Critical end point and singular point sets in phase diagrams

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The characterization of singular point sets in phase diagrams is surveyed in the light of catastrophe theory. The critical end point and the phase diagram near it, containing the unstable critical point, are particularly examined. Some diagrams of its sections are given, which extend beyond the standard analysis of the butterfly catastrophe. The interplaying phenomena between these points are also briefly discussed.

I. INTRODUCTION

The study and classification of singular points is the most powerful way to deal with phase diagrams of complex systems.[1] These are organized in a hierarchy in which the lower dimensional ones can be considered as sections of a particular diagram containing just one isolated multicritical point of highest order. In its neighborhood, the local properties of the system are described by the Landau potential. Catastrophe theory provides a way to establish the relevant topological features by analytic methods,[2,3] leading to a classification of general diagrams up to some dimension as sections of a given catastrophe.

However, it is necessary to distinguish clearly between the pure catastrophe-theoretic concepts and those traditionally used in thermodynamics. This is useful by itself and will also show the possibility of the appearance of some exotic phenomena in complex systems.

The tricritical system and the associated butterfly catastrophe[4–6] are appropriate to study these matters, and simple enough to allow analytic calculations and display of the relevant diagrams. In Ref. 6 we matched the well-known two-fluid-mixture phase diagrams with sections of the butterfly catastrophe. Here we proceed by developing methods for the representation of these diagrams, in order to clarify the various roles of singular points.

II. GENERAL DEFINITIONS

Singular point sets in phase diagrams are of two kinds.

(i) One set is defined as special configurations of the minima of the thermodynamical potential. They may be also subdivided into coexistence points, when some minima have the same depth, and multicritical points, when some minima coincide. There are also mixed points that exhibit coexistence of minima and multicritical points, called, in general, critical end points.

(ii) Another set is instability points, where one minimum merges with a maximum and disappears. It is the subject of catastrophe theory, where it is also called the bifurcation set.

The multicritical point may also be considered as a intersection of instability manifolds, because it is produced by merging minima and, therefore, the intermediate maxima.

The mathematical conditions for both kinds of singular points are different. In the first case, it is an algebraic condition on the potential, and in the second, a differential one.[3,7] The easiest example is the liquid-vapor transition, where phase coexistence is given by

$$g_L = g_V \tag{1}$$

(g is the potential and L and V stand for liquid vapor, the two minima of g), while the instability or the critical point (CP) is given by the first or both differential conditions

$$g_{vv} = 0 \ , \tag{2}$$

$$g_{vvv} = 0 \tag{3}$$

($g_v = \partial g / \partial v, \ldots$).

The already cited mixed points are given by a mixture of algebraic and differential conditions and can be understood as the intersection of pure coexistence manifolds and pure multicritical manifolds. The critical end point (CEP) is defined in a physical system when two coexisting phases become identical in the presence of a third. We shall be considering henceforth a system with at least three thermodynamical fields, for instance, a two-fluid mixture.[1,4–6] Its CEP is the intersection of a triple-point line and a critical line, with equations

$$g_{L_1} = g_{L_2} = g_V \ , \tag{4}$$

$$g_{xx} = g_{xxx} = 0 \ . \tag{5}$$

However, this critical line, Eq. (5), must have another singular point, when it becomes unstable, which, therefore, we shall call the unstable critical point (UCP). This point is the intersection of the line with another "critical line" of a different nature, defined as the line of points where two maxima merge; that is, where the medium phase (the vapor) becomes symmetrically unstable.[6] The UCP has been scarcely considered in the thermodynamical literature (however, it is mentioned in Ref. 7) because of its involved physical interpretation. However, it is crucial in catastrophe theory.

The analytical condition for the UCP (Refs. 6 and 7) is, besides (5),

$$g_{xxxx}=0 . \quad (6)$$

Since it has codimension 3, the phase diagram around it is described by the swallowtail catastrophe.[9] Nevertheless, the next-higher-order butterfly catastrophe,

$$\Gamma=x^6+tx^4+ux^3+wx^2+vx , \quad (7)$$

allowing for three phases and being compact, must be considered. In this light, we shall unveil the phase structure of the part of the diagram near the tricritical point (TCP), including both CEP and UCP.

III. ANALYTIC CALCULATION OF SINGULAR POINTS

The appropriate representation of the Landau potential for studying phase coexistence is[1,5,8]

$$\Gamma(T,P,\mu;x)=\prod_{i=1,2,3}[(x-b_i)^2+d_i] , \quad (8)$$

where d_1 can be taken to be null, $d_2,d_3>0$, and the remaining five variables satisfy an additional condition which removes the equivalence under x translation. If we want that condition to be the usual in catastrophe theory, the nonappearance of the derivative of the highest-order term (the germ), we must demand

$$b_1+b_2+b_3=0 . \quad (9)$$

This representation was also used in Ref. 10 in an analysis of the tricritical phase diagram, but no connection with the butterfly catastrophe was made.

In that parametrization, roughly speaking, b_i corresponds to the position of the minima, which we call A,B,C, taking $b_1<b_2<b_3$ and d_i to their height. The manifolds of double coexistence A-B or A-C are easily expressed as d_2 or $d_3=0$, while the one for B-C demands further elaboration (see Appendix). Triple coexistence is given by $d_2=d_3=0$. In the thermodynamic literature, they are usually represented in the (T,P,μ) phase diagram as surfaces intersecting in the triple line. However, if metastable phase coexistence is also considered, they extend beyond the triple line and a clearer picture is obtained from the coexistence lines in the constant P planes or, equivalently,[6] the constant (t,u) sections of the butterfly catastrophe (7). For example, we sketch how to obtain analytically the line of A-C (liquid-liquid) coexistence. Apart from $d_3=0$ we need the expression of (t,u) as functions of (b_i,d_i)

$$\begin{aligned} t&=d_2+d_3-(b_1^2+b_2^2+b_3^2)\\ &=d_2-(b_1^2+b_2^2+b_3^2) , \end{aligned} \quad (10)$$

$$\begin{aligned} u&=2b_2d_2+2b_3d_3-2b_1b_2b_3\\ &=2b_2d_2-2b_1b_2b_3 . \end{aligned} \quad (11)$$

They are the implicit equations of the line. To find the explicit ones in the (v,w) plane, using b_2 as a parameter,

$$v=v(t,u;b_2) , \quad (12)$$

$$w=w(t,u;b_2) , \quad (13)$$

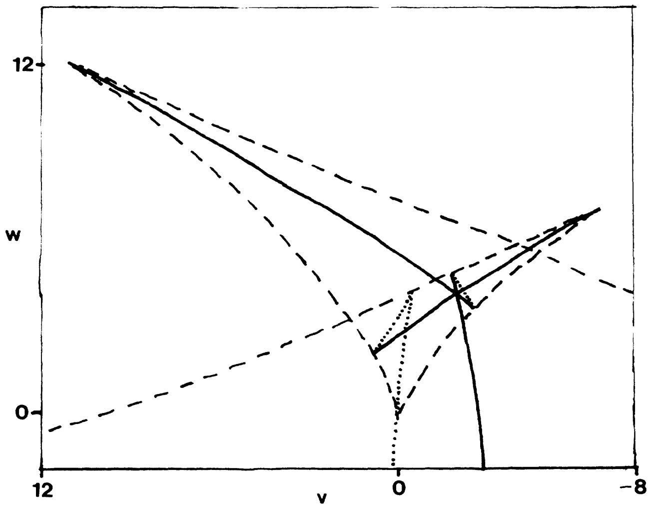

FIG. 1. Phase diagram in the (v,w) plane for $t=-4$, $u=1$. The physical coexistence lines are solid, while the unphysical ones are dotted. The dashed line is the usual instability line of the butterfly catastrophe.

first one solves for d_2,b_3 in (10) and (11); second, one finds (v,w) as functions of (b_i,d_i); and third, one inserts the previous functions for them. This rather cumbersome process is exposed in the Appendix.

All coexistence lines are shown in Fig. 1, with the instability line, for the case $t=-4$, $u=1$. The CEP, as an intersection of the triple line and the critical line BC, is given by

$$d_2=d_3=0, \quad b_2=b_3 . \quad (14)$$

Taking $b_2=b_3=b>0$, $b_1=-2b$, there is one free parameter in the four-dimensional phase diagram and it constitutes a line. The potential becomes

$$\Gamma=(x+2b)^2(x-b)^4 . \quad (15)$$

It was studied by Schulman[4] and is represented in Fig. 2.

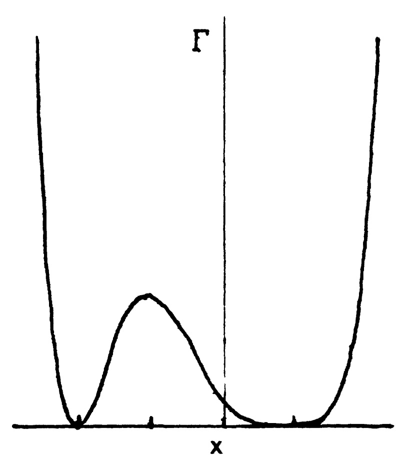

FIG. 2. Landau potential for the critical end point $(b=1)$.

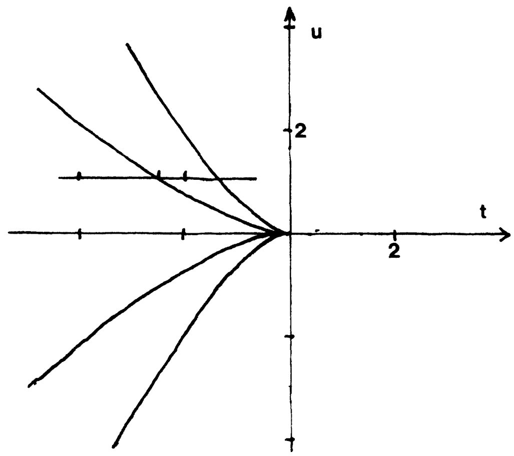

FIG. 3. CEP and UCP lines in the (t,u) plane. A physical trajectory of constant u, $u=1$, is displayed, with three marked points, phase diagrams of which are drawn in Figs. 4 and 5.

There is also another symmetric line of CEP (Ref. 1), given by $b_1=b_2$, which corresponds also to (15) with $b<0$. They join at the TCP.

It is useful to draw the CEP and UCP lines together in the (t,u) plane. For the first ones, we need the expression of (t,u) as functions of b, either extracted as a particular case of (10) and (11) or directly from (15):

$$t=-6b^2, \quad u=4b^3 . \tag{16}$$

Eliminating b,

$$u^2+2(t/3)^3=0 . \tag{17}$$

These two lines of CEP, joining in a cusp, have been previously described in a qualitative way [Ref. 11, Fig. 4(a)].

The UCP lines are given by the usual analysis of the butterfly catastrophe,[9] from the conditions [(5) and (6)]

$$u^2+\tfrac{64}{5}(t/3)^3=0 . \tag{18}$$

There is an error in the edition of Ref. 9 available to us. Both curves, which are similar, are drawn in Fig. 3. The CEP line is on the inside and is crossed first when moving at constant u from low t values, for which the "triangular pocket" in the (v,w) plane exists. In the crossing point, the curve for BC coexistence disappears (Fig. 4). Through the relation between t and P (Ref. 6) it is possible to deduce the features in the (T,P,μ) diagram.

IV. DISCUSSION

It is interesting to note that between the CEP and UCP lines we have at constant pressure a phase diagram like Fig. 4 (3), showing no medium phase (vapor) in equilibrium but having it still as metastable inside the triangle. The corresponding (T,x) diagram is rather peculiar. It is inferred from the (x,w) diagram, conveniently constructed by pulling up the coexistence curve to the equilibrium surface and then projecting it on the (x,w) plane. For different values of t around and on the CEP, we have the sequence shown in Fig. 5. The inner arc in Fig. 5 (3) corresponds to metastable B-C coexistence.

Other higher singular point sets of the first kind come up in higher-dimensional phase diagrams: the critical double point, etc.[3] As long as we restrict ourselves to corank 1, the analysis can be carried out with the representation (8) and the same techniques. The result is the appearance in the phase diagram of zones that correspond to phases only existing as metastable phases but exhibiting phenomena proper for equilibrium ones. For corank 2 or higher, the representation (8) is no longer possible and finer methods must be devised.[12]

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APPENDIX

We briefly comment here the mathematical methods used for the construction of the phase diagram in the (v,w) plane, Fig. 1. See also Refs. 10 and 5.

Let us start with the expression of v,w as function of (b_i,d_i):

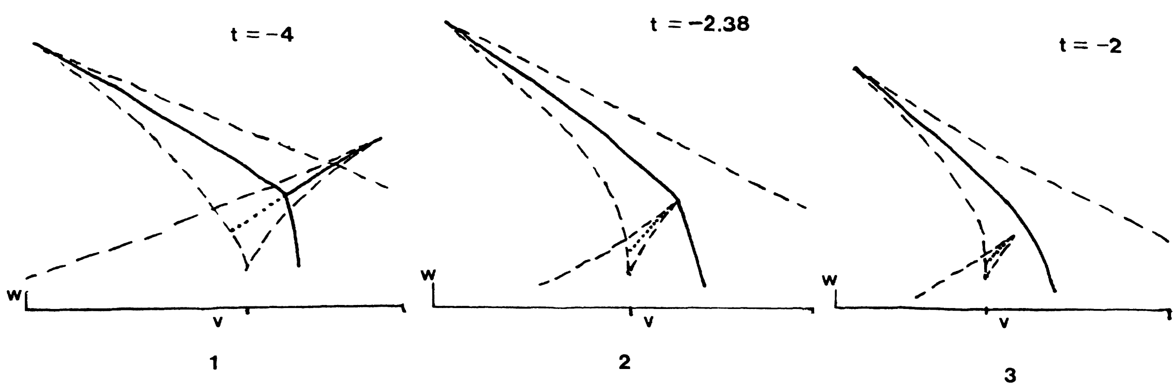

FIG. 4. Phase diagrams in the (v,w) plane, showing how the BC coexistence line disappears at the CEP but still remains metastable inside the triangle.

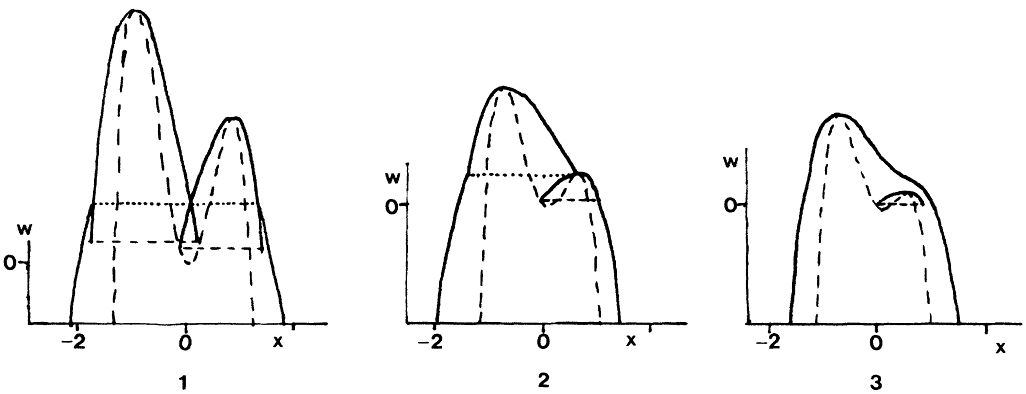

FIG. 5. Phase diagrams in the (x,w) plane for the cases of Fig. 4. The triple-point line is dotted. The ends below it correspond to metastable coexistence. Observe how at the CEP the ends of the *AB* coexistence line disappear (2) while the ones of the *BC* coexistence line become a whole arc, which still remains afterwards (3).

$$v=-2b_1(b_1b_2^2b_3+b_1b_2b_3^2+b_1b_2d_3+b_1b_3d_2+b_2^2b_3^2+b_2^2d_3+b_3^2d_2+d_2d_3)\ , \tag{A1}$$

$$w=b_1^2b_2^2+b_1^2b_3^2+b_2^2b_3^2+4b_1^2b_2b_3+4b_1b_2^2b_3+4b_1b_2b_3^2+b_1^2(d_2+d_3)+b_2^2d_3+b_3^2d_2+4b_1b_2d_3+4b_1b_3d_2+d_2d_3\ . \tag{A2}$$

For the *A-C* coexistence line, we make $d_3=0$ and solve for d_2,b_3 in (10) and (11),

$$b_3=[(-15b_2^4-12tb_2^2+6ub_2)^{1/2}-3b_2^2]/6b_2\ , \tag{A3}$$

$$d_2=(2b_2^3+tb_2+u)/3b_2^2\ . \tag{A4}$$

Upon substitution of them in (A1) and (A2), after making $b_1=-b_2-b_3$, we get its parametric equations

$$v=(8b_2^6+4tb_2^4+2ub_2^3+2tub_2-u^2)/12b_2\ , \tag{A5}$$

$$w=(20b_2^6+12tb_2^4+8ub_2^3+4t^2b_2-u^2)/12b_2^2\ . \tag{A6}$$

The *A-B* coexistence line is obtained with the analogous procedure from $d_2=0$, yielding formulas similar to (A3) and (A4), but interchanging 2 and 3. Inserting in (A1) and (A2), after making $b_1=b_2-b_3$, we find the same [(A5) and (A6)] with b_3 instead of b_2.

For the *B-C* coexistence line, it is necessary to leave the $d_1=0$ condition in (8), because otherwise the condition for it does not have a simple form. We can, instead, take $d_1<0$ and $d_2=d_3=0$. This represents *B-C* coexistence as long as

$$-d_1<(b_2-b_1)^2\ . \tag{A7}$$

In this case, the process goes as follows. In the first step the new t,u,w,v expressions are obtained. In the second, one solves for d_1 and b_2, finding (A3) and (A4), but substituting 1 for 2 and 2 for 3. Therefore (v,w) is again as in (A5) and (A6), this time with b_1 as parameter.

The startling conclusion is that the three coexistence lines are three parts of the same curve, which has a triple autointersection at the triple point. Each one is parametrized by the physically allowed range of b_1,b_2,b_3. While b_2 and b_3 are positive and always $b_2<b_3$, b_1 is negative and is such that (A7) is satisfied. We may label each part by the value of the parameter at the triple point. Taking $d_2=d_3=0$ in the first representation, or $d_1=0$ in the second, we have the same cubic equation

$$2b^3+tb+u=0\ , \tag{A8}$$

whose three solutions are b_1,b_2,b_3 at the triple point. It may be checked from the fact that they give the same (v,w) values. For the $t=-4$, $u=1$ case of Fig. 1, they are

$$b_1=-1.526,\quad b_2=0.259,\quad b_3=1.267\ ,\qquad v=-2,\quad w=4\ . \tag{A9}$$

If we consider only one parameter $b\in(-\infty,\infty)$ in (A5) and (A6), we describe the whole curve. It has two branches, one for $b\in(0,\infty)$ that includes the *A-B* and *A-C* coexistence lines, another for $b\in(-\infty,0)$ that includes the *B-C* coexistence line, and another line corresponding to the condition that the two maxima have the same height, which passes by the lower critical point. The two short links, also shown in Fig. 1, mean that one maximum and one minimum have the same height.

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