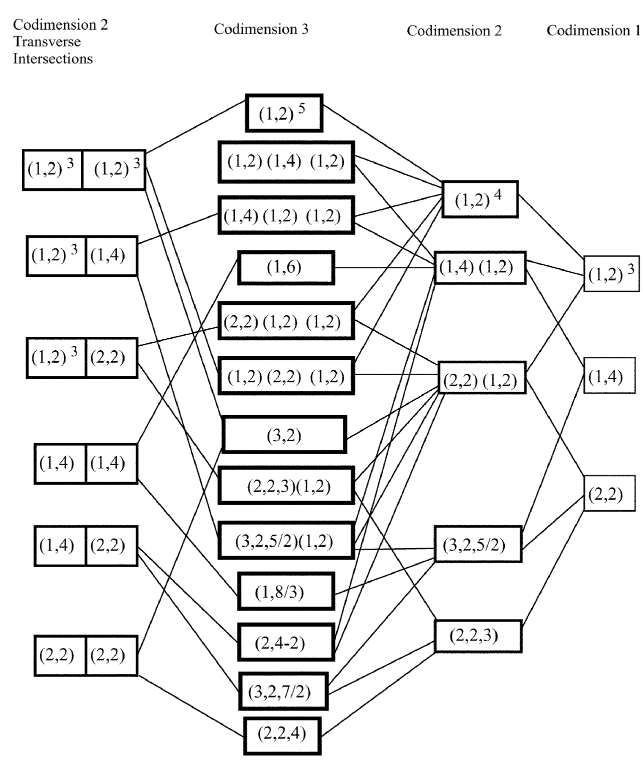

Fig. 12 Diagram of adjacencies for non-tangential singularities up to codimension three.

nity. Singularities of higher codimension have yet to be investigated.

Some of the singularities and the scenarios identified in this paper were missing in the previous classifications. A few of them can be observed in the published works about modeled and actual binary mixtures. We hope that experiment will lead to the observation of the remaining ones.

Appendix

We include here (Fig. 12) the diagram of adjacencies between the singularities discussed in this paper. It helps to present in a synthetic way the different items of the classification according to their codimension and to understand the relationships between them, *i.e.* how the different items piece together.

Acknowledgement

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