ON THE CLASSIFICATION OF GENERIC PHENOMENA IN THERMODYNAMIC BINARY MIXTURES

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ABSTRACT. A complete list of generic phenomena occurring in binary mixtures is given through the classification of singularities of convexification of two-parameter families of fronts. This work improves a preceding classification by Varchenko [Var90], adding to the list the birth of the azeotropy phenomenon by an exchange between a lower and an upper critical point. The occurrence of Legendrian singularities is also discussed.

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INTRODUCTION

An empirical list of generic phenomena occurring in binary mixtures was given by Landau and Lifchitz ([LL67]). A theoretical classification was firstly made by Varchenko ([Var90]) in a mathematical work probably unknown to most physicists. For example, in a recent classification by Nezbeda et al. ([NKS97]), the phenomenon of the birth of the double azeotrope, found by Varchenko, is missing (as well as in the Landau-Lifchitz list). The double azeotrope, although rare, do exist generically, (see [GS66]), and actually in a more recent work the phenomenon of its birth was pointed out in a model of binary mixture ([KNPS99]).

On the other hand, Varchenko's theory does not include another singularity of the Landau-Lifchitz list, and he concluded that this event is not generic. In fact, it is generic, and rather common in binary mixtures: it occurs when an azeotrope arises together with an exchange between an upper and a lower critical point. This singularity is called "critical azeotropic point" in [KNPS99] and [KNPS99]. I show in this paper that the theory of Varchenko, without a restriction he wrongly made, includes this singularity (which I called "wings").

The contact geometry in the last decades was successfully used to describe the properties of the equilibrium surfaces and to derive at once several facts of classical thermodynamics. An important result in contact geometry is that in contact spaces of dimension less or equal to 6 the singularities of Legendrian sub-manifolds (called Legendrian singularities) are simple (their mathematical model does not contain free parameters) and their list is finite. This implies that a priori in a thermodynamic mixture with at most 4 components we know all possible types of critical events that may generically occur ([AVSZ82]). However, this list has to be drastically reduced, as I remarked in [AFV00]: most singularities have no physical relevance,

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because they happen in the instability domain. In particular, in binary mixtures all singularities of maximal codimension are not detectable.

The main theoretical models of binary mixtures are the Van der Waals equation and their derivations. A seminal paper on this subject is the work of Konynenburg and Scott, where a whole set of Van der Waals systems (depending on three external parameters) is investigated. It is interesting to observe that such systems feature all possible singularities allowed by the theory but one: the birth of double azeotrope. In section 4 I shall use this model for different purposes: firstly (4.1), to verify the behavior, theorically predicted, of the thermodynamic potential near the wings-singularity; secondly (4.2), to show the presence of the 'invisible' A_4 singularity in some systems considered in [KS80] and to detect the occurrence of the A_5 singularity as a non generic event, namely appearing in some systems with particular values of parameters.

1. Phase-diagrams and Gibbs potential

Warnings. Throughout this paper, the vocabulary of contact geometry is used, mainly in some remarks which are clearly identified, and which the reader can skip. The interested reader might consult [AG90] for further details. The word *surface* is used for objects which are not necessarily of dimension 2.

In the pressure-temperature diagram (phase-diagram) of a one-component thermodynamical system, a line corresponds to a phase-change, the end-point of a line corresponds to a critical point and the meeting-point of three lines corresponds to a three-phase equilibrium.

Thermodynamical systems which consist in one mole of mixtures of two components are also described by pressure-temperature diagrams, where the loci of critical points, (resp. of azeotropies, of triple points) appear as lines.

To every point of the (p, T)-plane there corresponds an entire interval of equilibrium states, characterized by the molar fraction x of one of the components. The analogue of the one-component system phase-diagram is a partition of the 3-dimensional (p, T, x)-space by a two-dimensional surface in, which separates the regions of homogeneous equilibrium from those of the heterogeneous one. I shall refer to this surface as *C-surface*.

By classifying the generic phenomena of binary mixtures, I mean the description of all local features of such three-dimensional phase-diagrams which are stable up to small changes in the external parameters of the system.

The equilibrium states of a thermodynamical mixture with a fixed number of molecules form a 3-dimensional surface in the space M of dimension seven, whose coordinate are the extensive variables (volume V, entropy S and molar fraction x of the second component), the intensive conjugate variables (the pressure p, the temperature T, and the difference of chemical potentials $\mu_2 - \mu_1$ of the two components) and the internal energy U. *Remark.* The space M may be viewed as a *contact space*: the *contact* differential one-form, whose zeros define a field of hyperplanes on M, is nothing but the Gibbs form:

$$\alpha = dU - TdS + pdV - (\mu_2 - \mu_1)dx$$

The tangent space at each point of the equilibrium surface is contained in the contact hyperplane through this point. Such 3-dimensional surfaces are called *Legendrian.*

The graph of the internal energy in terms of the extensive variables, i.e. the projection of the Legendre sub-manifold to the (V, S, x, U)-space, is what is called the *front* of this Legendrian surface.

The internal energy U of the homogeneous equilibrium states is a smooth true function (i.e. one-valued) of the extensive variables. A point on the graph of the internal energy represents a state of stable equilibrium if the tangent plane at that point does not intersect the surface in other points. The points where the graph is locally but not globally convex represent metastable equilibria and those where the graph is non convex represent non stable equilibria. The entire set of stable equilibria is described by the convexified graph of the internal energy: the points where the convex envelope of the graph do not coincide with the graph represent heterogeneous equilibria.

The Gibbs potential G of the homogeneous equilibrium states is the Legendre transform of the internal energy with respect to the variables V and S. It is a multivalued function (whose graph might be singular) of the variables p, T and x.

Remark. In the language of contact geometry, the graph of the Gibbs potential is the front of a surface which is Legendrian with respect to the contact form $dG - Vdp + SdT - (\mu_2 - \mu_1)dx = 0$.

Denote by $G[p,T](x)$ the multivalued function of one variable x, obtained from G when p and T are fixed. Denote by $G[p,T]_{\bar{x}}$ the true function of x obtained after convexification of $G[p,T](x)$. The three dimensional phase diagram is separated into regions by the surface made of all points (p,T,x) such that the graph of $G[p,T]_{\bar{x}}$ is not smooth above x (these x correspond to the endpoints of the segments that were added in the convexification of $G[p,T]$). Since we have a 2-parameters (p and T) family of convexified functions, the classification of generic phenomena encountered in binary mixtures is reduced to the classification of the singularities of codimension one and two of the convex envelopes of sections of one-dimensional fronts. Varchenko studied families of smooth fronts. It is remarkable that this suffices to interpret all singularities but one.

2. The classification of singularities

2.1. Definition of Varchenko's singularities. Consider a set of smooth bounded functions $y = f_i(x)$ defined on $\mathbb{R}$ and convex outside an interval I. The convex hull of this set is the intersection of all half-planes which contain this set. The convex envelope $y = \bar{f}(x)$ is the function associating to x the minimum value of y of the convex hull on x (see fig 1).

At generic points where $\bar{f}(x)$ is locally convex the tangent line has a contact of order two with the graph of $\bar{f}(x)$, and no other points of the graph belong to this line. In the generic situation the graph of $\bar{f}(x)$ is subdivided into arcs and segments by a set of singular points. Also the interval I is thus subdivided into sub-intervals by the x-coordinates of the singular points. Consider the case where $\bar{f}(x)$ depends on some continuous parameters: higher codimension events are constituted by points where the order of tangency with the tangent line is bigger, or by the presence of a set of points (possibly coinciding) with a common tangent (having possibly different orders of tangency) belonging to the convex envelope. In figure 2 events of different codimensions are shown.

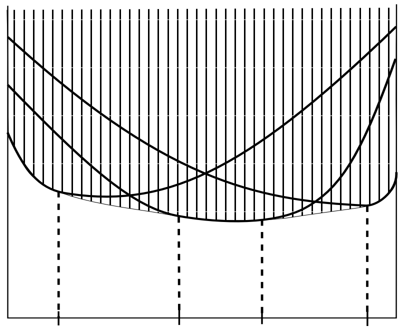


FIGURE 1. Three smooth functions on a interval, their convex hull (dashed domain) and the C-singularities of its convex envelope projected (dashed lines) on the interval

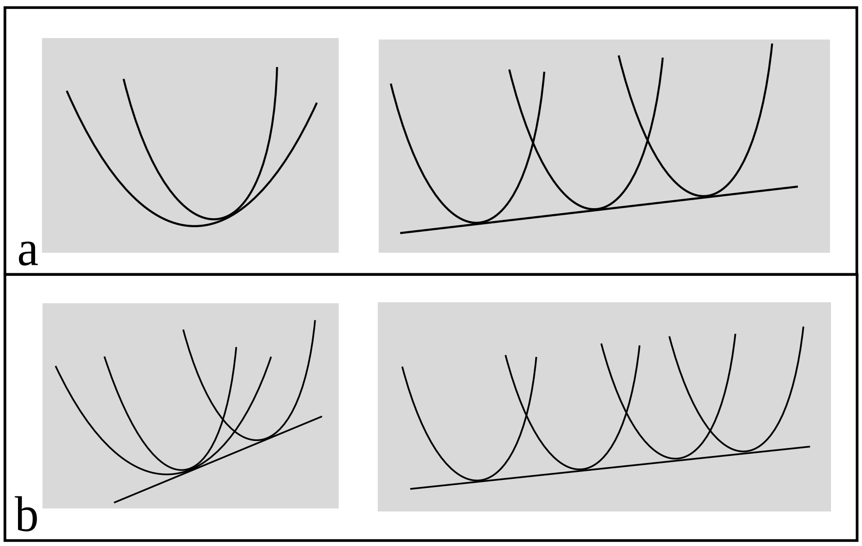


FIGURE 2. Singularities of codimension one (a) and of codimension two (b)

Varchenko proved that if $\bar{f}(x)$ depends on two parameters, the list of generic phenomena contains, besides the codimension zero situations, three codimension-one singularities (fold, double fold and dihedral angle) and four singularities of codimension two (double pleat, trihedral angle, split-pleat tail and dove).

I shall analyze all these singularities (and the missing "wings") for binary mixtures, where the two parameters are the pressure and the temperature, x is the molar fraction of the second component and $\bar{f}(x)$ is the Gibbs potential.

2.2. **The list of generic phenomena.** Consider a generic (p, T)-diagram. To every generic point there corresponds a particular $G[p, T]_{\bar{x}}(x)$, containing a number m of disjoint straight segments due to the convexification, and $2m$ singular points (their extremes). The projection of these points to the $[0, 1]$ interval of the x variable subdivide this interval in $k = 2m + 1$ segments, to which there correspond $m + 1$ homogeneous phases and m non homogeneous ones. These points actually define the C-surface of the phase diagram over the (p, T)-plane. When one moves

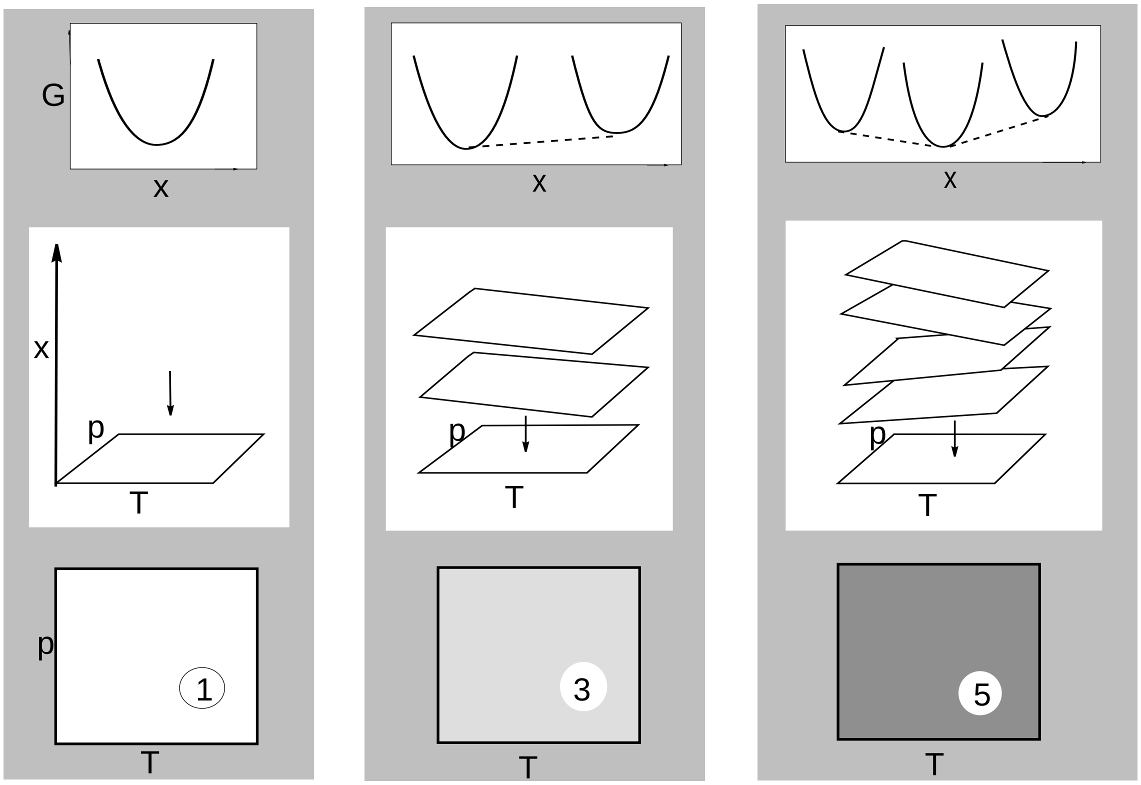


FIGURE 3. The generic point. Examples with $m = 0, 1, 2$. (*top*: the convexified potential, *middle*: the $2m$-sheeted surface over the generic point, *bottom*: the (p, T)-diagram)

along 1-dimensional path on this plane, one encounters generically - by definition - singularities of codimension 1 in the potential: the number $2m$ of singular points changes and consequently also the shape of the C-surface. The loci of these codimension one points form curved segments on the (p, T)-plane, whose end-points correspond to singularities of codimension two. Over such points the surface can be rather complicated: the number m varies in different ways along different paths on the (p, T)-plane which go trough the point of codimension two. To have a better understanding of the form of the surface over these points, I give pictures of its local shape and also pictures of its generic sections by planes containing the x-direction. I obtain in this way the pictures of generic local features of (x, T) or (x, p)-diagrams, to which physicists are more accustomed. (Following an old tradition, the regions of heterogeneous phases are filled by horizontal lines).

Codimension zero. The surface over a generic point is $2m$-sheeted. The number of phases (the odd k) is marked on the (p, T)-diagrams, and to each k there corresponds a gray-color code (darker color corresponds to bigger k). See figures 3 and 4.

Codimension 1. The codimension one singularities of the C-surface (corresponding to codimension one singularities of the convexified potential) projects on lines of the (p, T)-plane. The number k jumps at these lines: it is always possible to provide these lines with a *coorientation*, defining positive the side of the plane where k is bigger. In the figures the positive side is signaled by small strokes (hence pointing towards the darker region). The three types of codimension-one singularities are:

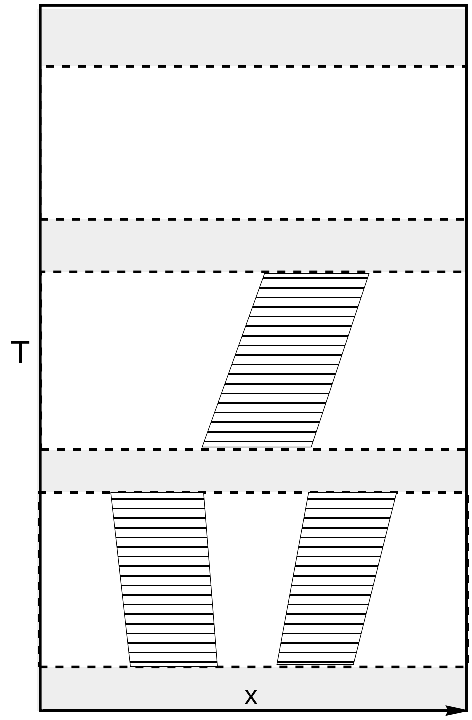


FIGURE 4. The (x, T)-diagram over a generic point

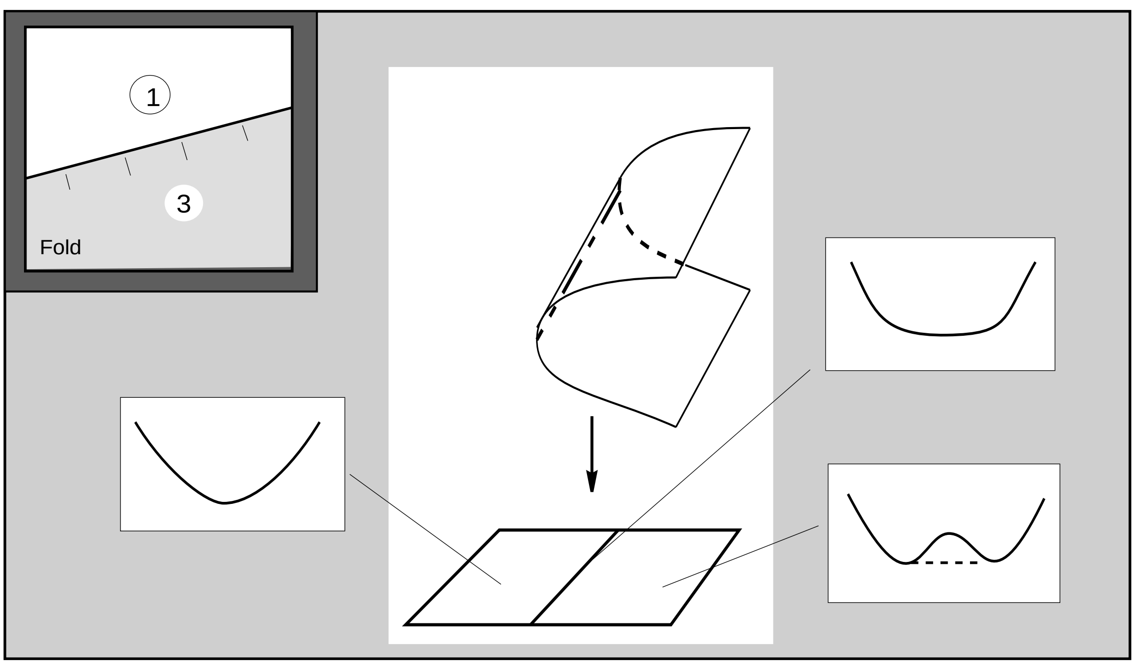


FIGURE 5. The fold. *Top-left*: the (p, T)-diagram; *centre*: the C-surface over the (p, T)-plane; *small boxes*: the convexified potential

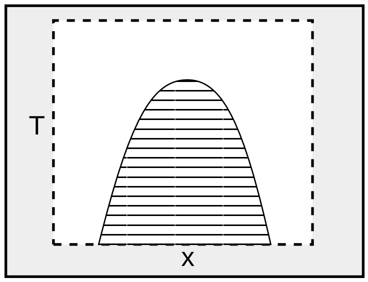


FIGURE 6. The (x, T)-diagram, section of the C-surface containing the critical point

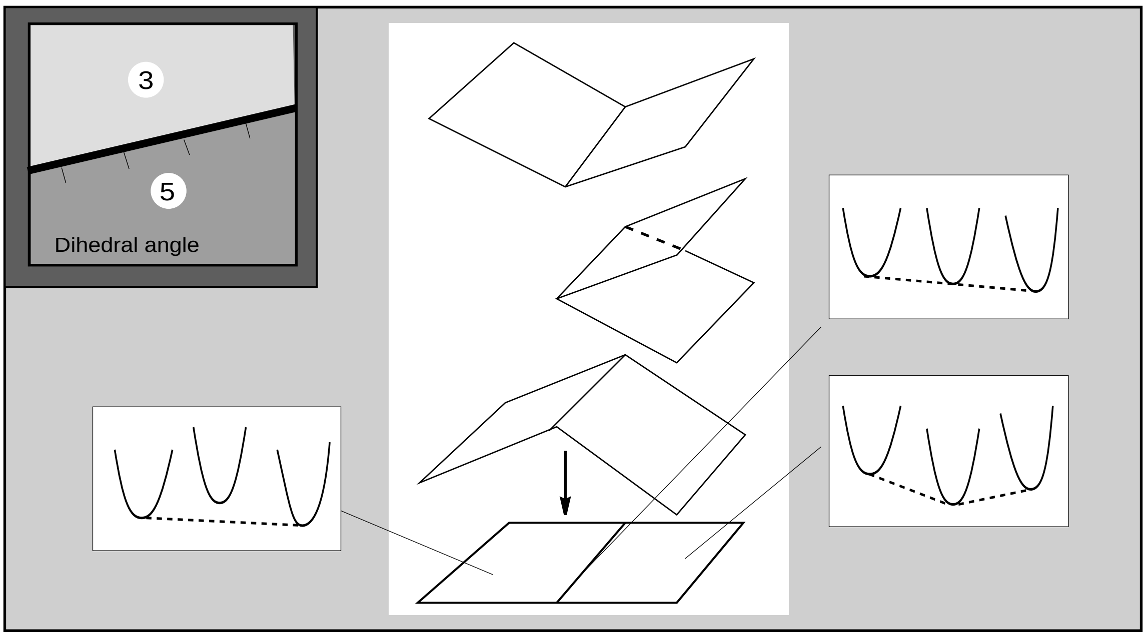


FIGURE 7. The dihedral angle. *Top-left*: the (p, T)-diagram; *centre*: the C-surface over the (p, T)-plane; *small boxes*: the convexified potential

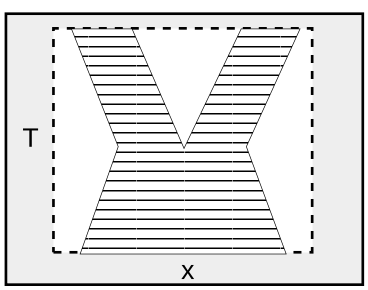


FIGURE 8. The (x, T)-diagram, section of the C-surface containing the triple point

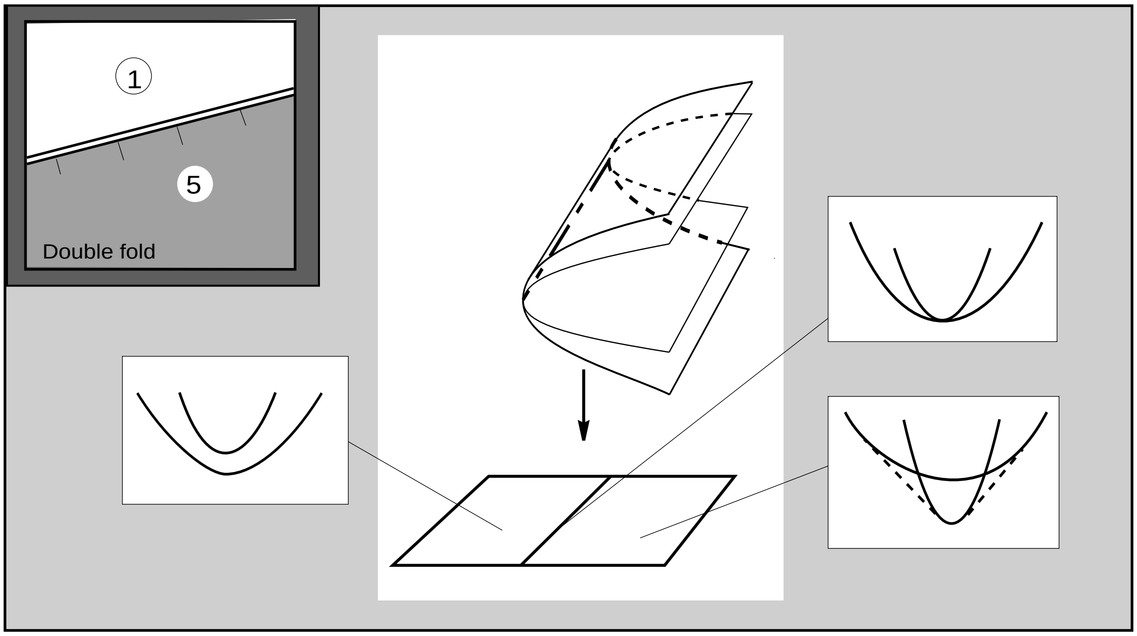


FIGURE 9. The double fold. *Top-left*: the (p,T)-diagram; *centre*: the C-surface over the (p,T)-plane; *small boxes*: the convexified potential

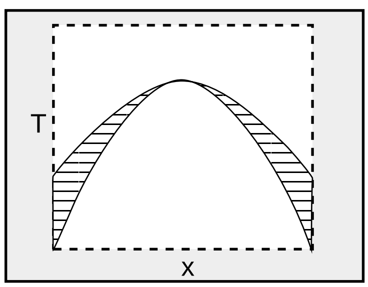


FIGURE 10. The (x,T)-diagram, section of the C-surface containing the azeotrope point

- I-1) *Fold.* Known as **critical point**, this event happens when the locally convex $G[p,T](x)$ stops being convex giving rise to a pair of inflection points. The convexified potential contains, after this event, the straight segment of the born heterogeneous phase (see figure 5). In the generic sections of the surface containing the x direction (ex. $p = \text{const}$, see figure 6) the critical point is a maximum or a minimum of the curve bounding the heterogeneous domain. It is called respectively upper or lower critical point.
  Remark. This singularity is the A_3 Legendrian singularity (see section 3).
- I-2) *Dihedral angle.* This singularity is known as **triple point** or three-phase equilibrium. It happens when in the potential there are three different points with a common tangent, all belonging to the convex envelope. The C-surface is composed of three dihedral angles over the triple point line. The system passes from k phases to $k+2$ phases when the (p,T) point crosses the line of triple points (see figures 7 and 8).

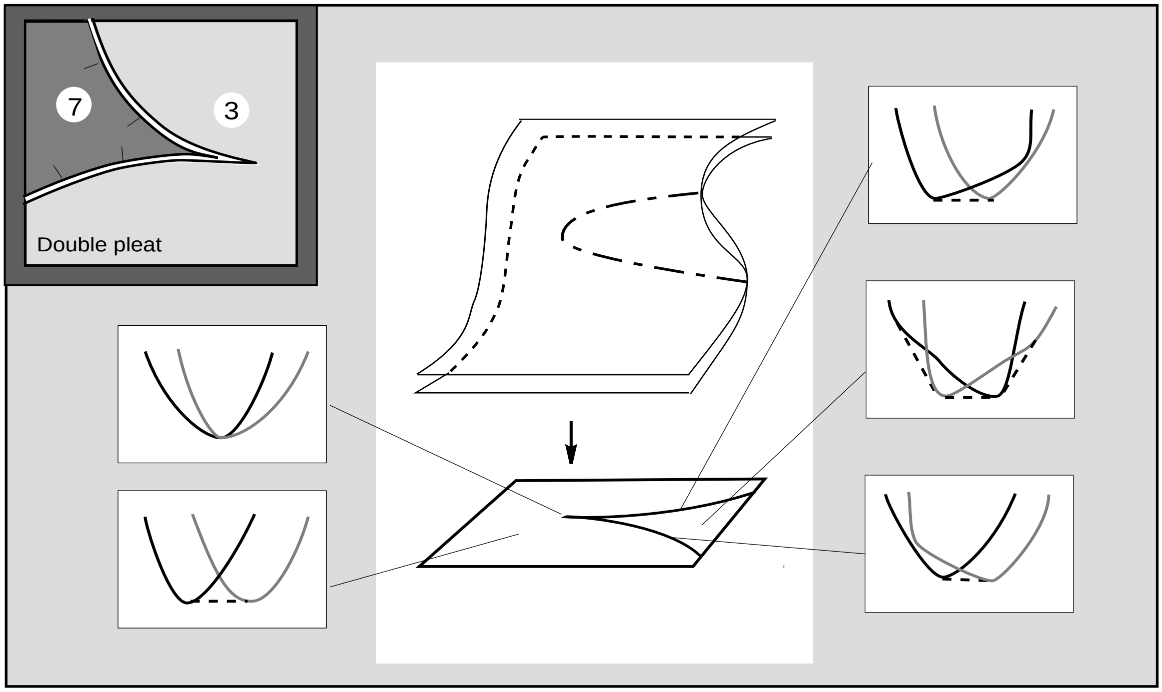


FIGURE 11. The double pleat. *Top-left corner*: the (p,T)-diagram; *centre*: the C-surface over the (p,T)-plane; *small boxes*: the convexified potential

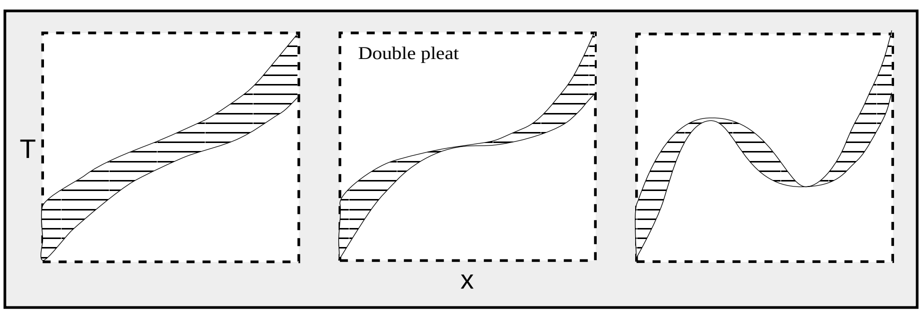


FIGURE 12. The (x,T)-diagrams, sections of the C-surface containing the birth of double azeotrope

- I-3) *Double fold.* This phenomenon is known as **azeotropy**. It happens when two convex branches of the potential become tangent each other. The lower potential stops being convex giving rise to two convexifying segments. The systems passes from k phases to $k+4$ phases, when the (p,T) point crosses the line of azeotropies (see figures 9 and 10).

  Codimension 2. The codimension two singularities of the C-surface (corresponding to codimension two singularities of the convexified potential) project on points of the (p,T)-plane. There are five types of such singularities:
- II-1) *Double pleat.* This phenomenon corresponds to the **birth of the double azeotrope**. It happens when two branches of the potential experience a second order tangency. The system, varying the pressure or the temperature, passes

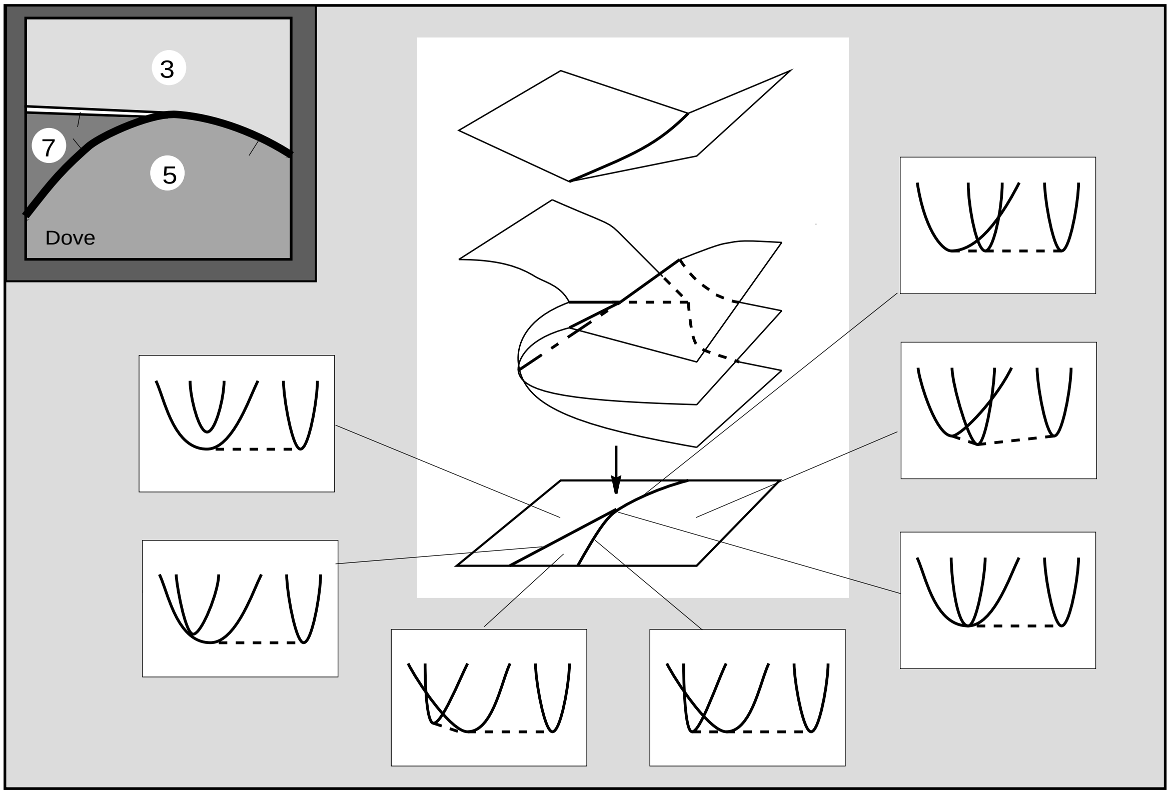


FIGURE 13. The dove. *Top-left*: the (p, T)-diagram; *centre*: the C-surface over the (p, T)-plane; *small boxes*: the convexified potential

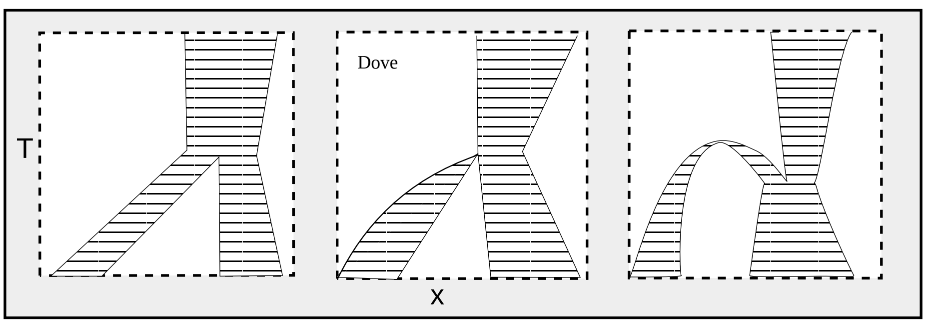


FIGURE 14. The (x, T)-diagrams, sections of the C-surface containing the birth of azeotrope from a triple points line

at this point from $k + 2$ to $k + 6$ phases (see figure 11). The generic section of the C-surface containing the x direction avoids the tangent to the azeotrope line in the (p, T)-plane at the singular point (figure 12).

- II-2) *Dove*. This singularity corresponds to the **birth/death of an azeotropy in a triple point line**. It happens when in the graph of the potential two adjacent points of the three points having a common tangent do coincide, giving rise to a mutual tangency of two branches, responsible of the azeotropy (see figure 13). On the (p, T)-plane, the azeotrope line at its end is tangent to the triple point line, which reverse the coorientation at the dove singularity. The

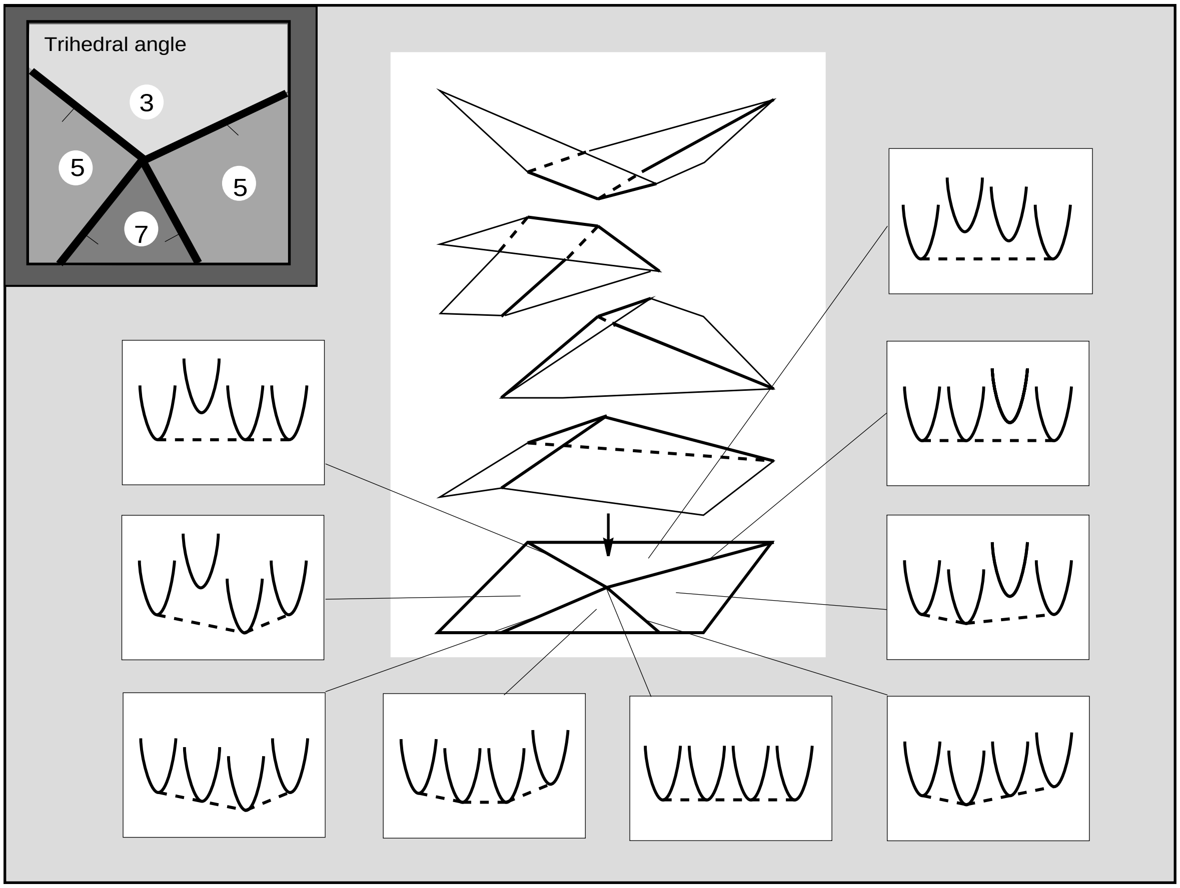


FIGURE 15. The trihedral angle. *Top-left*: the (p, T)-diagram; *centre*: the C-surface over the (p, T)-plane; *small boxes*: the convexified potential

generic section of the C-surface containing the x direction avoids the tangent to the triple points line in the (p, T) plane at the singular point (figure14)

- II-3) *Trihedral angle*. This singularity corresponds to the **quadruple point or four-phases equilibrium**. In the graph of the potential there are four different points having the same tangent line, all belonging to the convex envelope. At the singular point four three-phases lines meet, each of which is the projection on the (p, T)-plane of three dihedral angles, belonging to three of the four trihedral angles which form the C-surface (see figure 15). In this case there are three different generic types of sections of the C-surface containing the x direction (figure 16).
- II-4) *Split-pleat tail*. This singularity corresponds to the **birth or death of a critical point at the birth of a triple point**. In the graph of the potential, two adjacent points of three points with a common tangent merge in a point (fold) with a contact of order four with the tangent line. The surface over the singularity is (k+2) sheeted and (k+4) sheeted over an angle, which may reach π (it is acute in figure 17). There are two types of generic sections of the C-surface, containing the x direction, as shown in figure 18. In the first case the triple point and the critical points coexist and both disappear at the

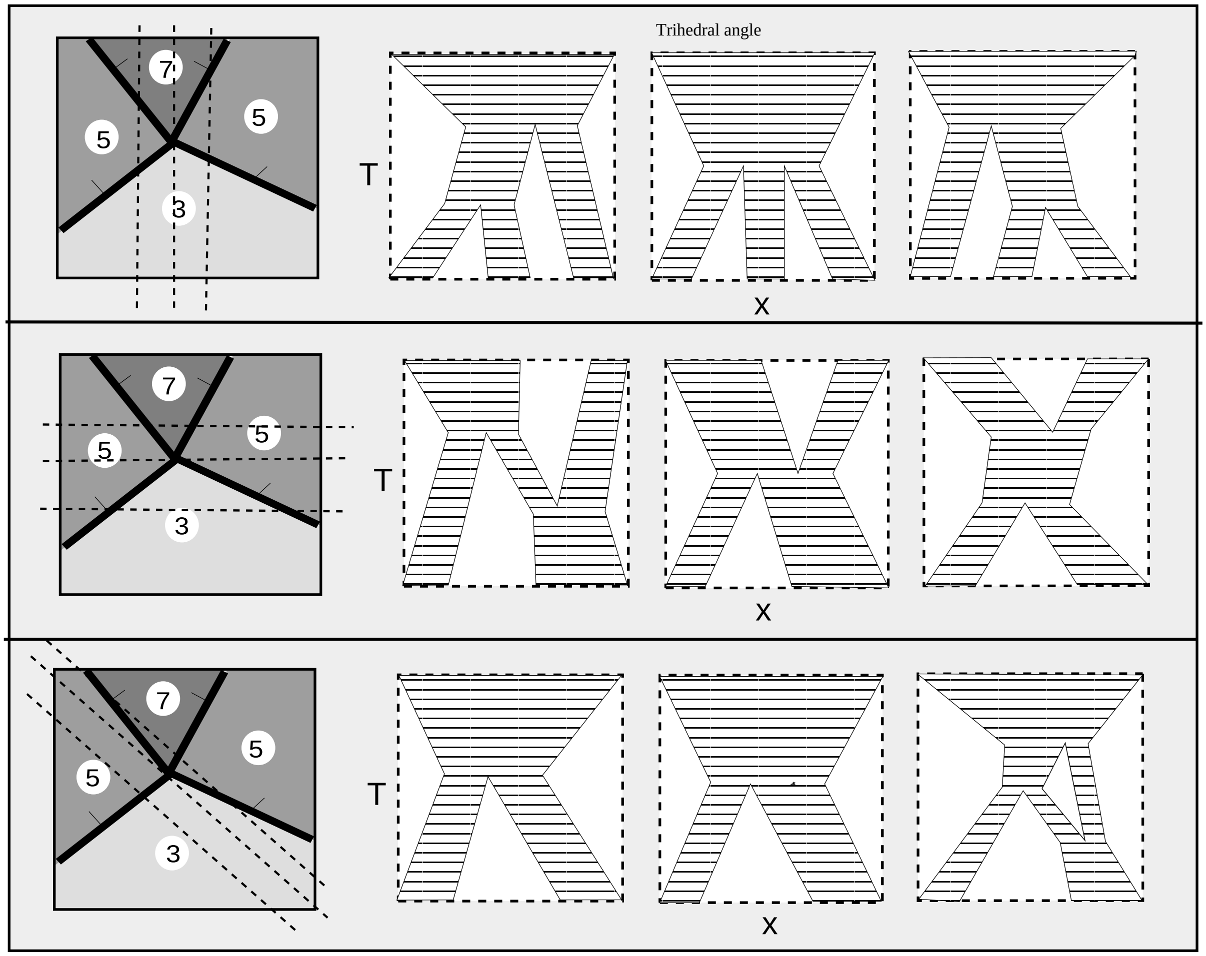


FIGURE 16. The (x, T)-diagrams, sections of the C-surface containing the quadruple point singularity

singularity, in the other one the critical point disappears and a triple point appears.

- II-5) *Wings*. This singularity happens when a **upper-critical (lower-critical) point disappears at a lower-critical (upper-critical) point appears together with an azeotrope**. The surface has a double-fold line which ends in a fold line. On the (p, T)-plane at the wings point the double fold (azeotrope) line ends and it is tangent to the critical line. The coorientation of the critical line reverses at the singular point. The graph of the potential experiences a singularity of fronts: a cusp point belonging to the interior of the convex hull become tangent to a locally convex branch, belonging to the convex envelope. Many singularities in the graph of the potential in the neighborhood of the wings are invisible because they belong to the interior of the convex hull and do not affect the convex envelope (see figure 19). A generic section of the C-surface containing the x direction does not contain the tangent to the critical line at the wings point (see figure 20).

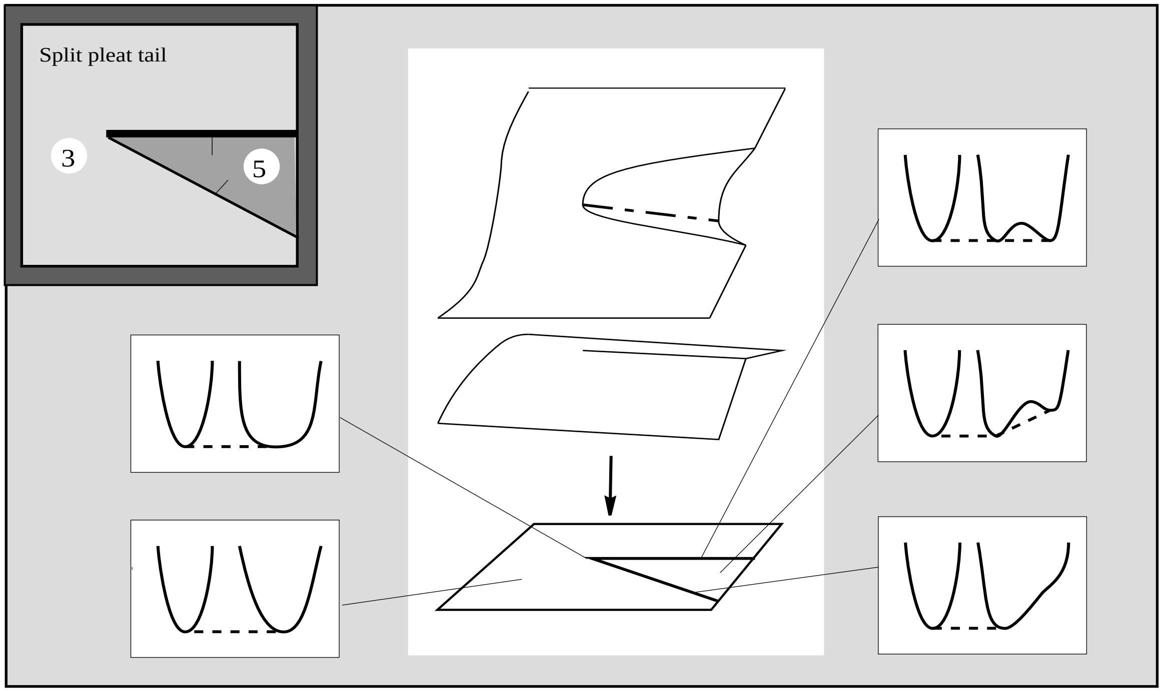


FIGURE 17. The split-pleat tail. *Top-left*: the (p,T)-diagram; *centre*: the C-surface over the (p,T)-plane; *small boxes*: the convexified potential

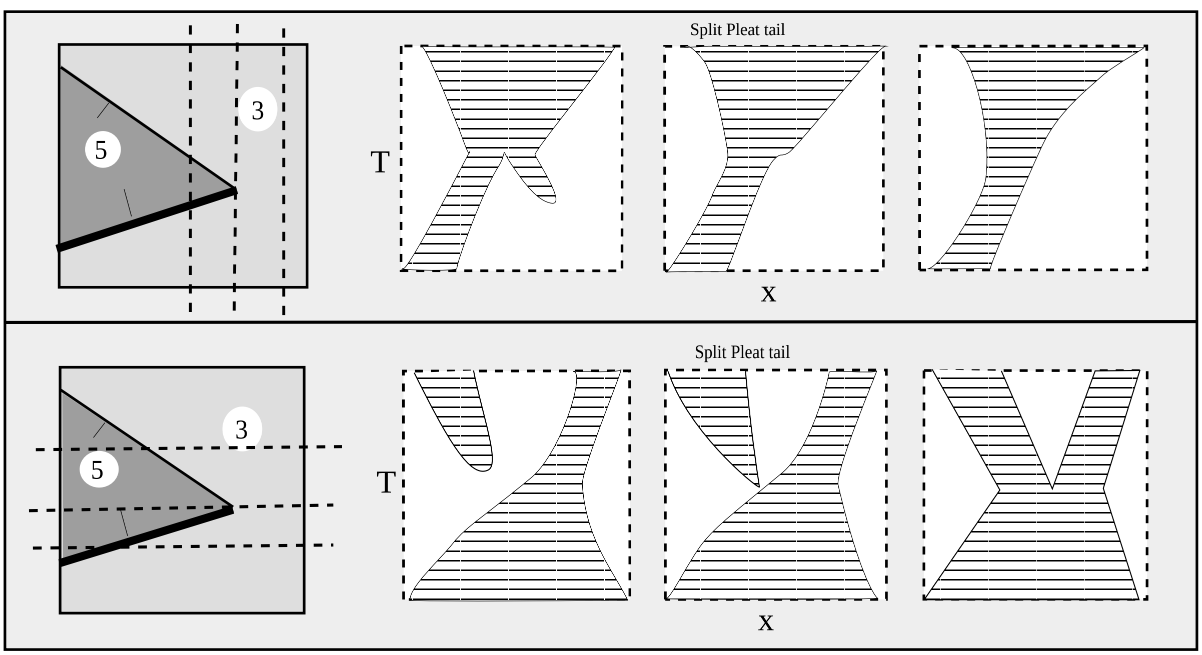


FIGURE 18. The (x,T)-diagrams, sections of the C-surface showing (top) the death of a critical point together with a triple point and (bottom) the death of a critical point with the birth in a triple point

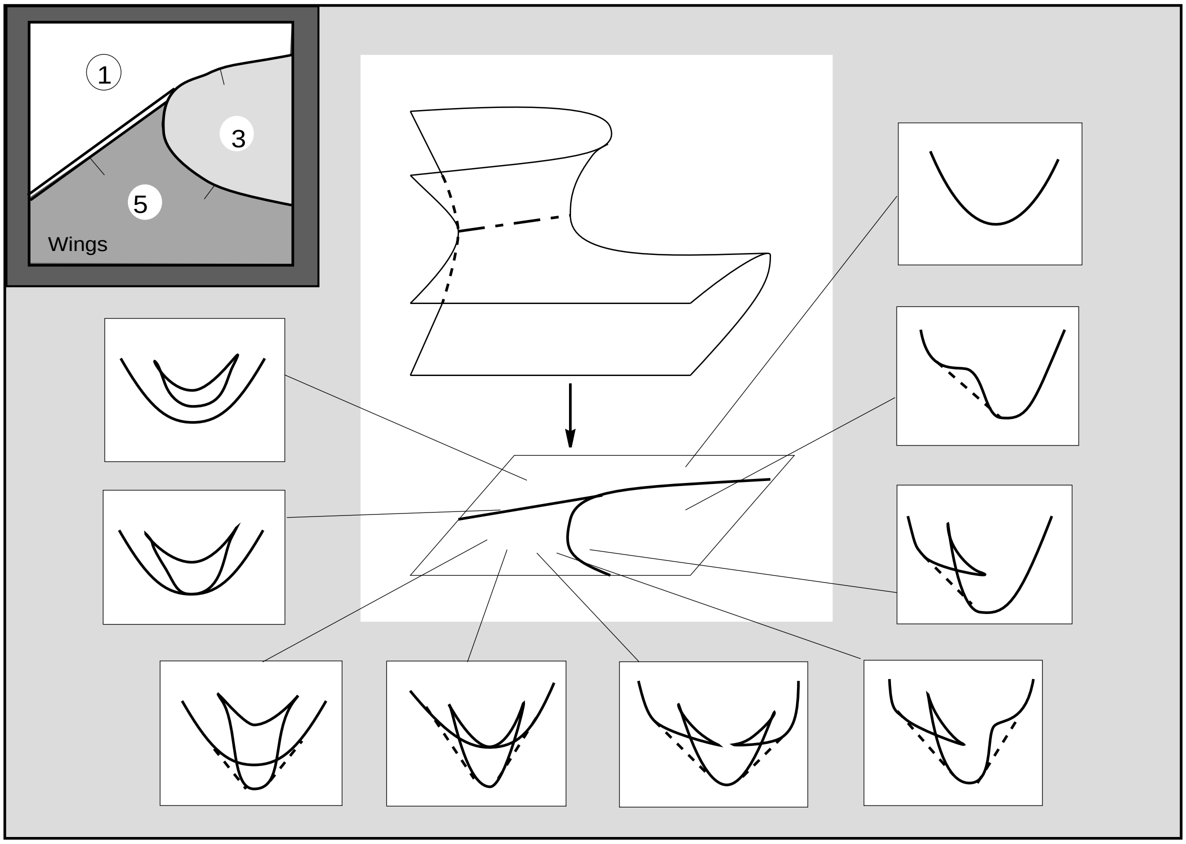


FIGURE 19. The wings. *Top-left*: the (p,T)-diagram; *centre*: the C-surface over the (p,T)-plane; *small boxes*: the convexified potential

3. Legendrian singularities

In the energy description the equilibrium states of a mole of a binary mixture consist in a 3d-surface L, graph of the internal energy U in terms of the extensive variables V (volume), S (entropy) and x (molar fraction of the second component). The stable equilibrium states consist in the convex envelope $\bar{L}$ of this graph. A point of the convex envelope represents a homogeneous equilibrium if the graph of the internal energy is locally convex, a heterogeneous equilibrium otherwise (the graph is locally a ruled surface or a hyperplane). In the contact space M, with the

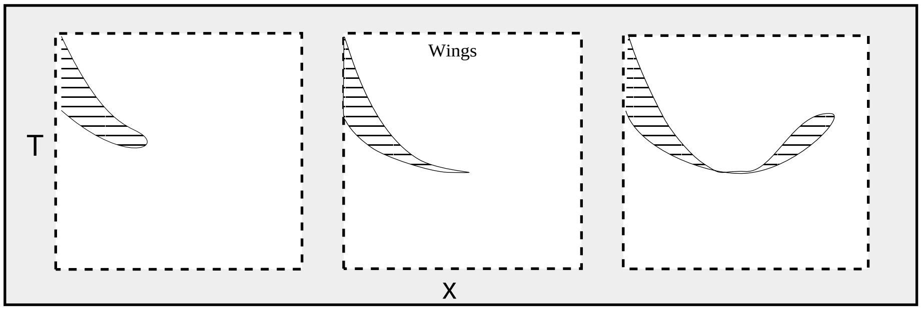


FIGURE 20. The (x, T)-diagrams, sections of the C-surface showing the death of a lower-critical point and the birth of an azeotrope together with an upper-critical point

additional intensive variables $p = -\partial U/\partial V$, $T = \partial U/\partial S$, $\mu_2 - \mu_1 = \partial U/\partial x$, the 3-d equilibrium surfaces are represented by Legendrian sub-manifolds $\mathfrak{L}$ and $\bar{\mathfrak{L}}$. Remind that $\mathfrak{L}$ is smooth, whereas $\bar{\mathfrak{L}}$ is non smooth because of convexification.

Legendrian singularities occur at those points of $\mathfrak{L}$ where the Hessian determinant of internal energy vanishes. Since in a neighborhood of such points the sign of the Hessian determinant changes, a singular point cannot belong to the interior of the homogeneous domain, where U is locally convex: a Legendrian singularity is always located at the boundary of a locally convex domain. On the other hand, after convexification a point represents a stable equilibrium only if it belongs to the convex envelope of the internal energy, hence a *'stable'* Legendrian singular point must belong also to $\bar{\mathfrak{L}}$ and it is therefore located on the C-surface separating the homogeneous from the heterogeneous states.

The generic Legendrian singularities of a 3-dimensional sub-manifold have codimension 1, 2 or 3. They are given by the following list [AG90]: A_2 (codimension 1); A_3 (codimension 2); A_4, D_4^+ and D_4^- (codimension 3). After the convexification the singularities of type D_n disappear (being located always at the interior of the complement of the elliptical domain); whereas the A_n singularities survive to the convexification only if n is odd (see [AFV00]). Therefore, in binary mixture we can see, generically, only the A_3 singularity. Such singular points form lines in the C-surface, namely the fold lines of critical points of the mixture.

4. Singularities in Van der Waals systems

In this section I utilize a 3-parameter family of Van der Waals models analyzed by Konynenburg and Scott ([KS80]) to investigate the presence of generic singularities.

The Van der Waals equation of state for a mole of binary mixture is

$$p = \frac{RT}{V - b(x)} - \frac{a(x)}{V^2} \tag{1}$$

where R is the molar gas constant, x is the mole fraction of the second component, and the function $a(x)$ et $b(x)$ are

$$a(x) = (1-x)^2 a_{11} + 2(1-x)x a_{12} + x^2 a_{22},$$

$$b(x) = (1-x)b_{11} + x b_{22}.$$

Constants a_{11} and a_{22} measure the attractive forces between pairs of molecules of the pure components 1 and 2, respectively, and a_{12} is the corresponding parameter for the interaction between molecules 1 and 2. Constants b_{11} and b_{22} are size parameters for the pure components.

According to [KS80], the three non dimensional parameters that characterize the Van der Waals model are:

$$\xi = \frac{(b_{22} - b_{11})}{(b_{11} + b_{22})}$$

$$\zeta = \frac{(\frac{a_{22}}{b_{22}^2} - \frac{a_{11}}{b_{11}^2})}{(\frac{a_{22}}{b_{22}^2} + \frac{a_{11}}{b_{11}^2})}$$

$$\Lambda = \frac{(\frac{a_{22}}{b_{22}^2} - \frac{2a_{12}}{b_{11}b_{22}} + \frac{a_{11}}{b_{11}^2})}{(\frac{a_{22}}{b_{22}^2} + \frac{a_{11}}{b_{11}^2})}$$

In fact, these parameters are functions of the ratios $m = a_{22}/a_{11}$, $n = a_{12}/a_{11}$ and $k = b_{22}/b_{11}$, so that the Van der Waals equation written in terms of the non dimensional variables $\mathtt{p}$, $\mathtt{T}$ and $\mathtt{V}$, given by:

$$\mathtt{p} = \frac{27b_{11}^2}{a_{11}}p \quad \mathtt{T} = \frac{27Rb_{11}}{8a_{11}}T \quad \mathtt{V} = \frac{1}{b_{11}}V$$

becomes

$$\mathtt{p} = \frac{8\mathtt{T}}{\mathtt{V} - b(x)/b_{11}} - \frac{27a(x)/a_{11}}{\mathtt{V}^2} \tag{2}$$

which depends only on the three parameters m, n and k.

Konynenburg and Scott analyzed [KS80] the behavior of system (1) varying the values of parameters ξ, ζ and Λ. The classification of the different kinds of behavior they gave, based on the global features of the (p, T)-diagrams, became standard in the literature on the binary mixtures.

¿From the point of view of singularities, varying the parameters values, the system (1) exhibits all the generic phenomena listed in the previous section, with the exception of the double pleat (the birth of the double azeotrope). The presence of the double azeotrope is quite rare in binary mixtures (it was experimentally found in 1966 [GS66]): this justifies the absence of the double pleat in the Landau-Lifchitz empirical classification.

4.1. **The Wings-singularity.** I am moreover specially interested in the wings singularity, the new singularity from the theoretical point of view. It is well visible in the (p, T)-diagrams of systems of type I-A, II-A, III-A, V-A in [KS80] (i.e., in all cases with azeotropy), where a single azeotrope line ends meeting a critical line.

One can indeed verify that the Gibbs potential is actually of the form given in figure 19 in a neighborhood of the singular point. Consider, for example, the system with $\zeta = -.263$, $\Lambda = -.579$ and $\xi = 1/3$. In the (p, T)-diagram of figure 41 in [KS80] a wings-singularity is visible for non dimensional pressure and temperature $\mathtt{p} = 0.82$ and $\mathtt{T} = 1.37$. For values of $\mathtt{p}$ and $\mathtt{T}$ indicated by a black circle in figure 21, the non dimensional Gibbs potential $\mathtt{G}[\mathtt{p}, \mathtt{T}](x) = G[p, T](x)/RT$ is calculated according to the formulae:

$$\mathtt{G}[\mathtt{p}, \mathtt{T}](x) = \ln \lambda_1(x)(1 - x) + \ln \lambda_2(x)x$$

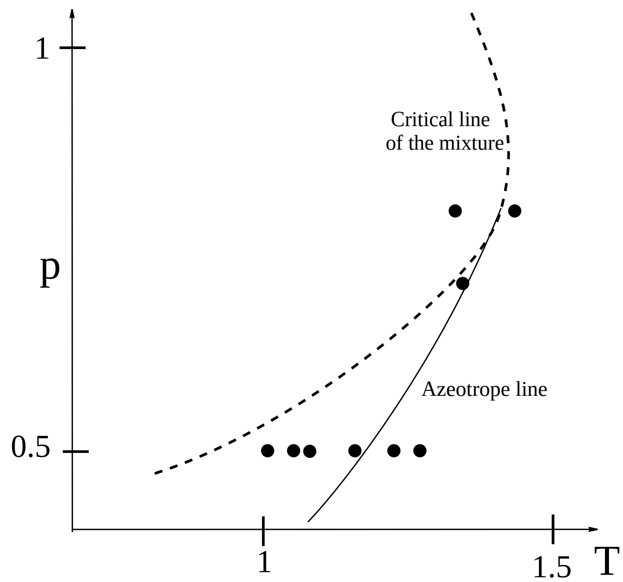
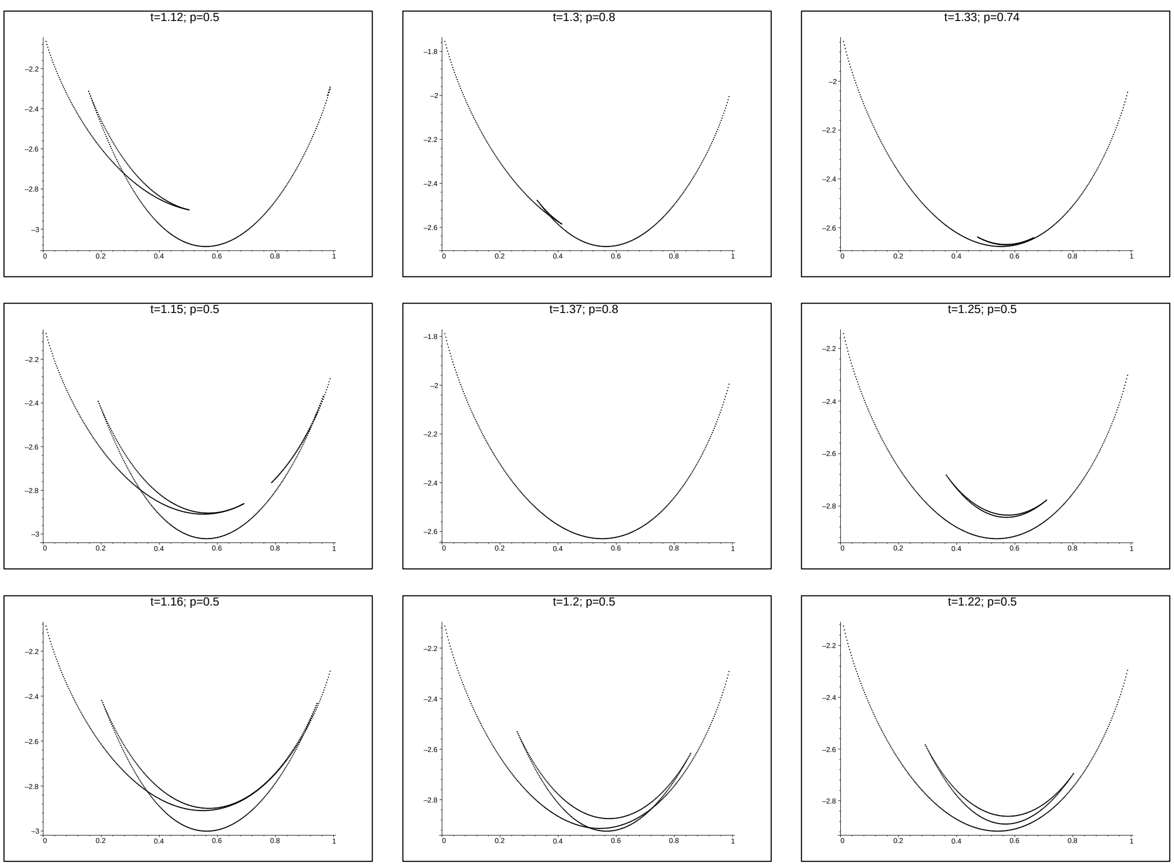


FIGURE 21. For nine values of (p, T) marked by small circles the non dimensional potential $G[p, T](x)$ is shown below



where the non dimensional activities are

$$\ln \lambda_1(x) = -\frac{27(1-x+nx)}{4\mathtt{TV}} + \ln\left(\frac{1-x}{\mathtt{V}-(1-x+kx)}\right) + \frac{\mathtt{V}}{\mathtt{V}-(1-x+kx)}$$

$$\ln \lambda_2(x) = -\frac{27(n-nx+mx)}{4\mathtt{TV}} + \ln\left(\frac{x}{\mathtt{V}-(1-x+kx)}\right) + \frac{\mathtt{V}}{\mathtt{V}-(1-x+kx)}$$

and, for every $x \in (0,1)$, $\mathtt{V}(x)$ is given by the solutions of equation 2 with the chosen values $\mathtt{p}$ and $\mathtt{T}$.

Then I show in figure 21 the graph of the multivalued $\mathtt{G}[\mathtt{p},\mathtt{T}](x)$, which are similar to the expected pictures (see figure 19).

4.2. **Legendrian singularities in Van der Waals systems.** Besides the projected lines of critical points (fold lines), in the calculated (p,T)-diagrams of the system (1), a singularity A_4 is visible in a case (figure A2 of [KS80]) where the authors extend the critical line to the metastable domain. In the projection to the (p,T)-plane this singularity is a cusp point of the critical line.

Moreover, the projection of a singularity A_5 is visible in figure 32 of [KS80], where a critical point line splits in a three-phases line and 2 critical lines (whose projections on the (p,T)-plane coincide). This singularity is non generic for binary mixture, i.e. it happens for special values of the parameters, but it is stable and thus detectable by experiments. For further details and explanations see [AFV00].

5. Conclusions

The singularity theory and specially the approach of Varchenko which was generalized here allows not only to classify all the possible phenomena of binary mixtures, but also to understand - looking at the (p,T)-diagrams - the whole features of the phase diagrams (see [AFV00])

Such a mathematical formulation in terms of singularities of convex envelopes is also convenient to classify all generic phenomena occurring when the system experiences a change in the external parameters.

This is essential to understand the geometrical properties of the so-called global phase diagrams, describing the different behaviors of systems depending on many parameters.

Moreover, this method could also be used to show that in the list of Nezbeda et al. [NKS97] of the codimension 3 singularities (i.e. occurring in generic 1-parameter families of models) five phenomena are missing.

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