Chapter 16: Thermodynamics of Fluids

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16.1 INTRODUCTION

A material is a fluid when its mechanical behavior is characterized by a single coordinate: the volume, V. The force conjugate to V is the hydrostatic pressure, -P, where the minus sign ensures that the pressure is ordinarily positive. Two types of material are fluids: liquids and gases that cannot support equilibrium shear stresses, and solids that are in unconstrained mechanical equilibrium with a fluid such as the atmosphere. While solids can support non-hydrostatic stresses, it can be shown that these inevitably disappear when the solid achieves unconstrained mechanical equilibrium with a medium that imposes a hydrostatic stress. Hence all materials are fluids under appropriate conditions.

Systems that are nominally fluid may still have a relatively complex mechanical behavior because of either of two complicating factors: electromagnetic fields or two-phase interfaces. Electromagnetic fields are most important when the material is a dielectric that can be polarized internally, or when it contains ion cores that have permanent magnetic moments. The electromagnetic field can usually be ignored when the field is small or the material is a conductor or non-polar insulator. Interfaces are present whenever the system contains several distinct phases. However, the thermodynamic contribution of the interfaces can usually be neglected when the single-phase regions are large and the interfaces are not highly curved.

In the following three chapters we avoid the complications introduced by interfaces, non-hydrostatic stresses, and electromagnetic fields by confining our attention to systems of simple fluids, where a simple fluid is defined as a system that is characterized by the coordinates \{S,V,\{N\}\}, or any equivalent set.

The present chapter develops the general theory of simple fluids, essentially as it was proposed by Gibbs (Equilibrium of Heterogeneous Substances). The chapter begins with a review of the fundamental equation of a fluid and the conditions of internal equilibrium and stability. It then discusses the nature and geometry of the fundamental surface, treats the equilibrium and stability of systems that contain several distinct phases, and introduces the phase rule and the general concept of a phase diagram. It finishes with a discussion of phase transformations, critical points and mutations in simple fluids. In the following two chapters we develop and illustrate these concepts through specific discussions of one-component simple fluids and multicomponent fluids, or solutions.

The equilibrium behavior of a fluid phase is determined by its fundamental equation, which expresses the thermodynamic potential as a function of a complete set of constitutive variables. The fundamental equation can always be represented as an \(n\)-dimensional surface in the \((n+1)\)-dimensional fundamental space that is spanned by the thermodynamic potential and the \(n\) constitutive coordinates. It is often easiest to understand the thermodynamic and phase relations of a system by visualizing the geometry of the fundamental surface. A simple example is the relation between the binary phase diagrams that map the equilibrium behavior of binary solutions and the free energy-composition curves of
the individual phases, which most students of materials science encounter very early in their technical education. Hence a good part of this chapter is concerned with the geometry of fundamental surfaces.

### 16.2 The Fundamental Equation of a Simple Fluid

The constitutive coordinates of a simple fluid are \( (S, V, \{N\}) \), where \( S \) is the entropy, \( V \) is the volume, and \( \{N\} \) is the set of independent chemical components.

#### 16.2.1 Chemical components

The set of independent chemical components includes only those components whose quantities must be specified to fix the composition of the system. The number of components \( (c) \) is most often equal to the number of different atomic species. However, the number of independent components may exceed the number of atomic species if it is useful to consider atomic vacancies as a component or if the atoms themselves are divisible. For example, the thermodynamics of conductors is often best phrased so that the conduction electrons are a separate component from the ion cores. If there is an external source of electrons the conduction electrons constitute an independent component. The number of components may also be less than the number of different atoms. For example, if the system is made by mixing stoichiometric compounds then the number of independent components is the number of compounds, irrespective of the number of different atom types.

#### 16.2.2 The energy function

The fundamental equation of a simple fluid can be written as the energy function

\[
E = \tilde{E}(S, V, \{N\}) = TS - PV + \sum_k \mu_k N_k
\]

The partial derivatives of \( \tilde{E} \) provide constitutive equations for the thermodynamic forces, as is evident from the differential form

\[
dE = T dS - P dV + \sum_k \mu_k dN_k
\]

The second partial derivatives provide constitutive equations for the thermodynamic properties.

Since the thermodynamic behavior of the fluid is independent of the quantity that is present, it is usually convenient to eliminate the quantity of fluid by dividing the energy by either the volume or the aggregate mole number. This procedure restates the fundamental equation in terms of the energy density, either
\[ E_v = \tilde{E}_v(S_v, \{n\}) \]  

where \( E_v \) is the energy per unit volume, \( S_v \) is the entropy per unit volume and \( n_k \) is the mole number of the \( k^{th} \) specie per unit volume, or

\[ e = \tilde{e}(s, v, \{x\}) \]

where \( e, s \) and \( v \) are the molar energy, entropy and volume and \( x_k \) is the mole fraction of the \( k^{th} \) specie. The differential forms of equations 16.3 and 16.4 were developed in the discussion of classical thermodynamics, and are

\[ dE_v = TdS_v + \sum_{k=1}^{c} \mu_k dn_k \]

where \( c \) is the number of independent chemical components, and

\[ de = Tds - Pdv + \sum_{k=1}^{c-1} \tilde{\mu}_k dx_k \]

where \( v \) is the molar volume, \( \tilde{\mu}_k \) is the relative potential of the \( k^{th} \) component,

\[ \tilde{\mu}_k = \mu_k - \mu_c \]

and the summation is truncated at the \((c-1)^{th}\) term since

\[ \sum_{k=1}^{c} x_k = 1 \]

### 16.2.3 Alternate forms of the fundamental equation of a simple fluid

The fundamental equation can also be written in the entropic form

\[ S = \tilde{S}(E, V, \{N\}) = \frac{E}{T} + \left[ \frac{P}{T} \right] V - \sum_k \left[ \frac{\mu_k}{T} \right] N_k \]

whose differential is

\[ dS = \left[ \frac{1}{T} \right] dE + \left[ \frac{P}{T} \right] dV - \sum_k \left[ \frac{\mu_k}{T} \right] dN_k \]
The Legendre transforms of the energy function yield the common alternative forms of the fundamental equation of a simple fluid. The *enthalpy* is

\[ H = \tilde{H}(S,P,\{N\}) = E + PV = TS + \sum_k \mu_k N_k \quad 16.11 \]

whose differential is

\[ dH = TdS + VdP + \sum_k \mu_k dN_k \quad 16.12 \]

The *Helmholtz free energy* is

\[ F = \tilde{F}(T,V,\{N\}) = E - TS = - PV + \sum_k \mu_k N_k \quad 16.13 \]

whose differential is

\[ dF = - SdT - PdV + \sum_k \mu_k dN_k \quad 16.14 \]

The *Gibbs free energy* is

\[ G = \tilde{G}(T,P,\{N\}) = E - TS + PV = \sum_k \mu_k N_k \quad 16.15 \]

whose differential is

\[ dG = - SdT + VdP + \sum_k \mu_k dN_k \quad 16.16 \]

The *work function* is

\[ \Omega = \tilde{\Omega}(T,V,\{\mu\}) = E - TS - \sum_k \mu_k N_k = - PV \quad 16.17 \]

whose differential is

\[ d\Omega = - SdT - PdV - \sum_k N_k d\mu_k \quad 16.18 \]

The thermodynamic potentials can also be written as densities by dividing through by the volume or total mole number (provided that these quantities are controlled). The values of the differentials change as was illustrated for the case of the energy density. One of the most important of these is the volume density of the work function,
\[ \Omega_V = -P \]  

which leads immediately to the \textit{Gibbs-Duhem function}

\[ P = \dot{P}(T, \{\mu\}) \]

whose differential is the \textit{Gibbs-Duhem equation},

\[ dP = S_v dT + \sum_k n_k d\mu_k \]

16.2.4 Thermodynamic properties of a simple fluid

The first-order thermodynamic properties of a simple fluid are most often defined from the Gibbs free energy. The second thermal derivative is

\[
\left[\frac{\partial^2 \tilde{G}}{\partial T^2}\right] = -\frac{C_p}{T} \tag{16.22}
\]

where the \textit{isobaric specific heat}, \(C_p\), is defined by the relation,

\[ C_p = N c_p = T \left[ \frac{\partial S}{\partial T} \right]_{P,N} \]

The second derivative with respect to the pressure is

\[
\left[\frac{\partial^2 \tilde{G}}{\partial P^2}\right] = -V \kappa_T \tag{16.24}
\]

where the \textit{isothermal compressibility}, \(\kappa_T\), is defined as

\[ \kappa_T = \frac{1}{V} \left[ \frac{\partial V}{\partial P} \right]_{T,N} \]

The cross derivative is

\[
\left[\frac{\partial^2 \tilde{G}}{\partial P \partial T}\right] = V \alpha \tag{16.26}
\]

where the \textit{coefficient of thermal expansion}, \(\alpha\), is defined as

\[ \alpha = \frac{1}{V} \left[ \frac{\partial V}{\partial T} \right]_{P,N} \]

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The first order chemical properties are
\[
\left[ \frac{\partial^2 \bar{G}}{\partial N_k^2} \right] = \left[ \frac{\partial \mu_k}{\partial N_k} \right]_{TP\{N\}'} = 16.28
\]
where the set \{N\}' includes all components except that used in the partial derivative, and
\[
\left[ \frac{\partial^2 \bar{G}}{\partial N_j \partial N_k} \right] = \left[ \frac{\partial \mu_j}{\partial N_k} \right]_{TP\{N\}'} = \left[ \frac{\partial \mu_k}{\partial N_j} \right]_{TP\{N\}'} = 16.29
\]
The properties that involve cross derivatives between the pressure and the composition are
\[
\left[ \frac{\partial^2 \bar{G}}{\partial N_k \partial P} \right] = \left[ \frac{\partial \mu_k}{\partial P} \right]_{T\{N\}} = \left[ \frac{\partial V}{\partial N_k} \right]_{TP\{N\}'} = 16.30
\]
The partial derivative on the right in 16.30 is called the partial molar volume of the kth component. The cross derivatives between the temperature and the composition are
\[
\left[ \frac{\partial^2 \bar{G}}{\partial N_k \partial T} \right] = \left[ \frac{\partial \mu_k}{\partial T} \right]_{P\{N\}} = -\left[ \frac{\partial S}{\partial N_k} \right]_{TP\{N\}'} = 16.31
\]
where the partial derivative on the right is called the partial molar entropy of the kth component.

The first-order thermodynamic properties in any other representation can be derived from this set by Jacobian transformations. Other properties that are commonly used are the isometric specific heat,
\[
C_V = C_p - \frac{TV\alpha^2}{\kappa_T} = 16.32
\]
and the isentropic compressibility,
\[
\kappa_S = \frac{C_V}{C_p} \kappa_T = 16.33
\]

16.3 THE CONDITIONS OF INTERNAL EQUILIBRIUM

The conditions of thermal and chemical equilibrium were derived earlier in the course. Thermal equilibrium always requires that the temperature be the same everywhere:
\[
T = \text{const}. = 16.34
\]
The conditions of chemical and mechanical equilibrium depend on whether potential fields must be taken into account.

In the absence of external potential fields chemical equilibrium requires that the chemical potential of each specie be the same everywhere in the fluid:

\[ \mu_k = \text{const.} \quad 16.35 \]

The corresponding condition of mechanical equilibrium can be found from the Gibbs-Duhem relation, equation 16.21, which shows that the pressure is uniform when the temperature and the chemical potentials are. It follows that

\[ \text{a simple fluid that is in mechanical equilibrium in the absence of external fields has a uniform pressure:} \]

\[ P = \text{const.} \quad 16.36 \]

When external fields cannot be neglected the condition of chemical equilibrium is changed to read

\[ \mu_k + \phi_k = \text{const.} \quad 16.37 \]

where \( \phi_k \) is the potential energy per mole (or per unit mass, depending on the definition of the chemical potential) in the external field. Taking the gradient of equation 16.37 we have

\[ \nabla \mu_k = - \nabla \phi_k \quad 16.38 \]

which, given the Gibbs-Duhem equation, shows that

\[ \text{when a simple fluid is in mechanical equilibrium in the presence of an external field that imposes the potential } \phi_k \text{ per mole, the gradient of the pressure has the value} \]

\[ \nabla P = \sum_k n_k \nabla \mu_k = - \sum_k n_k \nabla \phi_k \quad 16.39 \]

There are three potential fields that are commonly encountered in materials science: the gravitational field, the centrifugal field and the electric field. The gravitational potential has the constant gradient per unit mass

\[ \nabla \phi = g e_z \quad 16.40 \]

where \( g \) is the gravitational constant and \( e_z \) is a unit vector in the vertical direction. It follows that the condition of mechanical equilibrium for a simple fluid in a gravitational field is
\[ \nabla P = \frac{dP}{dz} \mathbf{e}_z = - \rho g \mathbf{e}_z \quad 16.41 \]

where \( \rho \) is the mass density of the fluid.

The centrifugal potential has the gradient per unit mass,

\[ \nabla \phi = - \omega^2 r \mathbf{e}_r \quad 16.42 \]

where \( \omega \) is the angular velocity of rotation, \( r \) is the distance from the axis of rotation and \( \mathbf{e}_r \) is a unit vector in the direction of \( r \). It follows that the condition of mechanical equilibrium for a simple fluid in a centrifugal field is

\[ \nabla P = \frac{dP}{dr} \mathbf{e}_r = \rho \omega^2 r \mathbf{e}_r \quad 16.43 \]

The electric field acts only on charged species and has the gradient

\[ \nabla \phi_k = - q_k \mathbf{E} \quad 16.44 \]

where \( q_k \) is the charge per mole of the \( k \)th specie and \( \mathbf{E} \) is the electric field. It follows that the condition of mechanical equilibrium for a simple fluid in an electric field is

\[ \nabla P = q \mathbf{E} \quad 16.45 \]

where

\[ q = \sum_k n_k q_k \quad 16.46 \]

is the net electric charge per unit volume.

16.4 The Fundamental Surface

16.4.1 The energy surface

The fundamental equation of a simple fluid

\[ E = \tilde{E}(S,V,\{N\}) \quad 16.47 \]

shows that the energy is a function of \( c+2 \) variables, where \( c \) is the number of independent components. It follows that the energy can be represented as a \((c+2)\)-dimensional hypersurface in a \((c+3)\)-dimensional space. This hypersurface is the energy surface, and is one
example of the \textit{fundamental surface} of the fluid. It provides a graphical representation of the equilibrium behavior of the fluid.

The stability of a fluid is governed by the curvature of the energy surface. It is easily shown that

\textit{the energy surface of a homogeneous stable fluid is concave}

that is, it has an upward curvature everywhere, as is illustrated for the two-dimensional case in Figure 16.1. [The modifier \textit{homogeneous} is needed because, as we shall see, the equilibrium state of a fluid may contain several distinct phases. We shall defer discussion of this case.]

\begin{center}
\begin{tikzpicture}
\begin{axis}[
view={0}{90},
axis lines=left,
axis line style={-},
xticklabels={E, η},
xtick={0,1},
yticklabels={0,1},
ytick={0,1},
width=0.5\textwidth,\]
\addplot[domain=0:1,samples=50,smooth,thick] {x^2};
\end{axis}
\end{tikzpicture}
\end{center}

Fig. 16.1: Projection of the fundamental surface on the E-η plane showing that the fundamental surface is concave.

To prove this note that the second derivatives of the energy function, \( E = \tilde{E}(\{u\}) \), form the \((n \times n)\) dimensional matrix of properties whose elements are

\[
E_{ik} = \left[ \frac{\partial^2 \tilde{E}}{\partial u_i \partial u_k} \right] \quad 16.48
\]

The conditions of stability require that

\[
E_{kk} = \left[ \frac{\partial^2 \tilde{E}}{\partial u_k^2} \right] > 0 \quad 16.49
\]

so that \( E(\{u\}) \) is necessarily concave in each of the independent variables, \( u_k \), over the range for which it is stable. The local condition of stability is

\[
\delta^2 E = \frac{1}{2} \sum_{k=1}^{n} \lambda_k (\delta u_k)^2 > 0 \quad 16.50
\]

where the \( \lambda_k \) are the \( n \) eigenvalues of the property matrix, \((E_{ij})\), and the \( \eta_k \) are the \( n \) corresponding eigenvectors. The eigenvectors and eigenvalues of \( E_{ij} \) are functions of the constitutive coordinates that may vary from point to point on the fundamental surface. How-
ever, the inequality 16.50 requires that at any point on the fundamental surface where the fluid is stable

$$\left[ \frac{\partial^2 \tilde{E}}{\partial \eta_k^2} \right] = \lambda_k > 0$$ 16.51

for all k. It is sufficient that the least eigenvalue, $\lambda_{\text{min}}$, be greater than zero. It follows that the fundamental surface is concave wherever the fluid is stable.

Since the equilibrium behavior of a fluid is independent of its quantity it is often more useful to consider the energy densities, $E_v(S_v, \{n\})$ or $\epsilon(s, v, \{x\})$. In either case the energy surface is a (c+1)-dimensional surface in a (c+2)-dimensional space. The condition of local stability requires that the eigenvalues of the property matrices $E_{vij}$ and $e_{ij}$ have only positive eigenvalues, so the energy surfaces $\tilde{E}_v(S_v, \{n\})$ and $\tilde{\epsilon}(s, v, \{x\})$ are also concave wherever the fluid is stable.

### 16.4.2 Alternate forms of the fundamental surface

A fundamental space and fundamental surface can be defined for any of the thermodynamic potentials that are derived from the energy function by Legendre transformation. In every case the stability of the fluid is associated, geometrically, with the curvature of the fundamental surface. However, the curvature of stable segments of the fundamental surface depends on the natural coordinates of the thermodynamic potential that generates the surface, and changes as the Legendre transform is used to replace deformation coordinates by their conjugate forces. The restrictions on the curvature of the fundamental surface can be found from the local conditions of stability and the properties of the Jacobian transformation.

To phrase the general results, consider the thermodynamic potential

$$\Phi_t = \Phi_t(p_1, \ldots, p_r, u_{r+1}, \ldots, u_n)$$

$$= E - \sum_{k=1}^{r} p_k u_k$$ 16.52

where $\Phi_t$ is the $t^{th}$ Legendre transformation of the energy function, $E = \tilde{E}(\{u\})$, and $p_k$ is the force conjugate to the deformation coordinate, $u_k$. The partial derivatives of $\Phi$ are

$$\left[ \frac{\partial \tilde{\Phi}}{\partial p_k} \right] = - u_k \quad (k = 1, \ldots, r)$$ 16.53

$$\left[ \frac{\partial \tilde{\Phi}}{\partial u_k} \right] = p_k \quad (k = r+1, \ldots, n)$$ 16.54
The thermodynamic properties that are determined by the potential, \( \Phi \), are the \( n(n+1)/2 \) independent elements of the matrix, \( \Phi_{ij} \), of second partial derivatives of \( \Phi \). The determinant of the property matrix, \( \Phi_{ij} \), is defined as the sum

\[
\text{det}(\Phi_{ij}) = \sum_{P} (-1)^{P} \Phi_{i1} \Phi_{2j} \cdots \Phi_{hk}
\]

where the sequence \( (i,j,...,k) \) is a permutation of the sequence of numbers \( (1,2,...,n) \), \( P \) is the order of the permutation, and the sum is taken over all permutations. Given equations 16.53 and 16.54 the determinant can also be written in the Jacobian form

\[
\text{det}(\Phi_{ij}) = \frac{\partial(-u_{1},...,u_{r},p_{r+1},...,p_{n})}{\partial(p_{1},...,p_{r},u_{r+1},...,u_{n})}
\]

As we discussed in the development of classical thermodynamics, the thermodynamic potentials that depend on mixtures of forces and deformation coordinates are useful to discuss the behavior of systems whose walls are such that the forces that appear in the set of constitutive variables are fixed by the environment while the deformation coordinates are fixed by the content of the system. We are hence usually interested in the changes in \( \Phi \) that occur either when the forces are altered by changes in the environment at a constant content of the system, or when the system is altered by changing its content in a fixed environment. The former involve changes in the set \( \{p_{1},...,p_{r}\} \) at constant \( \{u_{r+1},...,u_{n}\} \). The latter are variations in \( \{u_{r+1},...,u_{n}\} \) at constant values of \( \{p_{1},...,p_{r}\} \). It is straightforward to show that the fundamental surface that describes the dependence of \( \Phi \) on the variables \( \{u_{r+1},...,u_{n}\} \) is concave when the system is stable, while that which relates \( \Phi \) to the forces \( \{p_{1},...,p_{r}\} \) is convex.

To prove the first statement we use the local condition of stability, which requires that \( \Phi \) be a minimum with respect to variations of state at constant values of \( \{p_{1},...,p_{r}\} \). The second variation of \( \Phi \) is

\[
\delta^{2} \Phi = \frac{1}{2} \sum_{ij=r+1}^{n} \Phi_{ij} \delta u_{i} \delta u_{j} \geq 0
\]

which can only be true for all variations of \( \{u_{r+1},...,u_{n}\} \) if the \( (n-r)x(n-r) \) matrix of coefficients

\[
\Phi_{ij} = \left[ \frac{\partial^{2} \Phi}{\partial u_{i} \partial u_{j}} \right]
\]

has only positive eigenvalues. Hence
the fundamental surface of the potential \( \Phi(p_1, \ldots, p_r, u_{r+1}, \ldots, u_n) \) is concave with respect to variations of the deformation coordinates \( u_{r+1}, \ldots, u_n \) when the fluid is locally stable.

To determine the behavior of the fundamental surface of the potential \( \Phi \) with respect to variations of the forces, \( p_1, \ldots, p_r \), note that the Jacobian determinant of the coefficients

\[
\Phi^p_{ij} = \left[ \frac{\partial^2 \tilde{\Phi}}{\partial p_i \partial p_j} \right]
\]

16.59

can be written

\[
\det(\Phi^p_{ij}) = \frac{\partial(-u_1, \ldots, u_r)}{\partial(p_1, \ldots, p_r)} = \left[ \frac{\partial(p_1, \ldots, p_r)}{\partial(-u_1, \ldots, u_r)} \right]^{-1}
\]

16.60

The second form of the right-hand side is just the reciprocal of the determinant of the matrix whose elements are

\[
-E_{ij} = - \left[ \frac{\partial^2 \tilde{E}}{\partial u_i \partial u_j} \right]
\]

16.61

But the eigenvalues of the matrix \( E_{ij} \) are all positive, so the eigenvalues of the matrix whose elements are \(-E_{ij}\) are negative. Hence the eigenvalues of the matrix \( \Phi^p_{ij} \) are negative, and

the fundamental surface of the potential \( \Phi(p_1, \ldots, p_r, u_{r+1}, \ldots, u_n) \) is convex with respect to variations of the forces \( p_1, \ldots, p_r \) when the fluid is locally stable.

16.4.3 The Gibbs-Duhem function

As a first example of the relations derived above consider the Gibbs-Duhem function, which yields a fundamental equation that gives the fluid pressure in the form

\[
P = \tilde{P}(T, \{\mu\}) = - \Omega_v
\]

16.62

Equation 16.62 is the equation of a fundamental surface in the \((c+2)\)-dimensional space that is spanned by \( P, T, \) and \( \{\mu\} \). Since

\[
\left[ \frac{\partial \tilde{P}}{\partial T} \right] = S_v
\]

16.63

\[
\left[ \frac{\partial \tilde{P}}{\partial \mu_k} \right] = n_k
\]

16.64
the pressure increases monotonically with $T$ and $\{\mu\}$, and hence increases with any variation that involves positive changes in the constitutive variables.

![Diagram](image)

Fig. 16.2: A portion of the projection of the fundamental surface $\tilde{P}(T,\{\mu\})$ on the $P$-$\eta$ plane, where $\eta$ is a generalized coordinate that is a linear combination of the coordinates $T$ and $\{\mu\}$.

It can, moreover, be shown that the pressure surface is concave. Since the pressure is the negative of the work function per unit volume its second partial derivatives, which are the elements of the property matrix, $P_{ij}$, are the negatives of the second partial derivatives of $\Omega y$. The results of the previous section show that the eigenvectors of the matrix of second derivatives of $\Omega y$ are negative. Hence the eigenvectors of $P_{ij}^p$ are all positive, and the second variation of $P$ can be written in terms of its eigenvectors, $\eta_k$, as

$$\delta^2 P = \frac{1}{2} \sum_k \lambda_k^p (\delta \eta_k^p)^2 \tag{16.65}$$

Coupling this result with the positive definite character of the first partial derivatives of the function, $P$, it follows that the fundamental surface $P(T,\{\mu\})$ is monotonic and concave for any variation whatever. This behavior is illustrated in Figure 16.2 for the variation of $P$ with an arbitrary coordinate, $\eta_k$ which is any linear combination of the constitutive coordinates $(T,\{\mu\})$.

### 16.4.4 The Gibbs free energy

The potential that is usually most convenient for the treatment of fluid solutions is the Gibbs free energy

$$G = \tilde{G}(T,P,\{N\}) \tag{16.66}$$

or, in molar form,

$$g = \tilde{g}(T,P,\{x\}) \tag{16.67}$$
The natural variables of the Gibbs free energy are a mixture of the forces, \((T,P)\), and the deformation coordinates, \(\{N\}\) or \(\{x\}\). The results of the previous section show when the system is stable the fundamental surface that gives the Gibbs free energy in the space of its natural variables is convex with respect to variations of the forces \(T\) and \(P\), but is concave with respect to changes in the composition at given \(T\) and \(P\). The former behavior is illustrated in Fig. 16.3.

![Graph showing convex dependence of Gibbs free energy on temperature](image)

Fig. 16.3: The convex dependence of the Gibbs free energy on the temperature.

### 16.5 The Boundaries of the Fundamental Surface

#### 16.5.1 Types of boundaries

Let a homogeneous fluid be locally stable for at least some range of values of its constitutive coordinates. In this case its energy surface must be concave over the corresponding region of the fundamental space. The limit of the range of stability of the fluid falls at the boundary of the concave portion of the fundamental surface. The locus of the boundary is set by one of three conditions.

First, the fundamental surface terminates naturally where the constitutive variables cease to be defined. For example, the compositions, \(x_k\), satisfy the condition \(0 \leq x \leq 1\), and the fundamental surface \(e(s,v,\{x\})\) terminates at the two extremes.

Second, the fundamental surface terminates where the conditions of stability are violated. In the case of the energy surface the stability limit falls at an inflection point where the surface loses its concavity in the direction of the minimal eigenvector. It is often possible to estimate the shape that the fundamental surface would have if it were possible to continue the range of existence of the fluid beyond the stability limit (for example, by imposing kinetic constraints that prevent the fluid from transforming into something else). In this case the fundamental surface can be drawn so that the inflection in the surface that defines the limit of stability is clear, as in Fig. 16.4. We shall refer to this limit as an stability.

Third, the fluid may simply cease to exist outside a certain range of values of the constitutive variables in the sense that the system could not maintain itself as the fluid of in-
terest, but would necessarily become some other material with different properties. We shall refer to a stability limit of this type as a termination. A termination is not necessarily foreshadowed by the shape of the energy surface, which may be strongly concave arbitrarily close to the termination. An example is shown schematically in Fig. 16.4.

![Diagram](image)

**Fig. 16.4:** The g-x fundamental surface for a hypothetical fluid showing its stability range, which is bounded on the left by an inflection and on the right by a termination.

A termination of the fundamental surface is usually attributable to an instability with respect to an internal parameter whose value is set by the conditions of equilibrium so that it does not appear in the list of constitutive coordinates. Examples are common in the thermodynamics of solids since there are often many different possible ways of constructing the solid that are nominally consistent with given values of T, P and \{N\}. The different constructions of the solid can usually be described in terms of states of order characterized by order parameters that are internal variables. Terminations are associated with instabilities with respect to spontaneous changes in the values of the order parameters. The common examples include instabilities with respect to chemical order, in which different atomic species within a crystalline solid occupy distinct sets of lattice sites, magnetic order, in which the net magnetic moments of the ion cores within the solid align in a ferromagnetic or antiferromagnetic pattern, ferroelectric order, in which differently charged ion cores within a material undergo small relative displacements so that the material takes on a net polarization, and electronic order, in which the distribution of conduction electrons within the solid become unstable with reconfigurations into insulating or superconducting states. Similar types of reaction occur in some molecular liquids, where the axes of the molecular chains may spontaneously align to create liquid crystals.

### 16.5.2 Stability limits

The behavior of a fluid near a termination of its fundamental surface cannot usually be analyzed without recourse to a deeper model that takes hidden variables into account. However, the thermodynamic stability limits are determined by the properties of the fundamental equation. We have already derived the essential condition: the least eigenvalue of the property matrix, \(E_{ij}\), vanishes at the limit of stability which has the consequence that the determinant of the property matrix also vanishes. It is possible to rephrase this condition in an alternate, simple form that has a number of important applications.
Let the Gibbs-Duhem function be written

\[ P = \tilde{P}(\{p\}) \quad 16.68 \]

where \( \{p\} = \{T, \{u\}\} \) is the set of forces conjugate to the variables \( \{u\} = \{S_v, \{n\}\} \), the volume densities of the entropy and the mole numbers. The elements of the property matrix, \( P_{ij} \), that is formed by the second derivatives of the pressure with respect to the forces are

\[ \left[ \frac{\partial^2 \tilde{P}}{\partial p_i \partial p_j} \right] = \left[ \frac{\partial u_i}{\partial p_j} \right]_{\{p\}'} \quad 16.69 \]

where the set \( \{p\}' \) includes all forces in \( \{p\} \) except \( p_j \). An arbitrary diagonal term in the property matrix, \( P_{ii} \), can be written in the Jacobian form

\[ P_{ii} = \left[ \frac{\partial u_i}{\partial p_j} \right]_{\{p\}'} = \frac{\partial (p_1, \ldots, u_i, \ldots, p_n)}{\partial (p_1, \ldots, p_n)} \]

\[ = \left[ \frac{\partial (p_1, \ldots, u_i, \ldots, p_n)}{\partial (u_1, \ldots, u_n)} \right] \left[ \frac{\partial (p_1, \ldots, p_n)}{\partial (u_1, \ldots, u_n)} \right]^{-1} \quad 16.70 \]

The denominator on the right-hand side of 16.70 is the determinant of the property matrix, \( (E_v)_{ij} \), that is defined by the energy density. The numerator is the determinant of the minor of \( (E_v)_{ij} \) that is formed by removing the row and column associated with the variable \( u_i \). At the limit of stability

\[ \det[(E_v)_{ij}] = 0 \quad 16.71 \]

It follows that the diagonal term, \( P_{ii} \), is singular unless the numerator of the equation, the determinant of the \( i^{th} \) first minor of \( e_{ij} \), also vanishes. Since the least eigenvalue of a minor of a matrix cannot be less than the least eigenvalue of the matrix itself, the diagonal term, \( P_{ii} \), is infinite unless the least eigenvalue of \( (E_v)_{ij} \) is also an eigenvalue of the \( i^{th} \) first minor of \( (E_v)_{ij} \). That is, \( P_{ii} \to \infty \) unless \( u_i \) does not participate in the eigenvector that has the eigenvalue \( \lambda_{\min} \).

It is clearly impossible for the least eigenvalue of \( (E_v)_{ij} \) to be common to all of its first minors; at least one of these must be obtained by eliminating a quantity whose variation appears in the eigenvector that determines \( \lambda_{\min} \). We have hence proved the general result:
at the limit of stability at least one of the partial derivatives

\[
P_{ii} = \left[ \frac{\partial u_i}{\partial p_j} \right] \quad 16.72
\]

becomes infinite.

The minimal eigenvector that is associated with the least eigenvalue of \((E_\nu)_{ij}\) at the stability limit is a linear combination of members of the set \{u\}, and generally involves several of these coordinates. The partial derivative on the right-hand side of 16.72 is infinite for all the \(u_i\) that appear in the minimal eigenvector. Hence it is usually true that several of the thermodynamic properties of a fluid increase without bound as the stability limit is approached. The most familiar observation is the singularity in the specific heat, \(C_p\), at the instability point, which is observed at almost all stability limits. We shall explore this point further below.

### 16.6 PHASES OF A FLUID SYSTEM

Let a fluid be designated by the set of chemical components it contains, as is usually done in practice. Considering the whole range of temperature, pressure and composition, there will be many different ways in which the components can be assembled into stable materials. This is even true when there is only one component, which is a liquid or a gas when it is a physical fluid, may have any one of several crystal structures, or may be amorphous, in the solid state. It follows that the complete fundamental surface for the system has many distinct sheets, as illustrated in Fig. 16.5. Each distinct, stable portion of the fundamental surface identifies a material that is represented by a particular fundamental equation. These distinct materials are called the phases of the system.

The complete fundamental surface of a fluid maps the fundamental equation for all possible ways of assembling its components into materials. The phases of the system correspond to the distinct stable segments of the fundamental surface.

The concept of a phase is a fundamental one in elementary chemistry and physics as well as in materials science, and is usually presented in introductory courses in an intuitive way that may make the definition given above seem unnecessarily opaque and formal. This is not the case, as can be seen by considering the usual intuitive definitions of a phase. The idea that a system can exist in distinct phases is usually introduced in one of two ways: by noting that there are distinct physical "states of aggregation" of a given set of chemical components that have dramatically different properties, such as the gas, liquid, and various solid "phases", or by noting that a given system will generally consist of distinct, physically homogeneous regions that are separated by sharp interfaces, for example, a solid in equilibrium with its vapor. Both observations lead to the notion of different phases as recognizably different ways of assembling the system that have distinct properties. They can be transformed into one another, for example, by changing the temperature or pressure or
by displacing an interface that separates two phases in equilibrium. In all cases the transformation involves a discontinuity in the properties of the materials that is accomplished by an infinitesimal change in the constitutive coordinates.

![Diagram](image_url)

**Fig. 16.5:** Section through the fundamental surface of a system that has three phases, $\alpha$, $\alpha'$, and $\beta$. $\alpha$ and $\alpha'$ are separated by an instability; $\alpha$ and $\beta$ are separated by a termination of the fundamental surface.

These observations are usually gathered in the conventional definition of a "phase" as a volume of material with homogeneous composition and properties. But this definition is insufficient to distinguish a phase as the term is ordinarily used. For example, an infinitesimal change in the composition of a stable solution does not cause any discontinuity in its properties. In conventional terminology an infinitesimal change in composition preserves the phase of the material. Nor is a single-phase region necessarily homogeneous. A multicomponent solution develops an inhomogeneous composition in the presence of gravity, even within "single phase" regions.

The term "phase transition" is ordinarily used to describe a discontinuous change in properties that is brought about by an infinitesimal change in the values of the constitutive coordinates. A phase transition necessarily involves a displacement of the system from one stable segment of its fundamental surface to another, whether the transition is due to a change in the values of the constitutive coordinates or to movement across an equilibrium two-phase interface. The thermodynamic properties of a material are determined by its fundamental equation, which is continuous on any stable segment of the fundamental surface. Hence a transition that involves a discontinuous change in properties after an infinitesimal variation in the constitutive coordinates necessarily requires that the state of the system be displaced from one stable segment of the fundamental surface to another. Similarly, as we shall show below, a two-phase interface cannot separate materials that lie at different points on the same stable segment of the fundamental surface. If two distinct states are separated by an interface, their fundamental surfaces must be separated by a termination or an instability along the line that connects them in the fundamental space; they must lie on distinct stable portions of the fundamental surface. On the other hand, if two states of the system lie on different stable segments of the fundamental surface then any transition between them involves a discontinuity in at least some thermodynamic property, and a line connecting them necessarily crosses a discontinuity or instability. Hence the
definition of a phase given above is both necessary and sufficient to describe the concept of the distinct phases of a system as it is ordinarily used.

### 16.7 Global Equilibrium in a Multiphase System

Neglecting external fields, the global condition of equilibrium is the minimum energy principle:

\[ (\delta E)_{S,V,\{N\}} \geq 0 \quad 16.73 \]

which asserts that the internal energy of the given state of the system must be less than that of any other state that has the same total entropy, volume and mole number. When the system is restricted to contain only a single phase this criterion has a simple graphical interpretation: the most stable phase has the least energy for the given values of \( S, V \) and \( \{ N \} \). However, if the system has several possible phases then it may also lose equilibrium by spontaneously evolving into a multiphase state. We seek a global condition of equilibrium that specifically takes this possibility into account.

To ensure global equilibrium the system must be stable with respect to a variation of state that involves the formation of a small quantity of a new phase. The thermodynamic content of the new phase includes the energy, \( \delta E' \), entropy, \( \delta S' \), volume, \( \delta V' \), and chemical content, \( \{ \delta N' \} \). The total variation of the energy in the formation of the new phase is, then,

\[ \delta E_T = \delta E + \delta E' \quad 16.74 \]

where the unprimed quantity refers to the initial phase. Using the Lagrange multipliers \( \theta \), \( \pi \), and \( \{ \gamma \} \) to modify the variations of the entropy, volume and chemical content the global condition of stability can be rewritten

\[ \delta (E_T - \theta \delta S_T + \pi \delta V_T - \sum_k \gamma_k \delta N_k) \geq 0 \quad 16.75 \]

where the signs on the Lagrange multipliers are chosen for convenience. Using equation 16.74 and the variational form of the energy function, the condition of equilibrium becomes

\[ \delta E' - \theta \delta S' + \pi \delta V' - \sum_k \gamma_k \delta N_k' + (T-\theta)\delta S + (P-\pi)\delta V + \sum_k (\mu_k-\gamma_k) \delta N_k \geq 0 \quad 16.76 \]

The last three terms on the left-hand side of 16.76 are just the conditions of internal equilibrium for the initial phase, which is in equilibrium only if

\[ T = \theta \quad 16.77 \]

\[ P = \pi \quad 16.78 \]
\[ \mu_k = \gamma_k \]  

With these results the condition of equilibrium reads

\[ \delta E' - T\delta S' + P\delta V' - \sum_k \mu_k \delta N_k^i \geq 0 \]  

Assuming that the new phase is internally in equilibrium, which makes its formation most favorable, then the new phase is homogeneous and its deformation coordinates scale with its size. We can hence remove the variation signs. It follows that

\[ \text{a fluid phase is in equilibrium with respect to the formation of a new phase if and only if the quantity} \]

\[ E' - TS' + PV' - \sum_k \mu_k N_k^i \geq 0 \]  

\[ \text{where the forces are those of the original phase and the quantities are those of the hypothetical product phase.} \]

The inequality 16.81 is the general condition of equilibrium that was formulated by Gibbs. It is somewhat easier to use if the integrated form of the fundamental equation of an equal quantity of the initial phase is subtracted, giving

\[ \Delta E - T\Delta S + P\Delta V - \sum_k \mu_k \Delta N_k \geq 0 \]  

where

\[ \Delta E = E' - E \]

is the change in energy when a quantity of the initial phase is changed into an equal quantity of the product phase, and \( \Delta S, \Delta V \) and \( \{\Delta N\} \) have the same meaning.

The condition 16.82 can be immediately rewritten in terms of the appropriate form of the fundamental equation for any other experimental case. For example, if the pressure and temperature are fixed then the global condition of equilibrium is

\[ \Delta G - \sum_k \mu_k \Delta N_k \geq 0 \]  

Since the equilibrium of a phase is independent of its size (at least so long as we neglect surface effects) it is often more convenient to write 16.84 in the molar form

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\[ \Delta g - \sum_{k=1}^{c-1} \bar{\mu}_k \Delta x_k \geq 0 \]

where \( c \) is the total number of components and \( \bar{\mu}_k = \mu_k - \mu_c \) is the relative chemical potential of the \( k \)th component.

### 16.8 Maximum Pressure; The Phase Rule

#### 16.8.1 The maximum pressure principle

If a simple fluid phase is in equilibrium with respect to the formation of a new phase then it is necessarily true that any small subvolume of the fluid is in equilibrium with respect to a transition into the new phase. The small subvolume is an open system whose temperature and chemical potentials are fixed by the surrounding fluid, which functions as a reservoir. When \( T, V \) and the \( \{\mu\} \) are fixed the condition of equilibrium that is expressed by 16.81 reduces to the inequality

\[ (P - P')V' \geq 0 \]

where \( P' \) is the pressure of the product phase. Since \( V' > 0 \), the condition 16.86 establishes the maximum pressure principle:

\[ \text{a fluid is in equilibrium with respect to the formation of a new phase if and only if its pressure is greater than that of any other phase that might be formed with the given values of the temperature and chemical potentials.} \]

Fig. 16.6: P-T section through the fundamental space of a fluid showing fundamental surfaces for the three phases \( \alpha, \beta \) and \( \gamma \). The range of \( T \) for which each of the phases is stable is indicated.

The maximum pressure principle has a simple graphical interpretation that is illustrated in Fig. 16.6. Let the fundamental surfaces, \( P = P(T,\{\mu\}) \), be plotted for each distinguishable phase of the system. The stable phase for any given values of the constitutive variables, \( (T,\{\mu\}) \), is that which has the maximum pressure. Hence the stable, fundamental surface for the system is the outer envelope of the fundamental surfaces of the individual
phases. Transitions from one stable phase to another occur where the fundamental surfaces of the individual phases intersect one another.

Note that since the fundamental equation, \( \tilde{P}(T,\{\mu\}) \), is single-valued by definition, a homogeneous phase is never out of equilibrium with respect to a transformation to another example of itself. Distinct phases are represented by different branches of the fundamental surface.

### 16.8.2 Phase diagrams

The fundamental surface that is associated with the equation \( \tilde{P}(T,\{\mu\}) \) yields the simplest formal example of the phase diagram of a fluid system. For any set of values of the constitutive variables, T and \( \{\mu\} \), the stable phase is that which has the greatest pressure. Barring a fortuitous degeneracy in the fundamental equations of distinct phases, the stable phase is unique except where the fundamental surfaces intersect. Hence the \((c+1)\)-dimensional space that is spanned by T and \( \{\mu\} \) is divided into subvolumes within which a particular phase is stable. Multiphase equilibria occur for states that fall on the surfaces that bound these subvolumes. The T, \( \{\mu\} \) space can hence be used as a \((c+1)\)-dimensional phase diagram, which is a map that shows the phases that appear at equilibrium as a function of the constitutive coordinates T and \( \{\mu\} \).

An example is shown in two dimensions in Fig. 16.7, where we have assumed a one-component system. Stable phases fill areas in the T-\( \mu \) plot. Two-phase equilibria occur at values of T and \( \mu \) that fall along lines in the plane. Three-phase equilibria fall at isolated points.

![Phase diagram](image)

**Fig. 16.7:** Schematic drawing of the T-\( \mu \) phase diagram of a hypothetical fluid.

While the T-\( \{\mu\} \) phase diagram is the simplest to visualize (in the formal sense) of any of the phase diagrams of a multicomponent fluid, it is almost never used in practice because the relative difficulty of measuring the chemical potential makes it an awkward choice for a constitutive variable. Phase diagrams are usually based on the molar Gibbs free energy so that the constitutive variables are T, P, and \( \{x\} \). The geometry of these diagrams is more complicated, but the constitutive variables are the natural variables for most experimental situations. The phase diagram of a one-component fluid is usually plotted in
the P-T plane, and can be derived from the Gibbs free energy since $G = \mu$ for a one-component system.

### 16.8.3 The phase rule

In the phase diagram drawn in Fig. 16.7 the number of phases determines the dimension of the equilibrium phase field. Single phases fill two-dimensional areas, two-phase equilibria lie along one-dimensional lines, and three-phase equilibria fall at isolated, zero-dimensional points. The dimension of the figure that governs a given equilibrium also gives the number of geometric "degrees of freedom" of the changes of state that can be made without destroying the equilibrium. When the system consists of a single phase in a one-phase field the system can undergo arbitrary infinitesimal changes that alter both T and $\mu$ without changing phase; the equilibrium has two degrees of freedom. When the system contains two phases in equilibrium the only changes that do not destroy the equilibrium are those in which T and $\mu$ are simultaneously varied so that the system moves along the two-phase equilibrium line; the equilibrium has one degree of freedom. When three phases are in equilibrium any change of state whatever destroys the three-phase equilibrium; the number of degrees of freedom is zero.

The relation between the number of equilibrium phases and the dimension of the corresponding field in the T-$\mu$ diagram of a fluid can be phrased in a simple, general form that is known as the phase rule and was originally proposed by Gibbs. It is derived as follows.

Let a simple fluid contain r phases that are in equilibrium with one another in the absence of external fields or interfacial effects. Each phase obeys a fundamental equation that can be written in the Gibbs-Duhem form

$$ P = \tilde{P}(T,\{\mu\}) $$  \hspace{1cm} (16.87)

If the number of independent components is (c), equation 16.87 shows that the number of independent variables (degrees of freedom) is (c+1). The values of (c+1) of the forces that act on the fluid can be varied freely over the range of existence of the phase; the value of the other is set by the Gibbs-Duhem equation.

Now let there be two fluid phases in equilibrium. The phases obey different fundamental equations that have the generic form 16.87. The conditions of thermal and chemical equilibrium require that T and $\{\mu\}$ be the same in the two phases, and the condition of mechanical equilibrium has the consequence that P is the same. Hence whenever the two phases are in equilibrium,

$$ \tilde{P}^1(T,\{\mu\}) = \tilde{P}^2(T,\{\mu\}) $$  \hspace{1cm} (16.88)

Equation 16.88 governs changes of state that preserve the two-phase equilibrium. The equation can be solved for one member of the set $\{T,\{\mu\}\}$, so only (c) of the (c+1) variables $\{T,\{\mu\}\}$ remain free.
Generalizing this result, if \( r \) phases are in simultaneous equilibrium then \((r-1)\) equations of the form 16.88 hold, and must be preserved in any change of state that maintains the equilibrium. Each equation can be used to eliminate one of the \((c+1)\) independent variables of a single phase. The residual number of independent variables (degrees of freedom) is

\[
f = (c+1) - (r - 1) = c - r + 2
\]

Equation 16.89 is *Gibbs phase rule*.

The phase rule governs the geometry of phase diagrams of simple fluids whose coordinates are any \((c+1)\) of the thermodynamic forces. Single phases fill \((c+1)\)-dimensional volumes that are bounded by \((c)\)-dimensional hypersurfaces on which two phases are in equilibrium. The two-phase surfaces are bounded by \((c-1)\)-dimensional hypersurfaces on which three phases are in equilibrium. These are bounded by \((c-2)\)-dimensional surfaces of four-phase equilibria, etc. The geometry ultimately reduces to isolated points in the \((c+1)\) dimensional space at which \((c+2)\) phases coexist.

The phase rule is particularly useful for testing the validity of phase diagrams that are determined experimentally, and played an important role in the development of experimental thermodynamics. However, it has recently become fashionable for researchers to find and publish "exceptions" to the phase rule. To evaluate these "exceptions" recall the restrictions on the derivation of the phase rule. It assumes that all phases of the system are simple fluids and that interfaces and external fields have a negligible effect. If any of these assumptions is untrue the phase rule is inapplicable in the form derived here. If all of these assumptions hold the phase rule is as valid as the Second Law. The reported "exceptions" to the phase rule known to me involve situations in which one of the phases is obviously not a simple fluid.

It is, of course, possible to violate the phase rule fortuitously if two or more fundamental surfaces happen to be degenerate at a point of intersection with others. Since the fundamental space is continuous a fortuitous degeneracy at a point of intersection is extremely unlikely. To my knowledge, no example has ever been found.

### 16.9 Minimum Energy; the Common Tangent Rule

When the fundamental surface is the Gibbs-Duhem surface the constitutive variables are the thermodynamic forces. Multiphase equilibria occur at intersections of the fundamental surfaces. When the fundamental surface is the plot of a thermodynamic potential whose natural variables include deformation coordinates the geometric relations that govern multiphase equilibria are more complicated. Since distinct phases that are in equilibrium generally differ in their thermodynamic densities the points that represent the equilibrium states are spatially separated in the fundamental space. However, they do have a simple geometric relation to one another which is specified by the *common tangent rule*. The use
of the energy surface together with the common tangent rule has the advantage that it not only locates regions of multiphase equilibria but also determines the relative quantities of the phases that are present for given overall values of the constitutive coordinates.

16.9.1 The common tangent rule on the energy surface

We can establish the common tangent rule in the most general case by examining the equilibrium of phases on the energy density surface, \( \tilde{E}(S,V,\{N\}) \). To investigate equilibrium on the energy surface it is first important to recognize that the total energy depends on the size of the system while the phase equilibria do not. This is apparent from the fact that the rules governing phase equilibria can be derived from the Gibbs-Duhem function, whose value does not depend on the system size. To characterize multiphase equilibria it is sufficient to consider the fundamental surface that is generated by the volume energy density

\[
E_v = \tilde{E}_v(S_v,\{n\})
\]

or the molar energy density

\[
e = \tilde{e}(s,v,\{x\})
\]

Both are independent of system size, and lead to identical results. The molar form is usually more convenient.

The fundamental space of the molar energy density is the \((c+2)\)-dimensional space that is spanned by the variables \(e, s, v\) and \(\{x\}\). The fundamental surface in this space is given by equation 16.91. The molar form of the condition of equilibrium is

\[
e' \geq e + T\Delta s - P\Delta v + \sum_k \bar{\mu}_k \Delta x_k
\]

where \(\bar{\mu}_k = \mu_k - \mu_c\) is the relative chemical potential of the \(k\)th chemical component and the summation is taken over the \((c-1)\) independent composition variables.

The right-hand side of the condition 16.92 has a simple geometric interpretation. Using the notation \(e = e(\{q\})\) the inequality can be written

\[
e' \geq e + \sum_{k=1}^n \left[ \frac{\partial \tilde{e}}{\partial q_k} \right] \Delta q_k
\]
The right-hand side of 16.93 is just the equation of a plane in the (c+1)-dimensional fundamental space that is tangent to the fundamental surface at the state, Σ, whose equilibrium is to be tested. If the state Σ is in global equilibrium the inequality must be satisfied everywhere in the fundamental space. The plane tangent to the fundamental surface at Σ must pass beneath every segment of the fundamental surface; if the tangent plane intersected the fundamental surface at least some set of states beyond the intersection would violate the condition of equilibrium. Hence the global equilibrium of the state Σ is determined by its tangent plane.

The geometry of the tangent plane is illustrated for the two-dimensional case in Fig. 16.8, which shows sections of the fundamental surfaces of two stable phases. If the system is in state Σ of phase α then it is in global equilibrium since the plane tangent to this state does not intersect the fundamental surface. If the system is in state Σ it is not in global equilibrium. The tangent plane to Σ cuts the fundamental surface of phase β; hence a system in state Σ is out of equilibrium with respect to the formation of a small quantity of phase β in any of the states that fall on the fundamental surface in the shaded region of the figure.

![Diagram](image)

Fig. 16.8: An illustration of the manner in which the tangent plane to the energy surface determines global equilibrium. η is an arbitrary constitutive coordinate.

Now suppose that two states, Σ₁ and Σ₂, are in equilibrium with one another. The conditions of equilibrium must be satisfied for both of them. The temperature, pressure and chemical potentials of the two states must be the same, so their tangent planes must be parallel. Global equilibrium then requires that both tangent planes lie beneath the fundamental surface at every point. But this is only possible if the tangent planes are the same. Hence two states that are in equilibrium with one another lie on a common tangent plane.

The geometry of the common tangent rule is illustrated in Fig. 16.9 for the two-dimensional case. State Σ of phase α and state Σ of phase β can exist in equilibrium with one another. Since their tangent planes have the same slope, the thermodynamic forces are the same and they satisfy the internal conditions of equilibrium. Since their tangent planes are the same, they obey the same global condition of equilibrium. On the other hand, state Σ of phase γ cannot participate in the equilibrium. While its tangent plane is parallel, the plane is displaced so that Σ’ is out of equilibrium with respect to transformation to a mixture of Σ and Σ.
If two stable states lie on a common tangent plane they must be different phases of the system. A stable phase is represented by a concave segment of the fundamental surface. A tangent plane to a surface that is everywhere concave (or convex) touches the surface at only one point. Hence a phase cannot be in equilibrium with another example of itself. Equilibrium between distinct states requires that they lie on separate stable segments of the fundamental surface, and, hence, that they be distinct phases in the sense defined in Section 16.6.

These considerations apply equally well to a mixture of several phases. If several phases are simultaneously in equilibrium with one another then the equilibrium states must all lie on a common tangent plane that does not cut the fundamental surface. Multiphase equilibrium is hence governed by the common tangent rule:

*If a fluid system contains several distinct states in equilibrium then these states lie on a common tangent to the energy surface. The states represent different phases of the system. The multiphase system is in global equilibrium if the common tangent plane never cuts the fundamental surface.*

### 16.9.2 Multiphase equilibrium

The common tangent rule stated above is a necessary condition for multiphase equilibrium: if several distinct phases are in equilibrium they must lie on a common tangent. It is possible to develop it into a sufficient condition for multiphase equilibrium. The stronger form of the common tangent rule can be stated as follows.

*If the state of a system falls at an interior point of a common tangent plane the equilibrium state of the system is a multiphase mixture of the states that lie in the common tangent plane. The relative proportions of the phases present are determined by the thermodynamic densities of the system.*
To establish this statement and define the interior of a common tangent plane it is useful to begin with an examination of two-phase equilibrium. The geometry of a two-phase equilibrium is shown schematically in Fig. 16.9. Let the coordinate, \( \eta \), be that linear combination of the constitutive coordinates, \( \{q\} \), that connects the two states \( \Sigma \) and \( \Sigma \) that lie on a common tangent. The line that connects the equilibrium states \( \Sigma \) and \( \Sigma \) in the constitutive space, \( \{q\} \), is called the tie-line. Since the energy surfaces are concave, when \( \eta < \eta_c \) a single-phase state of phase \( \alpha \) is in equilibrium and when \( \eta > \eta_c \) a single-phase state of phase \( \beta \) is in equilibrium. However, when \( \eta_c < \eta < \eta_c \) neither \( \alpha \) nor \( \beta \) is in equilibrium by itself. A tangent to any point on the \( \alpha \) surface beyond \( \eta_c \) cuts the \( \beta \) surface, while a tangent to any point on the \( \beta \) surface below \( \eta_c \) cuts the \( \alpha \) surface. The states, \( \{q\} \), that fall on the tie-line specified by \( \eta_c < \eta < \eta_c \) are the interior points of the tangent line. When the state of the overall system lies at an interior point of the common tangent (that is, on the tie-line) the only state that satisfies the condition of equilibrium is a two-phase mixture of \( \Sigma \) and \( \Sigma \).

When a system contains a two-phase mixture the phases must be present in proportions that give the correct average densities for the system as a whole. The phase fractions can be found in terms of the coordinate \( \eta \) that characterizes the tie-line. If \( f^\beta \) is the mole fraction of the \( \beta \) phase and \( \eta^\alpha \) and \( \eta^\beta \) are the values of \( \eta \) in the two equilibrium states then the conservation of the thermodynamic densities requires that

\[
\eta = \eta^\alpha + f^\beta (\eta^\beta - \eta^\alpha)
\]

which requires that the mole fractions of the two phases be

\[
f^\beta = \frac{\eta - \eta^\alpha}{\eta^\beta - \eta^\alpha}
\]

\[
f^\alpha = 1 - f^\beta = \frac{\eta^\beta - \eta}{\eta^\beta - \eta^\alpha}
\]

Equations 16.95 are referred to as the lever rule because they resemble the equations for the mechanical balance of a lever about the point \( \eta \).

The analysis of two-phase equilibrium is readily generalized to multiphase equilibria. If several states are simultaneously in equilibrium the states must lie on a common tangent plane to the energy surface, and must represent distinct phases of the system. If the state of the system, as specified by the aggregate values of its constitutive coordinates, falls at an interior point of a common tangent to \( r \) phases, the equilibrium state is a multiphase mixture of \( r \) phases whose individual states are fixed by the points of tangency of the common tangent plane. The interior points of the common tangent plane are those that lie within the \((r-1)\)-dimensional figure formed by the tie-lines that join the equilibrium states.

The proportions of the various phases can be computed from the aggregate values of the constitutive coordinates and the dimension of the interphase connections on the common tangent plane. If states of \( r \) phases are in equilibrium then an \((r-1)\) dimensional
plane is required to connect them (a line for two-phase equilibria, a two-dimensional plane for three-phase equilibria, etc.). The projection of this (r-1) dimensional plane on the space of the constitutive coordinates is spanned by (r-1) generalized coordinates, \( \eta_k \), which are linear combinations of the constitutive coordinates. If \( \eta_k^\alpha \) is the value of the \( i \)th coordinate in the \( \alpha \)th phase, \( f^\alpha \) is the mole fraction of the \( \alpha \)th phase, and \( f^r \) is the fraction of the \( r \)th phase, which is used as a reference, the condition of conservation of the thermodynamic densities yields the \( r \) equations

\[
\eta_k = \eta_k^r + \sum_{\alpha=1}^{r-1} f^\alpha \eta_k^\alpha \quad (i = 1, \ldots, r-1)
\]

\[
f^r = 1 - \sum_{\alpha=1}^{r-1} f^\alpha \quad 16.96
\]

which are together sufficient to determine the mole fractions of the phases present.

### 16.9.3 The phase rule

The phase rule can be understood or developed in terms of the geometry of the energy density surface. First consider a stable state, \( \Sigma \), which corresponds to a single-phase state of the system. The tangent plane to the point \( \Sigma \) on the fundamental surface does not contact the fundamental surface at any other point. If the state \( \Sigma \) is varied through an arbitrary infinitesimal variation of the constitutive coordinates \( \{q\} \) the result is an infinitesimal tilt in the tangent plane. If the tangent plane bypasses the fundamental surface then a tilt through a sufficiently small angle will not cause it to contact the fundamental surface. Hence the stable phase has \( (c+1) \) degrees of freedom that do not destroy its equilibrium, which correspond to the \( (c+1) \) free constitutive variables.

As the state of the system is changed the tangent plane rolls over the fundamental surface, continuously changing its tilt. If several phases exist the tangent plane will eventually contact the fundamental surface of a second phase, which establishes a two-phase equilibrium. It is then possible to change the state without destroying the two-phase equilibrium by varying the constitutive variables in a direction that preserves the tangent contact between the two fundamental surfaces, that is, by rolling the tangent plane in a direction so that it rests against the two fundamental surfaces. The simultaneous contact with two surfaces imposes one algebraic relation between the \( (c+1) \) constitutive coordinates. Hence there are \( (c) \) degrees of freedom.

The two-phase equilibrium surface can be rolled freely until it contacts the fundamental surface of a third phase. In a three-dimensional space this would terminate the possibility of free variation since three (non-collinear) points of contact in three dimensions uniquely determine a plane, and the tangent plane could not be rotated further without penetrating one of the fundamental surfaces. However, in a \( (c+2) \)-dimensional space \( (c > 1) \) the three-phase contact simple imposes a second algebraic constraint between the constitu-
tive coordinates, and the plane can still be rolled in (c-1) dimensions until the fundamental surface of a fourth stable phase is contacted.

A continuation of this reasoning regenerates the phase rule

\[ f = c - r + 2 \]

where \( f \), the number of degrees of freedom of a system that contains \( r \) phases in equilibrium, corresponds to the number of independent directions in which the common tangent plane can be rolled on the underside of the fundamental surface while maintaining simultaneous contact with the fundamental surfaces of \( r \) distinct phases.

### 16.9.4 The minimum-energy surface and the phase diagram

The equilibrium states that are determined by the energy surface lie on the lower envelope of the set of surfaces that includes the energy surfaces of the stable phases and the interior points of the common tangent planes that define the multiphase regions. The lower envelope can be generated by constructing the fundamental surfaces of all possible phases, and then rolling a plane over the underside of the figure under the constraint that the plane always contact at least one of the energy surfaces without ever cutting any of them. The result is the minimum-energy surface that contains all equilibrium states. It consists of single-phase segments that are bounded by regions of two-phase equilibrium, which are bounded in turn by regions of three-phase equilibrium, etc. A simple portion of the equilibrium surface of a one-component system is shown in Fig. 16.10, which includes a schematic drawing of the energy surfaces of two phases together with the tangent surface that connects them.

![Diagram](image.png)

Fig. 16.10: A portion of the energy surface of a one-component fluid showing two stable phases and the two-phase field defined by the common tangent.

The projection of the minimum-energy surface on the space of the constitutive coordinates gives the equilibrium phase diagram of the system. The equilibrium phase diagram is a (c+1)-dimensional figure. The subvolumes of the phase diagram can be labelled to show the phases present. Because of the geometry of the common tangent plane, subvolumes in which \( r \) phases are in equilibrium are always bounded alternately by subvol-
umes in which \((r+1)\) and \((r-1)\) phases appear. If the tie-lines through the multiphase sub-volumes are known the terminal points of the tie-lines specify the thermodynamic states of the phases that are in equilibrium. The generalized lever rule, equation 16.96, then determines the relative quantities of the phases that are present.

A hypothetical two-dimensional s-v section of a phase diagram is shown in Fig. 16.16. Single-phase regions of equilibrium of the \(\alpha\), \(\beta\) and \(\gamma\) phases are separated by two-phase regions, which are shaded light in the figure. The two-phase regions meet in the three-phase region that is shaded dark. Note that the single-phase and three-phase regions do not share a common boundary.

![Phase Diagram](image)

Fig. 16.11: Two-dimensional s-v section of a phase diagram showing the one-phase regions of three stable phase and the intervening areas of two- and three-phase equilibria.

### 16.10 Phase Transformations

#### 16.10.1 Metastable extensions of the fundamental surface

Multiphase equilibria are determined by the existence of common tangent planes to the energy surfaces of the stable phases of a system. The boundaries of the equilibrium range of a single phase are hence determined by the shapes and positions of the fundamental surfaces of the other phases. The boundary normally falls along a line on the energy surface at which the phase is fully stable; no feature of its own geometry suggests that a common tangent plane has been touched. Hence there is usually a metastable extension of the fundamental surface that penetrates well inside the region of space where two phases are in equilibrium.

The metastable extensions are shown in the example energy surface given in Fig. 16.16. Fig. 16.12 is a two-dimensional cut through a surface like that shown in Fig. 16.10 that is labelled to indicate the behavior that may occur in different regions of the metastable portion of the energy surface. The concave energy surface of the \(\alpha\) phase extends beyond the intersection with the common tangent that governs two-phase equilibrium. In the first shaded region to the right of the intersection the \(\alpha\) phase is metastable with respect to a transformation into a two-phase mixture of \(\alpha\) and \(\beta\). In the second shaded region it is also metastable with respect to a transformation to homogeneous phase \(\beta\), although the \(\beta\)
product of such a transformation is itself metastable with respect to transformation into a two-phase mixture. The fundamental surface of the $\alpha$ phase terminates at the boundary between the second and third shaded regions. The $\alpha$ phase cannot exist in the third shaded region.

![Illustration of the regions of metastability of phase $\alpha$ beyond the point of two-phase equilibrium with phase $\beta$. In the region labelled $\alpha = 1$ the $\alpha$ phase is unstable and cannot be preserved.]

**16.10.2 Phase transformations**

A metastable phase obeys the internal conditions of equilibrium. It is only out of equilibrium with respect to a *phase transformation* that involves a finite displacement of at least a portion of the system to a distinct energy surface. Such a displacement is often called a *first-order phase transformation* since it necessarily involves a finite change in the thermodynamic densities of at least the part of the system that changes phase. Whenever a phase transformation is thermodynamically preferred it will eventually happen. However, since physical displacements are continuous, the transformation must follow some physical path in going from one state to another. The transformation path reflects the *mechanism* of the transformation, and usually includes intermediate states that do not appear in the fundamental space. Whether the phase transformation happens in finite time depends on the kinetics of the most favorable transformation mechanism. The kinetics of real transformations are often sluggish, with the consequences that metastable phases are preserved for arbitrarily long times. Almost all engineering materials are in metastable states in the form in which they are used.

The lifetime of a metastable state depends on the kinetics of the possible transformations that take it to equilibrium. The intermediate states along the transformation path include non-equilibrium states that do not fall on the fundamental surface. Hence equilibrium thermodynamics does not predict the lifetime of a metastable state. On the other hand, it is possible to gain insight into the possible transformation paths from an examination of the equilibrium surface.

Consider the metastability of the phase $\alpha$ in Fig. 16.12. In the first shaded region to the right $\alpha$ is only out of equilibrium with respect to a transformation to a mixture of $\alpha$ and
β. The transformation is usually triggered by the nucleation of a small quantity of the β phase. According to the common tangent rule the β phase that forms must be in a state that lies below the tangent plane to the metastable state of the α phase. Fig. 16.13 shows the states of phase β that satisfy this constraint for a particular metastable state, Σ, of phase α. Whenever the metastable state, Σ, lies outside the intersection of the fundamental surfaces of α and β then the states of β that can initiate two-phase decomposition differ from Σ in at least some of their thermodynamic densities, and must be nucleated. However, it is clear from the geometry of the fundamental surfaces that the nucleation of β out of state Σ of α requires two physical changes: the formation of a region of β phase, which ordinarily differs from α in its physical symmetry, and the adjustment of the thermodynamic densities to values appropriate to a stable state of β. Since the combined changes are often difficult to accomplish spontaneously, a state like Σ can often be preserved as long as desired.

![Diagram](image)

**Fig. 16.13:** Two-dimensional section of a fundamental surface. The shaded region contains the states of phase β that may form out of state Σ of phase α.

The phase transformation becomes easier to accomplish when the metastable state lies beyond an intersection of the fundamental surfaces of the two phases, as it does in the second shaded region to the right in Fig. 16.12. In this case the transformation from α to β can occur at constant values of the thermodynamic densities. The nucleation of phase β then requires only a change in physical structure, and is generally easier to accomplish.

A phase transformation becomes inevitable when the state of the initial phase reaches an instability or termination of its fundamental surface. The system then spontaneously transforms into some state that is in relative equilibrium, that is, a state that lies beneath the tangent plane at the termination. In the example given in Fig. 16.12 the only such state is phase β, so β must nucleate spontaneously. In most real cases there are several possible product states. The selection between them is made on kinetic grounds; the initial product is the phase that forms most easily.
16.11 **Critical States**

16.16.1 **The nature of critical states**

The transformations that were discussed in Section 16.10 were transformations between distinct phases whose fundamental surfaces were displaced from one another. However, it is possible for a single fundamental surface to bifurcate into two distinct stable surfaces. The states at which such bifurcations occur are called *critical states*. When the state of a single-phase system passes through a critical state the system spontaneously decomposes into two distinct phases that are in equilibrium with one another.

Familiar examples of critical states in real systems include *critical points* in one-component fluids where the liquid and gas phases become indistinguishable from one another, and *miscibility gaps* in liquid and solid solutions where a homogeneous solution spontaneously decomposes into two similar solutions of different compositions. The critical state is the terminal state at which the distinction between the two phases vanishes.

16.16.2 **The geometry of critical states**

![Diagram of critical state](image)

**Fig. 16.14:** A fundamental surface containing a two-phase equilibrium that terminates in a critical state. The equilibrium states lie on the lower face of the fundamental surface. The metastable extensions of the two phases beyond the critical state are also shown.

The critical states that are associated with a particular decomposition reaction lie on an (c-1)-dimensional hypersurface in the (c+2)-dimensional fundamental space of the Gibbs-Duhem function, which is spanned by the coordinates \{P,T,\{\mu\}\}. This follows from the fact that the critical states terminate a region of the fundamental space in which two phases coexist. By the phase rule, states that contain two phases in equilibrium lie on a (c)-dimensional hypersurface. Its boundary is a (c-1)-dimensional hypersurface; that is, a critical state can be displaced in (c-1) independent directions without changing its character. A critical state hence has the characteristics of a three-phase equilibrium, and corresponds
to a three-phase equilibrium in the sense that the parent phase and the two phases into which it decomposes are all in equilibrium at the critical state.

The geometry of a critical state in a one-component fluid is illustrated in Fig. 16.14, which shows a section of the fundamental surface in the space of the coordinates P, T and ρ. The geometry of the fundamental surface near the critical state can be constructed through an operation that resembles that by which dislocations are created in a solid. Beginning with the fundamental surface of a stable fluid, cut the surface along a line that terminates at the critical state, and then fold the surface around the critical state so that the free edges penetrate through one another. The result is a two-phase equilibrium line where the sheets on the two sides of the cut pass through one another that terminates at the critical state.

16.16.3 Stability relations at the critical state

The critical state (Σc) lies at a stability limit of the parent phase since the parent phase decomposes when the state is displaced beyond the critical state into the two-phase field. It follows that the least eigenvalue of the property matrix, eij, of the parent phase vanishes from the positive side as the critical state is approached. However, the critical state is a stable equilibrium state since it lies at a single-phase point on the fundamental surface.

To test the consequences of the stability of Σc we choose the constitutive variables of the system to be the (c+1) eigenvectors (\{η\}) of the property matrix (eij) at (Σc). Since the \{η\} are (c+1) linearly independent combinations of the (c+1) natural variables, \{q\}, of the function e(\{q\}) the sets \{η\} and \{q\} are equivalent. The condition of equilibrium (16.92) can then be written

$$\Delta e \geq \sum_{i=1}^{c+1} \left[ \frac{\partial e}{\partial \eta_i} \right] \Delta \eta_i$$

16.98

where \(\Delta e = e' - e_c\), \(\Delta \eta = \eta' - \eta_c\), and the subscript, c, indicates the value of the variable at the critical state, \(\Sigma_c\). Since the fundamental surface is everywhere continuous and concave near \(\Sigma_c\) (if we include the metastable portions of the energy surfaces of the two equilibrium phases beyond \(\Sigma_c\)) then \(\Delta e\) can be evaluated from a Taylor expansion about \(\Sigma_c\). To fourth order,

$$\Delta e = \sum_{i=1}^{c+1} \left[ \frac{\partial e}{\partial \eta_i} \right] \Delta \eta_i + \frac{1}{2} \sum_{ij=1}^{c+1} \left[ \frac{\partial^2 e}{\partial \eta_i \partial \eta_j} \right] \Delta \eta_i \Delta \eta_j + \frac{1}{3!} \sum_{i=1}^{c+1} \left[ \frac{\partial^3 e}{\partial \eta_i \partial \eta_j \partial \eta_k} \right] \Delta \eta_i \Delta \eta_j \Delta \eta_k$$

$$+ \frac{1}{4!} \sum_{i=1}^{c+1} \left[ \frac{\partial^4 e}{\partial \eta_i \partial \eta_j \partial \eta_k \partial \eta_m} \right] \Delta \eta_i \Delta \eta_j \Delta \eta_k \Delta \eta_m$$

16.99
Substituting 16.99 into 16.98 gives the condition of equilibrium in the form

\[
\sum_{i=1}^{c+1} \lambda_i (\Delta \eta_i)^2 + \frac{1}{3} \sum_{i=1}^{c+1} \left[ \frac{\partial^2 e}{\partial \eta_i \partial \eta_j} \right] \Delta \eta_i \Delta \eta_j \Delta \eta_k \Delta \eta_k
\]

\[
+ \frac{1}{12} \sum_{i=1}^{c+1} \left[ \frac{\partial^4 e}{\partial \eta_i \partial \eta_j \partial \eta_k \partial \eta_m} \right] \Delta \eta_i \Delta \eta_j \Delta \eta_k \Delta \eta_m \geq 0 \tag{16.100}
\]

where \( \lambda_i \) is the \( i \)th eigenvalue of \( e_{ij} \), and we have used the identity

\[
\left[ \frac{\partial^2 e}{\partial \eta_i \partial \eta_j} \right] = \lambda_i \delta_{ij} \tag{16.101}
\]

to simplify the first term on the left-hand side.

At the critical state the least eigenvalue of the property matrix vanishes; barring a fortuitous degeneracy in the eigenvalues (which we shall ignore) all other eigenvalues remain positive. Let \( \lambda_1 \) be the least eigenvalue and let \( \eta_1 \) be its corresponding eigenvector. If the change of state that is considered in 16.100 involves a change in the value of any coordinate, \( \eta_k \), with \( k > 1 \) then for small \( \Delta \eta_k \) the value of the right-hand side of 16.100 is dominated by the second-order term. Since this term is positive definite, \( \Sigma_c \) is automatically stable for any small variation of the state for which \( \Delta \eta_k \neq 0 \) for any \( k > 1 \).

It follows that we need only be concerned with variations of \( \eta_1 \). Since \( \lambda_1 = 0 \) at \( \Sigma_c \), the conditions of equilibrium for variations of \( \eta_1 \) simplifies to the form

\[
\left[ \frac{\partial^3 e}{\partial \eta_1^3} \right] (\Delta \eta_1)^3 + \frac{1}{4} \left[ \frac{\partial^4 e}{\partial \eta_1^4} \right] (\Delta \eta_1)^4 \geq 0
\]

\tag{16.102}

This inequality can only be satisfied for both positive and negative variations of \( \Delta \eta_1 \) if the third derivative vanishes:

\[
\left[ \frac{\partial^3 e}{\partial \eta_1^3} \right] = 0
\]

\tag{16.103}

The condition of equilibrium then reduces to the simple condition

\[
\left[ \frac{\partial^4 e}{\partial \eta_1^4} \right] \geq 0
\]

\tag{16.104}
Ordinarily, the fourth derivative is positive at the critical state, which ensures stability. If the fourth derivative vanishes, then the fifth derivative must also vanish and the sixth must satisfy a condition like 16.104. In any case

\[ \text{the first non-zero derivative of the energy density with respect to the minimal coordinate, } \eta_1, \text{ at the critical state, } \Sigma_c, \text{ beyond the first, is a derivative of even order.} \]

### 16.16.4 Two-phase equilibrium beyond the critical state

A similar argument permits an analysis of the nature of the two-phase equilibrium beyond the critical state. Assume that the fourth derivative of e is non-zero at \( \Sigma_c \). The minimal eigenvalue, \( \lambda_1 \), vanishes at \( \Sigma_c \) and is positive in the one-phase field. If \( \lambda_1 \) is continuous in the neighborhood of \( \Sigma_c \) then it must fall to a negative value if the state of the system is displaced beyond the critical state into the two-phase field. The condition of equilibrium slightly within the two-phase field is, then,

\[ \lambda_1(\Delta\eta_1)^2 + \left[ \frac{\partial^4 e}{\partial \eta_1^4} \right] (\Delta\eta_1)^4 \geq 0 \]

where we have ignored the third derivative since its magnitude should be no more than comparable to that of \( \lambda_1 \) and it is multiplied by the cube of a small number. The two phases that are in equilibrium have equal values of the left-hand side of the inequality. Hence they satisfy the homogeneous form of 16.105, whose solution is

\[ \Delta\eta_1 = \pm \sqrt{-\frac{\lambda_1}{\beta}} \]

where

\[ \beta = \left[ \frac{\partial^4 e}{\partial \eta_1^4} \right] \]

In this case, which is the usual situation near a critical state, the two phases that are in equilibrium beyond \( \Sigma_c \) are symmetrically split along the coordinate, \( \eta_1 \), that determines the stability limit at \( \Sigma_c \).

A typical geometry of a phase diagram near a critical state is shown in Fig. 16.15, where the T-\( \eta \) section is used for simplicity, on the assumption that the minimal eigenvector, \( \eta_1 \), does not involve the entropy. A two-phase region appears below the critical state in the diagram, and has the form of a symmetrical cap whose maximum lies at \( \Sigma_c \).

Note that the fundamental surface is continuous around a critical state, as shown in the example given in Fig. 16.16. If the state of the system is displaced around the critical state without passing through it the parent phase becomes one of the two equilibrium phases (e.g., \( \alpha \rightarrow \alpha' \) or \( \alpha'' \) in Fig. 16.15) without discontinuity. This is only possible if the
phases beyond the critical state are examples of the parent phase in the sense that they have
the same symmetry and physical characteristics. In the case of the critical point in a one-
component fluid the liquid and gaseous states below the critical point are random dis-
tributions of atoms just like the "fluid" phase beyond the critical point. In the case of a
miscibility gap in a solid solution the two solutions below the critical state have the same
essential symmetry. This requirement imposes strict constraints on the symmetry of phases
that may be joined at a critical state, which are often useful in the analysis of phase equi-
librium in solids. We shall examine this point further when we treat the thermodynamics of
solids.

![Phase Diagram](image)

Fig. 16.15: T-η section of the phase diagram of a system that contains a
critical state at which phase α decomposes into α' and α''. The
coordinate, η, is governs the stability limit at Σc. The critical
state, Σc, lies at the top of the two-phase region.

### 16.12 Continuous Phase Transitions: Mutations

#### 16.12.1 The nature of mutations

The final geometric feature of the fundamental surface that is necessary to under-
stand phase relations in fluid systems is the possibility of mutations of the fundamental
surface. A mutation is a line (or, more accurately, an (n-1)-dimensional hypersurface on the n-
dimensional fundamental surface) that defines a physical discontinuity of the fundamental
surface that is not associated with an obvious mathematical discontinuity. The phases on
the two sides of a mutation differ qualitatively in their physical characteristics, but merge
continuously into one another so that all thermodynamic densities are continuous and the
merged surface of the two phases everywhere satisfies the global condition of equilibrium.
The mathematical feature of a mutation line is a discontinuity or (more commonly) a
singularity of the curvature of the fundamental surface which marks a discontinuous change
in thermodynamic properties that does not introduce a discontinuous change in the
thermodynamic forces or densities.

Familiar physical examples of mutations include the onset of magnetic or ferro-
electric order, many of the ordering transition in crystalline solid solutions, and the super-
conducting transition in metals. Each of these transitions can be accomplished by cooling a
system at fixed pressure and composition, in which case the fundamental surface is the Gibbs free energy surface and the mutation occurs at a critical temperature, $T_c$, which is often called the Curie temperature because of its early identification in studies of ferromagnetism. The transition is marked by the appearance of an internal order in the system which discontinuously changes the symmetry and, consequently, the properties of the phase. While the phase transition at the Curie point is unambiguously identified by the symmetry change that is induced by the onset of order, the magnitude of the order parameters vanishes continuously as the Curie temperature is approached from below. Hence the thermodynamic forces and densities are continuous at the Curie point. The thermodynamic change at the Curie point is a change in thermodynamic properties, which alters the curvature of the fundamental surface without introducing an obvious discontinuity.

The early experimental studies of phase transitions of this type were done with imprecise instruments that did not reveal the detailed behavior of the thermodynamic properties at the transition, but did note the discrete change in thermodynamic properties that accompanied a finite displacement across the transition line. This data led to a classification in which the associated transitions were called second order phase transitions, since they changed the second derivatives of the thermodynamic potential without affecting the first derivatives, which are altered in the more common first order phase transitions. This classification was formalized by P. Ehrenfest, who constructed an early theory of second-order transitions. The terminology persists to this day, although it is misleading.

More recent work has shown that in almost all cases of transitions of this type (the superconducting transition still appears to be an exception) at least some of the thermodynamic properties are singular on the transition line. The isobaric specific heat, in particular, almost always increases without bound as the transition is approached from at least one side. These observations led to various attempts to classify transitions according to the shape of the $C_p$-$T$ curve when the transition is thermally induced. The most widely used was proposed by Pippard (Classical Thermodynamics) in the 1950's.

While the Pippard classification is useful for more detailed studies it obscures the common feature of this whole class of transformations: they change the phase without introducing a discontinuity in the fundamental surface. Excepting the possibility of a weak instability on the transition line itself, a fundamental surface that contains a mutation line is not only continuous but also stable over the joint range of stability of the two phases. Landau and Lifshitz call them continuous transitions (or rather J.L. Synge, who translated the work, does; I don't know the original Russian). This is a good descriptive term, but is ambiguous since the term "continuous transition" is a useful one for any change of state that follows a well-defined path, even when it includes a first-order phase transformation.

Here and in the following we shall adopt the general term mutation to describe such transitions, where

\[ \text{a mutation is a line \((n-1)\)-dimensional hypersurface on the fundamental surface where the phase that is represented by the fundamental surface} \]
changes while the surface remains continuous and differentiable to at least the first order.

The differentiability of the fundamental surface at a mutation guarantees that its slope is also continuous.

16.12.2 The geometry of a mutation

![Diagram of phase changes](image)

Fig. 16.16: Two-dimensional example of a mutation from phase $\alpha$ to phase $\alpha'$. The fundamental surface is continuous at the mutation (dashed line). The slope, $p$, has a discontinuity there.

A two-dimensional example of the behavior of the fundamental surface at a mutation is given in Fig. 16.16. The energy and slope are continuous as the constitutive coordinate, $\eta$, is varied through the mutation. There is a change in curvature at the transition point, but this is not apparent in the energy surface. The change in curvature usually appears as a discontinuity in the slope of the energy surface, and is apparent in a plot of the force, $p = \frac{\partial e}{\partial \eta}$, against the coordinate, $\eta$, near the mutation, as illustrated in Fig. 16.16. While the experimental situation is unclear, there may also be examples of mutations for which the curvature remains constant and the change in properties is governed by a higher derivative. While this behavior is consistent with the definition of a mutation, we shall not discuss it further here.

16.12.3 Properties of mutations

We shall consider particular examples of mutations in some detail in a later chapter that addresses the theory of ordering. However, it is possible and useful to discuss two particular properties of mutations at this point.

First, the two phases that are joined at a mutation cannot exist simultaneously in the same system:

* a phase cannot be in equilibrium with a mutation of itself.

The validity of this statement follows from the individual stability of the phases that are joined at the mutation and the continuity of the slope at the mutation line. An equilib-
rium between the two phases would require the existence of a common tangent plane. But since the joint fundamental surface is continuous a tangent plane can only touch it at two points if there is an inflection in the slope of the fundamental surface. Since both phases are stable the only place an inflection could occur is at the mutation line itself. But since all of the first derivatives of the fundamental equation are continuous across the mutation the tangent plane at the mutation is well-defined and common to the phase on either side. Hence the two phases cannot have a common tangent and cannot be in equilibrium with one another.

This result has many practical applications, some of which we shall address in later chapters. As one quick example, it is desirable for some applications to create magnetic materials that contain fine ferromagnetic domains in a normal matrix. It is impossible to accomplish this with an equilibrium state of a material whose ferromagnetic transition is a mutation. Unless a way can be found to "freeze" the system in an unstable state, one must use a multicomponent system that decomposes into two equilibrium phases, only one of which mutates into a ferromagnet.

Second, the continuity of the fundamental surface at a mutation does not rule out the possibility that the mutation falls at a stability limit of either or both of the mutant phases:

*a mutation may represent a line of instability, provided that the instability is weak.*

To establish this point we consider the curvature of the energy surface near a mutation. It is possible to phrase the problem in one dimension by transforming the n constitutive coordinates, \{u\}, to a set of n equivalent, orthogonal coordinates, \{\eta\}, which have the property that one coordinate, \eta_i, is normal to the mutation line at the point of interest while all others are tangent to it. The system can then be displaced into the mutation by varying \eta_i while all of the other coordinates are held constant. The mutation is a stability limit if

\[
\left[ \frac{\partial^2 \tilde{e}}{\partial \eta_i^2} \right] = \left[ \frac{\partial p_1}{\partial \eta_i} \right] \rightarrow 0
\]

as the mutation is approached, where \( p_1 \) is the force conjugate to the coordinate \( \eta_i \).

To see the physical problem that is posed by a stability limit like 16.107, and its resolution, consider the geometry near a mutation of the fundamental surface in the fundamental space that is defined by the coordinates \( (p_1, \{\eta\}) \). The fundamental equation in this space is given by the Legendre transform

\[
f' = e - p_1 \eta_i = \tilde{f}(p_1, \{\eta\})
\]

If equation 16.107 holds then at the mutation line
\[
\left[ \frac{\partial^2 \tilde{\rho}}{\partial p_1^2} \right] = -\left[ \frac{\partial \eta_1}{\partial p_1} \right] (\eta'), \quad \rightarrow -\infty
\]  
16.109

The condition 16.109 suggests that the thermodynamic density, \( \eta_1 \), has a discontinuity at the mutation when it is reached by varying the force, \( p_1 \), which violates the continuity of the fundamental surface at the mutation line.

To find the condition under which the mutation line can be a stability limit we define the variable

\[
C = \left[ \frac{\partial \eta_1}{\partial p_1} \right] (\eta'),
\]
16.110

If the mutation falls at a stability limit then equations 16.107 and 16.109 suggest that near the mutation \( C \) has the mathematical form

\[
C = A(p_1) + \frac{B}{(p_1 - p_c)^\alpha} \quad (\alpha > 0)
\]
16.111

where \( A \) is a function that is well-behaved at \( p_c \) and \( B \) is a constant. The change in \( \eta_1 \) when the mutation is crossed by varying \( p_1 \) is

\[
\Delta \eta_1 = \int_{p_c - \varepsilon}^{p_c + \varepsilon} C(p_1) \, dp_1
\]
16.112

where \( \varepsilon \) is a small number. The integral is defined and equal to zero provided that

\[
\alpha < 1
\]
16.113

on both sides of the mutation.

This argument can be generalized to show that any thermodynamic property of the form \( C = (\partial \eta / \partial p) \), where \( \eta \) is a thermodynamic density and \( p \) is its conjugate force can be written

\[
C = \left[ \frac{\partial \eta}{\partial p} \right] = A(p) + B(p - p_c)^\alpha
\]
16.114

in the immediate neighborhood of a mutation, where either \( B = 0 \), in which case the phase is stable or \( \eta \) does not participate in the instability, or \( \alpha > -1 \), in which case the mutation is a stability limit, but the fundamental surface is continuous and differentiable at the mutation. The coefficient, \( \alpha \), is known as the critical exponent for the property, \( C \).
The property to which this rule is most often applied in practice in the isobaric specific heat, \( C_p \). The specific heat is singular as \( T \to T_c \) for almost all known mutations (the superconducting transition is an exception), but its singularity has the form 16.114 with \( \alpha > -1 \).

16.12.4 Behavior near a mutation

![Graphs showing behavior near a mutation](image)

Fig. 16.17: Three characteristic forms of the coefficient, \( C \), near a mutation: (a) second-order phase transition; (b) \( \lambda \)-transition; (c) \( \Lambda \)-transition.

Since a mutation divides two stable phase fields it is a juncture of two fundamental surfaces, both of which terminate at the mutation line. The analysis of the previous section shows that the phases may have stability limits at the mutation line. But it is not necessary that they do; the mutation line may be a simple termination of either phase.

We are hence led to define three types of mutations, which can be distinguished on the basis of the behavior of the most critical thermodynamic property, \( C \), at the mutation line. The classification is similar to that proposed by Pippard on the basis of experimental measurements of the isobaric specific heat. The three characteristic behaviors are illustrated in Fig. 16.17.

Fig. 16.17a represents the case in which both phases are stable at the mutation, that is, both fundamental surfaces have terminations there. The result is a simple discontinuity in \( C \). Following Ehrenfest, we shall refer to this as a second-order phase transition. Fig. 16.17b illustrates the case in which one of the phases has a stability limit at the mutation line while the other does not. Following Pippard (and others) we shall refer to this as a \( \lambda \)-transition because of its characteristic shape. Fig. 16.17c illustrates the behavior of \( C \) when the mutation line is a stability limit of both phases. In this case the curve has roughly the shape of a capital lambda, and shall call it a \( \Lambda \)-transition. Other shapes of the \( C \)-\( T \) relation are theoretically possible, but there is no theoretical reason to expect them and we shall not consider them here. Pippard gives an extensive list.

The theory of mutations will be discussed further at several points in the course, particularly in the context of the theory of order. As we shall see, the behavior of the char-
acteristic behavior of the thermodynamic properties near the transition is often associated with instability in the state of order that causes large fluctuations in at least one of the bounding phases as the mutation is approached.

16.12.5 Boundaries of a mutation between phases

![Diagram showing three possible situations at the termination of a mutation line in the P-T plane: (a) split into two mutations; (b) transform into a two-phase equilibrium line; (c) intersect a two-phase equilibrium line.]

Fig. 16.18: Three possible situations at the termination of a mutation line in the P-T plane: (a) split into two mutations; (b) transform into a two-phase equilibrium line; (c) intersect a two-phase equilibrium line.

A mutation separates two phases that are distinct in the limit in which they have the same thermodynamic potential and thermodynamic densities. They must, therefore, be distinguished by some difference, usually a change in symmetry, that constitutes a physical discontinuity between them that remains defined even in the limit in which its magnitude disappears. It follows that a mutation line cannot simply terminate. It ends in one of the three situations diagrammed in Fig. 16.18.

First, the mutation may split into two mutation lines, as shown in Fig. 16.18a, that surround a third phase. The phase enclosed by the mutation beyond the split, labelled γ in the figure, must be a mutation of both of the original phases, α and β. As we shall see at a later point, this imposes strong restrictions on the symmetry of the γ phase.

Second, the mutation line may change into a line of two-phase equilibrium. The fundamental surfaces of the two phases overlap beyond the point at which the mutation changes into an equilibrium line so that a two-phase equilibrium is possible.

Third, the mutation line may intersect a two-phase equilibrium line beyond which a third phase, γ, is in equilibrium with respect to both of the phases α and β. Since the mutation does not cause a discontinuity in the fundamental surface, there is no break or discontinuity in the two-phase equilibrium line where the mutation intersects it.