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Critical phases in multicomponent fluid mixtures

L Mistura

Istituto di Fisica-Facoltà di Ingegneria, Università di Roma, Roma, Italy
and
Gruppo Nazionale di Struttura della Materia del CNR, Roma, Italy

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Abstract. An extension of Gibbs' theory of ordinary critical points is presented with the aim of describing and classifying higher-order critical phases in multicomponent fluid mixtures. A classification scheme based on two topological invariants, namely the dimensionality of the critical null space (corank) and the number of thermodynamic equations which characterize a critical phase (codimension) is proposed. A classical theorem of Marston Morse is used to discuss the phase diagram in the neighbourhood of critical phases of corank one and two.

1. Introduction

The classical, thermodynamic theory of ordinary critical points, at which two coexisting phases become identical, was developed by Gibbs (1876) one hundred years ago. In recent years higher-order critical points, at which three or more coexisting phases become identical, originally predicted upon phase rule arguments by Kohnstamm (1926), have been observed in various fluid mixtures (Griffiths and Widom 1973 for a number of references, Lang and Widom 1975) or predicted on the basis of model calculations (Griffiths 1975 and references quoted therein). Our purpose in this paper is to extend Gibbs' theory for describing and classifying higher-order critical phases in multicomponent fluid mixtures. With the aim of characterizing a tricritical phase (the only one so far observed in fluid mixtures) by thermodynamic equations, the problem of extending Gibbs' theory to higher-order critical points has already been considered by Krichevskii (1972) and Bartis (1973). However previous proposals for the classifications of critical points (Benguigui and Schulman 1973, Chang *et al* 1973, Griffiths 1975) do not rely on Gibbs' method. Benguigui and Schulman (1973) have used Thom's (1972) catastrophe theory to arrive at a classification by 'type', an integer which is a topological property for transitions derivable from a variational principle; Chang *et al* (1973) have attempted to characterize the topological properties of a critical surface in a field space by means of two integers, namely its dimensionality d and its order θ , while Griffiths' (1975) proposal, which is not limited to critical points, is in terms of the topological structure of the phase diagram in the field space in the immediate vicinity of the point in question. Some of the ideas introduced in these works fit quite naturally in our approach and will actually be adopted particularly to avoid, where possible, the introduction of new notations or terminology.

2. Gibbs' theory and the classification of critical points

We shall follow the convention of Griffiths and Wheeler (1970) and divide the thermodynamic variables into two classes: 'densities' and 'fields'. The fields (in contrast to the densities) have the property that they take on identical value in coexisting phases. A characteristic aspect of the classical theory is the use of a set of densities, like the energy density and mole fractions, to represent the thermodynamic states of a system in contrast to the modern approach (Griffiths and Wheeler 1970) in which use is made of a set of fields, like temperature and chemical potentials. A fluid of c components, in absence of external fields, will be described by $c + 1$ densities $\rho_1, \rho_2, \dots, \rho_{c+1}$ together with the corresponding fundamental equation

$$d\sigma = \sum_1^{c+1} h_i d\rho_i \tag{1}$$

where the quantities $h_i = \partial\sigma/\partial\rho_i$ ($i = 1, 2, \dots, c + 1$) are the fields conjugate respectively to the ρ_i . Thermodynamic stability requires that the surface $\sigma = \sigma(\rho_1, \dots, \rho_{c+1})$ is either convex or concave. Let us assume for definiteness convexity in all the arguments. This will actually be the case, for example, if σ represents the internal energy density. Now, provided that the second derivatives $\partial^2\sigma/\partial\rho_i \partial\rho_j = \partial h_i/\partial\rho_j$ exist, convexity of σ implies that the quadratic form

$$\sum_1^{c+1} \sum_{i,j} \frac{\partial h_i}{\partial \rho_j} \delta\rho_i \delta\rho_j \tag{2}$$

is positive definite or semi-definite. We may investigate this condition by means of a diagonalization procedure. A convenient set of diagonal coefficients in our problem is suggested by considering the Hessian

$$R(\rho_1, \dots, \rho_{c+1}) \equiv \partial(h_1, h_2, \dots, h_{c+1})/\partial(\rho_1, \rho_2, \dots, \rho_{c+1}) \tag{3}$$

which can be written as the product of $c + 1$ factors by iterating the following operation:

$$R(\rho_1, \rho_2, \dots, \rho_{c+1}) = \frac{\partial(h_1, \dots, h_{c+1})}{\partial(\rho_1, h_2, \dots, h_{c+1})} \frac{\partial(\rho_1, h_2, \dots, h_{c+1})}{\partial(\rho_1, \dots, \rho_{c+1})} = \left(\frac{\partial h_1}{\partial \rho_1}\right)_{h_2, \dots, h_{c+1}} R(\rho_2, \dots, \rho_{c+1}) \tag{4}$$

to get

$$R(\rho_1, \rho_2, \dots, \rho_{c+1}) = \left(\frac{\partial h_1}{\partial \rho_1}\right)_{h_2, \dots, h_{c+1}} \left(\frac{\partial h_2}{\partial \rho_2}\right)_{h_3, \dots, h_{c+1}} \dots \frac{\partial h_{c+1}}{\partial \rho_{c+1}} \tag{5}$$

where, at each step

$$\left(\frac{\partial h_i}{\partial \rho_i}\right)_{h_{i+1}, \dots, h_{c+1}} = \frac{R(\rho_i, \dots, \rho_{c+1})}{R(\rho_{i+1}, \dots, \rho_{c+1})} \tag{6}$$

and, for shortening the notation, only the fields held constant are made explicit in the partial derivatives. Obviously $(c + 1)!$ different factorizations can be obtained with this procedure and they are characterized by the fact that each factor is a derivative of a field with respect to the conjugate density. The diagonalization of the quadratic form (2) with the diagonal elements specified by equations (6) may be carried out by means of a

unimodular transformation of the sort described by Tisza (1961). Thermodynamic stability now implies that none of the diagonal coefficients can ever be negative, moreover the well known thermodynamic inequalities

$$\frac{\partial h_i}{\partial \rho_i} \geq \left(\frac{\partial h_i}{\partial \rho_i}\right)_{h_1} \geq \left(\frac{\partial h_i}{\partial \rho_i}\right)_{h_2} \geq \dots \geq \left(\frac{\partial h_i}{\partial \rho_i}\right)_{h_1, h_2, \dots, h_{i-1}} \geq 0 \tag{7}$$

which are usually referred to as the Le Chatelier principle, should be satisfied.

The classical theory proceeds by postulating a continuous variation of these thermodynamic derivatives from stable states, where they take on positive values, to unstable states, where at least one of these derivatives takes on negative values. These two regions are separated by the limits of stability, the so called spinodal ‘curve’. The main conclusion of the classical theory is that a critical phase is a stable one lying on the spinodal curve. It follows that the quadratic form (2) becomes positive semi-definite at a critical point and at least one of the diagonal elements will be zero. We therefore propose to divide critical phases into classes according to the rank or better the corank n of the quadratic form (2). By corank we mean the number of vanishing coefficients in a given diagonal form and it is to be preferred (in contrast to the rank) because it is independent of the number of components.

In order to understand the physical meaning of this classification we recall that, for constant values of the field variables, corresponding to the equilibrium of m phases, the coexistence region in the density space is, in general, an $(m - 1)$ simplex, i.e. a point for a single phase, a straight-line segment for two phases, a plane triangle for three, a tetrahedron for four and so on. If we have only two phases in equilibrium, the segment representing the coexistence region will determine a direction (one-dimensional affine subspace) in the density space. On approaching an ordinary critical point the two phases become identical and we assume that the direction of the coexistence region approaches a well defined limit, the critical direction. Now the existence of a single critical direction is a characteristic feature of critical points of corank 1 regardless of the maximum number of phases p which become identical.

If we have three phases in equilibrium the triangle representing the coexistence region will determine in the density space a plane (two-dimensional affine subspace). On approaching a critical point we may conceive two essentially different behaviours as shown schematically in figure 1.

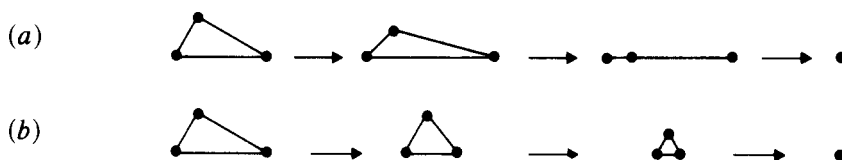


Figure 1.

In case (a), which corresponds to a tricritical point as it has been actually observed in fluid mixtures (Widom 1975), we have a single critical direction, while in case (b), which has been predicted for the two-dimensional three-state Potts model (Straley and Fisher 1973), the plane triangle approaches a well defined limit at the critical point. The existence of a single critical plane is a characteristic feature of critical points of corank 2 no matter what the value of p . It will be shown however in what follows that $p \geq 4$ if

$n = 2$. In general, the existence of a critical n -dimensional affine subspace, the null space of the quadratic form (2), is a characteristic feature of critical points of corank n .

We turn now to a description and classification of critical phases within a single class.

3. Critical phases of corank 1

For the first class, the critical direction will not, in general, be parallel to any coordinate axes or 'plane' in the density space. As a consequence all the thermodynamic derivatives of the same type of $(\partial h_1/\partial \rho_1)_{h_2, \dots, h_{c+1}}$ with c fields held constant, will vanish at the critical point. By contrast, according to the classical theory, those thermodynamic derivatives, like $(\partial h_1/\partial \rho_1)_{h_3, \dots, h_{c+1}}$, in which one or more densities are held constant, should remain finite and strictly positive. It may happen however that one or more densities take on identical values in coexisting phases. A well known example of this behaviour is an azeotropic line on the liquid-vapour equilibrium surface in binary systems. In these circumstances the critical direction will be parallel to some coordinate 'plane'. If, for example, ρ_2 is such a density the critical direction will be parallel to the $\rho_2 = \rho_2^{\text{crit}}$ 'plane' and $(\partial h_1/\partial \rho_1)_{h_3, \dots, h_{c+1}}$ will vanish while $(\partial h_2/\partial \rho_2)_{h_1, h_3, \dots, h_{c+1}}$ will remain positive at the critical point. In any case we may choose thermodynamic variables near the critical point such that the vanishing diagonal element will be $\partial h_{c+1}/\partial \rho_{c+1}$, i.e. with the ρ_{c+1} axes parallel to the critical direction. In this case the density ρ_{c+1} will play the role of the order parameter, being the only density, up to a constant factor, to take on different values in coexisting phases. The remaining c variables now actually behave like fields and are really irrelevant for the description of the critical behaviour. This change of variables is most conveniently obtained by means of a Legendre transform

$$g_1(x; h_1, h_2, \dots, h_c) = \sigma(\rho_1, \rho_2, \dots, \rho_c; x) - \sum_1^c h_K \rho_K \quad (8)$$

where $x \equiv \rho_{c+1}$ is the order parameter and g_1 is convex in x and concave in the field variables.

At a critical point we then have

$$\partial^2 g_1/\partial x^2 = \partial h_x/\partial x = 0 \quad (9)$$

where $h_x = \partial g_1/\partial x$ is the field conjugate to x and stability requires the first non-vanishing derivative of g_1 with respect to x to be of even order $2q$. At an ordinary critical phase $q = 2$, and we have therefore the two thermodynamic equations

$$\partial^2 g_1/\partial x^2 = 0 \quad \partial^3 g_1/\partial x^3 = 0 \quad (10)$$

while stability requires $\partial^4 g_1/\partial x^4 > 0$. At a tricritical point $q = 3$ (Bartis 1973, Widom 1975) and we have four thermodynamic equations

$$\partial^2 g_1/\partial x^2 = 0 \quad \partial^3 g_1/\partial x^3 = 0 \quad \partial^4 g_1/\partial x^4 = 0 \quad \partial^5 g_1/\partial x^5 = 0 \quad (11)$$

and stability requirements are satisfied if $\partial^6 g_1/\partial x^6 > 0$. The number of thermodynamic equations which characterize a critical phase will be called its codimension K . We have therefore $K = 2$ for an ordinary critical point, $K = 4$ for a tricritical point and in general $K = 2q - 2$. Either K or q may be used to make a complete list of different critical points

in the first class. For a given q the phase diagram in the critical region is then obtained expanding g_1 as a power series of x

$$g_1(x; h_1, \dots, h_c) = g_1(h_1, \dots, h_c) + a_1(h_1, \dots, h_c)(x - x_c) + a_2(h_1, \dots, h_c)(x - x_c)^2 + \dots + (x - x_c)^{2q} \tag{12}$$

where only terms up to the first non-vanishing coefficient have been retained and the coefficient of the highest power, which has to be positive, has been assumed to be 1. In general two or more phases in equilibrium should have the same value, say α , for h_x and the same value for $g_1 - xh_x$. These two conditions express the well known common tangent construction. The equation,

$$h_x(x; h_1, \dots, h_c) = \alpha \tag{13}$$

an algebraic equation of order $2q - 1$ with real coefficients, has at least one real root and a maximum of $2q - 1$ distinct real roots. A possible graph representing $g_1 - \alpha x$ as a function of x in a multiphase region is shown qualitatively in figure 2.

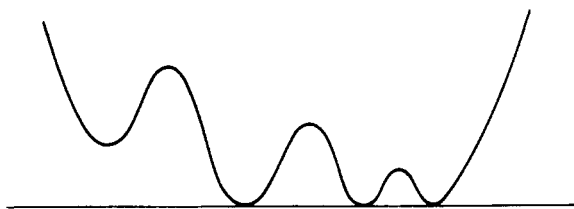


Figure 2. A possible graph representing $g_1 - \alpha x$ as a function of x in a multiphase region near a critical point of corank 1.

If we denote by m_1 the number of maxima in a graph like this and by m_0 the number of minima, we have the two relations

$$m_0 + m_1 \leq 2q - 1 \quad m_0 - m_1 = 1 \tag{14}$$

which provide the following inequality for m_0 :

$$m_0 \leq q \tag{15}$$

which in turn gives $p = q$. Note that p is the ‘order’ of the critical point according to Widom (1973) terminology.

The entire phase diagram could be determined by making a catalogue of the various possibilities for the solutions of equation (13), for example with the method proposed by Krinsky and Mukamel (1975) and adopted by Griffiths (1975).

In what follows we will show how this discussion may be extended to critical points of higher corank.

4. Critical phases of corank 2

If $n = 2$ we have a critical plane which, in general, will not be parallel to any axes or ‘plane’ in the density space. As a consequence the two vanishing diagonal coefficients will be $(\partial h_1 / \partial \rho_1)_{h_2, \dots, h_{c+1}}$ and $(\partial h_2 / \partial \rho_2)_{h_3, \dots, h_{c+1}}$ while those thermodynamic derivatives,

like $(\partial h_3/\partial \rho_3)_{h_4, \dots, h_{c+1}}$, in which two or more densities are held constant, should remain finite and strictly positive. As in the case of critical points of the first class special geometrical relationships may occur but in any case we may choose our variables near the critical point so that the vanishing diagonal elements are $\partial h_{c+1}/\partial \rho_{c+1}$ and $(\partial h_c/\partial \rho_c)_{h_{c+1}}$. With this choice, the densities $\rho_{c+1} \equiv x$ and $\rho_c \equiv y$ will play the role of order parameters, being the only two densities, up to a linear transformation, to take on different values in coexisting phases. In close analogy with the previous case, the change of variables is accomplished by the following Legendre transform of σ :

$$g_2(x, y; h_1, h_2, \dots, h_{c-1}) = \sigma(\rho_1, \dots, \rho_{c-1}; y, x) - \sum_{1^K}^{c-1} h_K \rho_K \tag{16}$$

which is convex in both x and y and concave in the field variables. The first three thermodynamic equations for a critical point of the second class are then

$$\partial^2 g_2/\partial x^2 = 0 \quad \partial^2 g_2/\partial y^2 = 0 \quad \partial^2 g_2/\partial x \partial y = 0 \tag{17}$$

and stability requires that the first non-vanishing derivative of g_2 with respect to x or y is of even order $2q$. For $q = 2$ we get the critical phase of lowest codimension. All the third-order derivatives vanish:

$$\partial^3 g_2/\partial x^3 = 0 \quad \partial^3 g_2/\partial y^3 = 0 \quad \partial^3 g_2/\partial x^2 \partial y = 0 \quad \partial^3 g_2/\partial y^2 \partial x = 0 \tag{18}$$

while the fourth-order derivatives should obey certain inequalities in order to guarantee the convexity of g_2 .

Equations (17) and (18) are the seven thermodynamic equations which characterize the critical phase of corank 2 of lowest codimension. It should be noted at this point that the four equations proposed by Krichevskii (1972) for a tricritical point are obtained by taking the first two in each set (17) and (18).

The next critical point with $n = 2$, corresponding to $q = 3$, will have $K = 18$ and in general $K = q(2q + 1) - 3$. In the spirit of the classical theory, in order to determine the phase diagram in the critical region, for a given value of q , g_2 will be represented by a polynomial in x and y of even order $2q$ whose coefficients are real, smooth functions of the fields h_1, h_2, \dots, h_{c-1} . In general, the points representing a set of coexisting phases should have a common tangent plane that is the same value for $h_x \equiv \partial g_2/\partial x$, $h_y \equiv \partial g_2/\partial y$ and $g_2 - xh_x - yh_y$. We have now a system of two real algebraic equations

$$h_x(x, y; h_1, \dots, h_{c-1}) = \alpha \quad h_y(x, y; h_1, \dots, h_{c-1}) = \beta \tag{19}$$

which has at least one real root and a maximum of $(2q - 1)^2$ distinct real roots. A possible graph representing $g_2 - xh_x - yh_y$ as a function of x and y in a multiphase region is qualitatively shown in figure 3. Under these conditions a general result, obtained by Morse (1925) for a real function of n independent variables and for a domain of definition not necessarily simply connected, seems to be applicable. Accordingly if we denote by m_0 the number of minima, by m_1 the number of saddle points and by m_2 the number of maxima in a graph like that in figure 3 we have

$$m_0 + m_1 + m_2 \leq (2q - 1)^2 \quad m_0 - m_1 + m_2 = 1 \tag{20}$$

from which

$$m_0 + m_2 \leq 2q(q - 1) + 1. \tag{21}$$

Let us consider in detail the case $q = 2$. If $m_2 = 0$ we have $m_0 \leq 5$ and therefore $m_1 \leq 4$. A configuration of this type with a maximum of five coexisting phases is expected to be

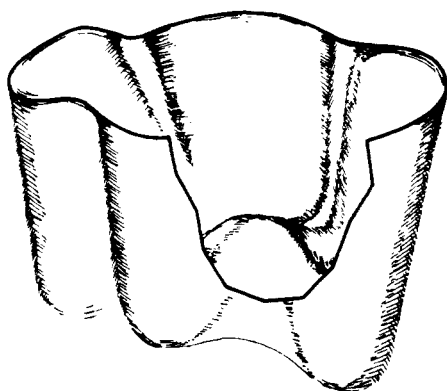


Figure 3. A possible graph representing $g_2 - \alpha x - \beta y$ as a function of x and y in a multiphase region near a critical point of corank 2.

found in the neighbourhood of the critical point of the first class with $K = 8$. We therefore exclude the possibility that the same situation might occur in the present case. With $m_2 = 1$ we get from equation (21)

$$p = 2q(q - 1) \tag{22}$$

which gives $p = 4$ for $q = 2$. This result confirms a previous suggestion by Griffiths (1975). When we have four coexisting phases there are two cases which must be distinguished. In the first, the four points of contact of g_2 with the quadruple tangent plane may be joined so as to form a convex quadrilateral; in the second, one of the points of contact lies within the triangle formed by joining the other three. Figure 4(a) gives a somewhat stylized representation of the approach to the critical point in the first case. (For the sake of comparison figure 4(b) shows schematically the approach of a quadruple point to a critical phase with $n = 1$ and $K = 6$.)

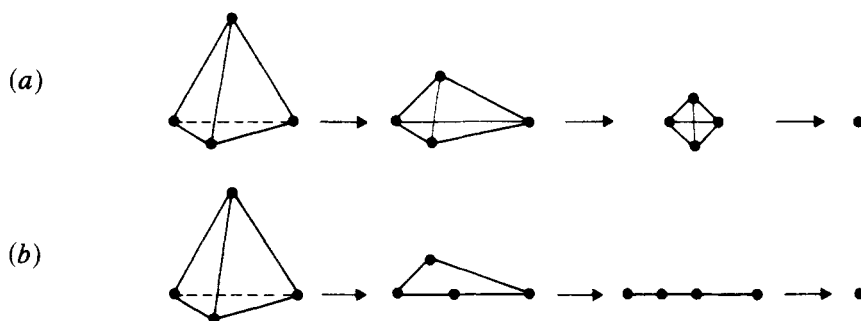


Figure 4.

The four vertices of the quadrilateral correspond to the four coexisting phases or hills of g_2 , the four sides to the cols and the intersection of the diagonal to the single basin. For this configuration we have $m_0 - m_1 + m_2 = 1$ and $m_0 + m_1 + m_2 = 9$ it may therefore occur in the neighbourhood of the critical point with $n = 2$ and $K = 7$. But when the point of contact lies within the triangle formed by joining the other three (figure 5), we

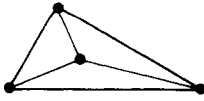


Figure 5.

have $m_0 = 4$, $m_1 = 6$ and $m_2 = 3$, therefore $m_0 + m_1 + m_2 = 13$ and such a configuration cannot occur in the neighbourhood of the critical point with $K = 7$, but we must have at least $K = 18$. It is interesting to remark at this point that a triple point which is essentially different from that observed in the tricritical region (figure 1(a)) should exist in the neighbourhood of the critical point with $K = 7$. Indeed for a configuration in which the system of equations (19) has seven distinct real roots we may have $m_0 = 3$ with $m_1 = 3$ and $m_2 = 1$, that is a graph for g_2 with three hills, three cols and a single basin which on approaching the critical point could behave as schematically shown in figure 1(b). These aspects of the phase diagram can also be studied, with the help of Morse (1925) theorem, for critical points of higher corank. However owing to the higher codimension of these critical phases we have not found this study of great interest so far.

5. Concluding remarks

A possible notation for the critical points discussed in the previous sections is as follows. A capital letter, as proposed by Griffiths (1975), to indicate the maximum number of phases which become identical, a subscript to indicate the codimension K and a preceding superscript will give the corank n . Accordingly an ordinary critical surface will be identified with the symbol 1B_2 a tricritical surface 1C_4 and the critical phase of lowest codimension with $n = 2$ will be 2D_7 and we should have next ${}^3N_{16}$, etc. Because the codimension K is related to the maximum number of phases our notation is redundant. We feel however it has the advantage of readily providing some relevant topological properties of a critical surface.

We should mention in conclusion that a more elegant geometric formulation of the theory is possible which has the advantage of introducing a coordinate-free language. Indeed even if a thermodynamic space, i.e. the set of all thermodynamic states of a system, can be regarded as a subset of a vector space it cannot be so regarded in any canonical way and in fact linear and non-linear changes of variables are frequently used in thermodynamics. We would therefore like to know what properties are independent of the description we give of the space. With this in mind we will now briefly outline a description of the concepts of thermodynamics within the framework of differential topology, i.e. that branch of differential geometry which studies the more general, purely topological properties of differentiable manifolds (Milnor 1969). We agree with Smale (1972) that a principal candidate for the state space of a system should be a differentiable manifold. We will assume therefore that the thermodynamic states of our system are represented by the points x of a $(c + 1)$ -dimensional differentiable manifold M so that at least locally, the states can be put into a one-to-one continuous correspondence (homeomorphism) with the points of an open set of the $(c + 1)$ -dimensional real linear space R^{c+1} . The mere differentiability of the manifold permits one to introduce curves (quasi-static processes), differentiable functions (thermodynamic state variables) and relations of local parallelism and linear differential forms, but does not mean

that such concepts as parallel transport, curvature and metric, which play a central role in the theory of gravitation, exist in it.

A coordinate system in the thermodynamic space is a set of $c + 1$ real differentiable functions $x_1(x), x_2(x), \dots, x_{c+1}(x)$ on M . Coordinate transformations $x'_i = x'_i(x_1, x_2, \dots, x_{c+1})$ should provide locally a one-to-one differentiable map, in particular, therefore, the Jacobian $\partial(x'_1, x'_2, \dots, x'_{c+1})/\partial(x_1, x_2, \dots, x_{c+1})$ should not vanish.

A basic role in Gibbs' theory of thermodynamic stability is played by the function

$$\Phi(x; p', T', \mu'_1, \dots, \mu'_c) = \epsilon(x) + p' - T'\sigma(x) - \sum_1^c \mu'_h \rho_h(x) \tag{23}$$

where $p', T', \mu'_1, \dots, \mu'_c$ are constants to be determined by the equilibrium conditions, ϵ is the internal energy density, σ the entropy density, $\rho_1, \rho_2, \dots, \rho_c$ the mass densities of the c components. The stable equilibrium states are defined by the following variational principle (Gibbs 1876): *if for a given state of the fluid, it is possible to assign such values to the constants $p', T', \mu'_1, \dots, \mu'_c$ that Φ is zero and positive for any other state in its neighbourhood then the given state of the fluid will be stable.*

The intrinsic nature of this statement is not usually recognized. By contrast, in order to work out from this principle the several conditions of stability a definite set of independent variables is introduced, namely the entropy density and the densities of the various components. Admittedly this particular choice is strongly suggested by the expression (23), we have therefore to show how the consequence of the principle may be worked out without any reference to a particular set of variables.

Stable states correspond to critical points of Φ in the sense of differential topology, i.e. points where the derivative of Φ vanishes (Milnor 1969). Following this terminology stable critical phases correspond to degenerate critical points of Φ . These two notions are independent from the choice of the coordinate system as can be readily verified directly. Indeed, in a given coordinate neighbourhood of a critical point $\partial\Phi/\partial x_l = 0$ ($l = 1, 2, \dots, c + 1$) and therefore also

$$\frac{\partial\Phi}{\partial x'_K} = \sum_1^{c+1} \frac{\partial\Phi}{\partial x_l} \frac{\partial x_l}{\partial x'_K} = 0.$$

On the other hand for the second-order derivatives we have in general

$$\frac{\partial^2\Phi}{\partial x'_K \partial x'_l} = \sum_{i,j}^{c+1} \frac{\partial^2\Phi}{\partial x_i \partial x_j} \frac{\partial x_i}{\partial x'_K} \frac{\partial x_j}{\partial x'_l} + \sum_1^{c+1} \frac{\partial\Phi}{\partial x_i} \frac{\partial^2 x_i}{\partial x'_K \partial x'_l} \tag{24}$$

but the second term on the right-hand side vanishes at a critical point with the consequence that the matrix $\partial^2\Phi/\partial x_i \partial x_j$ represent a tensor with respect to the basis $(\partial/\partial x_1, \partial/\partial x_2, \dots, \partial/\partial x_{c+1})$. The shape of Φ in the neighbourhood of a stable normal state is determined by the lemma of Morse (1925). To the author's knowledge there is no comparatively general result for the shape of Φ in the neighbourhood of a critical phase. According to the results obtained in this paper the study of phase diagrams near a critical point in multicomponent fluid mixtures may help to elucidate this problem.

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