

Chapter 2

Thermodynamics

We know from experience that a macroscopic system behaves in a relatively simple manner. For example, when liquid water is heated under atmospheric pressure, it will boil at 100 °C. If the vapor so produced is cooled at the same pressure, it will condense at 100 °C. These statements hold true regardless of the initial conditions from which the body of water under consideration has evolved. This situation is in stark contrast to that in classical mechanics, in which initial conditions play a far more prominent role. In fact, our experience tells us that results of measurements we make of a macroscopic body are quite insensitive to the detailed microscopic state of the body. Thermodynamics is built on this empirical observation and systematically elucidates interconnections among these *insensitive observations*. In this chapter, we review the framework of thermodynamics before attempting to interpret it from the classical mechanical point of view in Chaps. 3 and 4.

2.1 The First Law of Thermodynamics

A macroscopic system, such as a glass of water, consists of many molecules. While behavior of molecules is subject to the laws of quantum mechanics rather than those of classical mechanics, the latter framework can still provide a useful approximation in many situations. On the basis of conservation of energy we saw in the previous chapter, we may conclude that the work W' done on the system, which is a collection of molecules in this case, is equal to the change ΔE in its total energy:

$$\Delta E = W' . \quad (2.1)$$

In writing this equation, it is assumed that the number of mechanical degrees of freedom remains fixed while the work is performed on the system. In thermodynamics, a system that does not exchange particles with the surroundings is called a **closed system** or a **body**. In contrast, an **open system** allows for particles to freely

pass through its boundary, thereby changing its number of mechanical degrees of freedom. For a moment, we focus only on closed systems.

Our everyday experience tells us, however, that a change in the apparent state of the system can be brought about without exerting any work on it. For example, by immersing a piece of heated steel in a glass of cold water, we can cause the state of the water to change. It becomes warmer and, if the steel is sufficiently hot, the water may even start to boil. From this observation, we infer that its energy content has also changed. At the molecular scale, this may be understood as a result of kinetic energy being transferred from iron atoms to water molecules through collisions among them. The kinetic energy is also constantly redistributed within the piece of steel. It appears then that the process we are observing belongs to the realm of classical mechanics. While this is true aside from the abovementioned quantum nature of atomistic processes, a full description of the process from this mechanistic point of view demands that we be capable of knowing the position and velocity of each constituent particle in the system (a glass of water in this case) and in the surroundings (a block of steel) at some instant of time and that the equations of motion can be integrated from the initial conditions so determined. Even if this is somehow possible, it is not clear if the microscopic description we would obtain is particularly useful.

Thus, when we perform a macroscopic observation, which does not inquire into the molecular-level details of a process, we must acknowledge that there are two types of processes. Firstly, there are those processes for which the force and the resulting displacement can be identified at a macroscopic level. In this case, we can readily compute ΔE by means of (2.1). Then, there are other processes, such as those we have considered above, for which the relevant forces and displacements are detectable only at a microscopic level. In such a situation, we, as a macroscopic observer, cannot compute ΔE by means of (2.1).

It is then sensible to use separate notations and words referring to these two modes of affecting the energy content of the system. From this point on, we shall use the term **work** to mean the mode of energy transfer into a system in which the force and the resulting displacement are measurable at a macroscopic level. We use the symbol W to denote the work in this narrower sense of the word. The other mode of energy transfer is called **heat** and is denoted by the symbol Q . Thus, heat embraces all modes of energy transfer we cannot express in a form of a macroscopic force and the resulting macroscopic displacement. By means of the newly introduced quantities, (2.1) becomes

$$\Delta E = W + Q. \quad (2.2)$$

The principle of conservation of energy, when expressed in this form, is called the **first law of thermodynamics**.

Of course, (2.2) would not be very useful unless we can compute Q for a given process despite our inability to identify the relevant forces and displacements at the microscopic level. This question of quantifying Q will be taken up in the next section.

The state of a system defined in terms of the coordinates and momenta of all particles in the system is called the “microscopic state” or **microstate** of the system. In contrast, we use the phrase “macroscopic state,” or **macrostate** for short, to refer to the state in which the system appears to us when making observations that are insensitive to the microscopic details. Thus, *the notion of heat arises when we describe the behavior of the system in terms of macrostates as opposed to microstates.*

In thermodynamics, we are primarily interested in the “internal state of the system” and not in its macroscopic motion in space or change in its position relative to an external field. Accordingly, the kinetic energy due to translational motion of the system as a whole and the potential energy due to an external field are subtracted off from E , and we focus only on what is left, which is called the **internal energy** of the system and is denoted by U .

If we consider a system enclosed by rigid walls that are fixed in space, the location of its center of mass fluctuates at a microscopic level as a result of interaction between the system and its surroundings. Because of this, the procedure just described is not well defined if applied within the context of microscopic description of the system. However, the change in the kinetic or the potential energy due to such fluctuation is generally too small to be detectable by *macroscopic measurements*. Within the accuracy of such measurements, the separation of E into U and the rest will be a well-defined procedure.

In Sect. 1.6, we saw that E is an additive quantity. Since both the kinetic and potential energies we are considering here are additive, U also is an **additive quantity**. For a homogeneous body, U is also an **extensive quantity**. That is, U is proportional to the size of the system. To see this, we may imagine dividing the homogeneous body into two equal parts. If each part is still macroscopic, the interaction between them makes a negligible contribution to U . By the additivity of the internal energy, U of the whole system is equal to twice the internal energy of one of the parts.

Provided that neither the heat nor the work affects the translational motion of the system as a whole or its position in the external field, we may rewrite (2.2) as

$$\Delta U = W + Q. \quad (2.3)$$

Given two macrostate A and B accessible to a system, there are many distinct ways of bringing it from one to the other. The amount of work W involved usually depends on exactly how the change is brought about. We express this fact by saying that W is path dependent. A path-dependent quantity is called a **path function**.

Based on the classical mechanical notion of energy, however, we expect that the energy of a system has a uniquely determined value for a given macrostate of the system. Such a quantity, the value of which is determined *only* by the macrostate in question, is called a **state function**. Consequently, the energy difference $\Delta U := U_b - U_a$ between the two states is path independent. According to (2.3), then Q must be a path function.

We note that the classical mechanical work W' is, as seen from (2.1), path independent. In defining W , we have focused only on macroscopic forces and macro-

scopic displacements and lost track of the processes occurring at the microscopic level. This is what makes W a path function.

We will often be concerned with infinitesimal changes, in which W and Q are infinitesimally small. Using $\mathrm{d}W$ and $\mathrm{d}Q$ to denote, respectively, the amount of work done on and heat added to the system, and replacing ΔU by $\mathrm{d}U$ to indicate that only the leading term of ΔU is retained, we write (2.3) as

$$\mathrm{d}U = \mathrm{d}W + \mathrm{d}Q \quad (2.4)$$

for an infinitesimal process. As with W and Q , and in contrast to $\mathrm{d}U$, both $\mathrm{d}W$ and $\mathrm{d}Q$ are path-dependent quantities. We use the notation d to emphasize this fact.

Typically, the work term for an infinitesimal change is given by

$$\mathrm{d}W = -P\mathrm{d}V, \quad (2.5)$$

where P and V are the pressure and volume of the system, respectively. In Sect. 2.3, we examine how this expression arises and under what conditions.

2.2 Quantifying Heat

The notion of heat was introduced as a result of our inability to track the detailed mechanism of energy transfer at the microscopic level. Therefore, it is not clear if heat can be quantified at all. How do we compute Q if it is defined as everything that cannot be expressed as force times displacement?

For expediency, we accept the following statement: Using a purely classical mechanical device, it is always possible to change the state of a system between two distinct macrostates A and B.

In other words, at least one of the two changes, from A to B *or* from B to A, can always be realized. By a purely **classical mechanical device**, we imply our ability to track all of its generalized coordinates and momenta. As a result, the device does not exchange heat with the system, but it can exchange work with the system. This means that the difference in energy between any two states can be measured in terms of force and the displacement. For example, if the change from A to B is achievable, we have

$$U_b - U_a = W_{\text{cm}}, \quad (2.6)$$

where W_{cm} is the work done on the system by the purely classical mechanical device. Having determined the energy difference, we can compute the heat Q received by the system during *any* process that brings the system from A to B. In fact, from (2.3),

$$Q = (U_b - U_a) - W = W_{\text{cm}} - W, \quad (2.7)$$

where W is the work done on the system during the process that involves an exchange of heat.

2.3 ‡A Typical Expression for $\mathfrak{d}W$

Suppose that an external body exerts a force $\mathbf{t}dA$ on the system through a surface element of area dA on the boundary of the system. Further, let $d\mathbf{l}$ denote the infinitesimal displacement experienced by the surface element. The work done by the force $\mathbf{t}dA$ is then $d\mathbf{l} \cdot (\mathbf{t}dA)$. Repeating this computation for each of the surface elements, into which the system boundary A is divided, and adding together the results, we arrive at the total work done on the system:

$$\mathfrak{d}W = \int_A d\mathbf{l} \cdot (\mathbf{t}dA) , \quad (2.8)$$

where the integral is over the boundary A . If a part of the boundary is held fixed, then $d\mathbf{l} = \mathbf{0}$ for that part of the boundary.

The stress vector \mathbf{t} is given in terms of the stress tensor \hat{T} as

$$\mathbf{t} = \mathbf{n} \cdot \hat{T} , \quad (2.9)$$

where \mathbf{n} , called the outward unit normal, is a unit vector perpendicular to dA and pointing away from the system. By definition,

$$\hat{T} = -P\hat{I} + \hat{T}_v , \quad (2.10)$$

where \hat{I} is the unit tensor and \hat{T}_v is referred to as the extra (or viscous) stress tensor.

We recall that \hat{T}_v for Newtonian fluids is proportional to the *rate* of deformation. (The explicit expression for \hat{T}_v is of no importance in the present discussion. For further details, consult Ref. [5], for example.) The key observation here is that, if any imbalance of force at any point on the system boundary is infinitesimally small, then the boundary moves very slowly and \hat{T}_v will be negligibly small. Thus,

$$\hat{T} = -P\hat{I} . \quad (2.11)$$

Since $\mathbf{a} \cdot \hat{I} = \mathbf{a}$ for any vector \mathbf{a} , we have

$$\mathbf{n} \cdot \hat{T} = \mathbf{n} \cdot (-P\hat{I}) = -P\mathbf{n} \cdot \hat{I} = -P\mathbf{n} . \quad (2.12)$$

So,

$$\mathfrak{d}W = \int_A d\mathbf{l} \cdot (-P\mathbf{n})dA . \quad (2.13)$$

If P is uniform over the boundary A of the system, this may be written as

$$\mathfrak{d}W = -P \int_A d\mathbf{l} \cdot \mathbf{n}dA . \quad (2.14)$$

But, as seen from Fig. 2.1, $d\mathbf{l} \cdot \mathbf{n}dA$ is the volume swept out by the surface element dA as it moves by $d\mathbf{l}$. When this quantity is added together for all such surface elements, the end result is the net change in the volume of the system. In this way, we arrive at (2.5).

We note that solids can sustain nonzero \hat{T}_v even if the boundary does not move at all. This is because, according to Hooke's law, which is an excellent approximation

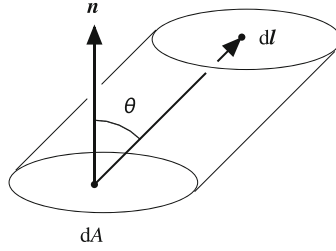


Fig. 2.1 The volume of the column swept out by the surface element dA as it moves by $d\mathbf{l}$ is given by $d\mathbf{l} \cdot \mathbf{n} dA = dA \|d\mathbf{l}\| \cos \theta$, in which \mathbf{n} is the outward unit normal of dA and $\|d\mathbf{l}\| \cos \theta$ is the height of the column.

for many solids as long as the deformation is sufficiently small, \hat{T}_v in a solid is proportional *not* to the rate of deformation but to the size of deformation itself. We can still apply (2.5) to a solid under hydrostatic pressures, for which $\hat{T}_v \equiv 0$.

2.4 The Second Law of Thermodynamics

The content of the **second law of thermodynamics** is the following: There is a *state function* of a system called **entropy** S . The value of S can change as a result of both interactions with the surroundings and internal processes. Denoting the change associated with these processes by dS_e and dS_i , respectively, we have

$$dS = dS_e + dS_i. \quad (2.15)$$

For *closed* systems, dS_e is given by

$$dS_e = \frac{dQ}{T} \quad (2.16)$$

where T is the **absolute temperature** and is a positive number. Thus, dS_e can be positive, negative, or zero depending on the sign of dQ . A process for which $dQ \equiv 0$ is called an **adiabatic process**. In contrast,

$$dS_i \geq 0 \quad (2.17)$$

regardless of whether the system is closed or open. For processes occurring in a closed system, therefore, we have

$$dS \geq \frac{dQ}{T}. \quad (2.18)$$

As shown more explicitly later in Example 2.1, the equality in (2.17) and (2.18) holds only for **reversible processes**. A process is called reversible if the sequence of states visited by the system can be traversed in an opposite direction by an

infinitesimal change in the boundary conditions. As an example, we may think of a very slow expansion and compression of a gas enclosed in a thermally insulated cylinder fitted with a frictionless piston. The gas will expand if the external pressure is infinitesimally smaller than that of the gas. By an infinitesimal increase in the external pressure, the process can be reversed. Heat transfer due to an infinitesimal temperature difference is another example.

As is the case with the internal energy, entropy is an additive quantity. To see this, we may consider a composite system consisting of subsystems, each at its own uniform temperature. For each of them, we can assign a reference state at which its entropy is zero. Using a combination of reversible adiabatic processes and reversible heat transfer, we can bring a subsystem from its reference state to the actual state of interest and compute the change in its entropy by means of (2.18) with equality. The entire process in which this is done, one subsystem after another, may be regarded as a single process in which the composite system is brought to the state of interest from its reference state. As long as the interaction among subsystems can be ignored, the resulting change in entropy of the composite system is equal to the sum of the entropy change for each of the subsystems. **Additivity** of S , when applied to a homogeneous body implies that entropy of the body is proportional to its size. In other word, S is an **extensive quantity**. This property of S are in stark contrast with such quantities as T and P , which are independent of the size of the system and is said to be **intensive**.

As we shall see later, classification of thermodynamic quantities into extensive and intensive variables is of fundamental importance in thermodynamics. Without it, one cannot derive important equations such as the Euler relation and the Gibbs–Duhem relation. (See Sects. 2.10, 2.11, 6.4, and 6.5.)

We will be concerned primarily with the consequence of the second law and the properties of entropy as summarized above and will not inquire how the law can be established solely on the basis of macroscopic observations. An interested reader should consult Ref. [2].

2.5 Equilibrium of an Isolated System

When a system is isolated from the surroundings and thus left undisturbed, it eventually reaches a particularly simple state, in which no further change is observed in any *macroscopic* quantities we can measure of the system. This final state is called an **equilibrium state**. The second law of thermodynamics leads to a precise formulation of the condition of equilibrium of an isolated system in terms of entropy.

Since $dQ = 0$ for an isolated system, (2.18) reduces to

$$dS \geq 0. \quad (2.19)$$

That is, during a spontaneous internal process that brings the system eventually to a state of equilibrium, the entropy of the system does not decrease. At the same time, the internal energy of the system remains constant since dW is also zero for an isolated system.

It seems unlikely that the entropy of a *finite* isolated system can increase indefinitely. Instead, we expect the entropy of the system to eventually reach the maximum possible value consistent with the given values of U , V , the total mass, and any other constraints that might be imposed on the system. Once the system reached this state of maximum entropy, any further change would require the entropy to decrease, which is impossible for an isolated system. Evidently, the same argument applies when S is only a local maximum. The entropy being (local) maximum is thus *sufficient* for an isolated system to be in equilibrium.

To establish its *necessity* for equilibrium, we may consider a system that is not at the state of maximum entropy under a given set of constraints. In this case, those processes that result in an increase of S are still possible while the processes in the opposite direction are not. Thus, we expect that the state of the system under consideration is not one of equilibrium.

In this way, we are led to accept the following formulation of the condition of equilibrium:

Condition of Equilibrium 1 *For the equilibrium of an isolated system, it is necessary and sufficient that the entropy of the system is (local) maximum under a set of constraints imposed on the system.*

For a more careful discussion aimed at establishing the necessity and the sufficiency of the condition, see pp. 58–61 of Ref. [3].

According to the second law, processes resulting in a decrease of the entropy are impossible for an isolated system. From a point of view of statistical mechanics, which provides a microscopic interpretation of the second law, this is not entirely accurate. In fact, the probability of finding the system with entropy S' which is less than the equilibrium value S is proportional to

$$e^{(S'-S)/k_B}, \quad (2.20)$$

where $k_B = 1.3806 \times 10^{-23}$ J/K is the **Boltzmann constant**. That the entropy of an isolated system can actually decrease by spontaneous fluctuation is directly responsible for the initial stage of the so-called first-order phase transition, the examples of which include freezing of a supercooled liquid, sudden boiling of superheated liquid, and condensation of supersaturated vapor. These phases of temporary existence, such as the supercooled liquid, superheated liquid, and supersaturated vapor, are said to be **metastable** and correspond to a *local* maximum of the entropy.

2.6 Fundamental Equations

The concept of fundamental equation is essential to thermodynamics. As we shall see, by merely accepting its existence and assuming that it meets some modest mathematical requirements, we can establish surprising interrelations among seemingly unrelated quantities almost effortlessly.

2.6.1 Closed System of Fixed Composition

For a moment, we restrict ourselves to reversible processes occurring in a closed system. For simplicity, we also assume that there is no chemical reaction in the system so that the number of moles of species i , to be denoted by N_i , is constant for each species ($i = 1, \dots, c$). Under these conditions, we may rewrite (2.4) using (2.5) and (2.18) to obtain

$$dU = TdS - PdV. \quad (2.21)$$

As of now, we have accepted the validity of this equation only for reversible processes during which N_1, \dots, N_c of the system remain constant. We now argue that it applies to irreversible processes as well.

The key idea here is that, as long as we limit ourselves to an isolated system that is in *equilibrium* and *homogeneous*, its entropy S is a function only of U , V , and N_1, \dots, N_c :

$$S = S(U, V, N_1, \dots, N_c). \quad (2.22)$$

This is so because the value of S , in the case of an isolated system in equilibrium, is determined by it being the maximum possible value for given values of U , V , and N_1, \dots, N_c . Equation (2.22) is an example of **fundamental equations** of the system.

The restriction on homogeneity stems from our use of (2.5). In the case of an inhomogeneous system, there may be no single value of P . Thus, the work done on the system by an infinitesimal displacement of an infinitesimal portion of the system boundary depends on the position of this surface element. In order to specify the state of the system, then, one generally has to specify the shape of the system boundary, and not just its volume.

For the processes under consideration, N_1, \dots, N_c are constant. Suppose now that we have changed the values of U and V by some infinitesimal amounts dU and dV , respectively. The value of S in this new state is simply

$$S(U + dU, V + dV, N_1, \dots, N_c). \quad (2.23)$$

To the first order, therefore, the resulting change in S is given by

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V,N} dU + \left(\frac{\partial S}{\partial V} \right)_{U,N} dV, \quad (2.24)$$

where we used (B.16) and included N in the subscripts to remind us that the derivatives are taken while holding all of N_1, \dots, N_c constant.

Note that (2.24) is obtained by applying (2.22) to the states before and after the infinitesimal change. Thus, so long as the system is in equilibrium and homogeneous both *before* and *after* the change and N_1, \dots, N_c remain unaffected, (2.24) applies to *any* process including irreversible ones.

According to (2.21), however,

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \quad (2.25)$$

for a reversible process. A comparison between (2.24) applied for a reversible process and (2.25) gives

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N} \quad \text{and} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{U,N} . \quad (2.26)$$

The differential coefficients on the right-hand side are obtained by comparing the values of S for infinitesimally different two equilibrium states. Since S is a state function, the partial derivatives depend only on the values of dU or dV , but not on how these changes are brought about. Therefore, (2.26) holds regardless of the nature of the process.

Combining (2.24) and (2.26) and noting that neither depends on the process being reversible, we conclude that (2.25), and hence (2.21), hold for *any* infinitesimal change that is occurring in a closed system without affecting N_1, \dots, N_c .

We emphasize that, given a pair of initial and final states, values of δQ and δW do depend on the actual path taken, since they are path functions. In particular, $\delta Q \neq TdS$ and $\delta W \neq -PdV$ for irreversible processes. Only the sum of these two, $dU = \delta W + \delta Q$, is independent of the path and is given by (2.21). We illustrate these points with the following example.

Example 2.1. Gas in a cylinder: Let us consider a gas enclosed in a cylinder that is fitted with a frictionless piston. We suppose that the gas is initially in equilibrium and has a uniform temperature T and pressure P . Then, we induce a change in the state of the gas by changing the external pressure acting on the piston to P_e and by changing the wall temperature of the cylinder to T_a .

The gas will expand if $P_e < P$ while it will be compressed if $P_e > P$. In both cases, the work δW done *on* the system by the surroundings is given by

$$\delta W = -P_e dV = -PdV + (P - P_e)dV . \quad (2.27)$$

Since temperature varies continuously across interfaces, T_a is also the temperature of the gas in the immediate vicinity of the wall. According to (2.16), the heat δQ received by the system during this process is

$$\delta Q = T_a \delta S_e , \quad (2.28)$$

which is positive if $T_a > T$ and negative if $T_a < T$.

Unless $P_e = P$ and $T_a = T$, the process will momentarily make the system inhomogeneous. Nevertheless, after the process has completed and the system is left alone for a while, it will reach a new state of equilibrium and the state function S , and hence dS , will have definite values. Let us introduce this dS in our expression for δQ . Using (2.15),

$$\delta Q = T \delta S_e + (T_a - T) \delta S_e = T(dS - \delta S_i) + (T_a - T) \delta S_e . \quad (2.29)$$



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