# CHAPTER 2

# ENERGY, WORK, AND HEAT

### 2.1 Introduction

Energy is a familiar concept, but most people would have a hard time defining just what it is. You may hear people talk about "an energy-burning workout," "an energetic personality," or "renewable energy sources." A few years ago people were very concerned about an "energy crisis." None of these uses of the word "energy" corresponds to its scientific definition, which is the subject of this chapter.

The most important characteristic of energy is that it is *conserved*: you can move it around or change its form, but you can't destroy it, and you can't make more of it.<sup>1</sup> Surprisingly, the principle of conservation of energy was not fully formulated until the middle of the 19th century. This idea certainly does seem nonsensical to anyone who has seen a ball roll across a table and stop, since the kinetic energy of the ball seems to disappear. The concept only makes sense if you know that the ball is made of atoms, and that the macroscopic kinetic energy of motion is simply converted to microscopic kinetic energy of the random atomic motion.

### 2.2 Work and Kinetic Energy

Historically, the concept of energy was first introduced in mechanics, and therefore this is an appropriate starting point for our discussion. The basic equation of motion of classical mechanics is due to Newton, and is known as Newton's second law.<sup>2</sup> Newton's second law states that if a net force **F** is applied to a body, its center-of-mass will experience an acceleration **a** proportional to **F**:

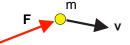
$$\mathbf{F} = m\mathbf{a}.\tag{2.1}$$

The proportionality constant m is the *inertial mass* of the body.

<sup>&</sup>lt;sup>1</sup>Thus, energy can't be burned (fuel is burned), it is a property matter has (not personalities), there are no sources of it, whether renewable or not, and there is no energy crisis (but there may be a usable energy, or availability, crisis).

<sup>&</sup>lt;sup>2</sup>For now we consider only classical, nonrelativistic mechanics.

Suppose a single external force **F** is applied to point particle moving with velocity **v**. The force is applied for an infinitesimal time dt, during which the velocity changes by  $d\mathbf{v} = \mathbf{a} dt$ , and the position changes by  $d\mathbf{x} = \mathbf{v} dt$ .



Taking the scalar product<sup>3</sup> (or dot product) of Eq. (2.1) with  $d\mathbf{x}$  gives

$$\mathbf{F} \cdot d\mathbf{x} = m\mathbf{a} \cdot d\mathbf{x}$$

$$= \left[m\left(\frac{d\mathbf{v}}{dt}\right)\right] \cdot [\mathbf{v}dt]$$

$$= m\mathbf{v} \cdot d\mathbf{v}$$

$$= d(mv^2/2). \qquad (2.2)$$

Here  $v = |\mathbf{v}|$  is the particle speed. Note that only the component of  $\mathbf{F}$  along the direction the particle moves is needed to determine whether v increases or decreases. If this component is parallel to  $d\mathbf{x}$ , the speed increases; if it is antiparallel to  $d\mathbf{x}$  the speed decreases. If  $\mathbf{F}$  is perpendicular to  $d\mathbf{x}$ , then the speed doesn't change, although the direction of  $\mathbf{v}$  may.

Since we'll have many uses for  $\mathbf{F} \cdot d\mathbf{x}$  and  $mv^2/2$ , we give them symbols and names. We call  $\mathbf{F} \cdot d\mathbf{x}$  the infinitesimal *work* done by force  $\mathbf{F}$ , and give it the symbol dW:

$$dW = \mathbf{F} \cdot d\mathbf{x} \tag{2.3}$$

(We'll see below why we put a bar through the d in dW.)

The quantity  $mv^2/2$  is the kinetic energy  $E_k$  of the particle:

$$E_k = \frac{mv^2}{2} \tag{2.4}$$

With these symbols, Eq. (2.2) becomes

$$dW = d(E_k). \tag{2.5}$$

Equation (2.5) may be interpreted in thermodynamic language as shown in Fig. 2.1. A system is defined which consists only of the particle; the energy

<sup>&</sup>lt;sup>3</sup>Recall that the scalar product of two vectors  $\mathbf{A} = \mathbf{i} A_i + \mathbf{j} A_j + \mathbf{k} A_k$  and  $\mathbf{B} = \mathbf{i} B_i + \mathbf{j} B_j + \mathbf{k} B_k$  is defined as  $\mathbf{A} \cdot \mathbf{B} = A_i B_i + A_j B_j + A_k C_k$ . Here  $\mathbf{i}, \mathbf{j}$ , and  $\mathbf{k}$  are unit vectors in the x, y, and z directions, respectively.

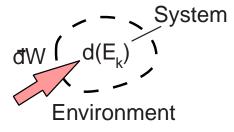


Figure 2.1: Energy accounting for a system consisting of a single point particle acted on by a single force for time dt.

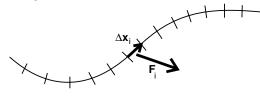
"stored" within the system (here just the particle kinetic energy) increases by  $d(E_k)$  due to the work dW done by external force **F**. Since force **F** is produced by something outside the system (in the environment), we may regard dW as an *energy transfer* from the environment to the system. Thus, work is a type of energy transfer. Of course, dW might be negative, in which case  $d(E_k) < 0$ . In this case, the direction of energy transfer is actually from the system to the environment.

The process of equating energy transfers to or from a system to the change in energy stored in a system we will call *energy accounting*. The equations which result from energy accounting we call *energy balances*. Equation (2.5) is the first and simplest example of an energy balance – we will encounter many more.

If the force **F** is applied for a finite time t, the particle will move along some trajectory  $\mathbf{x}(t)$ .



The change in the particle kinetic energy  $\Delta E_k = E_k(B) - E_k(A)$  can be determined by dividing the path into many very small segments, and summing Eq. (2.2) for each segment.



In the limit where each segment is described by an infinitesimal vector  $d\mathbf{x}$ ,



Figure 2.2: Energy accounting for a single particle acted on by (a) a single force (b) multiple forces for finite time.

the sum becomes an integral:

$$\int_{path} dW = \int_{path} d(E_k) \tag{2.6}$$

The right-hand side of this can be integrated immediately:

$$\int_{path} d(E_k) = \Delta E_k. \tag{2.7}$$

The integral on the left-hand side defines the total work done by **F**:

$$W = \int_{path} dW = \int_{path} \mathbf{F} \cdot d\mathbf{x}.$$
 (2.8)

Note that the integral is along the particular path taken. Eq. (2.6) becomes

$$W = \Delta E_k. \tag{2.9}$$

The thermodynamic interpretation of this equation is shown in Fig. 2.2 and is similar to that of Eq. (2.5): work is regarded as a transfer of energy to the system (the particle), and the energy stored in the system increases by the amount transferred in. (Again, if W < 0, then the direction of energy transfer is really from the system to the environment, and in this case  $\Delta E_k < 0$ .)

If two forces act simultaneously on the particle, then the total applied force is the vector sum:  $\mathbf{F} = \mathbf{F}_1 + \mathbf{F}_2$ . In this case, Eq. (2.9) becomes

$$W_1 + W_2 = \Delta E_k, \tag{2.10}$$

where  $W_1 = \int_{path} \mathbf{F}_1 \cdot d\mathbf{x}$  and  $W_2 = \int_{path} \mathbf{F}_2 \cdot d\mathbf{x}$ .<sup>4</sup> The generalization to N forces is obvious: the work done by all N forces must be considered to compute  $\Delta E_k$ .

 $<sup>^{4}</sup>$ For now we're considering a point particle, so the path followed is the same for both forces; this won't be true for extended objects, which will be considered in section 2.4.

### 2.3 Evaluation of Work

Since in general a force may depend on factors such as the instantaneous particle position  $\mathbf{x}$ , the instantaneous velocity  $\mathbf{v}$ , or may depend explicitly on time, the work done by the force will clearly depend on *the path* the particle takes from A to B, *how fast* it travels, and the particular *time* it passes each point. Since there are infinitely many possible trajectories  $\mathbf{x}(t)$  which start at point A at some time and pass through point B at some later time, there are infinitely many possible values for  $W = \int_{path} dW$ ; we need additional information [i.e.,  $\mathbf{x}(t)$ ] to evaluate W.

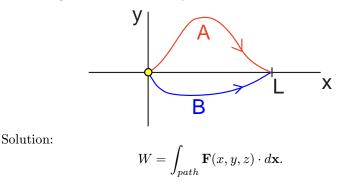
This is the reason we put the bar through dW but not through  $d(E_k)$ . It's always true that  $\int_{path} d(Q)$  may be formally evaluated to yield  $Q_B - Q_A$ , where Q is some function of the state (position, velocity, etc.) of the particle and of time, and  $Q_A$  and  $Q_B$  denote the values of Q when the particle is at endpoints of the path.

But dW is not like this: it's only the symbol we use to denote "a little bit of work." It really equals  $\mathbf{F} \cdot d\mathbf{x}$ , which is not of the form d(Q), so can't be integrated without more information. Quantities like dW are known as "inexact differentials." We put the bar in dW just to remind ourselves that it is an inexact differential, and so its integral depends on the particular path taken, not only on the state of the particle at the beginning and end of the path.

Example 2.1 The position-dependent force

$$\mathbf{F}(x, y, z) = \begin{cases} +\mathbf{i}C & \text{if } y > 0\\ -\mathbf{i}2C & \text{if } y \le 0 \end{cases}$$

is applied to a bead on a frictionless wire. The bead sits initially at the origin, and the wire connects the origin with (L, 0, 0). How much work does **F** do to move the bead along wire A? How much along wire B? Does the contact force of the bead against the wire do any work?



Since  $\mathbf{F}$  always points in the x direction,

$$\mathbf{F}(x, y, z) \cdot d\mathbf{x} = F_x(x, y, z)dx$$

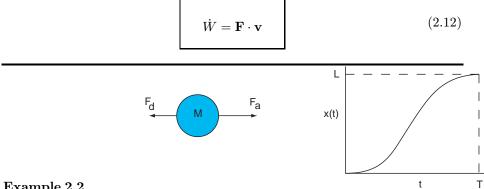
Therefore, along path A, W = CL, and along path B, W = -2CL.

Along path A, the force does work on the particle, while along path B the particle does work on whatever is producing the force. Of course, for motion along path B to be possible at all, the particle would have to have an initial kinetic energy greater than 2CL. The contact force does no work, since it is always perpendicular to the wire (and therefore to  $d\mathbf{x}$ ), so  $\mathbf{F}_{contact} \cdot d\mathbf{x} = 0$ .

If we do know  $\mathbf{x}(t)$ , we can convert the path integral definition of work [Eq. (2.8)] into a time integral, using  $d\mathbf{x} = \mathbf{v}(t)dt$ :

$$W = \int_{t_A}^{t_B} \mathbf{F}(\mathbf{x}(t), \mathbf{v}(t), t) \cdot \mathbf{v}(t) dt$$
(2.11)

This is often the easiest way to evaluate work. Note that the integrand is  $\mathbf{F} \cdot \mathbf{v}$ . Therefore,  $\mathbf{F} \cdot \mathbf{v}$  is the *rate* at which force  $\mathbf{F}$  does work, or in other words the instantanteous *power* being delivered by **F**. We denote the power by W:



#### Example 2.2

A ball initially at rest at x = 0 in a viscous fluid is pulled in a straight line by a string. A time-dependent force  $F_a(t)$  is applied to the string, which causes the ball to move according to

$$x(t) = \frac{L}{2} \left[ 1 - \cos\left(\frac{\pi t}{T}\right) \right].$$

At time t = T, the ball comes to rest at x = L and the force is removed. As the ball moves through the fluid, it experiences a drag force proportional to its speed:  $F_d = -C\dot{x}(t)$ . How much work is done by the applied force to move the ball from x = 0 to x = L?

Solution: Newton's second law requires

$$F_a + F_d = m\ddot{x}(t), \tag{2.13}$$

 $\mathbf{SO}$ 

$$F_a(t) = m\ddot{x}(t) + C\dot{x}(t).$$
 (2.14)

Since we know x(t), we can differentiate to find

$$\dot{x}(t) = \frac{L}{2} \left(\frac{\pi}{T}\right) \sin \tau \tag{2.15}$$

and

$$\ddot{x}(t) = \frac{L}{2} \left(\frac{\pi}{T}\right)^2 \cos \tau \tag{2.16}$$

where  $\tau = \pi t/T$ . Substituting these expressions into Eq. (2.14) results in

$$F_a(t) = \frac{CL}{2} \left(\frac{\pi}{T}\right) \sin \tau + \frac{mL}{2} \left(\frac{\pi}{T}\right)^2 \cos \tau.$$

To calculate the work done by  $F_a(t)$ , we need to evaluate

$$W_a = \int_{path} \mathbf{F}_{\mathbf{a}} \cdot d\mathbf{x} = \int_0^L F_a \, dx.$$

Since we know both  $F_a(t)$  and x(t), it is easiest to convert this path integral to a time integral using  $dx = \dot{x}(t)dt$ :

$$W_a = \int_0^T F_a(t)\dot{x}(t) \, dt.$$

Changing the integration variable to  $\tau$   $(d\tau = (\pi/T)dt)$ ,

$$W_a = \left(\frac{L}{2}\right)^2 \frac{\pi}{T} \int_0^{\pi} \left[C\sin^2\tau + \left(\frac{\pi}{T}\right)\sin\tau\cos\tau\right] d\tau.$$

Since  $\int_0^{\pi} \sin^2 \tau \, d\tau = \pi/2$  and  $\int_0^{\pi} \sin \tau \cos \tau \, d\tau = 0$ ,

$$W_a = \frac{\pi^2 C L^2}{8T}.$$

If there were no drag (C = 0), then the work would be zero, since the work done to accelerate the ball for t < T/2 would be fully recovered in decelerating the ball for t > T/2. But in the presence of a drag force, a finite amount of work must be done to overcome drag, even though the ball ends as it began with no kinetic energy.

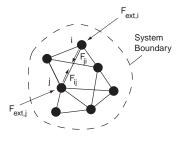


Figure 2.3: External and internal forces acting on two masses of a rigid body.

Note that the work is inversely proportional to the total time T. It takes more work to push the ball rapidly through the fluid (short T) than slowly. By carrying out the process very slowly, it is possible to make  $W_a$  as small as desired, and in the limit of  $T \to \infty$  the process requires no work. This behavior is characteristic of systems which exhibit viscous drag.

### 2.4 Energy Accounting for Rigid Bodies

Up until now we have only considered how to do energy accounting for point masses. To develop energy accounting methods for macroscopic matter, we can use the fact that macroscopic objects are composed of a very large number of what we may regard as point masses (atomic nuclei), connected by chemical bonds. In this section, we consider how to do energy accounting on a macroscopic object if we make the simplifying assumption that the bonds are completely rigid. We'll relax this assumption and complete the development of energy accounting for macroscopic matter in section 2.8.

Consider a body consisting of N point masses connected by rigid, massless rods, and define the system to consist of the body (Fig. 2.3). The rods will transmit forces between the masses. We will call these forces *internal forces*, since they act between members of the system. We will assume the internal forces are directed along the rods. The force exerted on (say) mass j by mass iwill be exactly equal in magnitude and opposite in direction to that exerted on mass i by mass j ( $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$ ), since otherwise there would be a force imbalance on the rod connecting i and j. No force imbalance can occur, since the rod is massless and therefore would experience infinite acceleration if the forces were unbalanced. (Note this is Newton's third law.)

Let the masses composing the body also be acted on by arbitrary *external* forces from the environment. The external force on mass i will be denoted

 $\mathbf{F}_{ext,i}$ .

The energy balance in differential form for one mass, say mass i, is

$$dW_{ext,i} + \left(\sum_{j} \mathbf{F}_{ji}\right) \cdot d\mathbf{x}_i = d(E_{k,i}),$$
(2.17)

where  $dW_{ext,i} = \mathbf{F}_{ext,i} \cdot d\mathbf{x}_i$  and of course  $\mathbf{F}_{ii} = 0$ . Summing the energy balances for all masses results in an energy balance for the entire system:

$$\sum_{i} dW_{ext,i} + \sum_{i} \sum_{j} \mathbf{F}_{ji} \cdot d\mathbf{x}_{i} = d(E_{k}), \qquad (2.18)$$

where

$$d(E_k) = \sum_i d(E_{k,i}) = \sum_i d(m_i v_i^2/2)$$
(2.19)

is the change in the total kinetic energy of the body.

Equation (2.18) can be simplified considerably, since the second term on the left is *exactly zero*. To see this, recall that the rods are rigid, so

$$d(|\mathbf{x}_i - \mathbf{x}_j|) = 0 \tag{2.20}$$

for all i and j. Equation (2.20) can be written as

$$(\mathbf{x}_i - \mathbf{x}_j) \cdot d(\mathbf{x}_i - \mathbf{x}_j) = 0.$$
(2.21)

Now  $\mathbf{F}_{ij}$  is parallel to  $(\mathbf{x}_i - \mathbf{x}_j)$ , so multiplying Eq. (2.21) by  $|\mathbf{F}_{ij}|/|\mathbf{x}_i - \mathbf{x}_j|$  results in

$$\mathbf{F}_{ij} \cdot d(\mathbf{x}_i - \mathbf{x}_j) = 0. \tag{2.22}$$

Since  $\mathbf{F}_{ji} = -\mathbf{F}_{ij}$ , we can re-write this as

$$\mathbf{F}_{ji} \cdot d\mathbf{x}_i = -\mathbf{F}_{ij} \cdot d\mathbf{x}_j. \tag{2.23}$$

Therefore, because the body is rigid, the work done by  $\mathbf{F}_{ji}$  on mass *i* is precisely equal to the negative of the work done by  $\mathbf{F}_{ij}$  on mass *j*. Thus, the internal forces  $\mathbf{F}_{ij}$  cause a transfer of kinetic energy from one mass within the body to another, but considering the body as a whole, do no *net* work on the body.

Mathematically, the second term on the left of Eq. (2.18) is a sum over all pairs of mass indices (i, j). Because of Eq. (2.23), for every i and j, the (i, j) term in this sum will exactly cancel the (j, i) term, with the result that the double sum is zero.

With this simplification (for rigid bodies), Eq. (2.18) reduces to

$$\sum_{i} dW_{ext,i} = d(E_k).$$
(2.24)

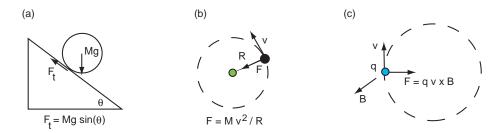


Figure 2.4: Some forces which do no work: (a) traction force on a rolling wheel; (b) centrifugal force; (c) Lorentz force on a charged particle in a magnetic field

We see that to carry out an energy balance on a rigid body, we only need consider work done by external forces, not by internal ones. We can always tell which forces are external ones – they are the ones which cross the system boundary on a sketch.

A macroscopic solid object is composed of a huge number of essentially point masses (the atomic nuclei) connected by chemical bonds (actually rapidly moving, quantum-mechanically smeared out electrons). If we ignore for the moment the fact that bonds are not really rigid, a solid object can be approximated as a rigid body. If this approximation holds, then the appropriate energy balance equation will be Eq. (2.24).

For simplicity, assume that the external forces act only at L discrete locations on the surface of the object, where it contacts the environment.<sup>5</sup> In this case, the external work term in Eq. (2.24) becomes  $\sum_{\ell=1}^{L} \mathbf{F}_{\ell} \cdot d\mathbf{x}_{\ell}$ , where  $d\mathbf{x}_{\ell}$  is the displacement of the surface of the object at the point where the force  $\mathbf{F}_{\ell}$  is applied. The energy balance Eq. (2.24) becomes

$$\sum_{\ell=1}^{L} \mathbf{F}_{\ell} \cdot d\mathbf{x}_{\ell} = d(E_k).$$
(2.25)

It is very important to remember that the displacements to use in this equation are those *where the forces are applied*, and may differ for each force. Do not make the mistake of using the displacement of some other point (e.g. the center of mass).

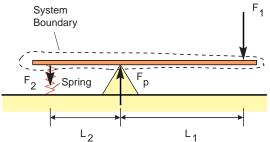
If a force is applied to a macroscopic object at a point where it is stationary, the force does no work no matter how large the force is. (If you push against a stationary wall, you may exert yourself, but you do no work on it.) Also, a force

<sup>&</sup>lt;sup>5</sup>If the macroscopic force is exerted over some small but finite contact area, the macroscopic force  $\mathbf{F}_{\ell}$  in Eq. (2.25) is simply the sum over the atomic-level forces  $\mathbf{F}_{ext,i}$  in Eq. (2.24) for all atoms *i* in the contact area.

applied *perpendicular* to the instantaneous direction of motion of the contact area can do no work.

Some common forces which do no work are shown in Fig. 2.4. A traction force  $|\mathbf{F}_t| = mg\sin\theta$  in the plane of the surface keeps a rolling wheel from sliding down a hill; but since the wheel is instantaneously stationary where it contacts the ground,  $\mathbf{F}_t \cdot d\mathbf{x} = 0$  and therefore the traction force does no work. A centrifugal force and the Lorentz force a charged particle experiences in a magnetic field are both perpendicular to the direction of motion, and thus can do no work.

**Example 2.3** A downward force  $\mathbf{F}_1$  is applied to a rigid, horizontal lever a distance  $L_1$  to the right of the pivot point. A spring connects the lever to the ground at a distance  $L_2$  to the left of the pivot, and exerts a downward force  $\mathbf{F}_2$ . An upward force  $\mathbf{F}_p$  is exerted on the lever at the pivot. Evaluate the work done by each force if end 2 is raised by  $dy_2$ , and determine the value of  $\mathbf{F}_1$  which achieves this motion without changing the kinetic energy of the lever.



**Solution**: Define the system to consist of the lever only (a rigid body). The body is acted on by three external forces, and so we must evaluate the work input to the system from each force. Since the lever is rigid, if the height of end 2 changes by  $dy_2$  while the height at the pivot point is unchanged, then the height of end 1 must change by  $dy_1 = -(L_1/L_2)dy_2$ . So the three work inputs are:

$$dW_1 = (-\mathbf{j}F_1) \cdot (-\mathbf{j}L_1 dy_2/L_2) = (F_1 L_1/L_2) dy_2 > 0 \qquad (2.26)$$

$$dW_2 = (-\mathbf{j}F_2) \cdot (+\mathbf{j}dy_2) = -F_2 dy_2 < 0 \tag{2.27}$$

$$dW_p = (+\mathbf{j}F_p) \cdot (0) = 0. \tag{2.28}$$

Note that the work due to the pivot force is zero, since the lever does not move at the pivot. Force  $\mathbf{F}_1$  does positive work on the lever, since the force and displacement are in the same direction. The spring which produces force  $\mathbf{F}_2$  does *negative* work on the lever, since the force and displacement are in opposite directions. In this case, we say that the lever does positive work on the spring, since the force exerted by the lever on the spring is oppositely directed

to  $\mathbf{F}_2$  (Newton's third law).

The energy balance on the lever is then

If we wish to move the lever without increasing its kinetic energy, then we must choose

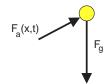
$$F_1 L_1 = F_2 L_2. (2.30)$$

This is the familiar law of the lever, but note that we obtained it from an energy balance, not by balancing torques as would be done in mechanics.

### 2.5 Conservative Forces and Potential Energy

# 2.5.1 A Uniform Gravitational Field

Suppose a point particle near the surface of the earth is acted on by gravity, which exerts a constant downward force  $\mathbf{F}_g = -\mathbf{j}mg$ . It is also acted on by an arbitrary external applied force  $\mathbf{F}_a(\mathbf{x}, t)$ .



In this case, Eq. (2.10) becomes

$$W_a + W_g = \Delta E_k \tag{2.31}$$

where

$$W_a = \int_{path} \mathbf{F}_a \cdot d\mathbf{x} \tag{2.32}$$

is the work done by the applied force, and

$$W_g = \int_{path} \mathbf{F}_g \cdot d\mathbf{x} \tag{2.33}$$

is the work done by the gravitational force. Due to the special character of  $\mathbf{F}_g$ (a constant force),  $W_g$  can be evaluated for an arbitrary path from A to B:

$$W_g = -\int_{path} \mathbf{j}mg \cdot d\mathbf{x}$$

$$= -\int_{y_A}^{y_B} mgdy$$
  
=  $-mg(y_B - y_A)$  (2.34)

$$= -mg\Delta y. \tag{2.35}$$

If  $\Delta y < 0$ , gravity does work *on* the particle, and its kinetic energy increases. If  $\Delta y > 0$ ,  $W_g < 0$ , which means that the particle must do work against gravity. In this case the kinetic energy decreases.

Note that  $W_g$  can be expressed solely in terms of the difference in a property (the height) of the particle at the beginning and end of its trajectory: *any* path connecting A and B would result in the same value for  $W_g$ . This is due to the special nature of the force  $\mathbf{F}_g$ , which is just a constant. Of course, for an arbitrary force such as  $\mathbf{F}_a(\mathbf{x}, t)$ , this would not be possible. The force  $\mathbf{F}_g$  is the first example of a *conservative force*.

Since  $W_g$  is independent of the particular path taken, we can bring it to the other side of Eq. (2.31):

$$W_a = (-W_g) + \Delta E_k$$
  
=  $mg\Delta y + \Delta E_k$   
=  $\Delta(E_k + mgy)$  (2.36)

We define mgy to be the gravitational potential energy  $E_g$  of the particle in this uniform gravitational field:

$$E_g = mgy. \tag{2.37}$$

With this definition, Eq. (2.31) becomes

$$W_a = \Delta(E_k + E_g). \tag{2.38}$$

Equations (2.31) and (2.38) are mathematically equivalent, but have different interpretations, as shown in Fig. 2.5. In Eq. (2.31), the gravitational force is considered to be an *external* force acting on the system; the work  $W_g$  it does on the system is included in the energy balance but not any potential energy associated with it. In (b), the source of the gravitational force (the gravitational field) is in effect considered to be part of the system. Since it is now internal to the system, we don't include a work term for it, but *do* include the gravitational potential energy (which we may imagine to be stored in the field) in the system energy. It doesn't matter which point of view we take – the resulting energy balance is the same because  $\Delta E_g$  is defined to be identical to

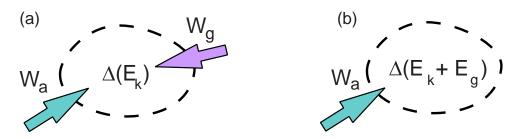


Figure 2.5: Two energy accounting schemes to handle the effects of a constant gravitational force. In (a), the gravitational field is considered to be external to the system, while in (b) the field is part of the system.

 $-W_g$ . But remember not to *mix* these points of view: don't include *both*  $W_g$  and  $\Delta E_g$  in an energy balance!

We may generalize this analysis to a macroscopic body. In this case, the gravitational potential energy becomes

$$E_g = \int_{body} \rho(\mathbf{x}) gy \, dV, \tag{2.39}$$

where  $\rho(\mathbf{x})$  is the local mass density (kg/m<sup>3</sup>) at point  $\mathbf{x}$  within the body. This can be re-written as

$$E_g = Mgy_{cm}, (2.40)$$

where

$$M = \int_{body} \rho(\mathbf{x}) \, dV \tag{2.41}$$

is the total mass of the body and  $y_{cm}$  is the y-component of the center of mass, defined by

$$\mathbf{x}_{cm} = \frac{1}{M} \int \rho(\mathbf{x}) \, \mathbf{x} \, dV. \tag{2.42}$$

### 2.5.2 General Conservative Forces

A constant force, such as discussed above, is the simplest example of a conservative force. The general definition is as follows:

a force is conservative if and only if the work done by it in going from an initial position  $\mathbf{x}_A$  to a final position  $\mathbf{x}_B$  depends only on the initial and final positions, and is *independent of the path taken*.

Mathematically, this definition may be stated as follows:

$$W_c = \int_{path} \mathbf{F}_c \cdot d\mathbf{x} = f(\mathbf{x}_B) - f(\mathbf{x}_A), \qquad (2.43)$$

where f is some single-valued scalar function of position in space.

For the special case of a closed path ( $\mathbf{x}_B = \mathbf{x}_A$ ), Eq. (2.43) reduces to

$$\oint \mathbf{F}_c \cdot d\mathbf{x} = 0, \tag{2.44}$$

where  $\oint$  denotes integrating all the way around the path. Therefore, the work done by a conservative force on a particle traversing any arbitrary closed loop is exactly zero. Either Eq. (2.43) or Eq. (2.44) may be taken as the definition of a conservative force.

Only very special functions  $\mathbf{F}(\mathbf{x}, \mathbf{v}, t)$  can satisfy the conditions for a conservative force. First of all, consider the dependence on velocity. The only way Eq. (2.44) can be satisfied by a velocity-dependent force for all possible loops, traversing the loop in either direction at arbitrary speed, is if the velocitydependent force does no work. This is possible if  $\mathbf{F}(\mathbf{x}, \mathbf{v}, t)$  is always perpendicular to  $\mathbf{v}$ . Thus, any conservative force can have an arbitrary velocity-dependent force  $\mathbf{F}_v$  added to it and still be conservative as long as  $\mathbf{F}_v \cdot \mathbf{v} = 0$  at all times.

It seems that in nature there is only one velocity-dependent conservative force, which is the Lorentz force felt by a charged particle moving through a magnetic field  $\mathbf{B}$ . This Lorentz force is given by

$$\mathbf{F}_L = q\mathbf{v} \times \mathbf{B},\tag{2.45}$$

which is always perpendicular to both  $\mathbf{v}$  and  $\mathbf{B}$ . Unless stated otherwise, we will assume from here on that conservative forces do not have a velocity-dependent part, keeping in mind that the Lorentz force is the one exception.

Having dealt with the allowed type of velocity dependence, consider now the time dependence. It is clear that  $\mathbf{F}_c$  can have no *explicit* time dependence (i.e.,  $\mathbf{F}(\mathbf{x}(t))$  is OK but  $\mathbf{F}(\mathbf{x}(t), t)$  is not). If  $F_c$  depended explicitly on time, then the result for  $W_c$  would too, rather than on just the endpoint positions in space. So we conclude that a conservative force (or at least the part which can do work) can depend explicitly only on position:  $\mathbf{F}_c(\mathbf{x})$ .

### 2.5.3 How to Tell if a Force is Conservative

If we are given a force function  $\mathbf{F}(\mathbf{x})$ , how can we tell if it is conservative? First consider the inverse problem: If we know the function  $f(\mathbf{x})$ , can we derive what  $\mathbf{F}_c$  must be? Consider a straight-line path which has infinitesimal length:  $\mathbf{x}_B = \mathbf{x}_A + d\mathbf{x}$ . Then equation 2.43 reduces to

$$\mathbf{F}_c(\mathbf{x}_A) \cdot d\mathbf{x} = f(\mathbf{x}_A + d\mathbf{x}) - f(\mathbf{x}_A). \tag{2.46}$$

Since  $d\mathbf{x}$  is infinitesimal, we may expand  $f(\mathbf{x}_A + d\mathbf{x})$  in a Taylor series:<sup>6</sup>

$$f(\mathbf{x}_A + d\mathbf{x}) = f(\mathbf{x}_A) + \nabla f(\mathbf{x}_A) \cdot d\mathbf{x} + O(|d\mathbf{x}|^2), \qquad (2.47)$$

where the gradient of f is defined by

$$\nabla f = \mathbf{i}\frac{\partial f}{\partial x} + \mathbf{j}\frac{\partial f}{\partial y} + \mathbf{k}\frac{\partial f}{\partial z}.$$
(2.48)

As we let  $|d\mathbf{x}|$  go to zero, the higher-order terms go to zero rapidly, so Eq. (2.46) becomes

$$\mathbf{F}_c(\mathbf{x}) \cdot d\mathbf{x} = \nabla f(\mathbf{x}_A) \cdot d\mathbf{x} \tag{2.49}$$

The only way this equation can hold for arbitrary  $\mathbf{x}_A$  and  $d\mathbf{x}$  is if

$$\mathbf{F}_c(\mathbf{x}) = \nabla f(\mathbf{x}). \tag{2.50}$$

Therefore, a conservative force which depends only on position must be the gradient of some scalar function of position in space  $f(\mathbf{x})$ .

How can we tell if a given vector function  $\mathbf{F}(\mathbf{x})$  is the gradient of some unknown scalar function  $f(\mathbf{x})$ ? The easiest way is to write them both out explicitly:

$$\mathbf{F}(x,y,z) = \mathbf{i}F_i(x,y,z) + \mathbf{j}F_j(x,y,z) + \mathbf{k}F_k(x,y,z)$$
(2.51)

$$\nabla f(x, y, z) = \mathbf{i} \frac{\partial f}{\partial x} + \mathbf{j} \frac{\partial f}{\partial y} + \mathbf{k} \frac{\partial f}{\partial z}.$$
 (2.52)

If these are equal, then each component must be equal, so

$$F_i(x, y, z) = \partial f(x, y, z)/dx$$
(2.53)

$$F_j(x, y, z) = \partial f(x, y, z)/dy$$
(2.54)

$$F_k(x, y, z) = \partial f(x, y, z)/dz.$$
(2.55)

Consider now the mixed second derivatives of f(x, y, z). It doesn't matter which order we do the differentiation:

$$\frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right) = \frac{\partial^2 f}{\partial x \partial y}, \tag{2.56}$$

with similar results for the partial derivatives involving z. Therefore, if  $\mathbf{F} = \nabla f$ , we may substitute eqs. (2.53) and (2.54) into Eq. (2.56) and obtain

$$\frac{\partial F_j}{\partial x} = \frac{\partial F_i}{\partial y}.$$
(2.57)

<sup>&</sup>lt;sup>6</sup>If this is not clear to you in vector form, write it out component by component.

Similarly,

$$\frac{\partial F_i}{\partial z} = \frac{\partial F_k}{\partial x},\tag{2.58}$$

and

$$\frac{\partial F_j}{\partial z} = \frac{\partial F_k}{\partial y},\tag{2.59}$$

Equations (2.57)–(2.59) provide a simple test to determine if  $\mathbf{F}(\mathbf{x})$  is conservative. If  $\mathbf{F}$  passes this test, it should be possible to integrate equations (2.53)– (2.55) and find a function  $f(\mathbf{x})$  such that  $\mathbf{F} = \nabla f$ . If  $\mathbf{F}$  fails the test, then no such  $f(\mathbf{x})$  exists.

#### 2.5.4 Energy Accounting with Conservative Forces

We can easily generalize the analysis of the mass in a constant gravitational field to handle an arbitrary conservative force acting on a particle. The energy balance is

$$W_a + W_c = \Delta E_k. \tag{2.60}$$

Since the force is conservative,  $W_c = f(\mathbf{x}_B) - f(\mathbf{x}_A) = \Delta f$ . Therefore, we may write the energy balance as

$$W_a = \Delta E_k - \Delta f = \Delta (E_k - f). \tag{2.61}$$

Now define the potential energy associated with this conservative force as follows:

$$E_p(\mathbf{x}) = -f(\mathbf{x}) + C. \tag{2.62}$$

Since only differences in potential energy have any physical significance, we can set the additive constant C to any convenient value. The energy balance now becomes

$$W_a = \Delta(E_k + E_p). \tag{2.63}$$

As with the gravitation example, the energy balances (2.60) and (2.63) are completely equivalent mathematically, and we can use whichever one we prefer. They differ only in interpretation. Using Eq. (2.60), we regard whatever produces the conservative force (e.g. a gravitational, electric, or magnetic field, a frictionless spring, etc.) as part of the *environment* – external to the system. Therefore, we include the work  $W_c$  done by this force on our system when we do energy accounting. If we write the energy balance as in Eq. (2.63), we are regarding the source of the conservative force as part of the system. Since in this case the force becomes an internal one, we don't include the work  $W_c$  in the energy balance, but we must account for the potential energy stored in the field or spring as part of the system energy.

### 2.6 Elementary Forces and Conservation of Energy

Elementary forces are those forces which are part of the basic structure of physics, such as the gravitational force, electromagnetic forces, nuclear forces, etc. These forces are responsible for all atomic-level or subatomic behavior, including chemical and nuclear bonding and the forces atoms feel when they collide with one another. (But quantum mechanics, rather than classical mechanics, must be used to correctly predict these features).

As far as we know now, *every* elementary force of nature is conservative - that is, it may be derived from some potential energy function. Considering how special conservative forces are (there are infinitely more functions  $\mathbf{F}(\mathbf{x})$  which are *not* the gradient of some  $f(\mathbf{x})$  than there are functions which are), this can be no accident – it must be a deep principle of physics.

The universe can be thought of as a very large number of elementary particles interacting through conservative, elementary forces. If we do an energy accounting for the entire universe, treating the conservative interactions between particles by adding appropriate potential energy terms to the system energy as discussed in section 2.5.4, we find<sup>7</sup>

$$\Delta(E_k + E_p) = 0, \qquad (2.64)$$

where  $E_k$  and  $E_p$  represent the kinetic and potential energies, respectively, of the entire universe. Of course there can be no external work term, since the entire universe is inside our system!

Therefore, the total energy of the universe (kinetic + all forms of potential) is constant. Everything that has happened since the birth of the universe — its expansion, the condensation of protons and electrons to form hydrogen gas, the formation of stars and heavy nuclei within them, the formation of planets, the evolution of life on earth, you reading this book — all of these processes simply shift some energy from one type to another, never changing the total.

The constancy of the energy of the universe is the *principle of conservation* of energy. Of course, any small part of the universe which is isolated from the rest in the sense that no energy enters or leaves it will also have constant total energy. Another way of stating the principle of conservation of energy is that there are no sinks or sources for energy — you can move it around or change its form, but you can't create it, and you can't destroy it.

<sup>&</sup>lt;sup>7</sup>Of course, to calculate  $E_k$  and  $E_p$  correctly we would have to consider not only quantum mechanics but general relativity. These change the details in important ways, but not the basic result that the energy of the universe is constant.

Why is the energy of the universe constant? This is equivalent to asking why all elementary forces are conservative. Quantum mechanics provides some insight into this question. In quantum mechanics, a system has a well-defined constant total energy if two conditions are met: a) there are no interactions with external forces, and b) the laws governing the elementary forces are constant in time. If this is applied to the whole universe condition a) is automatically satisfied, and b) says simply that the basic laws of physics have always been the same as they are now. As far as we know, this is true – the laws of physics don't depend on time.

### 2.7 Non-Conservative Forces

Since all elementary forces are conservative, it might be thought that any macroscopic forces between macroscopic objects (which, after all, are composed of elementary particles interacting through elementary forces) should be conservative. This is actually *not true*, as a simple thought experiment demonstrates.

Imagine sliding an object around in a circle on a table, returning to the starting point. If the table were perfectly frictionless, it would take no net work to do this, since any work you do to accelerate the object would be recovered when you decelerate it. But in reality, you have to apply a force just to overcome friction, and you have to do net work to slide the object in a circle back to its original position. Clearly, friction is not a conservative force.

If we were to look on an atomic scale at the interface between the object and the table as it slides, we don't see a "friction force" acting at all. Instead, we would notice the roughness of both the table and the object – sometimes an atomic-scale bump sticking out of the object would get caught behind an atomic-scale ridge on the table. As the object continued to move, the bonds to the hung-up atoms stretch or bend, increasing their potential energy (like springs or rubber bands); finally, the stuck atoms break free and vibrate violently, as the energy due to bond stretching is released. The increased vibrational kinetic energy of these few atoms is rapidly transferred through the bonds to all of the other atoms in the object, resulting in a small increase in the random, thermal energy of the object.<sup>8</sup>

If we reverse the direction we slide the object, the apparent friction force

<sup>&</sup>lt;sup>8</sup>Essentially the same process happens in earthquakes as one plate of the earth's crust attempts to slide past another one along faults (such as the San Andreas fault or the many other faults below the LA basin). The sliding slabs of rock get hung up, and as the plates keep moving, huge strain energy is built up. Eventually, the plates break free, converting the pent-up strain energy (potential energy) into the kinetic energy of ground motion, which we experience as an earthquake. Sliding friction is a microscopic version of an earthquake!

reverses direction too, always opposing the direction of motion. This means that the friction force depends on the velocity of the object. For sliding friction, the dependence is usually only on the direction of the velocity vector (not its magnitude). But viscous drag in a fluid (also a type of friction) depends on the magnitude also, increasing with speed. This behavior is in sharp contrast to conservative forces, which only depend on position. For example, the gravitational force on an object of mass m is always mg directed in the same direction (toward the center of the earth) no matter what the velocity of the object is.

We see then that macroscopic forces which are non-conservative (friction) are actually "effective" forces which result from very complex atomic-level motion. Frictional forces always result in an irreversible conversion of macroscopic kinetic energy (the motion of the object) to disorganized, random thermal energy, and always oppose the direction of motion, so  $\mathbf{F}_{nc} \cdot d\mathbf{x}$  is always negative.

### 2.8 The First Law of Thermodynamics

We now wish to do energy accounting for arbitrary macroscopic material systems. We're already part way there – in Section 2.4 we developed an energy balance equation for macroscopic matter valid if the bonds between atoms were rigid. Unfortunately, this is not really the case. Bonds in solids can stretch and bend like springs, so the atoms are continually vibrating. This means that a solid will have kinetic energy associated with this motion, and potential energy due to stretching bonds. In liquids and gases, molecules can move and rotate, as well as vibrate.

In this section, we extend our previous analysis to account for these effects, and develop a purely macroscopic statement of energy accounting, which is the celebrated First Law of Thermodynamics.

#### 2.8.1 The Internal Energy

Consider a macroscopic sample of matter (solid, liquid, or gaseous) at rest. Although no motion is apparent, on a microscopic level the atoms composing the sample are in continual, random motion. The reason we don't perceive this motion, of course, is that all macroscopic measurements we can do average over a *huge* number of atoms. Since the atomic motion is essentially random, there are just as many atoms travelling to the right with a given speed as to the left. Even though individual atomic speeds may be hundreds of meters per second, the atomic velocities tend to cancel one another when we sum over a large number of atoms.

But the kinetic energies due to the atomic motion don't cancel, since the

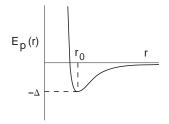


Figure 2.6: Potential energy of a chemical bond as a function of bond length r. The unstretched length is  $r_0$ .

kinetic energies are all positive, scalar numbers. Even a sample of matter at rest (no center-of-mass motion) has microscopic kinetic energy, which we will call the internal kinetic energy:

$$E_{k,int} = \sum_{j} m_j v_j^2 / 2,$$
 (2.65)

where the sum is over all atoms in the sample.

The sample has microscopic potential energy too. As the atoms move, they stretch or compress the bonds holding them together. The bonds may be modeled as springs, although ones with a spring constant which depends on bond length. The potential energy of these "springs" as a function of length typically looks something like the curve in Fig. 2.6. If the bond is compressed so that it is shorter than  $r_0$ , the potential energy rises rapidly. If it is stretched, the potential energy rises, too. The bond can be broken  $(r \to \infty)$  if work  $\Delta$  is done to pull the atoms apart.

Other types of interactions between atoms can be modeled in a similar way. Molecules in a gas hardly feel any force from other molecules far away, but when two molecules approach closely (collide) the potential energy rises rapidly, causing them to repel one another and move apart again. Similarly, the interaction of two atoms which are charged may be described by a repulsive or attractive electrostatic potential energy which depends on their separation. If the atoms or molecules have a magnetic moment (e.g. iron or nickel atoms, oxygen molecules), then their interaction is described by a potential energy function which depends on their separation and the relative alignment of their magnetic moment vectors. In fact, *every* atomic-level interaction between atoms can be described in terms of some potential energy function. We know this is possible, since we know atomic-level forces are conservative.

At any instant in time, the sample has a microscopic, internal potential energy, which is the sum of all of the potential energy contributions describing the interactions between the atoms or molecules:

$$E_{p,int} = \sum_{k} E_{p,k}.$$
(2.66)

The index k runs over all pairs <sup>9</sup> of atoms which exert forces on one another in any way.

Of course, since the particles are constantly moving and interacting, both the atomic positions and atomic velocities keep changing. Hence, both  $E_{k,int}$ and  $E_{p,int}$  are constantly changing, as energy shifts from kinetic to potential and back again (for example, as two atoms in a gas collide and rebound).

In doing energy accounting for this sample, we will first of all choose the system to consist of the sample itself (a closed system). We will furthermore choose to treat the conservative interactions between atoms within it by including  $E_{p,int}$  in the system energy, rather than accounting explicitly for the work done by these forces. Therefore, the only work terms which will appear are those due to external forces.

If no external forces act on the atoms of the sample (if it is completely isolated from the environment), then energy accounting leads to the conclusion that the sum of  $E_{k,int}$  and  $E_{p,int}$  must be constant:

$$\Delta(E_{k,int} + E_{p,int}) = 0. \tag{2.67}$$

We define the *internal energy* U by

$$U = E_{k,int} + E_{p,int},\tag{2.68}$$

For a stationary sample which is isolated from the environment  $\Delta U = 0$ .

The internal energy includes all of the kinetic energy associated with the atomic-level, random motion of the atoms of the system, and all of the potential energy associated with all possible interactions between the atoms. Since the potential energy associated with chemical bonds is included in  $E_{p,int}$ , chemical energy is part of the internal energy. Chemical energy is essentially the energy required to break chemical bonds ( $\Delta$  in Fig. 2.6). Since  $\Delta$  differs for every different type of bond, if a chemical reaction occurs which breaks bonds of one type and forms bonds of another type,  $E_{p,int}$  may go up or down. If the system is isolated, U must be constant, and therefore  $E_{k,int}$  must change oppositely to

<sup>&</sup>lt;sup>9</sup>The potential energy of some interactions – for example, bending of chemical bonds – may depend on the positions of three or more atoms. This doesn't change anything – we simply add these terms too to  $E_{p,int}$ .

the change in  $E_{p,int}$ . The change in  $E_{k,int}$  would be experienced as a change in temperature.<sup>10</sup>

**Example 2.4** At sufficiently low density and a temperature of 300 K, the internal energy of gaseous  $H_2$  is -2441 kJ/kmol<sup>11</sup> and the internal energy of gaseous  $I_2$  is 59,993 kJ/kmol. (We will show later that in the limit of low density the internal energy per mole of a gas is a function only of temperature – assume this limit applies here.) The internal energy of gaseous hydrogen iodide HI is given by the formula

$$U_{HI} = 17,655 + 21.22T \text{ kJ/kmol}$$
(2.69)

which is valid for 300 < T < 600 K.

If one kmol of  $H_2$  is reacted with one kmol of  $I_2$  to form two kmol of HI in a closed, constant-volume container with no energy transfer to the environment, what is the final temperature if the initial temperature is 300 K?

Solution: The internal energy of the initial mixture of  $H_2$  and  $I_2$  at 300 K is

$$U = (1 \text{ kmol})(-2441 \text{ kJ/kmol}) + (1 \text{ kmol})(59,993 \text{ kJ/kmol}) = 57,552 \text{ kJ}.$$
(2.70)

Since the system is isolated (no energy transfer to the environment), U does not change during the reaction. The final state consists of 2 kmol of HI, so the final internal energy per kmol of HI is 28,776 kJ/kmol. From Eq. (2.69), the final temperature is 524 K.

Note that the internal energy of  $H_2$  is negative at 300 K. This is not a problem, since only differences in internal energy matter. It simply reflects a particular choice for the arbitrary constant C in the internal potential energy for  $H_2$ .

Nuclear or even relativistic mass energy  $(E = mc^2)$  could be included in U if we like. A nuclear physicist would certainly want to do this. But since only changes in energy have physical significance, we can disregard these forms of energy if we don't plan to consider processes in which they change.

The internal energy is defined in a reference frame in which the sample is at rest. If this frame is moving and/or rotating with respect to the lab frame, then the macroscopic kinetic energy associated with these motions must be added to

 $<sup>^{10}</sup>$ Temperature will be formally introduced in the next chapter. For now, think of it as a measure of the internal kinetic energy per atom. This would be exactly true if atomic motions were really described by classical mechanics, but when quantum effects are important (and the usually are) it is only approximately true.

 $<sup>^{11}</sup>$  One kmol is  $6.023\times10^{26}$  molecules. The mass of 1 kmol in kg equals the molecular weight of the molecule.

U to determine the total sample energy E in the lab frame:

$$E = U + \frac{1}{2}Mv_{cm}^2 + \frac{1}{2}I\omega^2, \qquad (2.71)$$

where  $v_{cm}$  is the center-of-mass speed and  $\omega$  is the rotation rate (assumed to be about a principal axis which has moment of inertia I).<sup>12</sup>

It is important to note that  $E_{p,int}$  does not include any potential energy arising from interactions of atoms in the sample with gravitational, electric, or magnetic fields produced by *external* sources. If we choose to include these macroscopic potential energy terms in the sample energy, we have to add them explicitly. If the sample is near the surface of the earth and has charge q, the total energy including potential energy terms would be

$$E = U + \frac{1}{2}Mv_{cm}^2 + \frac{1}{2}I\omega^2 + Mgy + q\mathcal{E}, \qquad (2.72)$$

where  $\mathcal{E}$  is the value of the electrostatic potential (volts).

With macroscopic kinetic and potential energy modes, the energy balance for an isolated sample is

$$\Delta E = 0, \qquad (2.73)$$

not  $\Delta U = 0$ . For example, a rubber ball dropped onto a rigid table will eventually come to rest, even if there is no energy loss to the environment. The gravitational potential energy Mgy is converted into an increase in U, which would be experienced as an increase in temperature. E, however, remains constant.

### 2.8.2 Atomic Level Energy Transfer: Microscopic Work

No sample of matter can really be completely isolated from the environment. Usually, it is in contact with other matter (e.g., a container for a gas or liquid; a table a solid rests on). Even if it were floating in interstellar space it would still exchange energy with the environment through radiation.

We now need to consider how to do energy accounting for a macroscopic sample allowing for external work done by forces from the environment. Consider a sample of gas in a container such as shown in Fig. 2.7 which has one movable wall (a piston). We will take the system to be the gas, and container to be part of the environment.

On an atomic level, both the gas and container consist of atoms which are in constant motion. The atoms of the gas are moving randomly in all directions,

<sup>&</sup>lt;sup>12</sup>We assume here that all parts of the sample are moving or rotating macroscopically together. If not, then the macroscopic kinetic energy must be determined as  $(1/2) \int \rho(\mathbf{x}) v(\mathbf{x})^2 dV$ , where the integration is over the sample and  $\rho$  is the mass density.

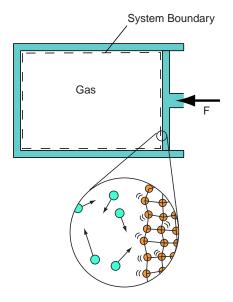


Figure 2.7: A gas in a container, as seen from the macroscopic and microscopic points of view.

colliding with one another and occasionally with the container walls. The atoms in the container are vibrating chaotically about their equilibrium positions as they are buffeted by the neighboring atoms they are bonded to, or (at the surface) by gas atoms.

When a gas atom collides with a wall atom, the gas atom may rebound with either more or less kinetic energy than it had before the collision. If the wall atom happens to be moving rapidly toward it (due to vibration) when they hit, the gas atom may receive a large impulse and rebound with more kinetic energy. In this case, the wall atom does microscopic work on the gas atom: positive microscopic work is done by the environment on the system.

On the other hand, the wall atom may happen to be moving away when the gas atom hits it, or it may rebound significantly due to the impact. In this case, the gas atom will rebound with *less* kinetic energy than it had before — therefore, the gas atom does microscopic work on the wall atom: negative microscopic work is done by the environment on the system.

We see that collisions between the gas atoms and the walls can do microscopic work even if macroscopically the walls appear stationary. If we let time dt elapse,

then the energy balance on the gas is

$$dW_{micro} = dU, (2.74)$$

where  $dW_{micro}$  is the total work done on the gas by wall collisions during time dt.

#### 2.8.3 Energy Transfer as Heat

Suppose the piston is held fixed, but the container starts out "hotter" than the gas, meaning that the container atoms have more kinetic energy per atom than do the gas atoms.<sup>13</sup> Then over time the gas atoms on average will pick up kinetic energy from collisions with wall, and wall atoms will lose kinetic energy:  $dW_{micro}$  will be positive,  $U_{gas}$  will tend to go up, and  $U_{container}$  will tend to go down. Of course, if the gas started out hotter, then  $dW_{micro}$  would be negative, and the changes in internal energy would be reversed.

Eventually, when their kinetic energies per atom are comparable,<sup>14</sup> the number of collisions per unit time which impart extra energy to the gas atoms will just balance the number per unit time which remove energy from the gas atoms, and  $U_{gas}$  and  $U_{wall}$  will stop changing on average. There would still be very rapid statistical fluctuations about these average values, but for a reasonable sized sample these fluctuations are not observable, since it can be shown from statistics that random fluctuations like this have a relative magnitude proportional to  $1/\sqrt{N}$ . For example, if  $N = 10^{20}$ , then  $\delta U/U \sim 10^{-10}$ : the internal energy is constant to one part in  $10^{10}$  in this case.

The process we have just described is energy transfer between the wall (part of the environment) and the gas (the system) due to microscopic work. However, *macroscopically* it doesn't appear that any work is being done, since the piston isn't moving, and we can't see the microscopic deflections due to atomic motion. Therefore, there is no *observable, macroscopic*  $\mathbf{F} \cdot d\mathbf{x}$ , and no macroscopic work.

We call this process of energy transfer by microscopic work without observable macroscopic work energy transfer as heat, or heat transfer for short. The amount of energy transferred in this way is denoted by the symbol Q. For an infinitesimal amount, we use the symbol dQ. As for work, the bar in dQ reminds us that it is not the differential of any function, it only means "a little bit of heat." (Or the other way to say it is that dQ, like dW, is an inexact differential.)

 $<sup>^{13}{\</sup>rm Of}$  course, "hotness" is really related to temperature, which we'll introduce in the next chapter.

<sup>&</sup>lt;sup>14</sup>More precisely, when their temperatures are equal.

The energy balance for this process is then

$$dQ = dU. \tag{2.75}$$

#### 2.8.4 Energy Transfer as Macroscopic Work

Each collision of a gas atom with a wall delivers an impulse to the wall. At typical gas densities, the number of collisions per unit area of wall per unit time is very large. For example, objects sitting in room temperature ambient air experience roughly  $10^{24}$  collisions per cm<sup>2</sup> per second. Macroscopically, it is not possible to detect the individual impulses from so many frequent collisions. Instead, a macroscopic force on the wall is felt, which is proportional to wall area:

$$F_{wall} = PA. \tag{2.76}$$

The proportionality constant P is the gas *pressure*.

Suppose the piston is now moved slowly toward the gas a distance dx. The macroscopic work required to do this is

$$dW_{macro} = \mathbf{F} \cdot d\mathbf{x} = (PA)dx. \tag{2.77}$$

The gas atoms which collide with the moving piston have their kinetic energy increased on average slightly more than if the pison had been stationary; therefore,  $U_{gas}$  increases. If dQ = 0, then the energy balance is

$$dU = dW_{macro} = PAdx. (2.78)$$

Of course, there may also be microscopic work occurring which is not visible macroscopically (heat transfer). To account for this, we must write the energy balance as

$$dU = dQ + dW_{macro}. (2.79)$$

For a more general system, macroscopic kinetic energy and potential energy may also be part of the system energy. If energy is transferred to such a system by macroscopic work and by heat transfer, the most general energy balance for a closed system is

$$dE = dQ + dW. (2.80)$$

We have to stipulate that the system is closed, since if matter were to enter or leave the system, it would carry energy with it which is not accounted for

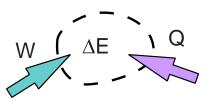


Figure 2.8: The First Law for a Closed System.

in Eq. (2.80). Note that we have removed the subscript "macro" on the work term. In thermodynamics generally, and from here on in this book, the term *work* means *macroscopic work*, unless otherwise stated.

Equation (2.80) is known as the *First Law of Thermodynamics*. The First Law simply states that the change in the total energy of a system equals the energy transfer to it as heat, plus the energy transfer to it as work. It is simply a statement of conservation of energy for a macroscopic system.

Note that there is no formula for dQ like  $dW = \mathbf{F} \cdot d\mathbf{x}$ . In practice, dQ is determined from equation 2.80 once dW and dE have been evaluated.

We can integrate Eq. (2.80) for some finite change from an initial state to a final one, yielding

$$\Delta E = Q + W \tag{2.81}$$

where

$$W = \int_{i}^{f} dW = \int_{i}^{f} \mathbf{F}_{macro} \cdot d\mathbf{x}_{macro}$$
(2.82)

and

$$Q = \int_{i}^{f} dQ. \qquad (2.83)$$

The interpretation of Eq. (2.81) is as shown in Fig. 2.8. Both work and heat represent energy transfers across the system boundary; the energy E stored within the system (in whatever form) changes by the amount of energy transferred in.

Alternatively, we may divide Eq. (2.80) by the elapsed time dt to obtain

$$\frac{dE}{dt} = \dot{Q} + \dot{W} \tag{2.84}$$

where the ratio dQ/dt is the heat transfer rate  $\dot{Q}$  and the ratio dW/dt is the power input or work rate we've defined previously.

All three equations (2.80), (2.81), and (2.84) are different forms of First Law of Thermodynamics for a closed system. In solving problems involving the First Law, you should carefully consider which form is most appropriate to use. If the process occurs during an infinitesimal time dt, use Eq. (2.80). If you are given initial and final states of the system, often Eq. (2.81) is the best choice. If you are given a heat transfer or work *rate*, then probably Eq. (2.84) would be easiest to use.

For many processes, both Q and W will be significant, and must be included to correctly calculate the change in the system energy E from the First Law. But in some cases, either Q or W may be very much smaller than the other. In analyzing such processes, it is often acceptable to only include the dominant energy transfer mechanism, although this all depends on how accurate an answer is required for  $\Delta E$ .

For example, if a solid is heated, it usually expands a little bit. But in many cases the work done in the expansion against atmospheric pressure is so small that  $W \ll Q$ . In this case, it might be OK to neglect W in calculating  $\Delta E$  due to heating.

The opposite case would occur, for example, if a rubber band were rapidly stretched. Since heat transfer takes some time to occur, if the stretching is rapid enough it might be OK to neglect Q in calculating the increase in internal energy of the rubber band due to the work done to stretch it.<sup>15</sup> Processes for which Q = 0 are called *adiabatic*.

#### 2.9 Reversible and Irreversible Work

An important concept in thermodynamics is the idea of *reversible work*. Work  $dW = \mathbf{F}(\mathbf{x}, \mathbf{v}) \cdot d\mathbf{x}$  is reversible if and only if the work done in moving  $d\mathbf{x}$  is exactly recovered if the motion is reversed. That is,

Forward: 
$$dW_{forward} = \mathbf{F}(\mathbf{x}, \mathbf{v}) \cdot d\mathbf{x}$$
 (2.85)

Reverse: 
$$dW_{reverse} = - dW_{forward} = \mathbf{F}(\mathbf{x}, -\mathbf{v}) \cdot (-d\mathbf{x}).$$
 (2.86)

Note that the velocity changes sign when the direction of motion is reversed. This condition is satisfied if

$$\mathbf{F}(\mathbf{x}, \mathbf{v}) \cdot \mathbf{v} = \mathbf{F}(\mathbf{x}, -\mathbf{v}) \cdot \mathbf{v}. \tag{2.87}$$

 $<sup>^{15}</sup>$  You can verify for yourself that rubber bands heat up when stretched by rapidly stretching one and holding it to your lip.

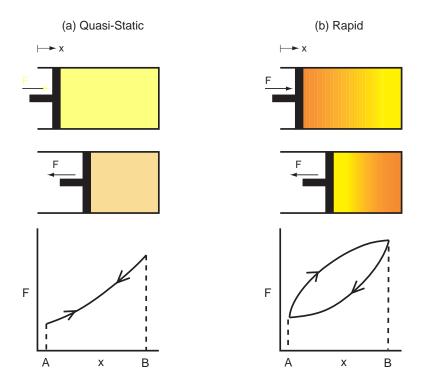


Figure 2.9: (a) Quasi-static and (b) rapid compression and expansion of a gas.

Therefore, the condition is that the force component in the direction of  $\mathbf{v}$  be the same for forward and reverse motion. A force which depends only on position  $\mathbf{x}$  will satisfy this, and therefore work done by any  $\mathbf{F}(\mathbf{x})$  is reversible.

Friction and drag forces always depend on velocity, and act opposite to the direction of motion, changing sign when the direction of motion is reversed. Therefore, work done on a system by a friction or drag force is *always negative* (i.e., the system must do work against the friction force). Work done by or against such forces is never reversible – work must always be done to overcome friction, and you can never recover it.

Consider compressing a gas in a cylinder by pushing in a piston, as shown in Fig. 2.9. As discussed above, the gas exerts a force on the piston due to collisions of gas atoms with the piston surface. To hold the piston stationary, a force F = PA must be applied. We will assume the piston is lubricated, and is well-insulated so the compression process is adiabatic. The piston can be moved very slowly by applying a force just slightly greater than PA. If the piston velocity is sufficiently small, then the work required to overcome viscous drag in the lubricant will be negligible (example 2.2). Also, if the piston speed is slow enough, the gas molecules which collide with the piston have plenty of time to move away from it and distribute their excess energy with other molecules through collisions before the piston has moved any significant distance. In this case, the state of the gas is the same as would occur if the piston were stationary at the instantaneous value of x: The gas molecules are uniformly distributed in the cylinder, and the force on the piston is the same as if the piston were not moving – it is PA.

In this limit of zero piston speed, the force on the piston approaches PA, no matter whether the piston is moving in or out. In this limit, the compression or expansion process is called *quasi-static*, since the force on the piston is the same as if the piston were static. Therefore, the work done during quasi-static compression of a gas is reversible work.

If the piston velocity is high, two things happen which make the process irreversible. First, the work to overcome viscous drag in the lubricant may no longer be negligible. Second, if the piston velocity is comparable to the average molecular speed in the gas, then the piston will tend to sweep up molecules near it, forming a high-density region just in front of it (similar to a snowplow). Since the rate at which molecules collide with the piston is proportional to their number per unit volume, the piston will experience more collisions at a given xlocation than if it were moving slowly. Therefore, the applied force F to move the piston must be greater than the quasi-static force, and thus the work to compress the gas is greater than in the quasi-static limit. A typical plot of F(x)for rapid compression is shown in Fig. 2.9(b).

If this process is now reversed and the gas is rapidly expanded, we still have to do work to overcome viscous drag in the lubricant (not only do we not get back the work done to overcome drag during compression, we have to do *still more work* to overcome it during expansion). Also, there is now a *low density* gas region near the piston, since the piston is moving away so fast the molecules lag behind. So the gas pushes on the piston with *less* force than if the expansion were done very slowly. Therefore, *the work we get back in the expansion is less than we put in during compression*.

Since  $W = \int \mathbf{F} \cdot d\mathbf{x}$ , the work input  $W_{AB}$  to move the piston from A to B is  $\int_{A}^{B} F_{comp}(x) fx$ , where  $F_{comp}(x)$  is the force applied along the compression part of the curve. This of course is simply the area under the  $F_{comp}(x)$  curve. The work input to expand the gas from B to A is  $W_{BA} = \int_{B}^{A} F_{exp}(x) dx =$ 

 $-\int_{A}^{B}F_{exp}(x)dx.$ 

If we consider the entire process  $A \to B \to A$ , then the total work input  $W = W_{AB} + W_{BA}$ . In the quasi-static case  $F_{comp}(x) = F_{exp}(x) = PA$ , so  $W = W_{AB} + (-W_{AB}) = 0$ . No net work is required to return the piston to its starting point. From the first law for this process (remember Q = 0)

$$W = \Delta U = 0. \tag{2.88}$$

Therefore, the gas internal energy returns to its starting value after quasi-static compression followed by quasi-static expansion.

In the non-quasi-static case,  $F_{comp}(x) > F_{exp}(x)$ . Therefore, W > 0: net work input must be done if the piston is rapidly moved from A to B and then back to A. From the First Law then,  $\Delta U > 0$ . The gas ends up with more internal energy (hotter) at the end of the process than at the beginning.

### 2.10 Some Reversible Work Modes

There are several different ways of doing reversible (quasi-static) work on matter. A few of these are described here.

### 2.10.1 Compression

We saw in the last section that if a gas is slowly compressed, the work required to move the piston dx is dW = (PA)dx. The same analysis would apply if the gas in the cylinder were replaced by any compressible substance, so this result is quite general. The volume change of the substance is dV = -Adx, so we may write this as

$$dW_{qs} = -PdV. (2.89)$$

We add the subscript "qs" since this only applies if the compression is done quasi-statically. Note this expression is for the work done on the substance (input to the system); For compression, dV < 0 and  $dW_{qs} > 0$ , for expansion dV > 0 and  $dW_{qs} < 0$ .

### 2.10.2 Stretching a Liquid Surface

If a liquid film is suspended on a wire frame, as shown in Fig. 2.10, a force is exerted on the wire that is proportional to its wetted length L that results from a tensile force<sup>16</sup> per unit length in the surface of the liquid. This is known as the

 $<sup>^{16}</sup>$ A tensile force is the opposite of a compression force – it pulls, rather than pushes.

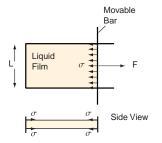


Figure 2.10: Surface tension in a liquid.

surface tension  $\sigma$ , and has units of N/m. For example, for a water/air interface at 25 °C,  $\sigma = 0.072$  N/m.

The physical origin of the surface tension is that molecules in a liquid exert attractive forces on one another, which hold the liquid together. These forces are much weaker than covalent chemical bonds, but nevertheless have a dependence on distance similar to that shown in Fig. 2.6. A molecule will have lower potential energy in the bulk, where it is surrounded by molecules on all sides, than at the surface, where it feels the attractive force only on one side. Therefore, surface molecules will try to move into the bulk, until as many have crowded into the bulk as possible and there is a shortage of surface molecules left to cover the area. The remaining surface molecules will be spaced slightly further apart than ideal  $(r > r_0)$ , and therefore they will pull on their neighboring surface molecules, resulting in the surface tension.

Since the film has two surfaces, the force required to hold the movable wire stationary is

$$F = 2\sigma L. \tag{2.90}$$

If the wire is now quasi-statically pulled, so that F is only infinitesimally greater than  $2\sigma L$ , the work done to move dx is

$$dW_{qs} = 2\sigma L dx. \tag{2.91}$$

During this process the total surface area of the film has increased by 2Ldx. Therefore, we may write

$$dW_{qs} = \sigma dA. \tag{2.92}$$

This expression for the work required to quasi-statically increase the surface area of a liquid is valid for arbitrary geometry.

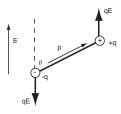


Figure 2.11: Forces exerted by an electric field on a polar diatomic molecule.

### 2.10.3 Electric Polarization

Many materials are *polar*, which means that although they are electrically neutral, they are composed of positively and negatively charged atoms. Any ionic crystal (NaCl) is polar, as is water (the hydrogen atoms have positive charge, and the oxygen atom has negative charge). If an electric field is applied to a polar material, it is possible to do work on it.

Consider the situation shown in Fig. 2.11. A polar diatomic gas molecule is oriented at a particular instant in time at an angle  $\theta$  with respect to an applied electric field. (Due to collisions between the gas molecules, at any instant in time there is a distribution of orientations – they are not all lined up with the field, except at absolute zero.)

The force on a charge q in an electric field **E** is given by

$$\mathbf{F} = q\mathbf{E}.\tag{2.93}$$

Therefore, the positive end of the molecule at position  $\mathbf{x}_+$  feels a force  $q\mathbf{E}$ , and the negative end at  $\mathbf{x}_-$  feels a force  $-q\mathbf{E}$ . The molecule will turn and may be stretched by the forces due to the electric field acting on each end. (The center of mass motion is unaffected, since there is no net force.) If, due to the field, the atoms move by  $d\mathbf{x}_+$  and  $d\mathbf{x}_-$ , respectively, then the work done on this one molecule is

$$dW_1 = (q\mathbf{E} \cdot d\mathbf{x}_+) + (-q\mathbf{E} \cdot d\mathbf{x}_-)$$
(2.94)

$$= q\mathbf{E} \cdot d(\mathbf{x}_{+} - \mathbf{x}_{-}). \tag{2.95}$$

The *electric dipole moment*  $\mathbf{p}$  of the molecule is defined by

$$\mathbf{p} = q(\mathbf{x}_{+} - \mathbf{x}_{-}). \tag{2.96}$$

The dipole moment is a vector which points along the direction from the negative charge to the positive charge. In terms of  $\mathbf{p}$ , the work done is

$$dW_1 = \mathbf{E} \cdot d\mathbf{p}. \tag{2.97}$$

This is the work done on one polar molecule; to determine the work done on the entire polar gas, we must sum over all N molecules in the gas:

$$dW = \sum_{n=1}^{N} \mathbf{E} \cdot d\mathbf{p}_n = \mathbf{E} \cdot d\left(\sum_{n=1}^{N} \mathbf{p}_n\right).$$
(2.98)

The quantity in parenthesis is the total dipole moment of the gas. This may be rewritten in terms of purely macroscopic quantities by defining the *polarization*  $\mathbf{P}$  to be the dipole moment per unit volume:

$$\mathbf{P} = \frac{1}{V} \left( \sum_{n=1}^{N} \mathbf{p}_n \right). \tag{2.99}$$

Then Eq. (2.98) becomes

$$dW = \mathbf{E} \cdot d(V\mathbf{P}). \tag{2.100}$$

Although we derived this equation for a polar gas, it is in fact completely general and applies to polar solids and liquids also.

For static polarization, P is some function of **E** and temperature T. Except in extremely strong fields, the dependence on **E** is linear, so that **P** may be expressed as  $\mathbf{P} = \epsilon_0 \chi_e(T) \mathbf{E}$ . In Rationalized MKSA units (the most common electromagnetic unit system for engineering work),  $\epsilon_0 = 8.90 \times 10^{-12} \text{ C}^2 \cdot \text{s}^2/\text{kg} \cdot \text{m}^3$ . The dimensionless material property  $\chi_e(T)$  is the *electric susceptibility*.

The susceptibility for many materials may be expressed as

$$\chi_e(T) = A + B/T,$$
 (2.101)

where A and B are constants. The A term describes polarization due to stretching of polar chemical bonds, a process which is not strongly temperature dependent. The B/T term describes orientation of polar molecules in a liquid or a gas, as we considered above.

It is not hard to see why this orientation process should be temperaturedependent. If  $\mathbf{E} = 0$ , then the dipoles are oriented randomly, so just as many point up as down. In this case,  $\mathbf{P} = 0$ . For non-zero  $\mathbf{E}$ , the field will try to align **p** for each molecule with **E**, but collisions between molecules will upset this alignment, tending to randomize **p**. The net effect of the competition between alignment by **E** and randomization by collisions is that molecules point in all directions, but  $\mathbf{p} \cdot \mathbf{E}$  is somewhat more likely to be positive than negative. This means that there is non-zero polarization, with **P** directed along **E**. Since higher **E** increases the tendency to align, and higher *T* increases the tendency to randomize direction, **P** typically increases with increasing **E**, and decreases with increasing *T*.

#### Example 2.5

A dielectric material is one which may be polarized, but has no mobile free charges, so no electrical currents can flow through it. Dielectrics are often used to fill the space between the plates in capacitors. A particular dielectric liquid, which obeys Eq. (2.101) with A = 0, is quasi-statically polarized at constant temperature starting at  $\mathbf{E} = 0$  and ending at  $\mathbf{E} = \mathbf{E}_1$ . For this material, the internal energy depends only on T. Determine the work and heat transfer during this process.

Solution:

$$W = \int dW = \int \mathbf{E} \cdot d(V\mathbf{P}). \qquad (2.102)$$

For quasi-static polarization, the static relationship between  $\mathbf{P}$ ,  $\mathbf{E}$ , and T holds, so

$$W_{qs} = \int_0^{E_1} Ed(V\epsilon_0 BE/T) = \frac{\epsilon_0 V BE_1^2}{2T}.$$
 (2.103)

Since this process is carried out isothermally, and for this particular material U = U(T),  $\Delta U = 0$  for this process. The first law applied to this system is

$$\Delta U = 0 = Q + W_{qs}, \qquad (2.104)$$

from which we conclude that  $Q = -\epsilon_0 V B E_1^2/2T$ . Therefore, heat must be removed (Q < 0) to polarize this material at constant temperature; if no heat were removed (adiabatic polarization), U would increase by  $W_{qs}$ , and the temperature would increase.

#### 2.10.4 Magnetization

Some materials are magnetic – that is, they contain atoms which have magnetic dipole moments and behave just like atomic-scale magnets. Magnetic atoms are usually ones with unpaired electrons, such as iron, nickel, or rare-earth elements. Some molecules can have unpaired electrons also, for example  $O_2$ .

An applied magnetic field can do work on magnetic materials. The analysis is very similar to that for electric polarization. If a single magnetic dipole with dipole moment  $\mathbf{m}$  is placed in a uniform magnetic field  $\mathbf{H}$ , the field exerts a torque on the dipole given by

$$\tau = \mu_0 \mathbf{m} \times \mathbf{H}.\tag{2.105}$$

where  $\mu_0$  is a constant which depends on the unit system we use to measure **m** and **H** known as the *permeability of free space*. In Rationalized MKSA units  $\mu_0 = 4\pi \times 10^{-7} \text{ kg} \cdot \text{m/C}^2$ .

The work done by this torque is

$$dW_1 = \mu_0 \mathbf{H} \cdot d\mathbf{m}. \tag{2.106}$$

Summing over all magnetic dipoles in the material and defining the magnetization  $\mathbf{M}$  by

$$\mathbf{M} = \frac{1}{V} \sum_{n=1}^{N} \mathbf{m}_n, \qquad (2.107)$$

we obtain an expression for the work required to change the magnetization of a magnetic material:

$$dW = \mu_0 \mathbf{H} \cdot d(V\mathbf{M}) \tag{2.108}$$

Analogous to the discussion above for dielectrics, if a magnetic material is placed in a static magnetic field, it will develop some static magnetization  $\mathbf{M}(\mathbf{H}, T)$ , which results from the balance between the field trying to align the dipoles and random thermal motion (collisions, vibrations) upsetting perfect alignment. If the field is increased very slowly (quasi-statically), then this relation between  $\mathbf{M}$ ,  $\mathbf{H}$ , and T will still hold, and we may write

$$dW_{qs} = \mu_0 \mathbf{H} \cdot d\left[V\mathbf{M}(\mathbf{H}, T)\right] \tag{2.109}$$

Example 2.6 A Curie substance is one for which the static magnetization is

$$\mathbf{M} = C \frac{\mathbf{H}}{T},\tag{2.110}$$

where C is a material-specific constant. Most magnetic materials behave as Curie substances in the limit of high temperature and low field strength.

A Curie substance in a uniform magnetic field  $\mathbf{H}_0$  is quasi-statically, isothermally magnetized by slowly increasing the field to  $\mathbf{H}_1 > \mathbf{H}_0$ . Calculate the work done on the substance, and the change in its internal energy. It may be shown that for a Curie substance U = U(T). Calculate the heat transfer which must occur in this process.

**Solution:** Since the process is quasi-static, the static relationship  $\mathbf{M}(\mathbf{H}, T)$  holds at every step in the process. Therefore,

$$W = \int_{H_0}^{H_1} \frac{\mu_0 C}{T} \mathbf{H} \cdot d\mathbf{H}$$
  
=  $\frac{\mu_0 C}{2T} (H_1^2 - H_0^2).$  (2.111)  
(2.112)

The First Law for this process is

$$\Delta U = Q + W. \tag{2.113}$$

Since the process is isothermal and we are given U = U(T),  $\Delta U = 0$ . Therefore,

$$Q = -W = -(\mu_0 C/2T)(H_1^2 - H_0^2).$$
(2.114)

Example 2.6 shows that heat must be given off to the environment in order to quasi-statically (reversibly) magnetize a Curie substance at constant temperature. If the process had been done adiabatically instead (Q = 0), the internal energy and temperature of the substance would have increased. The reason for this is that the microscopic torque exerted on the individual dipoles by the field imparts to them some rotational kinetic energy, which is then transferred to the rest of the substance by collisions. The reverse process of quasi-static isothermal demagnetization require heat *input* to maintain the sample temperature; if no heat is supplied (adiabatic demagnetization), the sample temperature drops.

These processes may be combined to produce useful devices, such as magnetic engines or magnetic refrigerators. Magnetic refrigerators are used in practice to achieve very low temperatures (T < 1 K), where conventional refrigerators cannot function.

### 2.10.5 Generalized Forces and Displacements

The expressions for quasi-static work are always of the general form  $\mathcal{F}dX$  or  $\mathcal{F} \cdot d\mathbf{X}$ : -PdV,  $\sigma dA$ ,  $\mathbf{E} \cdot d\mathbf{P}$ ,  $\mu_0 \mathbf{H} \cdot d\mathbf{M}$ , etc. We can think of these as generalizations of  $\mathbf{F} \cdot d\mathbf{x}$ . We call the  $\mathcal{F}$  terms  $(-P, \sigma, \mathbf{E}, \mathbf{H})$  generalized forces and the X terms  $(V, A, \mathbf{P}, \mathbf{M})$  generalized displacements.

The work done by any of these for a finite change is

$$W = \int_{path} \mathcal{F} \cdot d\mathbf{X}.$$
 (2.115)

This is still a path integral, but note it is not an integral in physical coordinate space, but in the space defined by **X**. For example, polarization work would involve integrating  $\mathbf{E} \cdot d\mathbf{P}$  along some  $\mathbf{P}(t)$  trajectory.

### 2.11 Some Irreversible Work Modes

If any of the processes discussed in the last section are done too rapidly, the work done will not be reversible. For example, if the magnetic field is increased too rapidly, the induced magnetization will lag behind the static  $\mathbf{M}(\mathbf{H}, T)$ . This will result in  $\mu_0 \mathbf{H} \cdot d\mathbf{M}$  being *greater* than the quasi-static value for a given  $d\mathbf{M}$ . Therefore, more magnetization work must be done to effect a given change in magnetization; less work is recovered during demagnetization.

Some other ways of doing work are *inherently* irreversible – if the direction of the motion is reversed, the force changes sign, so you can't recover *any* of the work put in. As we've already discussed, work done to overcome friction or viscosity is like this.

#### 2.11.1 Stirring a Viscous Fluid

An example of purely irreversible work is stirring a viscous fluid.<sup>17</sup> Work must be done to turn the stirrer, no matter which direction it is turned. The fluid will have some macroscopic kinetic energy for a while due to stirring, but eventually it will come to rest, with the energy transfer as work to the system due to stirring appearing finally as an increase in internal energy U.

In fact, the state of the fluid after it is stirred and has come to rest again is no different than if the same amount of energy had been added to it as heat. Fully irreversible work is equivalent to heat addition.

### 2.11.2 Electrical Current Flow Through A Resistor

Another common type of fully irreversible work is electrical current flow through a resistor. As electrons move through a resistor with an electrical potential  $\Delta \mathcal{E} > \prime$  across it, they lose electrostatic potential energy in the amount  $|e\Delta \mathcal{E}|$  by doing this amount of irreversible work. The work is done by colliding with atomic scattering centers within the resistor, which transfers energy to them, increasing the internal energy of the resistor.

If the number of electrons flowing through the resistor per second is  $N_e$ , then the rate at which irreversible work is done is

$$\dot{W}_e = \dot{N}_e |e\Delta \mathcal{E}| = \mathcal{I} \cdot \mathcal{E}.$$
(2.116)

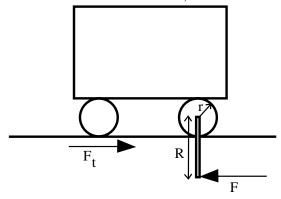
 $<sup>^{17}\</sup>mathrm{All}$  fluids, even water and gases, have some viscosity.

where  $I = e\dot{N}_e$  is the electrical current. The current through the resistor is proportional to the voltage across it:  $I = \Delta \mathcal{E}/R$ , where R is the resistance. Therefore, Eq. (2.116) can be also written  $\dot{W}_e = I^2 R$ , or  $\dot{W}_e = (\Delta \mathcal{E})^2/R$ .

As was true for stirring a fluid, passing a current through a resistor is fully irreversible, since changing the sign of the voltage also reverses the direction of current flow. The irreversible electrical work done on the resistor is equivalent thermodynamically to heat addition to the resistor.

## Problems

**2.1** A cart is sitting near the edge of a flat, horizontal table. The wheels of the cart have radius r, and a lever of length R > r is attached to one wheel. When the lever is straight down, it is pushed by a force  $\vec{F}$  to the left, causing the wheels to turn a small amount  $d\theta$  and the cart to move to the right. A traction force is also present on the wheels, which keeps the cart from sliding when the force  $\vec{F}$  is applied. Determine the work done by force  $\vec{F}$  and by the traction force. (Hint: calculate displacements with respect to the table carefully, remembering the cart moves. Make sure your answer is sensible when R = r.)



**2.2** Which of the following forces are conservative? The forces are all twodimensional – the component in the z direction is zero. Here  $\hat{i}$  is a unit vector in the x direction, and  $\hat{j}$  is a unit vector in the y direction.

$$\vec{F}_1 = \mathbf{i}y - \mathbf{j}x \tag{2.117}$$

$$\vec{F}_2 = \frac{\mathbf{i}x + \mathbf{j}y}{x^2 + y^2}$$
 (2.118)

$$\vec{F}_3 = \mathbf{i}2xy + \mathbf{j}x^2 \tag{2.119}$$

$$\vec{F}_4 = \mathbf{i}2x + \mathbf{j}x^2 \tag{2.120}$$

$$F_5 = \mathbf{i}a\sin(ax)\sin(by) - \mathbf{j}b\cos(ax)\cos(by) \qquad (2.121)$$

$$\vec{F}_6 = \mathbf{i}\sin(ax)\cos(by) + \mathbf{j}\cos(ax)\sin(by) \qquad (2.122)$$

- **2.3** Show that any force with the properties listed below which acts between two particles must be conservative.
  - 1. The force is directed along the line connecting the particles.
  - 2. The force depends only on the distance r between the particles.
- **2.4** A ball of mass m is dropped at height y = H onto a plate which at the moment the ball hits is at y = 0 and is travelling upward with constant speed  $v_p$ . Assuming the ball rebounds elastically and assuming air resistance is negligible, how high does the ball bounce? How much work does the plate do on the ball?
- **2.5** You are a scientist on your way to the new research station on Mars in the year 2020. Your spacecraft has just undocked from the space station in earth orbit, and is beginning to accelerate to cruising speed for the trip to Mars. The ion engines are turned on at t = 0, and the engine thrust begins to increase, producing for a while a spacecraft acceleration linear in time: a = Ct. Within the spacecraft, the effects of the acceleration are identical to those of a linearly-increasing gravitational field. Free-floating objects at t = 0 begin "falling" toward the rear wall. You notice a ball which at t = 0 is a distance H from the rear wall. In terms of the mass of the ball, C, and H, what is the kinetic energy (in the local reference frame within the spacecraft) of the ball when it strikes the wall? Is the concept of potential energy useful to solve this problem? Why or why not?
- **2.6** An ideal gas is defined to be one which satisfies  $PV = N\hat{R}T$ , where N is the number of kg-moles (kmol) of gas, and  $\hat{R} = 8.3143 \text{ kJ/kmol/K}$ . Consider an ideal gas contained in a vertical cylinder, with a piston of mass M at the top.
  - 1. Initially, no external force is applied to the piston, and it comes to some equilibrium height. If the atmospheric pressure is  $P_0$  and the cylinder area is A, what is the gas pressure in the cylinder?
  - 2. The gas is now heated quasi-statically at constant pressure until its volume is tripled. How much work does the gas do against the environment (which includes the massive piston) during this process?

- 3. Finally, a force is applied to the top of the piston, and the gas is quasi-statically, isothermally compressed back to its initial volume. How much work must be done?
- 2.7 A Curie substance undergoes a three-step quasi-static process:
  - 1. The substance is isothermally magnetized from  $(H_0, M_0)$  to  $(H_1, M_1)$ , where  $H_1 = 2H_0$
  - 2. The field is reduced back to  $H_0$ , holding M fixed
  - 3. The magnetization is reduced to  $M_0$ , holding H fixed

At the end of this process, the substance is back in its initial state. Sketch this process on a plot of H vs. M. For each step, determine

- 1. Whether work is done on or by the substance, and how much
- 2. Whether heat is transferred to or from the substance, and how much
- 3. The temperature at the end of the step.

Explain how this process might be used as the basis for a magnetic refrigerator.

- **2.8** For a particular dielectric material, the susceptibility is given by  $\chi_e = A + B/T$ . With  $\vec{E}$  held constant, the material is cooled to half its initial temperature, causing the polarization to increase. How much work is done on the material by the electric field in this process?
- **2.9** Due to surface tension, the pressure inside a small water droplet will be greater than the air pressure outside. Show that

$$\Delta P = P_i - P_o = \frac{2\sigma}{r},$$

where  $\sigma$  is the surface tension and r is the droplet radius. Hint: consider a *force* balance in the x direction on the system defined by the dotted line, which cuts the droplet in half.

$$\sigma$$
  $P_{i}$   $P_{o}$   $P_{o}$ 

Small water droplets in a fog may be only a few microns in size. Evaluate numerically the pressure inside a water droplet for diameter  $D = 1 \ \mu \text{m}$  and for  $D = 10 \ \mu \text{m}$  if the air pressure is 1 atm. (1 atm =  $1.01325 \times 10^5 \text{ N/m}^2$ ). Express your answer in atmospheres.

**2.10** An ideal gas has the properties described in problem 2.6. In addition, for *monatomic* ideal gases (He, Ar, etc.) the internal energy is related to N and T by

$$U = \frac{3}{2}N\hat{R}T.$$

Consider a process in which a monatomic ideal gas is quasi-statically *adiabatically* compressed from a state with  $V_0, P_0, T_0$  to a final state with properties V, P, T.

- 1. Derive an expression for how the temperature varies with volume during this process that is, find the function T(V). Do your analysis *systematically*: draw a sketch showing the system and any energy transfers from the environment, state any assumptions, invoke the first law, use necessary property data, etc.
- 2. Using this formula, evaluate the final temperature (K), final pressure (MPa), and work input (J) if argon at 300 K and 0.1 MPa is quasistatically, adiabatically compressed to one-fourth of its initial volume. (Recall 1 Pa = 1 N/m2.)