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

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

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

$$\oint \delta z = 0. \qquad (2.5)$$

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

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}. \qquad (2.6)$$

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

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 ($k = 1.38 \times 10^{-23}$ $\mathrm{J\,K^{-1}}$) (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

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

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

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

or

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

or

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

where $\left\langle \overline{\frac{m_{\mathrm{p}}v^2}{2}} \right\rangle$ 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.
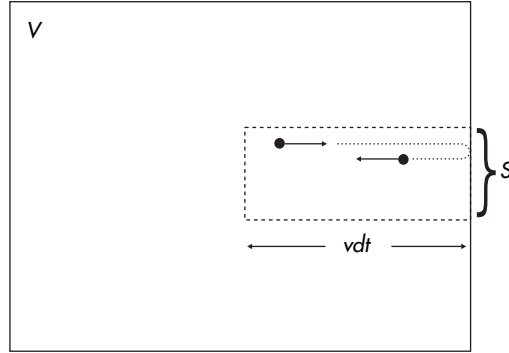
The kinetic theory of heat has found many applications in the kinetic theory of *ideal gases*. An ideal gas is one for which the following apply:

(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

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.

$$dP = 2m_\mathrm{p}vdN \qquad (2.10)$$

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

$$dN = \frac{N}{6V}Svdt \qquad (2.11)$$

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

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

Recalling the definition of pressure, p (pressure = force/area), and Newton's second law we obtain

$$p = \frac{1}{3}\frac{N}{V}m_\mathrm{p}v^2.$$

The above formula resulted by assuming that all molecules move with the same speed. This is not true, and because of that $m_\mathrm{p}v^2$ in the above equation should be replaced by the average of all points, $\langle \overline{m_\mathrm{p}v^2} \rangle$. We thus arrive at

$$p = \frac{1}{3}\frac{N}{V}\langle \overline{m_\mathrm{p}v^2} \rangle. \tag{2.12}$$

It can easily be shown that by combining equations (2.9) and (2.12), we can derive an equation that includes all three state variables:

$$pV = NkT. \tag{2.13}$$

Equation (2.13) provides the functional relationship of the equation of state $f(p, V, T)$ and it is called the *ideal gas law*. More details follow in the next chapter.