

Analysis of a three-component model phase diagram by catastrophe theory

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We analyze the thermodynamical potential of a lattice-gas model with three components and five parameters using the methods of the catastrophe theory. We find the highest singularity, which has codimension five, and establish its transversality. Hence the corresponding seven-degree Landau potential, the canonical form *wig-wam* or A_6 , constitutes the adequate starting point to study the overall phase diagram of this model. We also consider a singularity of lower codimension, which we relate to the phenomenon of critical azeotropy. [S0163-1829(98)01021-2]

I. INTRODUCTION

The study of phase diagrams of complex systems is an important part of thermodynamics and applied physics. Phase diagrams can be constructed either from experimental data or from theoretical models (for example, molecular models). Among these, the wide class of lattice-gas models is particularly suitable for a mathematical analysis. Here we will focus our attention on the lattice-gas model for a system with three components which simulates, in particular, a binary fluid mixture. A wide literature has already been devoted to it from different points of view (Refs. 1–4, and references therein). We are mainly interested in attempting to present an overall analysis of its phase diagram, with particular attention to its highest multicritical point, that is, the one with the highest codimension in the five-dimensional parameter space that we consider.

In the mean-field theory, the Gibbs potential is a function of the concentration of two of the three components and depends on three thermodynamical parameters, which can be taken as the temperature and the chemical potentials of the two components, and on three molecular parameters. The phase diagram deduced from this function is an accurate description of the system, except close to the (multi)critical points, where fluctuations become important and alter significantly the mean-field theory predictions. For this reason, the Gibbs potential has been the basis for determining the overall phase diagram.^{2,3} The method used in Ref. 2 establishes the qualitative features of the phase diagram, namely, the instability and (multi)critical (hyper)surfaces which divide its various regions, as well as some coexistence (hyper)surfaces. Those methods are considerably powerful but not sufficiently rigorous by mathematical standards. However, a well established mathematical theory for the analysis of singularities of potentials and hence the associated phase diagrams does exist, namely, catastrophe or singularity theory (CT).

Catastrophe theory has indeed been applied to the description of phase transitions^{5,6} and, in particular, of phase diagrams of complex thermodynamical systems including fluid mixtures.⁶ The philosophy behind these applications is different from ours: There one starts with a system on which some knowledge of the phase diagram is available, perhaps its salient features, and surmises a polynomial (Landau) potential from among the variety supplied by the CT classification (called canonical forms), which is supposed to em-

body the properties of the thermodynamical potential of the system near the phase transition of interest. Usually, this potential is well analyzed in the mathematical literature and its other properties can be safely assigned to the physical system. In summary, this procedure is phenomenological in nature and amounts to a fitting of phase diagrams. Although it utilizes CT, it is only to take advantage of well studied potentials. It is very intuitive since one is matching topological objects, whose properties can be realized many times by inspection. However, we shall adopt here the approach determining the polynomial potentials from a complete singularity analysis of the actual mean-field thermodynamical potential. A big advantage of our approach is that it is presented as a well-defined algorithm leading to a systematic way to analyze any general problem susceptible to be studied within the context of CT.

Furthermore, this second alternative agrees with the methods of Refs. 4,2, which in fact approach those of CT from the point of view of classical thermodynamics. (See Ref. 4 in regard to the convergence of both techniques). We intend to take the best of both worlds for the problem in hand: to draw intuition from thermodynamical methods and mathematical soundness from the theorems of CT. In particular, we emphasize the study of transversality of the actual thermodynamical potentials which guarantees that those simple forms (polynomial potentials or canonical forms) represent indeed up to a diffeomorphism the original thermodynamical potential. We shall give a brief account of the CT algorithm utilized throughout the paper together with an Appendix for more mathematical details.

Our results essentially agree with and support those in Ref. 2. However, we hinge less on the visualization of the phase diagram and more in the *classification* of its singularities, relying for the construction of the phase diagram on the straightforward method of gluing patches, each described by a standard canonical form for which the phase diagram can be found in the literature. Besides, we clearly establish the possibility of Landau potentials in two variables, that is, of corank-2 canonical forms, for the system with three components. This possibility was dismissed in Ref. 2. Nevertheless, this case is sufficiently complex on its own to postpone it for future work. The general issue of elimination of extraneous variables and the possibility of Landau potentials with several order parameters has already been studied.⁷

This work is organized as follows: In Sec. II we introduce the fundamental concepts of CT, the more technical points of

which are left for the Appendix. In Sec. III we describe the thermodynamical potential to be analyzed, give its physical interpretation and discuss general stability questions which help connect usual concepts in thermodynamics with those in catastrophe theory. In Sec. IV we apply the CT program to the potential previously introduced, reducing it first to a one-variable potential. In Sec. V we show a solution with the highest codimension and its transversality, thereby concluding that it is the *wigwam catastrophe*. We also consider in this section a peculiar singularity of lower codimension, associated with the physics of critical azeotropy. The last section is devoted to a discussion of the previous results and of the structure of the phase diagram entailed by them.

II. GENERALITIES ABOUT CATASTROPHE THEORY

In this section we are going to review very briefly the main concepts of CT. The reader desirous of more technical details is referred to Refs. 8,9. As is well known, CT deals with the singularities of smooth real-valued functions. The nature of these singularities is revealed by perturbing those functions. If as a result of a perturbation the qualitative properties of the function remain unaffected we will say that this function is stable or structurally stable. In other words, a function is said to be locally stable at a given point if there is a smooth change of coordinates so that the new function has the same structure as the old function. If a function is stable at all points then we will say that this function is globally stable. In a more precise way, a given function is a perturbation of another one at a given point if the distance between both functions is arbitrary small. The concept of distance leads us to topology. We can define the Taylor-series topology in the space \mathbb{R}^d where d gives the number of the Taylor-series coefficients. Thus the k jet of a given function at a given point is the Taylor series truncated beyond terms of degree k . Several definitions of distances can be given and all of these are expressed in terms of the k jets of each function.

Now the next important question is what information is lost when we truncate the Taylor series of a function around a given point, namely, the problem of determinacy. It consists of determining whether a function can be truncated and if so, for what value of the degree of the Taylor expansion it can be truncated without any loss of substantial information. Furthermore, to determine the most general family of functions of the smallest dimension d which contains the original function is called the problem of unfolding. The unfolding dimension is the number of parameters describing a general perturbation and the minimum number to describe it is called the codimension. When all the unfolding terms go to zero, the remainder of the universal unfolding is called the *germ* of the canonical form.

The next step is to introduce the concept of transversality as a means to study structure stability and genericity. This concept was originally introduced by Thom¹⁰ and, in general, is not widely used to classify physical phenomena in terms of elementary catastrophes. A property is called generic if the subset for which the property is valid is open and dense in the original set. In other words, when a property is invariant under a perturbation, this property is called generic or structurally stable. The theorem of transversality shows that

it is a generic property of functions to have only isolated *critical points* and such functions are stable under perturbations. We warn the reader not to confuse thermodynamical and mathematical terminology. In thermodynamical terms a critical point is just an equilibrium point and the word critical is reserved for a higher singularity. Two manifolds of \mathbb{R}^n intersect transversally if either their intersection is empty or they intersect transversally at all their points of intersection, that is, the direct sum of their tangent spaces at the point has dimension n or they span the tangent space \mathbb{R}^n at that point.

CT has usually not been applied in a rigorous way using all these concepts and theorems needed for its correct implementation. We claim in this work that if this is done so, the procedure proposed by the theory is not by any means cumbersome and time consuming. The catastrophe program proposed here provides a very useful and systematic way to examine and classify with not very much effort general behaviors of physical systems.

Let $F(x, \lambda)$ be a real function with state variables x_1, \dots, x_n ($x \in \mathbb{R}^n$) and control parameters $\lambda_1, \dots, \lambda_r$ ($\lambda \in \mathbb{R}^r$); that is, $F: \mathbb{R}^{n+r} \rightarrow \mathbb{R}$. We are to proceed as follows:

- (1) We pick (x_0, λ_0) such that x_0 is a *degenerate critical point* of $F(x, \lambda)$ and we consider the unfolding $f(x, \lambda) = F(x + x_0, \lambda + \lambda_0) - F(x_0, \lambda_0)$ and $h(x) = f(x, 0)$.
- (2) One calculates the determinacy and codimension of h from the k jet of h (see Appendix). Of course, if h is k determined then $h \sim j^k(h)$, that is, the function h is equal to $j^k(h)$ up to a change of coordinates and hence they are equivalent and have qualitatively the same properties; therefore, $\text{cod}(h) = \text{cod}(j^k(h))$.
- (3) One studies the k transversality of F and if this function is k transversal we can affirm that F and the canonical form of the unfolding of h are isomorphic and we can replace the original F function for this canonical unfolding. If not, we can claim that the F function is not susceptible to be studied by CT.

Following this CT program we do not need to invoke any convention (for example, delay or Maxwell convention) in order to classify degenerate or non-degenerate critical points on the state variables space. Both conventions are not intrinsic to CT. Only when we deal with the time evolution or when dynamical considerations about the physical system are considered, could a given convention be advisable. It is important to have in mind that these two conventions represent only the two extreme cases in a continuum of possibilities. The separatrices we obtain when a given convention is adopted (from the bifurcation equations for the delay convention or the Clausius-Clapeyron equations for the Maxwell convention) are different and very much related to the local or nonlocal behavior of the physical system, respectively. However, the adequacy or inadequacy of conventions has been largely discussed in the literature and the reader interested in more information is referred to Refs. 10 and 9.

III. DESCRIPTION OF THE GIBBS POTENTIAL

According to Ref. 2 a phenomenological model for a ternary mixture is obtained by assuming the Gibbs potential in the form

$$\bar{G} = N[a'yz + b'xz + c'xy + RT(x \ln x + y \ln y + z \ln z)], \quad (1)$$

where $N = N_x + N_y + N_z$ gives the number of total moles and N_x , N_y , and N_z are the moles of each component. The variables x, y, z are the mole fractions defined by $x = N_x/N$, $y = N_y/N$, and $z = N_z/N$; and hence we have the constraint

$$x + y + z = 1, \quad (2)$$

where $0 < x, y, z < 1$. Finally, a' , b' , and c' are phenomenological energy parameters. The energy part is the most general quadratic term, given that $x + y + z = 1$. This model can be derived from the mean-field theory of a lattice model Hamiltonian with variables taking three different states, representing the molecules of the three components.¹¹ Then a' , b' , and c' represent molecular interaction parameters. Let us consider the Gibbs potential Eq. (1) in a reduced form, dividing by NRT , and thus

$$G(x, y, z, a, b, c) = ayz + bxz + cxy + x \ln x + y \ln y + z \ln z \quad (3)$$

where now the new parameters a, b, c are defined with respect to the old ones a', b', c' dividing them by RT . The concentrations are supposed to be determined by some boundary conditions, such as the values of the chemical potentials of two components, say μ_x and μ_y . The mean-field theory prescription is then to minimize the *nonequilibrium Gibbs potential* $G - \mu_x x - \mu_y y$ with respect to x and y to obtain the equilibrium conditions

$$\frac{\partial G}{\partial x} = \mu_x, \quad \frac{\partial G}{\partial y} = \mu_y.$$

They allow us to solve for x and y as functions of μ_x, μ_y and the parameters a, b , and c , provided that the Jacobian $\det(\partial(\mu_x, \mu_y)/\partial(x, y)) = \det \partial_{ij}^2 G$ is not zero.

Thermodynamical stability further requires that the matrix $\partial_{ij}^2 G$ be positive definite. This property is called *convexity* and must hold for any thermodynamical potential, except on the instability hypersurfaces, which are the simplest singularities we may encounter in a phase diagram. An instability can occur only near a phase transition, when two equilibrium states, one unstable—hence unphysical—and the other metastable coalesce and disappear. In other words, a metastable state becomes unstable and, consequently, we speak of instability. This is the kind of sudden change in the configuration of a system to which CT owes its name. In mathematical terms we say that the *critical point* (equilibrium state) is degenerate. As a consequence, one cannot solve for x and y as functions of μ_x, μ_y or the solution is multivalued, corresponding to the existence of various equilibrium states. The simplest instability occurs when only one eigenvalue of the stability matrix vanishes; that is, the instability only affects one variable. One is to focus on this variable, which is called *relevant*, to consider further singularities. Therefore, it is convenient to transform the potential into a function of just the relevant variable by solving the equilibrium conditions for the other variables and substituting for them. The standard thermodynamical procedure that performs this operation is the Legendre transform. In fact, this procedure can be used for potentials in other fields, whenever there is an un-

derlying geometrical structure in the total space of variables, including state and control variables, called a *contact structure*. We address the reader interested in the general formulation to the literature.¹² How the Legendre transform is implemented in our case will be seen in the next section. Further singularities are studied afterwards with the one-variable potential. Next comes what can be called critical instability, followed by the tricritical point and onwards.

Several systems of interest are described by this Gibbs potential Eq. (1): A ternary mixture at constant volume, for example, a mixture of metals; a spin lattice where the molecules have spin one; a binary fluid mixture, where one of the three states represents a vacancy instead of a new molecule and the corresponding concentration is associated to a variable total volume. In the last case, the possible phases are vapor, miscible liquid mixture, and immiscible liquid mixture. The convenient extensive variables are the specific volume v and the relative concentration $\bar{x} = x/(x+y)$ of the two fluids and the intensive variables are the pressure and the chemical potential of one of the fluids. Moreover, the thermodynamical potential Eq. (1) depends on T, v , and \bar{x} and is therefore the Helmholtz potential $F(T, v, \bar{x})$. This system is perhaps the most interesting for applications, given the great amount of experimental data on binary fluid mixtures.^{13,14} However, the potential (1) is not the most popular for fitting data; a related form which has similar dependence on the relative concentration of the two fluids but is of the Van der Waals type for the volume is usually considered instead. We believe that this form, which is much more difficult to analyze, gives essentially the same qualitative behavior.

IV. APPLYING THE CT PROGRAM

From Eqs. (3) and (2), we have a function depending only on two variables, x and y , namely,

$$H(x, y, a, b, c) = ay(1-x-y) + bx(1-x-y) + cxy + x \ln x + y \ln y + (1-x-y) \ln(1-x-y). \quad (4)$$

Now consider the function $H_y(x, y, a, b, c) - \mu_2$ (where the subindices indicate derivatives with respect to the variable explicitly written and $\mu_2 \equiv \mu_y$) and let the point $(x_0, y_0, a_0, b_0, c_0, \mu_2^0)$ be such that $H_y(P_0) - \mu_2^0 = 0$ and $H_{yy}(P_0) > 0$, where $P_0 = (x_0, y_0, a_0, b_0, c_0)$. The first condition is the equilibrium condition for y and the second one is required by stability in the y direction. Then, by the implicit function theorem, there exists a unique function $\psi(x, a, b, c, \mu_2)$ defined in a neighborhood of $(x_0, a_0, b_0, c_0, \mu_2^0)$ with values in a neighborhood of y_0 such that $H_{yy}(x, y, a, b, c) > 0$, in these neighborhoods, and $H_y(x, \psi(x, a, b, c, \mu_2), a, b, c) - \mu_2 = 0$ in the domain of ψ and $\psi(x_0, a_0, b_0, c_0, \mu_2^0) = y_0$.

By solving for y as a function of μ_2 and substituting into $H - \mu_2 y$ we have performed a Legendre transformation, effectively eliminating the variable y . Next we subtract $\mu_1 x$ (where $\mu_1 \equiv \mu_x$) to obtain the function

$$L(x, a, b, c, \mu_1, \mu_2) = H(x, \psi(x, a, b, c, \mu_2), a, b, c) - \mu_2 \psi(x, a, b, c, \mu_2) - \mu_1 x, \quad (5)$$

representing a one variable nonequilibrium Gibbs potential. In order to have a function defined in a neighborhood of $\bar{0} = (0,0,0,0,0)$ we consider the new function

$$L_1(x,a,b,c,\mu_1,\mu_2) = L(x+x_0,a+a_0,b+b_0,c+c_0,\mu_1+\mu_1^0,\mu_2+\mu_2^0) - L(x_0,a_0,b_0,c_0,\mu_1^0,\mu_2^0). \quad (6)$$

Then we have the following equations:

$$L_1(\bar{0}) = 0 \quad (7)$$

and

$$L_{1,x}(x,a,b,c,\mu_1,\mu_2) = H_x[x+x_0,\psi(x+x_0,a+a_0,b+b_0,c+c_0,\mu_2+\mu_2^0),a+a_0,b+b_0,c+c_0] + H_y\psi_x - (\mu_2+\mu_2^0)\psi_x - (\mu_1+\mu_1^0), \quad (8)$$

so that

$$L_{1,x}(\bar{0}) = H_x(P_0) - \mu_1^0. \quad (9)$$

Suppose now that $H_x(P_0) - \mu_1^0 = 0$ (the remaining equilibrium condition). Then 0 would be called a *critical point* of $L_1(x,0,0,0,0,0)$ (in mathematical terminology). This function will be denoted by $g_1(x)$, which is the *germ* to be studied. Of course, $g_1(0) = 0$ and $g_1'(0) = 0$ from Eqs. (7) and (9). The two first derivatives of g_1 are

$$g_1'(x) = H_x[x+x_0,\psi(x+x_0,a_0,b_0,c_0,\mu_2^0),a_0,b_0,c_0] - \mu_1^0 \quad (10)$$

and

$$g_1''(x) = H_{xx}[x+x_0,\psi(x+x_0,a_0,b_0,c_0,\mu_2^0),a_0,b_0,c_0] + H_{xy}(-)\psi_x(-). \quad (11)$$

In particular

$$g_1''(0) = H_{xx}(P_0) + H_{xy}(P_0)\psi_x(x_0,a_0,b_0,c_0,\mu_2^0) \quad (12)$$

with

$$\psi_x(x_0,a_0,b_0,c_0,\mu_2^0) = \frac{-H_{xy}(P_0)}{H_{yy}(P_0)}, \quad (13)$$

as deduced from $H_y - \mu_2 = 0$ by taking the derivative with respect to x . Suppose that the Hessian of H is such that

$$H_{xx}(P_0)H_{yy}(P_0) - H_{xy}^2(P_0) = 0, \quad (14)$$

then $g_1''(0) = 0$ and 0 is a degenerate critical point of g_1 . Finally, we also assume that $g_1'''(0) = g_1^{iv}(0) = g_1^v(0) = g_1^{vi}(0) = 0$. Then we have imposed five conditions on g_1 altogether and we should be able to solve for (x_0,y_0,a_0,b_0,c_0) . In this case, we say that we have reached the highest codimension. We will see in the next section that there is indeed such a solution.

V. RESULTS

A. Highest singularity

Now we look for a point which fulfills the five conditions for the highest singularity mentioned above. We successively have that

$$y_0 = 1 - 2x_0, \quad (15)$$

$$b_0 = x_0^{-1}, \quad (16)$$

$$a_0 = c_0 = \frac{1 + 2x_0}{8x_0(1 - 2x_0)}, \quad (17)$$

and

$$36x_0^2 + 4x_0 - 1 = 0. \quad (18)$$

Thus from the last equation we have that $x_0 = (\sqrt{10} - 1)/18 = 0.120\ 127$. Moreover,

$$g_1^{vii}(0) = 6x_0^{-2} \left(\psi_{5x} - \frac{1472}{27} x_0^{-4} \right) \neq 0,$$

where

$$\psi_{5x} = \frac{256}{162} x_0^{-2} \left[\frac{157}{10} x_0^{-2} - 17(1 - 2x_0)^2 + 5 \frac{3x_0^2 - 4x_0 + 1}{x_0^2(1 - 2x_0)^2} \right].$$

The ensuing values of the control parameters are $a_0 = c_0 = 3(5 + 2\sqrt{10})/20 = 1.698\ 68$, $b_0 = 2(1 + \sqrt{10}) = 8.324\ 56$ and $\mu_1^0 = (-2 + 7\sqrt{10})/4 = 5.033\ 99$, $\mu_2^0 = (1 - \sqrt{5}/2)/2 + \ln[2\sqrt{10}] = 1.553\ 87$.

Now we apply results of singularity theory:^{10,15}

- (i) The 7 jet of g_1 is $j^7(g_1) = 1/7! g_1^{vii}(0)x^7$ with $g_1^{vii}(0) \neq 0$.
- (ii) The essence of g_1 respect the identity is 7 and therefore $\sigma(g_1) \geq 7$, where $\sigma(g_1)$ is the determinacy of g_1 (see the Appendix for the definition of this concept).
- (iii) The codimension of $j^7(g_1)$ is $\text{cod}(j^7(g_1)) = \dim \text{vect}(\langle x \rangle / \langle x^6 \rangle) = 5$ (see the Appendix) and $\sigma(j^7(g_1)) \leq 7$. Thus $j^7(g_1)$ is 7 determinate, $j^7(g_1) \sim g_1$ and g_1 is 7 determinate. Moreover, $\text{cod}(g_1) = 5$ and $\sigma(g_1) = 7$. A basis of this quotient vector space is given by the set $\{[x], \dots, [x^5]\}$. Then $\bar{g}_1(x, \lambda_1, \dots, \lambda_5) = g_1(x) + \lambda_1 x + \lambda_2 x^2 + \dots + \lambda_5 x^5$ is a *canonical unfolding* k transversal of the *germ* g_1 for every $k > 0$; in particular, for $k = 7$. Finally $g_1 \sim x^7$.
- (iv) The L_1 function is an unfolding 7 transversal of g_1 because one can prove (see the Appendix)

$$\langle x \rangle = \langle x^6 \rangle + V_{L_1} + \langle x \rangle^{7+1}, \quad (19)$$

where V_{L_1} is the real linear space generated by

$$\{L_{1,a}(x, \bar{0}) - L_{1,a}(0, \bar{0}), \dots, L_{1,\mu_2}(x, \bar{0}) - L_{1,\mu_2}(0, \bar{0})\},$$

where the subindices a, \dots, μ_2 denote derivatives with respect to the corresponding parameters. Note that Eq. (19) has the following expression:

$$\begin{aligned}
\langle x \rangle = \langle x^6 \rangle + & \left\{ x(-1+2x_0) + x^2 \frac{2}{3} x_0^{-1} (1-3x_0) + x^3 \left(\frac{2}{3} x_0^{-1} + \frac{4}{9} x_0^{-2} (-1+3x_0) \right) \right. \\
& + x^4 \left(-x_0^{-2} \frac{8}{9} + (3x_0-1)x_0^{-3} \frac{-352}{1080} \right) + x^5 \left(\psi_{5x}(3x_0-1) \frac{1}{5!} + \frac{1}{4!} \frac{352}{45} x_0^{-3} + \frac{16}{27} x_0^{-3} \right), \\
& - \frac{1}{3} x^2 + x^3 \frac{2}{9} x_0^{-1} + x^4 \left(-\frac{4}{9} x_0^{-2} + \frac{1}{24} \frac{352}{45} x_0^{-2} \right) + x^5 \left(\frac{1}{24} \frac{352}{45} x_0^{-3} - x_0 \frac{1}{5!} \psi_{5x} \right), \\
& x(1-2x_0) - \frac{2}{3} x^2 + x^3 \frac{-2}{9} x_0^{-1} + x^4 \frac{1}{24} \frac{128}{45} x_0^{-2} + x^5 \frac{1}{5!} \left(x_0 \psi_{5x} - \frac{352}{9} x_0^{-3} \right), \\
& \left. - x, x^2 \frac{2}{3} x_0^{-1} - x^3 \frac{4}{9} x_0^{-2} + \frac{1}{4!} x^4 x_0^{-3} \frac{352}{45} + \frac{1}{5!} x^5 (-\psi_{5x}) \right\}, \tag{20}
\end{aligned}$$

where the Taylor expansions in V_{L_1} have been truncated at x^5 because the terms of degree sixth and higher are already included in $\langle x^6 \rangle$. Solving Eq. (20) amounts to proving that a generic fifth-degree polynomial with no independent term can be generated as a linear combination of the five polynomials between the curly brackets. Hence it implies the resolution of a linear system whose determinant is $x_0(-58944x_0^2 + 729\psi_{5x}) \neq 0$.

Finally, this equality, Eq. (20), holds and consequently \bar{g}_1 and L_1 are isomorphic as unfoldings and L_1 can be qualitatively studied by the polynomial

$$x^7 + \lambda_1 x + \lambda_2 x^2 + \lambda_3 x^3 + \lambda_4 x^4 + \lambda_5 x^5,$$

which in the terminology of CT corresponds to the *wigwam* or A_6 *catastrophe*.

As a result of this analysis we can affirm that there are three changes of coordinates φ_1 , φ_2 , and φ_3 and a perturbation ε of parameters such that

$$\begin{aligned}
L_1(x, a, b, c, \mu_1, \mu_2) = & u^7 + \lambda_1 u + \lambda_2 u^2 + \dots + \lambda_5 u^5 \\
& + \varepsilon(a, b, c, \mu_1, \mu_2) \tag{21}
\end{aligned}$$

with

$$u = \varphi_3 p_1 \varphi_1(x, a, b, c, \mu_1, \mu_2),$$

$$\varphi_2(a, b, c, \mu_1, \mu_2) = (\lambda_1, \dots, \lambda_5),$$

where p_1 means the *first projection*, $p_1: \mathbb{R}^{1+5} \rightarrow \mathbb{R}$, that is, $p_1(x_1, \dots, x_6) = x_1$.

Moreover, the bifurcation set of Eq. (6) and that corresponding to

$$u^7 + \lambda_1 u + \lambda_2 u^2 + \dots + \lambda_5 u^5 \tag{22}$$

are diffeomorphic and we work rather with Eq. (22) due to its simplicity. The equilibrium manifold in $(u, \lambda_1, \dots, \lambda_5)$ is obtained from Eq. (22) by equating the first derivative to zero

$$7u^6 + \lambda_1 + 2\lambda_2 u + 3\lambda_3 u^2 + 4\lambda_4 u^3 + 5\lambda_5 u^4 = 0,$$

and, furthermore, instability occurs if the second derivative also vanishes,

$$42u^5 + 2\lambda_2 + 6\lambda_3 u + 12\lambda_4 u^2 + 20\lambda_5 u^3 = 0.$$

Now the bifurcation set is obtained by a projection onto the parameter space, that is, by eliminating the variable u in this system of two equations.

B. Critical azeotropy as a singularity

In the process of solving the equations that lead to the highest singularity one goes through singularities of lower codimension. They have no particular interest by themselves except in one case, which we proceed to describe.

Thus we analyze now the five conditions one by one. The equilibrium conditions allow one to express x_0 and y_0 as functions of the parameters, resulting in $y_0 = \psi(x_0, a_0, b_0, c_0, \mu_2^0)$, already used to define $g_1(x)$, and an equation for x_0 derived from equating Eq. (9) to zero. However, we prefer to keep x_0 and y_0 in the equations to follow, for it is simpler, understanding that they are to be substituted in the end.

The first condition on $g_1(x)$ is $g_1''(0) = 0$ or

$$\det H_{ij} = H_{xx}(P_0)H_{yy}(P_0) - H_{xy}^2(P_0) = 0. \tag{23}$$

The Hessian matrix is

$$(H_{ij}) = \begin{pmatrix} \alpha_3 + \alpha_1 & \alpha_3 \\ \alpha_3 & \alpha_3 + \alpha_2 \end{pmatrix}, \tag{24}$$

with $\alpha_3 = c - a - b + z^{-1}$, $\alpha_1 = a - c - b + x^{-1}$, and $\alpha_2 = b - a - c + y^{-1}$. We have reinstated $z = 1 - x - y$ for the sake of symmetry and we suppress the subindices zero relative to P_0 in the next equations. From Eq. (24),

$$\det H_{ij} = \alpha_3 \alpha_1 + \alpha_3 \alpha_2 + \alpha_1 \alpha_2 = 0, \tag{25}$$

which is a quadratic equation on either a, b, c or x, y . The next condition $g_1'''(0) = 0$ is equivalent to

$$\frac{1}{x^2} \alpha_2^3 + \frac{1}{y^2} \alpha_1^3 - \frac{1}{x^2} (\alpha_1 + \alpha_2)^3 = 0 \tag{26}$$

or

$$\frac{1}{x^2} \alpha_3^3 - \frac{1}{y^2} (\alpha_3 + \alpha_1)^3 + \frac{1}{z^2} \alpha_1^3 = 0 \quad (27)$$

or

$$-\frac{1}{x^2} (\alpha_3 + \alpha_2)^3 + \frac{1}{y^2} \alpha_3^3 + \frac{1}{z^2} \alpha_2^3 = 0. \quad (28)$$

Each of these is an equation of third degree in a, b, c .

Next we consider $g_1^{iv}(0) = 0$. Again this equation can be separated into three symmetric options. Each one imposes new conditions on α_i and hence on the elements of the Hessian matrix. Furthermore, they can only be fulfilled if two new quantities vanish. In other words, the codimension increases by two units with only one condition, a nongeneric situation. We choose the solution $\alpha_3 = \alpha_1 = 0$ such that $H_{xx}(P_0) = H_{xy}(P_0) = 0$. There are two more solutions, obtainable by cyclic permutation of the labels of the α 's. As a counterpart of the previous extra increase of the codimension by one unit, the next condition is identically fulfilled, $g_1^v(0) = 0$. Finally, from $g_1^{vii}(0) = 0$ one obtains the solution quoted in the subsection above.

Let us compare the foregoing analysis with the one in the previous literature on this model.^{11,2} This analysis goes as follows. The first condition $g_1^{ii}(0) = 0$ or, equivalently, that the Hessian of H be null has two types of solutions, namely, a simple solution, $\alpha_1^{-1} + \alpha_2^{-1} + \alpha_3^{-1} = 0$, and a second triple solution that requires that two of the α_i vanish simultaneously. The first type is more generic but, unfortunately, does not lead to a high codimension singularity, since the equation $g_1^{iv}(0) = 0$ has no solution for it. One of the second-type solutions is the one we have considered in the previous subsection. They are called symmetric solutions because the additional condition on the Hessian matrix elements implies a symmetry in the phase diagram, for example, $a = c$ in our solution.

Alternatively, we can avoid making any choice on the type of solution until the last moment, namely, when we demand $g_1^{iv}(0) = 0$. Then this condition implies by itself $g_1^v(0) = 0$. In other words, the singularities given by these two conditions are inextricably linked: the first one entails the second one. Moreover, the first condition led us to take $H_{xx}(P_0) = H_{xy}(P_0) = 0$ in addition to $\det H_{ij} = 0$. We may recall here that the vanishing of these two elements of the stability matrix for a binary fluid mixture has a thermodynamical interpretation: It occurs when there is critical azeotropy (Ref. 13, pp. 197–199). Azeotropy is not a singularity on its own but when it superposes on a critical point it enhances its singularity producing a new one. We see what kind of singularity it is in our case, namely, the one given by $g_1^v(0) = 0$ —a tricritical point. At this moment, we are not able to say if this is just a peculiarity of the particular three-component model we study or in fact constitutes a general feature.

VI. DISCUSSION

The solution with the highest codimension, namely, five, which has been found above must be isolated; that is, it cannot belong to a continuous family of solutions. Nevertheless, there can be a discrete set of solutions. Indeed, we can

obtain two other solutions from this one by using the symmetry of the original potential $G(x, y, z, a, b, c)$ under simultaneous permutations of (x, y, z) and (a, b, c) . The way in which they arise is clear in the last subsection. It is clear as well that there are no further solutions with codimension five.

Some readers may be concerned by the fact that our solution, Eq. (22), is a Landau potential which is not bounded below. This means that the equilibrium states are actually not stable but metastable. The catastrophe point P_0 corresponds to a degenerate instability rather than to a multicritical point. To be precise, it arises as a tricritical point, with Landau potential x^6 , merges with an unstable equilibrium state and disappears, for which the appropriate name is tricritical unstable point. Since $g_1^{vii}(0) \neq 0$, there is no tetracritical point in the phase diagram. In this we disagree with Ref. 2, where they assert to have three tetracritical points with $g_1^{vii}(0) = 0$. The conditions they obtain for their tetracritical points are precisely the same five conditions we have for our tricritical unstable point but the codimension of a generic tetracritical point is six. Thus it seems that they are calling tetracritical points what actually are tricritical unstable points.

In some contexts the existence of potentials not bounded below is perfectly natural; for example, in optics, where caustics can be studied as stationary values (not necessarily minima) of the eikonal¹⁸ with the CT algorithm we have followed. However, in thermodynamics the presence of metastable states must imply the existence of lower stable equilibrium states. We must remember that the Landau potential is a local object and provides no information on the behavior of the thermodynamical potential far from the point P_0 . Whether there is an absolute minimum or not is a global question beyond the methods of CT. To check the presence of other minima for the values of the parameters $(a_0, b_0, c_0, \mu_1^0, \mu_2^0)$ which produce the *wigwam catastrophe* we may solve the equations $H_x(x, y, a_0, b_0, c_0) - \mu_1^0 = 0$ and $H_y(x, y, a_0, b_0, c_0) - \mu_2^0 = 0$ for the whole range of the variables x and y . Since they are transcendental equations, they must be solved numerically. The result is that there are no more solutions. However, there is in fact an *absolute* minimum on the boundary at $x = 1, y = 0$, which does not show with the previous equations because the derivatives of the potential diverge on it. Nevertheless, it can be found by a numerical study of $H(x, y, a_0, b_0, c_0)$. That minimum corresponds to the phase with a pure first component, far from the value $x_0 \approx 0.12$. If one does not want to deal with metastable states, one may choose two ways: The first is to consider the highest singularity unphysical and to restrict to lower codimension singularities which are bounded below, as is sensible for binary fluid mixtures—see the next paragraph. The other is to complicate the original model adding new control parameters in the potential—like with energy terms of higher degree—and look for the next (or higher) codimension singularity.

The topology of the overall phase diagram is formed by gluing three patches, each corresponding to the phase diagram of the *wigwam catastrophe*, as given in the literature.¹⁷ The Taylor-series expansions on which the CT is based are supposed to be valid in each patch. The coordinates on each patch are not related and therefore we can only obtain topo-

logical information. Even the topological matching is not a trivial matter when we deal with high-dimensional spaces. Since the highest singularities in our analysis are essentially the same as those in Ref. 2, so is the phase diagram. The phase diagram is of great utility for experimentalists and we should like to obtain some more concrete information. We must notice that in a particular model, for example, a binary fluid mixture, the energy parameters are fixed and one can only tune the chemical potentials—one of which is to be interpreted as pressure in the binary mixture—and the temperature. Therefore, one is interested in three-dimensional sections of the overall phase diagram. In these sections it is not generic to have a tricritical point, (which has codimension four,) a fact well known to experimentalists. Generic and nongeneric sections of the phase diagram of the *wigwam catastrophe* are expected to cover all the possibilities. In regard with the nonboundness below of the *wigwam catastrophe* pointed out above, codimension-four sections provide the physically meaningful information, including generic tricritical points.

Another solution of $\det H_{ij}=0$ is, of course, that all the matrix elements be null so the matrix has rank zero or corank 2. This means that one cannot use the implicit function theorem to reduce to a function of one variable and one is to proceed with the CT program for a function of two variables. The next step is to analyze the 3 jet of this function, that is, the form given by the third derivatives. According to its signature, given by the sign of its discriminant, there are three possible cases: If it is negative, the canonical form is $x^3 - 3xy^2$, called the *elliptic umbilic catastrophe*; if it is positive the canonical form is $x^3 + 3xy^2$, called the *hyperbolic umbilic catastrophe*; if it is null, the 3 form is degenerate, and one is to analyze the 4 jet to determine the type of singularity, which may be the *parabolic umbilic catastrophe* or a type even more complex. The calculations driving at establishing the highest singularity in our five-dimensional parameter space are complicated and the results for corank 2 shall be reported in the future.¹⁹

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APPENDIX

In this Appendix we are going to present the main mathematical concepts widely introduced in Refs. 15, 16, and it is necessary to follow the main steps developed in Sec. V. Let us consider real functions of class ∞ and defined in a neighborhood of $0 \in \mathbb{R}^n$. We establish that two functions are equivalent if they coincide in a neighborhood of 0. The classes we obtain are called *germs* of functions and the set of *germs* is denoted by $E(n)$. The operations $f+g$ and $f \cdot g$ give to $E(n)$ the structure of a ring and $M(n)=\{f \in E(n)/f(0)=0\}$ is a maximal ideal of this ring. Moreover,

the operations $f+g$ and $\lambda \cdot f$ with $\lambda \in \mathbb{R}$ give to $E(n)$ the structure of a real vector space of dimension ∞ . The ideal $M(n)$ is generated by x_1, \dots, x_n , that is, $M(n)=\{f_1x_1 + \dots + f_nx_n/f_1, \dots, f_n \in E(n)\}$. In general, if $f_1, \dots, f_n \in E(n)$, we designate by $\langle f_1, \dots, f_n \rangle$ to the ideal generated by f_1, \dots, f_n , that is,

$$\langle f_1, \dots, f_n \rangle = \{f_1g_1 + \dots + f_ng_n/g_1, \dots, g_n \in E(n)\}.$$

In particular, $M(n)=\langle x_1, \dots, x_n \rangle$.

It is possible to define powers of $M(n)$ as $M(n)^k$. It can be proven that $M(n)^k$ is equal to the ideal of $E(n)$ generated by the monomials in x_1, \dots, x_n of degree k . In particular, for example, $\langle x, y \rangle^2 = \langle x^2, xy, y^2 \rangle$. We have also that $M(n)^{k+1} = \{f \in E(n)/D^i f(0)=0, i \leq k\}$, where with D^i we mean the derivative of degree i .

In a similar way, we can define the *germs* of diffeomorphisms of class ∞ from \mathbb{R}^n in \mathbb{R}^n which transform 0 in 0. This set is denoted by $G(n)$. We say that two *germs* are equivalent if there exists a change of coordinates $\varphi \in G(n)$ such that $f=g\varphi$ and it is denoted by $f \sim g$. When the k jets ($k \in \mathbb{N}$) of two functions are equal we say that these functions are k equivalent ($f \sim_k g$). A *germ* f is k determinate if for every *germ* g such that both k jets are equal we have that $f \sim g$. The determinacy of a *germ* f is the smallest number $k \in \mathbb{N}$ such that f is k determinate and it is called $\sigma(f)$. Therefore, we notice that if f is k determinate then $f \sim_j k^k f$, if f is k determinate and $f \sim_k g$ then g is k determinate, if f is k determinate and $f \sim g$ then g is k determinate.

The ideal of Jacobi of a *germ* f is defined by

$$\Delta(f) = \langle D_{x_1}f, \dots, D_{x_n}f \rangle,$$

where D_{x_1}, \dots, D_{x_n} are the partial derivatives with respect to the x_1, \dots, x_n variables. If $f \sim g$ then $\Delta(f) \equiv \Delta(g)$.

Now let us assume that $f \in M(n)^2$. Then $\Delta(f) \subset M(n)$ and we can speak of the quotient vector space $M(n)/\Delta(f)$. The dimension of this vector space is called a codimension of f , $\text{cod}(f)$. It can be proven that if $f \in M(n)$ then $\text{cod}(f)$ is finite if and only if $\sigma(f)$ is finite and in this case $\sigma(f) - 2 \leq \text{cod}(f)$. Moreover, if $f \sim g$ then $\text{cod}(f) = \text{cod}(g)$. Thus the codimension generally coincides with the number of conditions necessary to specify a function germ up to diffeomorphisms, which is the usual geometrical concept.

If $g \in M(n+r)$ and $f \in M(n)^2$, we say that g is a r unfolding of f if $g(x,0)=f(x)$ (with r parameters which we define as y_1, \dots, y_r). Now let us assume that $g \in M(n+r)$ is an unfolding of $f \in M(n)^2$ and $k \in \mathbb{N}$. We say that g is k transversal if

$$M(n) = \Delta(f) + M(n)^{k+1} + V_g,$$

where V_g is the real vector subset of $M(n)$ generated by the vectors $D_{y_1}g(x,0) - D_{y_1}g(0,0), \dots, D_{y_r}g(x,0) - D_{y_r}g(0,0)$.

Finally, the theorem of k transversality for unfoldings can be stated as follows: Let us consider $f \in M(n)^2$ k determinate and g and h two unfoldings of f with r parameters which are k transversal. Then g and h are isomorphic.

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