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CHAPTER ONE

Basic definitions

- *Thermodynamics* is defined as the study of *equilibrium states* of a *system* which has been subjected to some *energy transformation*. More specifically, thermodynamics is concerned with transformations of heat into mechanical work and of mechanical work into heat.

- A *system* is a specific sample of matter. In the atmosphere a parcel of air is a system. A system is called *open* when it exchanges matter and energy with its surroundings (Figure 1.1). In the atmosphere all systems are more or less open. A *closed* system is a system that does not exchange matter with its surroundings. In this case, the system is always composed of the same point-masses (a point-mass refers to a very small object, for example a molecule). Obviously, the mathematical treatment of closed systems is not as involved as the one for open systems, which are extremely hard to handle. Because of that, in atmospheric thermodynamics, we assume that most systems are closed. This assumption is justified when the interactions associated with open systems can be neglected. This is approximately true in the following cases. (a) The system is large enough to ignore mixing with its surroundings at the boundaries. For example, a large cumulonimbus cloud may be considered as a closed system but a small cumulus may not. (b) The system is part of a larger homogeneous system. In this case mixing does not significantly change its composition. A system is called *isolated* when it exchanges neither matter nor energy with its surroundings.

- The *state* of a system (in classical mechanics) is completely specified at a given time if the position and velocity of each point-mass is known. Thus, in a three-dimensional world, for a system of N point-masses, $6N$ variables need to be known at any time. When

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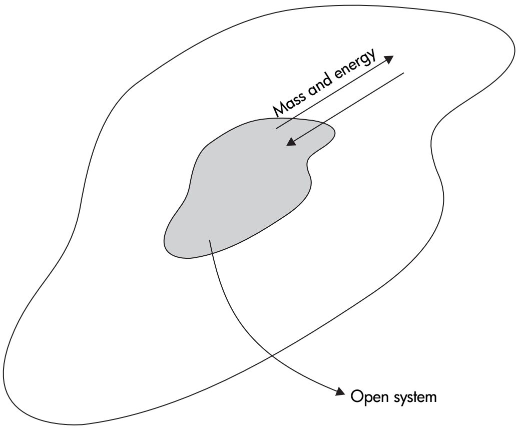

Figure 1.1
In an open system mass and energy can be exchanged with its environment. A system is defined as closed when it exchanges energy but not matter with its environment, and as isolated if it exchanges neither mass nor energy.

N is very large (like in any parcel of air) this dynamical definition of state is not practical. As such, in thermodynamics we are dealing with the average properties of the system.

If the system is a homogeneous fluid consisting of just one component, then its thermodynamic state can be defined by its geometry, by its temperature, T, and pressure, p. The geometry of a system is defined by its volume, V, and its shape. However, most thermodynamic properties do not depend on shape. As such, volume is the only variable needed to characterize geometry. Since p, V, and T determine the state of the system, they must be connected. Their functional relationship $f(p, V, T) = 0$ is called the *equation of state*. Accordingly, any one of these variables can be expressed as a function of the other two. It follows that the state of a one-component homogeneous system can be completely defined by any two of the three state variables. This provides an easy way to visualize the evolution of such a system by simply plotting V against p in a rectangular coordinate system. In such a system, states of equal temperature define an isotherm. Any other thermodynamic variables that depend on the state defined by the two independent state variables are called *state functions*. State functions are thus dependent variables and state variables are independent variables; the two do not differ in other respects. That is why in the literature there is hardly any distinction between state variables and state functions. State variables and state functions have the property that their changes depend only on the initial and final states, not on the particular way by which the change happened. If the system is composed of a homogeneous mixture of several components, then in order to define the state of the system we need, in addition to p, V, T, the concentrations of the different components. If the system is nonhomogeneous, we must divide it into a number of homogeneous parts. In this case, p, V, and T of a given homogeneous part are connected via an equation of state.

For a closed system, the chemical composition and its mass describe the system itself. Its volume, pressure, and temperature describe the state of system. Properties of the system are referred to as extensive if they depend on the size of the system and as intensive if they are independent of the size of the system. An extensive variable can be converted into an intensive one by dividing by the mass. In the literature it is common to use capital letters to describe quantities that depend on mass (work, W, entropy, S) and lower case letters to describe intensive variables (specific work, w, specific heat, q). The mass, m, and temperature, T, will be exceptions to this rule.

- An *equilibrium state* is defined as a state in which the system's properties, so long as the external conditions (surroundings) remain unchanged, do not change in time. For example, a gas enclosed in a container of constant volume is in equilibrium if its pressure is constant throughout and its temperature is equal to that of the surroundings. An equilibrium state can be stable, unstable, or metastable. It is stable when small variations about the equilibrium state do not take the system away from the equilibrium state, and it is unstable if they do. An equilibrium state is called metastable if the system is stable with respect to small variations in certain properties and unstable with respect to small changes in other properties.

- A *transformation* takes a system from an initial state i to a final state f. In a (p, V) diagram such a transformation will be represented by a curve I connecting i and f. We will denote this as $i \xrightarrow{I} f$. A transformation can be reversible or irreversible. Formally, a reversible transformation is one in which the successive states (those between i and f) differ by infinitesimals from equilibrium states. Accordingly, a reversible transformation can only connect those i and f states which are equilibrium states. It follows that a reversible process is one which can be reversed anywhere along its path in such a way that both the system and its surroundings return to their initial states. In practice a reversible transformation is realized only when the external conditions change very slowly so that the system has time to adjust to the new conditions. For example, assume that our system is a gas enclosed in a container with a movable piston. As long as the piston moves from i to f very slowly the system adjusts and all intermediate states are equilibrium states. If the piston does not move slowly, then currents will be created in the expanding gas and the intermediate states will not be equilibrium states. From this example, it follows that turbulent mixing in the atmosphere is a source of irreversibility. If a system goes from i to

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f reversibly, then it could go from f to i again reversibly if the same steps were followed backwards. If the same steps cannot be followed exactly, then this transformation is represented by another curve I' in the (p, V) diagram (i.e. $f \xrightarrow{I'} i$) and may or may not be reversible. In other words the system may return to its initial state but the surroundings may not. Any transformation $i \longrightarrow f \longrightarrow i$ is called a cyclic transformation. Given the discussion above we can have cyclic tansformations which are reversible or irreversible (Figure 1.2). A transformation $i \xrightarrow{I} f$ is called isothermal if I is an isotherm, isochoric if I is a constant volume line, isobaric if I is a constant pressure line, and adiabatic if during the transformation the system does not exchange heat with its surroundings (environment). Note and keep in mind for later that adiabatic transformations are not isothermal.

- *Energy* is something that can be defined formally (we have to wait a bit for this), but its concept is not easily understood by defining it. We all feel we understand what is meant by energy, but if we verbally attempt to explain what energy is we will get upset with ourselves. At this point, let us just recall that for a point-mass with a mass m_p moving with speed v in a uniform gravitational field g, Newton's second law takes the form

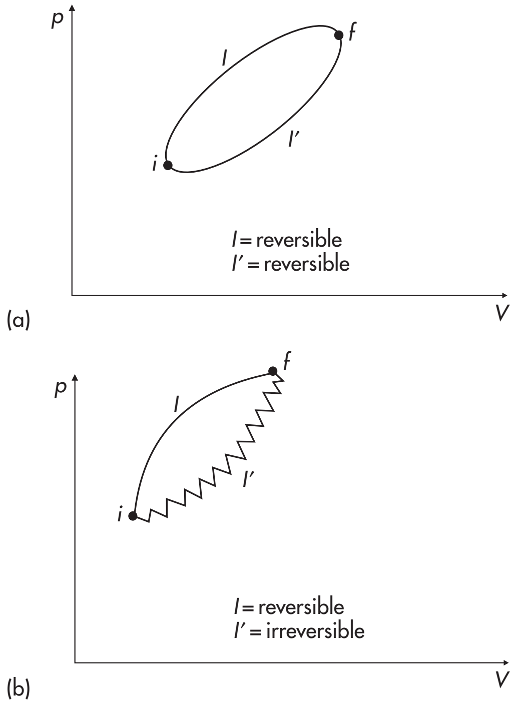

Figure 1.2
(a) A reversible cyclic process; (b) an irreversible cyclic process.

$d(K + P)/dt = 0$ where $K = m_{\mathrm{p}}v^2/2$, $P = m_{\mathrm{p}}gz$, t is the time, and z is the height. K is called the kinetic energy and P is called the potential energy. The total energy of the point-mass $E = K + P$ is, therefore, conserved. If we consider a system of N interacting point-masses that may be subjected to external forces (other than gravity), then the total energy of the system is the sum of the kinetic energy about the centre of gravity of all point-masses (internal kinetic energy), the kinetic energy of the centre of gravity, the potential energy due to interactions between the point-masses (internal potential energy), and the potential energy due to external forces. The sum of the internal kinetic and internal potential energy is called the internal energy of the system, U. A system is called conservative if $dU/dt = 0$ and dissipative otherwise. For systems considered here we are interested in the internal energies only.

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CHAPTER TWO

Some useful mathematical and physical topics

2.1 Exact differentials

If z is a function of the variables x and y, then by definition

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{2.1}$$

where dz is an exact differential. Now let us assume that a quantity δz can be expressed according to the following differential relationship

$$\delta z = M dx + N dy \tag{2.2}$$

where x and y are independent variables and M and N are functions of x and y. If we integrate equation (2.2) we have that

$$\int \delta z = \int M dx + \int N dy.$$

Since M and N are functions of x and y, the above integration cannot be done unless a functional relationship $f(x, y) = 0$ between x and y is chosen. This relationship defines a path in the (x, y) domain along which the integration will be performed. This is called a *line integral* and its result depends entirely on the prescribed path in the (x, y) domain. If it is that

$$M = \left(\frac{\partial z}{\partial x}\right)_y, \quad N = \left(\frac{\partial z}{\partial y}\right)_x \tag{2.3}$$

then equation (2.2) becomes

$$\delta z = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy.$$

The right-hand side of the above equation is the exact or total differential dz. In this case δz is an exact differential. If we now integrate δz from some initial state i to a final state f we obtain

$$\int_i^f \delta z = \int_i^f dz = z(x_f, y_f) - z(x_i, y_i). \tag{2.4}$$

Clearly, if δz is an exact differential its net change along a path $i \longrightarrow f$ depends only on points i and f and not on the particular path from i to f. We say that in this case z is a point function. All three state variables are exact differentials (i.e. $\delta p = dp$, $\delta T = dT$, $\delta V = dV$). It follows that all quantities that are a function of any two state variables will be exact differentials.

If the final and initial states coincide (i.e. we go back to the initial state via a cyclic process), then from equation (2.4) we have that

$$\oint \delta z = 0. \tag{2.5}$$

The above alternative condition indicates that δz is an exact differential if its integral along any closed path is zero. At this point we have to clarify a point so that we do not get confused later. When we deal with pure mathematical functions our ability to evaluate $\oint \delta z$ does not depend on the direction of the closed path, i.e. whether we go from i back to i via $i \xrightarrow{I} f \xrightarrow{I'} i$ or via $i \xrightarrow{I'} f \xrightarrow{I} i$ (see Figure 1.2). When we deal with natural systems we must view the condition $\oint \delta z = 0$ in relation to reversible and irreversible processes. If, somehow, it is possible to go from i back to i via $i \xrightarrow{I} f \xrightarrow{I'} i$ but impossible via $i \xrightarrow{I'} f \xrightarrow{I} i$ (for example, when I' is an irreversible transformation), then computation of δz depends on the direction and as such it is not unique. Therefore, for physical systems, the condition $\oint \delta z = 0$ when δz is an exact differential applies only to reversible processes.

Note that since

$$\frac{\partial}{\partial y}\frac{\partial z}{\partial x} = \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial x}\frac{\partial z}{\partial y}$$

it follows that an equivalent condition for δz to be an exact differential is that

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}. \tag{2.6}$$

Equations (2.3)–(2.6) are equivalent conditions that define z as a point function and subsequently δz as an exact differential. If a thermodynamic quantity is not a point function or an exact differential then its change along a path depends on the path. Moreover, its change along a closed path is not zero. Such quantities are path functions. For a path function the thermodynamic processes must be specified completely in order to define the quantity. For the rest of this book an exact differential will be denoted by dz whereas a non-exact differential will be denoted by δz. Finally, note that if δz

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is not an exact differential and if only two variables are involved, a factor λ (called the integration factor) may exist such that $\lambda \delta z$ is an exact differential.

2.2 Kinetic theory of heat

Let us consider a system at a temperature T, consisting of N point-masses (molecules). According to the kinetic theory of heat, these molecules move randomly at all directions traversing rectilinear lines. This motion is called *Brownian motion*. Because of the complete randomness of this motion, the internal energies of the point-masses not only are not equal to each other, but they change in time. If, however, we calculate the mean internal energy, we will find that it remains constant in time. The kinetic theory of heat accepts that the mean internal energy of *each* point-mass, $\overline{U}$, is proportional to the absolute temperature of the system (a formal definition of absolute temperature will come later; for now let us denote it by T),

$$\overline{U} = \text{constant} \times T \tag{2.7}$$

Let us for a minute assume that $N = 1$. Then the point has only three degrees of freedom which here are called thermodynamic degrees of freedom and are equal to the number of independent variables needed to completely define the energy of the point (unlike the degrees of freedom in Hamiltonian dynamics which are defined as the least number of independent variables that completely define the position of the point in state space). The velocity v of the point can be written as

$$v^2 = v_x^2 + v_y^2 + v_z^2.$$

Because we only assumed one point, then the total internal energy is equal to its kinetic energy. Thus,

$$U = \frac{m_\mathrm{p} v^2}{2}$$

or

$$U_x = \frac{m_\mathrm{p} v_x^2}{2}, \quad U_y = \frac{m_\mathrm{p} v_y^2}{2}, \quad U_z = \frac{m_\mathrm{p} v_z^2}{2}$$

where to each component corresponds one degree of freedom. According to the equal distribution of energy theorem, the mean kinetic energy of the point, $\overline{U}$, is distributed equally to the three degrees of freedom i.e. $\overline{U}_x = \overline{U}_y = \overline{U}_z$. Accordingly, from equation (2.7) we can write that

$$\overline{U}_i = AT, \quad i = x, y, z$$

where the constant A is a universal constant (i.e. it does not depend on the degrees of freedom or the type of the gas). We denote this constant as $k/2$ where k is Boltzmann's constant ($k = 1.38 \times 10^{-23}$ J K^{-1}) (for a review of units, see Table A1 in the Appendix). Therefore, the mean kinetic energy of a point with three degrees of freedom is equal to

$$\overline{U} = \frac{3kT}{2} \tag{2.8}$$

or

$$\frac{\overline{m_\mathrm{p} v^2}}{2} = \frac{3kT}{2}.$$

The theorem of equal energy distribution can be extended to N points. In this case, the degrees of freedom are $3N$ and

$$\sum_{i=1}^{N} \frac{\overline{m_\mathrm{p} v_i^2}}{2} = \frac{3NkT}{2}$$

or

$$\frac{1}{N} \sum_{i=1}^{N} \frac{\overline{m_\mathrm{p} v_i^2}}{2} = \frac{3}{2} kT$$

or

$$\left\langle \frac{\overline{m_\mathrm{p} v^2}}{2} \right\rangle = \frac{3}{2} kT \tag{2.9}$$

where $\langle \frac{\overline{m_\mathrm{p} v^2}}{2} \rangle$ is the average kinetic energy of *all* N points. Note that the above is true only if the points are considered as monatomic. If they are not, extra degrees of freedom are present that correspond to other motions such as rotation about the center of gravity, oscillation about the equilibrium positions, etc.

The kinetic theory of heat has found many applications in the kinetic theory of *ideal gases*. An ideal gas is one for which the following apply:

(a) the molecules move randomly in all directions and in such a way that the same number of molecules move in any direction;
(b) during the motion the molecules do not exert forces except when they collide with each other or with the walls of the container. As such the motion of each molecule between two collisions is linear and of uniform speed;
(c) the collisions between molecules are considered elastic. This is necessary because otherwise with each collision the kinetic energy of the molecules will be reduced thereby resulting in a temperature decrease. Also, a collision obeys the law of specular reflection (the angle of incidence equals the angle of reflection);
(d) the sum of the volumes of the molecules is negligible compared with the volume of the container.

Now let us consider a molecule of mass m_p whose velocity is v and which is moving in a direction perpendicular to a wall (Figure 2.1). The molecule has a momentum $P = m_\mathrm{p} v$. Since we accept that the

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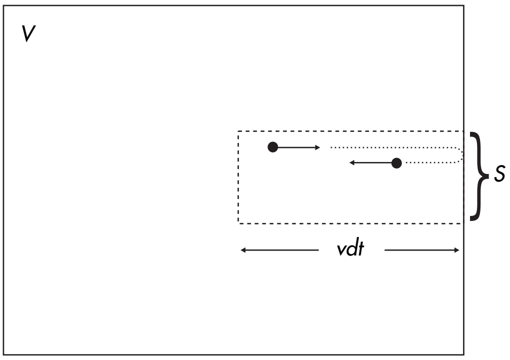

Figure 2.1
A molecule of mass m_p moving with a velocity v and hitting a surface S. If this collision is assumed elastic and specular, then the change in momentum is $2m_\mathrm{p}v$.

collision is elastic and specular, the magnitude of the momentum after the collision is $-m_\mathrm{p}v$. Thus the total change in momentum is $m_\mathrm{p}v - (-m_\mathrm{p}v) = 2m_\mathrm{p}v$. According to Newton's second law, $F = dP/dt$. If we consider N molecules occupying a volume V we can calculate the change in momentum dP of all molecules in the time interval dt by multiplying the change in momentum of one molecule $(2m_\mathrm{p}v)$ by the number of molecules dN that hit a given area S on the wall, i.e.

$$dP = 2m_\mathrm{p}v\,dN \tag{2.10}$$

Note that here we have assumed that all molecules have the same speed. The number dN of molecules hitting area S during dt is equal to the number of molecules which move to the right and which are included in a box with base S and length vdt. Since the motion is completely random, we can assume that $\frac{1}{6}$ of the molecules will be moving to the right, $\frac{1}{6}$ will be moving to the left, and $\frac{4}{6}$ will be moving along the directions of the other two coordinates. Since the volume of the box is $Svdt$ and the number of molecules per unit volume is N/V then the number of molecules inside the box is

$$\frac{N}{V}Svdt.$$

Accordingly, the number of molecules moving to the right and colliding with S is

$$dN = \frac{N}{6V}Svdt \tag{2.11}$$

From equations (2.10) and (2.11) it follows that

$$dP = 2m_\mathrm{p}v^2\frac{N}{6V}Sdt.$$