

Chapter 1

Elements of Thermodynamics

Thermodynamics provides a phenomenological description of nature, self-contained from an axiomatic point of view, considering, as a principle, matter in an aggregated form without any microscopic assumption. During the 20th Century, the common presentation of this theory followed the historical developments, with laws and examples fundamentally based on and explained by considering the classical problems of thermal engineering. Following this trend, it was, and still is, usual to see the formulation of the second law based on the Kelvin and Clausius prescriptions. Historically, with such a law, by using the Carnot cycle and the Clausius theorem, the existence of a state function called *entropy* (from the Greek, *transformation*) is then formulated. Tisza [1] and Callen [2], in a rigorous presentation, used the entropy function and the notion of an extremum principle as an ontological starting point to build the thermodynamic theory. This procedure equips a physicist with a readable formalism, providing a way to encompass the effect of time in the context of thermal approaches and yet bringing notions of thermal laws to the realm of the quantum field theory. We present an outline of the main elements of the equilibrium thermodynamics along the lines introduced by Tisza and Callen.

We describe four formulations of thermodynamics and the compatibility among them, that is: (i) the formulation based on the fundamental relation (or equation) in which the function of state entropy, S , or the energy, E , is given explicitly; (ii) the formulation using the Legendre transformation of S or E , giving rise to the thermodynamical potentials, such as the Helmholtz free energy and enthalpy; (iii) the formulation based on the set of equations of state, involving the first derivative of the extensive quantities as S or E . Such derivatives are zero-order homogeneous functions, and describe intensive variables such as pressure ($P = -\partial E/\partial V$), temperature ($T = \partial E/\partial S$), and so on; and (iv) the formulation based on second derivatives, describing quantities like specific heat, among others. The importance of formulations (iii) and (iv) relies on the straightforward connection with experiments.

Regarding the theoretical structure of the thermal formalism, it is worth emphasizing that it is similar to the theory of a mechanical system, in the sense that, first a definition for the notion of thermal state is introduced, and subsequently

the changes in the states are analyzed with causal laws. Although, in equilibrium, thermodynamics time does not play a role as it does in mechanics, we can still distinguish the kinematic and the dynamic aspects of the theory. The former is related to the definition of thermodynamic (thermal) variables, the measurability, the definition of the state of a thermal system, and the definition of specific processes. The dynamical aspects are related to changes in the state and laws regulating such changes. This scheme also works when time is a relevant parameter, such that nonequilibrium processes take place. For further readings, we suggest Refs. [1–7].

1.1 Kinematical aspects of thermal physics

The theoretical description of a physical system can be carried out by, first of all, defining the points in space and time where processes of measurement and tests of such a theory are supposed to take place. This leads us to the usual notion of a reference frame, defined by the of transformation from one point to another in space and time. One important aspect associated with the introduction of a reference frame is that the notion of space and time are defined simultaneously. For equilibrium thermal processes space only plays a significant role and is defined by a proper definition of a ruler. In this chapter we consider non-relativistic thermodynamics, then we have Galilean reference frames. We assume as a reference frame the laboratory system, without addressing to any change of coordinates. The characterization of a thermal system will then be given by a set of macroscopic variables selected in advance by an observer located in the laboratory. These variables are, for example, internal energy (E), pressure (P), volume (V), number of moles (N), temperature (T), among others. The definition of such thermal variables is given in association with the measurement process through the use of constraints and walls. Volume is measured by rulers; temperature, which is interpreted in a first moment as a quantity providing the degree of warmth of a body, is measured by thermometers. We say that walls define a volume when their sizes are fixed. Walls restrictive to energy of any kind give rise to an *isolated system*. When the walls of a system permit a very slow flow of energy to a system via mechanical work only, the walls are called *adiabatic*. Walls are called *diathermic* when changes of the energy between two systems are permitted via a difference of temperature.

There are two kinds of thermal variables. To realize that, consider a macroscopic homogeneous system, divided into a number of similar subsystems. For instance, a gas in a box can be seen as formed by a collection of sub-boxes. A variable is said to be *extensive* when its value is equal to the sum of values of each subsystem. Examples of such type of variables are energy, volume and number of moles. A variable is said to be *intensive* if its value is independent of subsystems. As examples we have temperature, pressure and all the densities defined from the extensive variables as energy density, volume density, number of moles density (or simply, density), and so on.

The *state* of a macroscopic system is defined by specifying a set of thermal variables, or in a more general sense, by a function of the state of the system. Usually, the evolution of an isolated system is such that, after some time, the system reaches a final state in which its variables no longer change in time. Such a state is the so-called *thermal equilibrium state*, and is defined by a set of extensive parameters, including energy necessarily. An equilibrium state will be denoted by $x = \{x_0, x_1, \dots, x_r\}$, with $x_0 = E$. A *simple system* is defined by setting $x_1 = V$, $x_2 = N_1$, $x_3 = N_2, \dots$, where N_1, N_2, \dots are the number of moles of different substances; this is the case, for instance, of a mixture of gases in a box with no chemical reactions.

The measurability of the variables like V and N , as we have said, follows standard methods. The measurement of the energy E , however, requires a careful discussion. To begin, we have to recall that the notion of energy has its origin in mechanics. That is, energy is defined in terms of the notion of work, measured in the MKS system in Joules, J, with $1 \text{ J} = 1 \text{ Nm}$, such that the difference between two energy levels of a system is physically associated with the change of the mechanical state. Therefore, even treating a thermal system, the internal energy has to be measured by a process involving mechanical work. The concept of energy conservation, however, is supported by the Joule experiment.

Consider a change in a system from a state a to a state b . The Joule experiment assures that if we isolate this system by adiabatic walls, then always there exists a mechanical procedure by which we can take the system from a to b or vice versa. In this way the quantity of energy that the system receives from or liberates to its neighborhood can be measured by a well defined mechanical method. Take, for instance, a gas in a box of volume V_a at pressure P_a and temperature T_a . The system is set in contact with a block of ice, such that at the final equilibrium new values for volume, temperature and pressure are, respectively, V_b , T_b and P_b , with $T_a > T_b$. It is not so simple to generate a mechanical procedure to bring the system from a to b , but is much more trivial to find a mechanical apparatus to raise the temperature of the system from the state b , taken as the initial state, to the final state a . In both situations we assume that the energy flow is the same. This is an example where there are energy flows to or from a system conditioned by the difference of temperature, via diathermic walls. This flow is called *heat* and was initially measured in arbitrary units called *calorie* (Cal). With Joule, the energy content of each *cal* was established experimentally resulting in $1 \text{ Cal} = 4.184 \text{ J}$.

If we treat equilibrium states, we assume that two arbitrary states can be connected to each other through a process composed of an infinity of intermediary states. Processes like that are called *quasi-static*. This notion is necessary in order to give a proper definition to a differentiable thermal quantity. The mechanical work associated with a system described by the parameters $x = \{E, x_1, \dots, x_r\}$ can

Table 1.1 Mechanical works and generalized forces

Infinitesimal work dW	Type of force
$-PdV$	Pressure P
$\sum_{j=1}^l \mu_j dN_j$	Chemical potential μ_j
$\mu_0 \mathbf{H}_{ext} \cdot d\mathbf{I}_j$	Magnetic field \mathbf{H}
$\mathbf{E}_{ext} \cdot d\mathbf{p}$	Electric field \mathbf{E}

be written as

$$dW = f \cdot dx = \sum_{j=1}^l f_j dx_j, \quad l \leq r, \quad (1.1)$$

where f_j is the applied generalized force and x_j is the corresponding extensive parameter modified by the action of f_j . Expressions for mechanical work are given in Sec. 1.1 for different systems, where P stands for pressure; μ_j for the chemical potential; μ_0 for the vacuum permissivity; \mathbf{H}_{ext} for the external magnetic field; \mathbf{I}_j for the magnetic dipole moment, where $\mu_0 \mathbf{H}_{ext}$ is the force associated with the extensive variable \mathbf{I}_j ; \mathbf{E}_{ext} for the electrical field and \mathbf{p} the electric dipole moment.

Up to now the characterization of a thermal system has been based on aspects involving the definition of a thermal state, without a specification of the laws describing the changes in the state. This dynamical characterization is the subject of the following section.

1.2 Dynamical aspects of thermal physics

First law of thermodynamics

In order to establish laws controlling the evolution of a thermal equilibrium state, first consider an infinitesimal energy flow to a system via work (dW) and heat (dQ), and let us assume the conservation of energy. Then from the Joule experiment we can write infinitesimal changes in the internal energy (dE) in the following way

$$dE = dQ + dW. \quad (1.2)$$

This expression is called the *first law of thermodynamics*, and it expresses the energy conservation taken as a fundamental law. Observe that the content of the mathematical differential can be assumed for dE , since E can be taken as a function of variables of the thermal system — a function of state. But this is not the case for dQ and dW , which express only small flows to or from the system.

Second law of thermodynamics

The first law is not enough to treat all the richness of thermal processes. For instance, it is a well-established experimental result that if two simple systems are

set forth in thermal contact with one another, the flow of heat will take place from the hotter system to the colder one. The reversal of this process, without any external intervention, is not observed, although it does not contradict the first law. In order to address this question, let us consider a system in a state given by the set $x = \{E, x_1, \dots, x_r\}$ and assume the existence of a state function $S = S(E, x_1, \dots, x_r)$ to be called *entropy*. The entropy $S(E, x_1, \dots, x_r)$ is, by definition, an extensive, analytical and monotonically increasing function in the variable E . Besides that, in the absence of internal constraints, values of extensive variables are those that make S maximum for an equilibrium state. That is,

$$\begin{aligned}\delta S|_{\text{equilibrium}} &= 0, \\ \delta^2 S|_{\text{equilibrium}} &< 0.\end{aligned}$$

This principle is called *the second law of thermodynamics*.

With the second law, thermal processes can be classified as *reversible* or *irreversible*. An irreversible process is that one which, if taken as reversible, would tend to minimize S , contradicting the second law. A typical example of such a process is the free expansion of a gas, which is a nonequilibrium process. In the case of equilibrium, a process is reversible when it can be recovered quasi-statically through a set of equilibrium states. In this case, the entropy is constant, in agreement with the second law.

Third law of thermodynamics

The *third law* states that by a number of finite steps, it is impossible to lower the temperature to $T = 0$. A consequence of this principle is that if a system, in a state characterized by a variable x (finite), is cooled to another state characterized by $x + \delta x$, then at $T = 0$, $\delta S|_a = 0$, or

$$\left(\frac{\partial S}{\partial x}\right)_{T \rightarrow 0} = 0. \quad (1.3)$$

An experimental result derived from this principle is that

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial P}\right)_{T \rightarrow 0} = - \lim_{T \rightarrow 0} \left(\frac{\partial V}{\partial T}\right)_P = 0.$$

This law, formulated by Nerst in 1905, is interpreted sometimes in statistical mechanics as an entropy condition, fixing the value of the entropy as $S = 0$ at $T = 0$ [2, 8].

1.3 Equations of state

Due to the second law, the entropy S is an analytical function in the energy variable. Then we can write in a unique way

$$S = S(E, x_1, \dots, x_r) \quad (1.4)$$

or equivalently

$$E = E(S, x_1, \dots, x_r). \quad (1.5)$$

Relations given by Eqs. (1.4) and (1.5) are called *fundamental equations* (or *relations*). “Fundamental” in the sense that if we know one of these relations, the properties of a thermal system can be obtained. We write the fundamental equation as

$$\Psi = \Psi(x_0, x_1, \dots, x_r) \equiv \Psi(x), \quad (1.6)$$

such that taking $\Psi = S$ and $x_0 = E$, Eq. (1.4) is recovered and the fundamental equation is said to be in the *entropy representation*. On the contrary, taking $\Psi = E$ and $x_0 = S$, Eq. (1.5) is obtained and the description is referred to as the *energy representation*.

Since S is an extensive function, it is a first-order homogeneous function. Indeed, for a system composed of m subsystems, the entropy can be written as

$$\begin{aligned} S &= S(E, x_1, \dots, x_r) \\ &= \sum_{k=1}^m S_k, \end{aligned} \quad (1.7)$$

where S_k is the entropy of the k -th system. Then taking for instance a system characterized by the state E, x_1, \dots, x_r , with the fundamental equation given by $S(E, x_1, \dots, x_r)$, another system can be constructed by a dilation of the former one by writing $\lambda E, \lambda x_1, \dots, \lambda x_r$ such that the new fundamental equation is λS . As a result of Eq. (1.7), the entropy of the new system is given by

$$S(\lambda E, \lambda x_1, \dots, \lambda x_r) = \lambda S(E, x_1, \dots, x_r). \quad (1.8)$$

The same result is true for the fundamental equation in the energy representation, that is,

$$E(\lambda S, \lambda x_1, \dots, \lambda x_r) = \lambda E(S, x_1, \dots, x_r). \quad (1.9)$$

We have stated that Ψ is a first-order homogeneous function, that is

$$\Psi(\lambda x_0, \lambda x_1, \dots, \lambda x_r) = \lambda \Psi(x_0, x_1, \dots, x_r). \quad (1.10)$$

As a consequence, differentiating Eq. (1.10) with respect to λ , we have

$$\sum_j \frac{\partial \Psi(\dots \lambda x_j)}{\partial (\lambda x_j)} x_j = \Psi(x_0, \dots, x_r). \quad (1.11)$$

On the other hand, taking the differential of Eq. (1.6), we obtain

$$d\Psi = \sum_{j=0}^r F_j dx_j, \quad (1.12)$$

where

$$F_i = \left(\frac{\partial \Psi}{\partial x_i} \right)_{x_0 \dots x_{i-1}, x_{i+1} \dots x_r}; \quad i = 0, \dots, r. \quad (1.13)$$

The notation $(\dots)_y$ means that y is held fixed. For simplicity, we drop this index. Notice that λ is an arbitrary parameter; then setting $\lambda = 1$ in Eq. (1.11), and using Eq. (1.13), we find

$$\Psi = \sum_{j=0}^r F_j x_j. \quad (1.14)$$

This is a basic result showing that if we know the set of $(r + 1)$ -relations given by Eq. (1.13), then we can solve, in principle, the thermodynamical problem by writing the fundamental relation as given in Eq. (1.14). The $(r + 1)$ -relations given by Eq. (1.13) are called the set of *equations of state*.

The interest in equations of state lies in practical aspects. To see this, let us analyze the physical content of the functions F_j . Observe that since $\Psi(x_0, \dots, x_k)$ is a first-order homogeneous function, its derivatives, $F_i = (\partial\Psi/\partial x_i)$, are zero-order homogeneous functions, that is

$$F_i(\lambda x_0, \dots, \lambda x_r) = F_i(x_0, \dots, x_r). \quad (1.15)$$

The functions $F_i(x_0, \dots, x_r)$, also called “forces,” are natural candidates to stand for intensive variables, like temperature, pressure and density of moles. Then the equations of states (1.13), relating intensive variables, are directly accessible by experiment, which is not the case for Ψ .

Since F_i are zero-order homogeneous functions, we have

$$\begin{aligned} F_i &= \left(\frac{\partial\Psi}{\partial x_j} \right) = F_i(x_0, \dots, x_r) \\ &= F_i(\lambda x_0, \dots, \lambda x_r) \\ &= F_i\left(\frac{x_0}{x_r}, \dots, \frac{x_{r-1}}{x_r}, 1 \right), \quad i = 0, \dots, r, \end{aligned} \quad (1.16)$$

where in the last line we have taken the arbitrary quantity λ to be $\lambda = 1/x_r$. Therefore, we have $r + 1$ functions F_i , each one depending on r intensive variables, since a ratio like x_{r-1}/x_r is an intensive quantity. Thus Eq. (1.16) show that the set of equations of state can be written exclusively in terms of intensive variables. The decrease in the variable number (originally Ψ required $(r + 1)$ variables, while each intensive function is written in terms of r variables) reflects the fact that, for instance, the molar density, rather than the number of moles, is important in this description. The elimination of the r variables from Eq. (1.16) gives rise to a relation among the $r + 1$ intensive variables. This relation can be derived from general arguments and it is called the Gibbs-Duhem relation. We proceed with the physical identification of each intensive variable $F_i(x_0, \dots, x_r)$.

1.4 The meaning of intensive variables

We consider a simple isolated system composed of two subsystems, denoted by a and b , such that V_a , V_b , N_a and N_b are kept fixed. Suppose there is a virtual flow

of heat between a and b , that is E_a and E_b can suffer a variation, where the total energy is given by

$$E = E_a + E_b. \quad (1.17)$$

The *equilibrium conditions* are specified by considering S as constant at equilibrium. Notice that E is constant since the system is isolated. Let us then analyze this fact in the entropy representation. In this case we denote,

$$\Psi = S \quad \text{and} \quad F_j^{(s)} = \frac{\partial S}{\partial x_j}.$$

For the composite system, the entropy can be written as

$$S = S_a(E_a) + S_b(E_b).$$

If the system reaches equilibrium, the second law states that $\delta S = 0$; therefore

$$\frac{\partial S}{\partial E_a} = \frac{\partial S_a}{\partial E_a} + \frac{\partial S_b}{\partial E_b} \frac{\partial E_b}{\partial E_a} = 0.$$

Using Eq. (1.17) with E being constant, i.e. $\delta E_a = -\delta E_b$, we derive

$$\frac{\partial S_a}{\partial E_a} = \frac{\partial S_b}{\partial E_b}. \quad (1.18)$$

In terms of the forces we write

$$F_{0,a}^{(s)} = \frac{\partial S_a}{\partial E_a}, \quad F_{0,b}^{(s)} = \frac{\partial S_b}{\partial E_b},$$

where $F_{0,\alpha}^{(s)}$ stands for the force in the entropy representation (s), considering $\alpha = a$ or $\alpha = b$. From Eq. (1.18) we obtain

$$F_{0,a}^{(s)} = F_{0,b}^{(s)}. \quad (1.19)$$

This equation is the equilibrium condition written in terms of the intensive variable $F_{0,\alpha}^{(s)}$.

At this point, we have to analyze the stability conditions of the systems. That is, suppose the system is virtually displaced from equilibrium with $E = \text{constant}$, such that two systems are set in thermal contact with each other. During the evolution of the system up to the final equilibrium state, S increases, and this fact can be expressed by $\delta S > 0$. Under this condition we have

$$\begin{aligned} \delta S &= \delta S_a + \delta S_b = \left(\frac{\partial S_a}{\partial E_a} - \frac{\partial S_b}{\partial E_b} \right) \delta E_a \\ &= (F_{0,a}^{(s)} - F_{0,b}^{(s)}) \delta E_a > 0. \end{aligned}$$

Assuming $F_{0,a}^{(s)} > F_{0,b}^{(s)}$, it follows that $\delta E_a > 0$ and $\delta E_b < 0$. Writing

$$F_{0,\alpha}^{(s)} = \frac{1}{\tau_\alpha},$$

then we have

$$\tau_a < \tau_b. \quad (1.20)$$

Table 1.2 Extensive variables

$\partial E/\partial S = T$	temperature
$\partial E/\partial V = -P$	pressure
$\partial E/\partial N = \mu$	chemical potential

In the reverse way, assuming $F_{0,a}^{(s)} < F_{0,b}^{(s)}$, we have $\delta E_a < 0$ and $\delta E_b > 0$. As a consequence

$$\tau_a > \tau_b. \quad (1.21)$$

In conclusion, in either case, heat flows from a system with the higher τ to the one with lower τ ; and at equilibrium, from Eq. (1.19) we obtain $\tau_a = \tau_b$, implying that there is no heat flow between the two systems. Therefore, since τ is an intensive quantity, it is the natural variable to represent the temperature, T , in accordance with the intuitive notion of temperature as a measure of the perception of coldness and warmth.

Recall that S increases monotonically with E , such that $(\partial E/\partial S) = T \geq 0$. This result ensures that T is positive definite. The third law fixes, as stated, $S = 0$ for the state at $T = 0$. The temperature, T , is measured in Kelvin degrees, denoted by K . Observe that this interpretation for $(\partial S/\partial E) = 1/T$ could be derived in the energy representation. In this case, we use the notation $F_{0,\alpha}^{(E)} = \partial E/\partial S = T$.

We proceed with this analysis for the sake of identification of the physical meaning of other intensive variables. Some results are given in Sec. 1.2 for a simple system. By this procedure, temperature is the “force” regulating the equilibrium for the energy flow in the form of heat. Pressure is the “force” regulating the equilibrium for the energy flow in the form of mechanical work defined via the variation of volume, and the chemical potential regulates the equilibrium for the exchange of matter among systems.

For a simple system in the energy representation, Eqs. (1.12) and (1.14) are given by

$$dE = TdS - PdV + \sum_{j=1}^k \mu_j dN_j \quad (1.22)$$

and

$$E = TS - PV + \sum_{j=1}^k \mu_j N_j. \quad (1.23)$$

Comparing Eq. (1.22) with Eq. (1.2), it results in

$$dQ = TdS. \quad (1.24)$$

Therefore, a quasi-static flow of heat to a system is associated with the increasing of the entropy.

With the result given in Eq. (1.24), the physical content of the second law as enunciated by Kelvin and Clausius is [2, 3]:

Kelvin: *It is not possible to realize a process, in which the only effect is to remove heat from a heat bath to give rise to an equivalent quantity of work.*

Clausius: *It is not possible to realize a process, in which the only effect is to transfer heat from a colder body to another one that is hotter.*

These two statements are equivalent to each other and can be derived from the second law as presented by following the Clausius procedure. Clausius introduced the entropy function as a theorem from the above enunciations. Here we have reversed the order.

Finally, Eqs. (1.12) and (1.14) in the entropy representation are given by

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{1}{T} \sum_{j=1}^k \mu_j dN_j. \quad (1.25)$$

and

$$S = \frac{1}{T}E + \frac{P}{T}V - \frac{1}{T} \sum_{j=1}^k \mu_j N_j. \quad (1.26)$$

1.5 Thermodynamical potentials

We find that the set of relations given in Eq. (1.13) provides an alternative procedure to treat thermal systems. In addition, as already observed, an advantage of this formalism based on $r + 1$ equations of state is that the intensive variables are more easily handled from an experimental perspective. For instance, for a dilute and hot gas, experiments shows that $P \sim \rho T$, where $\rho = N/V$ is the density. This is a state equation for the so-called *ideal gas*. The other equations for such a system are also available experimentally. A problem here is that despite experimental advantages, the full set of state equations remains inscrutable for a general situation. Such a difficulty naturally suggests a search for other formulations of thermodynamics. We can think of a thermal system considering the state defined by a set of mixed, intensive and extensive, variables. To find such a formalism, a preliminary step should be to define the fundamental equation via a function of state depending on a set of mixed variables, keeping compatibility with the aforementioned formulation.

For a specific situation, consider a system described by the fundamental equation

$$E = E(S, x_1, \dots, x_r).$$

Then we look for an equivalent representation for E , such that the state of the system is characterized by the set of mixed variables $\{T, x_1, \dots, x_r\}$, being the fundamental equation described by

$$F = F(T, x_1, \dots, x_r).$$

Note that a formulation in terms of F is of interest to describe the process of a system with constant temperature (an *isothermal process*). In this case, the system

is no longer isolated in reaching the equilibrium state, which is quite often the experimental situation. Beyond that, we have a reduction in the number of variables from $r+1$, with the fundamental equation for E , to r , with the fundamental equation written in terms of F .

Introducing the function F , observe that the difference between E and F is in the variable S : in the function $E(S, x_1, \dots, x_r)$, the variable S was changed to $T = \partial E / \partial S$ in F . Therefore, the function F can be introduced from E via a Legendre transformation. Since the motivation and the solution for the problem have been identified, there is no need to work with the specific energy representation.

Consider then the fundamental equation $\Psi = \Psi(x_0, x_1, \dots, x_r)$. The Legendre transformation of Ψ in $r - k$ variables x_{k+1}, \dots, x_r , is defined by

$$L = \Psi - \sum_{i=k+1}^r F_i x_i, \quad (1.27)$$

where $F_i = \partial \Psi / \partial x_i$. The differential of L is given by

$$dL = \sum_{i=0}^k F_i dx_i - \sum_{i=k+1}^r (x_i) dF_i. \quad (1.28)$$

This shows that L is a function in the variables $(x_0, \dots, x_k, F_{k+1}, \dots, F_r)$, i.e. $L = L(x_0, \dots, x_k, F_{k+1}, \dots, F_r)$. The functions L are the *thermodynamical potentials*, and F_i is said to be the *conjugate* of x_i . Therefore Eq. (1.27) defines the potential, while Eq. (1.28) shows its dependence on the variables. In the following the thermodynamical potentials for simple systems are identified explicitly using Eqs. (1.27) and (1.28) in the energy representation.

Helmholtz free energy

Define the Helmholtz free energy, F , as

$$F(T, V, N_1, \dots, N_k) = E - TS, \quad (1.29)$$

such that

$$dF = -SdT - PdV + \sum_{j=1}^k \mu_j dN_j. \quad (1.30)$$

This free energy is useful to describe isothermal processes. Part of the internal energy is then used to keep the temperature constant, and only the rest can be used for the realization of mechanical work.

Enthalpy

Defining the function

$$H = H(S, P, N_1, \dots, N_K) = E + PV \quad (1.31)$$

we have

$$dH = TdS + VdP + \sum_{j=1}^k \mu_j dN_j . \quad (1.32)$$

The enthalpy, $H(S, P, N_1, \dots, N_K)$, is useful to describe processes at constant pressure (*isobaric process*), as for instance a chemical reaction in an open container, such that P is the atmospheric pressure.

Gibbs free energy

The Gibbs free energy is defined as

$$G(T, P, N_1, \dots, N_k) = E - TS + PV, \quad (1.33)$$

so that

$$dG = -SdT + VdP + \sum_{j=1}^k \mu_j dN_j . \quad (1.34)$$

This free energy combines aspects of the Helmholtz free energy and enthalpy.

Grand thermodynamical potential

Finally the grand thermodynamical potential is given as

$$\Omega_G(T, V, \mu_1, \dots, \mu_k) = E - TS - \sum_{i=1}^k \mu_i dN_i \quad (1.35)$$

with

$$d\Omega_G = -SdT - \sum_{i=1}^k N_j d\mu_j - PdV.$$

This potential is useful to determine the full set of state equations, as we will see in the next section.

The Legendre transformations can be introduced in the entropy representation, in which $\Psi = S$. Following the same procedure as in the energy representation, with Eqs. (1.27) and (1.28), we can derive the thermodynamical potentials in the entropy representation. These potentials are called *Massieu functions*.

Previously the thermal state was introduced by a set of extensive variable. However, if the thermodynamic formalism is given in terms of potential functions, the state is represented by a set of mixed, intensive and extensive, variables. In this case, the restriction is that the state is not described by pairs of conjugate variables. For instance (S, P, N) can be used to describe the state of a simple system. But this is not the case for (S, T, N) , since S and T are conjugate variables.

1.6 Gibbs-Duhem relation

In this section we go back to the equations of state. We have seen that the fundamental equation, $\Psi = \Psi(x_0, \dots, x_r)$, can be written as in Eq. (1.14), that is

$$\Psi = \sum_{i=0}^r F_i x_i.$$

Taking the differential of Eq. (1.14) we have

$$d\Psi = \sum_{j=0}^r (dF_j x_j + F_j dx_j).$$

Using the differential of $\Psi = \Psi(x_0, \dots, x_r)$,

$$d\Psi = \sum_{i=0}^r F_i dx_i,$$

we find the following relation among the intensive variables

$$\sum_{i=0}^r x_i dF_i = 0. \quad (1.36)$$

This equation is the Gibbs-Duhem *relation*.

An immediate consequence of the Gibbs-Duhem relation is in the number of state equations. As mentioned before, we have to find $r + 1$ state equations for the F_j , functions of r variables. For instance, for a simple system with (S, V, N) the intensive variables are (T, P, μ) . Therefore, we have to look for three equations of state. We can use experimental results to infer only two of them, since the third one can be written by using the Gibbs-Duhem relation.

For a simple system in the energy representation with $E = E(S, V, N)$, the Gibbs-Duhem relation, Eq. (1.36), reads

$$SdT - VdP + Nd\mu = 0. \quad (1.37)$$

Using Eq. (1.34), the differential for the Gibbs free energy, that is

$$dG = -SdT + VdP + \mu dN,$$

and Eq. (1.37), we find $d(\mu N) = dG$. Writing $g = G/N$, it follows that

$$g = \mu.$$

Therefore, for simple systems the density of the Gibbs free energy is the chemical potential.

In the entropy representation, where $\Psi \equiv S = S(E, V, N)$, the Gibbs-Duhem relation is given by

$$d(\mu/T) = \varepsilon d(1/T) + \frac{1}{n} d(P/T),$$

where $\varepsilon = E/N$ and $n = N/V$.

1.7 Second derivatives

We analyze in this section the formulation of thermodynamics using second derivatives of the fundamental relations. The importance of this is that it brings the formulation of thermodynamics still closer to the experimental language.

The starting point of this formulation is an attempt to establish relations involving the variation of extensive variables. Consider the variables $F_i = F_i(x_0, \dots, x_j, \dots, x_r)$ and $F_j = F_j(x_0, \dots, x_j, \dots, x_r)$. Notice that by isolating x_j in the function F_i , and using this in F_j , we obtain, for any $i, j = 0, 1, 2, \dots, r$, the following equation

$$F_j = F_j(x_0, \dots, x_{j-1}, F_i, x_{j+1}, \dots, x_r);$$

or in terms of infinitesimals,

$$dF_j = dF_i \left(\frac{\partial F_j}{\partial F_i} \right)_{x_0, \dots, x_{j-1}, x_{j+1}, \dots, x_r}.$$

These equations can be solved for particular systems if we specify derivatives $\partial F_j / \partial F_i$, which is just a function of second derivatives of the fundamental equation, since we can write, for instance

$$dF_j = \left(\frac{\partial F_j}{\partial x_i} \right) \left(\frac{\partial x_i}{\partial F_i} \right) dF_i.$$

This result demands a carefully analysis of second derivatives and relations among them. The connection among all second derivatives is known as *Maxwell relations*. We consider a specific situation of a simple system.

Consider a simple system described by the fundamental equation

$$E = E(S, V, N), \tag{1.38}$$

in a closed container of adiabatic walls, with the number of moles, N , fixed. Initially the system is at a temperature T_i with a pressure P_i . The system is squeezed quasi-statically up to a final pressure P_f . The thermodynamical problem is then to find final values for the volume, V_f , the temperature, T_f , the internal energy, E_f , the entropy, S_f , and the chemical potential, μ_f .

As the process is quasi-static and adiabatic, then $dQ = 0$. As a consequence $dS = dQ/T = 0$, such that $S_i = S_f$. Assuming that Eq. (1.38) is given, by taking derivatives, we write equations of state, which are three in number. Two of them are written as

$$T = T(S, V, N), \tag{1.39}$$

$$P = P(S, V, N). \tag{1.40}$$

The third equation for μ is derived from the Gibbs-Duhem relation. An equation between T and P can be derived by elimination of V in Eqs. (1.39) and (1.40). The result is written as

$$T = T(S, P, N).$$

Since S and N are constant, the variation of T is

$$dT = \left(\frac{\partial T}{\partial P} \right)_{S,N} dP. \quad (1.41)$$

Besides

$$\left(\frac{\partial T}{\partial P} \right)_{S,N} = \left(\frac{\partial T}{\partial V} \right)_{S,N} \left(\frac{\partial V}{\partial P} \right)_{S,N}. \quad (1.42)$$

Similarly, we verify changes in the temperature with volume, using Eq. (1.39), that is,

$$dT = \left(\frac{\partial T}{\partial V} \right)_{S,N} dV. \quad (1.43)$$

These types of equations, as Eqs. (1.41) and (1.43), are all we need to provide an understanding of the thermodynamical problem; but above all, such relations are very useful for experimental tests. On the other hand, if we assume that Eqs. (1.41) and (1.43) are given in advance, then we can reverse the reasoning and write the state equations, as well as fundamental equations.

Relations as given by Eqs. (1.41) and (1.43) can be determined if we find a way, may be experimentally, to provide the derivatives like $(\partial T/\partial V)_{S,N}$, which are second derivatives of E or S . This requires an analysis of such second derivatives and the relations among them.

For this simple system we have only three independent second derivatives, for instance

$$\frac{\partial^2 E}{\partial S^2}; \quad \frac{\partial^2 E}{\partial V \partial S}; \quad \frac{\partial^2 E}{\partial V^2}. \quad (1.44)$$

Any other relation can be written as a combination of these three derivatives. To see that this is the case, consider for instance the derivative in Eq. (1.43), $(\partial T/\partial V)_{S,N}$, which can be written as

$$\left(\frac{\partial T}{\partial V} \right)_{S,N} = \frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S} \right) = - \left(\frac{\partial P}{\partial S} \right)_{V,N}. \quad (1.45)$$

By experimental necessity, for a simple system with N being constant, the set of three independent second derivatives is usually the following.

Thermal expansion coefficient

The thermal expansion coefficient, α_P , provides a measure for the fraction of volume increased by raising the temperature, when N and P are fixed.

$$\alpha_P = -\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P; \quad v = V/N = n^{-1}. \quad (1.46)$$

Isothermal compressibility

The isothermal compressibility, κ_T , provides a measure for the fraction of the decreasing volume by an increase of pressure, when T and N are constant.

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T. \quad (1.47)$$

Specific heat

The specific heat provides a measure for the heat flow by mole, necessary to increase the temperature by one degree. As a matter of convenience, this measure is carried out at constant pressure or at constant volume, that is

$$C_p = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P = \frac{1}{N} \left(\frac{dQ}{dT} \right)_P \quad (1.48)$$

and

$$C_V = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_V = T \left(\frac{\partial s}{\partial T} \right)_V = \frac{1}{N} \left(\frac{dQ}{dT} \right)_V. \quad (1.49)$$

Observe that the second derivative $(\partial T/\partial P)_{S,N}$ in Eq. (1.41) can be written as

$$(\partial T/\partial P)_{S,N} = VT\alpha_P/C_P$$

such that

$$dT = VT \frac{\alpha_P}{C_P} dP. \quad (1.50)$$

This result shows that a knowledge of the second derivatives C_P , α_P and κ_T provides an alternative way to introducing the thermodynamical theory.

We close this section with a brief discussion about a thermal magnetic system, defined by the fundamental equation which is a function of S, V, \mathcal{M}, N , that is

$$E = E(S, V, \mathcal{M}, N).$$

where \mathcal{M} is the magnetic dipole moment. The magnetic coefficients similar to α_P , κ_T , C_P and C_V are:

Coefficient of thermal variation of the magnetic moment

(analogous to α_P)

$$\alpha = \left(\frac{\partial \mathcal{M}}{\partial T} \right)_{P, H_{ex}}. \quad (1.51)$$

Magnetic susceptibility, κ_P , and isothermal susceptibility κ_T

$$\kappa_{T,P} = \frac{1}{V} \left(\frac{\partial \mathcal{M}}{\partial H_{ex}} \right)_{T,P} = \left(\frac{\partial M}{\partial H_{ex}} \right)_{T,P}. \quad (1.52)$$

Specific heat

$$C_{P, H_{ex}} = T \left(\frac{\partial S}{\partial T} \right)_{P, H_{ex}} \quad \text{or} \quad C_{P, \mathcal{M}} = T \left(\frac{\partial S}{\partial T} \right)_{P, \mathcal{M}}, \quad (1.53)$$

$$C_{V,H_{ex}} = T \left(\frac{\partial S}{\partial T} \right)_{V,H_{ex}} \quad \text{or} \quad C_{V,\mathcal{M}} = T \left(\frac{\partial S}{\partial T} \right)_{V,\mathcal{M}}. \quad (1.54)$$

The magnetic properties are often described by the susceptibility as a function of temperature, that is

$$\chi_{T,P} = \chi_{T,P}(T, P, H_{ex}) = \left(\frac{\partial M}{\partial H} \right)_{T,P}. \quad (1.55)$$

Since the relation among H , H_{ex} and M is given, we can find the relation between $\chi_{T,P}$ and $\kappa_{T,P}$, and the state equation

$$M = M(T, P, H_{ex}), \quad (1.50)$$

by integration.

1.8 Example: ideal gas and generalizations

Now we treat an example, by considering a simple system as a model characterized by a mono-component ideal gas, to exemplify the aforementioned thermodynamical formalism. Later we treat the problem to find a prescription to derive generalized state equations.

1.8.1 State equation for an ideal gas

An ideal gas is a chemically inert gas satisfying the following state equation

$$P = \frac{RT}{v} \quad \text{and} \quad T = \frac{2}{3R}\varepsilon,$$

where $v = V/N$ and $\varepsilon = E/N$. The quantity $R = 1,986 \text{ cal/mole } K$ is called *the universal constant of gases*. Another way to write the state equations is.

$$PV = NRT \quad \text{and} \quad E = \frac{3}{2}NRT. \quad (1.56)$$

These equations were established by experiments and are usually valid for a gas at high temperature and low pressure.

In order to write the fundamental relations, thermodynamical potentials and second derivatives, observe first of all that we have two state equations, but three independent extensive variables, that is, E , V and N . Then in order to use Eq. (1.14) to write the fundamental equation we have at our disposal another state equation (since, in principle, we need three of them). The third equation can be found by integrating the Gibbs-Duhem relation, Eq. (1.36), that is

$$\frac{\mu}{T} - \left(\frac{\mu}{T} \right)_0 = -\frac{3}{2}R \ln \frac{E}{E_0} - R \ln \frac{V}{V_0}, \quad (1.57)$$

where E_0, V_0, N_0 are the values for a reference state. Let us now write Eq. (1.14) in the entropy representation. This gives rise to

$$S = \frac{1}{T}E - \frac{P}{T}V - \frac{\mu}{T}N. \quad (1.58)$$

Using the state equations, Eqs. (1.56) and (1.57), we get the entropy function in terms of extensive quantities, that is,

$$S = \frac{N}{N_0} S_0 + \frac{3}{2} NR \ln \frac{E}{E_0} + NR \ln \frac{V}{V_0} - \frac{5}{2} NR \ln \frac{N}{N_0}, \quad (1.59)$$

where

$$S_0 = \frac{5}{2} N_0 R - N_0 \left(\frac{\mu}{T} \right)_0.$$

From Eq. (1.59), writing in the energy representation and using the Legendre transformation, thermodynamic potentials can be introduced. We leave these steps for the reader. Let us write the second derivative functions $\alpha_P, \kappa_T, C_V, C_P$:

$$\begin{aligned} \alpha_P &= \frac{1}{T}, \quad \kappa_T = \frac{1}{P}, \\ C_P &= \frac{5}{2} R, \quad C_V = \frac{3}{2} R. \end{aligned}$$

Therefore with this simple example we have established the usefulness of the different thermodynamical formulations.

1.8.2 The van der Waals equation

Although thermodynamics presents a well-defined formal structure, it would be interesting to find some prescription, at a theoretical level, to write down the fundamental equations or the equations of state, in particular, to describe more complex systems other than the ideal gas. This situation is quite close in nature to the mechanical problem to write Lagrangians explicitly. In this case the underlying symmetries can be used as a guide to write, for instance, models for the interactions. For thermal systems, such a prescription can be found if we recall that originally thermodynamics did not say a word about the microscopic nature of matter. However, we can use this microscopic viewpoint, assuming that matter is composed of particles, i.e. molecules, atoms, and so on, to implement thermodynamics. We proceed with a naive example, just to provide some flavor to this kind of reasoning.

As we have seen, an ideal gas is described by Eq. (1.56), where V is the volume of the gas container and P is the pressure. Taking into consideration that this gas is made of particles, some corrections in the ideal gas equation should be considered, resulting in a more general theory. In the case of the volume in Eq. (1.56), we can write

$$V \rightarrow V - Nb, \quad (1.60)$$

where b is a constant measuring the volume of each particle.

Assuming a molecular attraction, we expect a decrease in the pressure. That is, due to the attraction, collisions of particles with walls induce a reduction in the change of momentum, thus reducing the force on the wall; as a consequence the

pressure is lowered. Such a decrease in pressure can be considered as proportional to the number of pairs of molecules near to the wall region, that is, proportional to $n^2 = (N/V)^2$. Then the pressure should be modified to

$$P \rightarrow P - a \frac{N^2}{V^2}, \quad (1.61)$$

where a is a parameter related to the molecular interaction. Using the results of Eq. (1.60) and (1.61) in Eq. (1.56), we find

$$(V - Nb) \left(P - \frac{N^2}{V^2} a \right) = NRT.$$

or

$$P = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}, \quad (1.62)$$

which is called the van der Waals equation. In Eq. (1.62) instead of R we have written $k_B = R/N = 1.38065 \times 10^{-23} \text{ J/K}$. And thus N is to be interpreted as particle number, not moles. There is no need to use another notation since from now on N will be taken for the particle number only. The constant k_B is the Boltzmann constant.

1.9 Stability conditions and phase transitions

The second law ensures a maximum principle for the entropy, $\delta S = 0$ and $\delta^2 S < 0$, imposing stability conditions on thermodynamic systems. If the system is forced to go along a way conflicting with these conditions, then a phase transition may take place. We analyze some of these aspects in this section.

Consider a system receiving an infinitesimal amount of heat, dQ , from a heat bath at temperature T_0 and pressure P_0 . In this case, as a consequence of the second law of thermodynamics, the entropy change of the system, dS , is related to dQ by

$$dQ \leq T_0 dS.$$

The equality sign holds for reversible processes. Writing $dW = -P_0 dV$ for the work done on the system by the heat bath and using the first law of thermodynamics, $dQ = dE - dW$, we have

$$dA = dE + P_0 dV - T_0 dS \leq 0,$$

where the quantity

$$A = E + P_0 V - T_0 S,$$

called *availability* of the system, describes the maximum amount of work which may be extracted from a system in contact with a heat bath. Any process taking place in the system leads to a decrease of A , which has a minimum value at equilibrium. This

stability condition can also be stated for thermodynamic potentials, implying that Helmholtz and Gibbs free energies are a minimum at equilibrium. Such stability conditions can be used to prove that $C_V > 0$ and $C_P > 0$ [7].

The equilibrium state of a simple system is determined by specifying a set of thermodynamic variables such as (E, V, N) . The specification of (E, V, N) , however, is not a sufficient condition to ensure a uniform state of the system. That means, we can find different states coexisting in equilibrium, which belong to different *phases* of the system. A well-known example is the coexistence of phases in water, as liquid and vapor, or even three phases, liquid, solid and vapor. The phases can be

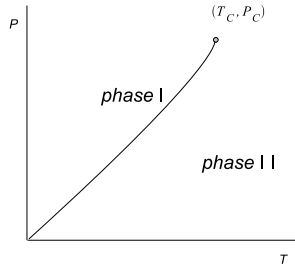


Fig. 1.1 First-order phase transition.

considered as different thermodynamic systems in equilibrium with each other; and thus, for a single system with two phases we have to state the following equilibrium phase conditions:

$$T_1 = T_2 = T, \quad (1.63)$$

$$P_1 = P_2 = P, \quad (1.64)$$

$$\mu_1(P, T) = \mu_2(P, T) = \mu. \quad (1.65)$$

We have written Eq. (1.65) with the explicit dependence on T and P to emphasize that the two phases cannot be in equilibrium at arbitrary T and P .

In a $P \times T$ diagram a phase transition can be represented by a line, as given in Fig. 1.1. If we go from region *I* to region *II*, crossing the line, we have an abrupt change in the nature of the system. That is, we find a separation of phases, at each point on the curve. The point (T_c, P_c) is called a *critical* point. Beyond that point, one can go from one region to another in a continuous way. In this case we do not meet any abrupt discontinuity among the phases.

In this type of phase transitions, we identify some specific characteristics. While the free energies of different phases are equal at the transition point, their first derivatives are discontinuous. This happens, for example, when water turns into vapor, in which case the discontinuity of entropy implies the existence of latent heat associated with the transition. This is called a *first-order phase transition*.

If the first derivatives of the free energy are continuous at the transition point, but not the thermodynamic quantities described by the second derivatives, like specific heat, compressibility and magnetization, then the system undergoes a *second-order phase transition*. Well-known examples of this transition are normal-metal to superconductor and para- to ferro-magnetic phases. In the later case, lowering the temperature below a critical value, T_c , implies a non-null magnetization, \mathbf{M} , appearing in the system. This ferromagnetic phase corresponds to ordered states, which have lower symmetry when compared with the disordered paramagnetic phase, where $\mathbf{M} = 0$. Distinctly from the first-order phase transition, no coexistence of phases occurs in the second-order phase transition; that is, there are no meta-stable states in either of the transition point.

The ordered phase is characterized by a non-vanishing order parameter, ϕ , which in the magnetic case can be identified with the magnetization. On the other hand, the symmetric phase has $\phi = 0$. Notice that the symmetry changes discontinuously at the transition point, since if $\phi \neq 0$ (no matter how small it is) the system presents the symmetry of the full ordered phase. Nevertheless, decreasing the temperature, ϕ changes continuously from zero to non-vanishing values at T_c . The overall behavior of order parameter with temperature is depicted in Fig. 1.2.

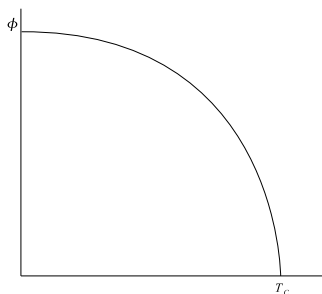


Fig. 1.2 Dependence of the order parameter with temperature.

A quantitative, phenomenological theory of second-order phase transition was proposed by Landau [7] in 1937. At a given temperature T and pressure P , for a system in equilibrium, the order parameter is determined in both phases. To describe the transition, Landau generalized the free energy allowing it to be, a function of, not only the state variables, but also of ϕ , which is taken as an independent variable. The actual value assumed by ϕ is determined by the equilibrium stability conditions, requiring that the free energy be a minimum for the given values of T and P . The next step is to assume an expansion of the generalized free energy, $\tilde{G}(P, T, \phi)$, near the transition point, $T \sim T_c$, in powers of the order parameter, as

$$\tilde{G}(T, \phi) = \tilde{G}_0(T) + A(T)\phi^2 + B(T)\phi^4. \quad (1.66)$$

For simplicity, we have taken P fixed. Notice that no monomial of odd order has

been written, a fact that is justified by symmetry arguments [7]. Also the expansion is truncated at the fourth power, since the order parameter is small, $\phi \sim 0$, close to T_c and the second degree monomial alone is not enough to describe the transition. In order to guarantee that $\tilde{G}(T, \phi)$ is bounded from below, and thus has a minimum, we take $B(T) > 0$. If $A > 0$, the minimum occurs at $\phi = 0$, the disordered phase. To have a minimum of $\tilde{G}(T, \phi)$ for $\phi \neq 0$, corresponding to ordered phase, we should have $A < 0$. Since $\tilde{G}(T, \phi)$ is continuous at the critical point, we must have $A(T_c) = 0$. Thus in the vicinity of T_c , we can expand $A(T)$ up to the first order in $T - T_c$, that is

$$A(T) = \alpha(T - T_c),$$

where $\alpha > 0$. With a similar reasoning, we find that at the critical point $B(T)$ is a positive constant, to be denoted by $B(T_c) = b$. Therefore, Eq. (1.66) is written as

$$\tilde{G}(T, \phi) = \tilde{G}_0(T) + \alpha(T - T_c)\phi^2 + b\phi^4. \quad (1.67)$$

The behavior of the Landau free energy as a function of the order parameter is illustrated in Fig. 1.3.

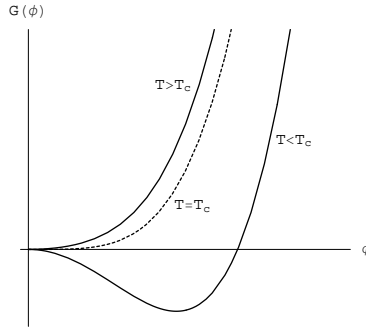


Fig. 1.3 Landau free energy, $G(\phi) = \tilde{G}(T, \phi) - \tilde{G}_0(T)$, in a second-order phase transition.

The extrema of $\tilde{G}(T, \phi)$ are determined by

$$\frac{\partial \tilde{G}(T, \phi)}{\partial \phi} = 2\alpha(T - T_c)\phi + 4b\phi^3 = 0,$$

having solutions, $\phi = 0$ and

$$\phi^2 = -\frac{\alpha(T - T_c)}{2b},$$

corresponding to the minima for $T > T_c$ and $T < T_c$, respectively, since in both cases

$$\frac{\partial^2 \tilde{G}(T, \phi)}{\partial \phi^2} = 2\alpha(T - T_c) + 12b\phi^2 > 0.$$

The entropy is given by

$$S = -\frac{\partial \tilde{G}(T, \phi)}{\partial T} = S_0 + \alpha \phi^2;$$

and thus we observe that it varies continuously through the transition. On the other hand, the specific heat for the ordered phase, $\phi \neq 0$, is

$$C = T \frac{\partial S}{\partial T} = C_0 + \alpha^2 \frac{T_c}{2D},$$

while for the symmetric phase, $\phi = 0$, $C = C_0$. This shows that the specific heat has a discontinuity at the critical temperature.

The main features of first-order phase transitions can also be cast within a Landau thermodynamic theory. In this case, the expansion of the free energy is taken in the form

$$\tilde{G}(T, \phi) = \tilde{G}_0(T) + a(T)\phi^2 - b\phi^4 + c\phi^6, \quad (1.68)$$

where b and c are positive constants and $a(T) = \alpha(T - T_0)$, T_0 being a temperature parameter that does not correspond to the critical temperature. The behavior of this free energy, as a function of ϕ , is presented in Fig. 1.4.

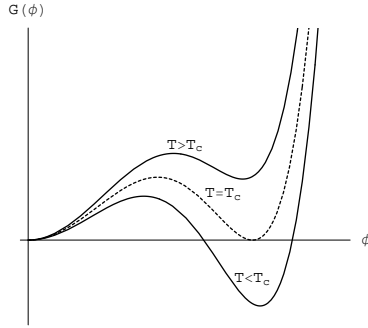


Fig. 1.4 Landau free energy, $G(\phi) = \tilde{G}(T, \phi) - \tilde{G}_0(T)$, in a first-order phase transition.

The free energy (1.68) has two local minima occurring at $\phi = 0$ and

$$\phi_0(T) = \frac{1}{3c} \left[b + \sqrt{b^2 - 3a(T)c} \right]; \quad (1.69)$$

which minimum value of \tilde{G} is the lowest one depends on the temperature. While the absolute minimum prevails in the stable phase, the other local minimum corresponds to metastable states that show up in the supercooling. The transition temperature, at which the distinct phases can coexist in equilibrium, is determined by requiring that the two minimum values of \tilde{G} are equal, i.e. by imposing that $\tilde{G}(T_c, \phi_0(T_c)) = 0$. This condition is equivalent to $a(T) = b^2/4c$, which implies that

$$T_c = T_0 + \frac{b^2}{4\alpha c}. \quad (1.70)$$

Note that, in a first order phase transition, the order parameter is discontinuous at T_c so that both the state and its symmetry change abruptly at the transition point. We could find the discontinuity of the entropy at the transition point, thus determining the latent heat, but we will not pursue this issue any further.

The Landau theory of phase transitions in thermodynamics can be extended to consider inhomogeneous systems, taking into account spatial fluctuations of the order parameter, such that ϕ is a field, that is $\phi = \phi(\mathbf{x})$. In this case, the expansion of $\tilde{G}(T, \phi)$ has to include derivatives of $\phi(\mathbf{x})$. For long-wavelength fluctuations, we keep only the lowest derivative terms, which has the form $(\nabla\phi)^2$. Hence, for instance, concerning a second-order phase transition we write

$$\tilde{G}(T, \phi) = \tilde{G}_0(T) + \alpha_0(T - T_c)\phi^2 + b\phi^4 + e(T_c)(\nabla\phi)^2. \quad (1.71)$$

Such a free energy can be viewed as an Euclidian field theory. In the quantum field theory, the thermodynamic description of the second-order phase transition is analyzed in terms of spontaneous symmetry breaking, and gives rise to new concepts such as Goldstone bosons that are related to collective states in many body systems. We will elaborate this theory including the temperature effects in the following chapters.