Chapter 8

The Equipartition Theorem

Topics

Equipartition and kinetic energy. The one-dimensional harmonic oscillator. Degrees of freedom and the equipartition theorem. Rotating particles in thermal equilibrium. Heat capacities revisited.

There is an important principle lurking behind many of the calculations we have carried out so far – the principle of the *Equipartition of Energy*. This is a very powerful concept in *classical statistical physics* and has general applicability *for systems in thermal equilibrium*. We will find that the principle has to be somewhat modified when we take quantum concepts into account, but let us first develop the classical version of the principle.

8.1 Equipartition and Kinetic Energy

In Section 3.4, our numerical simulations demonstrated that, using Newton's laws of motion and the randomising effects of collisions, the same Maxwellian velocity distribution is set up in the (x, y, z) directions. Furthermore, by averaging over the one-dimensional and three dimensional Maxwell distributions, we showed in Section 4.4.2 that the *average energies* in the three directions and the total

kinetic energy are:

$$\tfrac{1}{2}m\overline{v_x^2} = \tfrac{1}{2}kT; \tag{8.1}$$

$$\tfrac{1}{2}m\overline{v_y^2} = \tfrac{1}{2}kT;$$

$$\tfrac{1}{2}m\overline{v_z^2} = \tfrac{1}{2}kT;$$

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{1}{2}m\overline{v_x^2} + \tfrac{1}{2}m\overline{v_y^2} + \tfrac{1}{2}m\overline{v_z^2} = \tfrac{3}{2}kT. \tag{8.2}$$

Then, in Section 5.3, we extended the simulations to mixtures of gases, the particles having masses m_1 and m_2. Again, using only Newton's laws of motion and the randomising effect of collisions, we found that $\tfrac{1}{2}m_1\overline{v_1^2} = \tfrac{1}{2}m_2\overline{v_2^2} = \tfrac{3}{2}kT$. In other words, in thermal equilibrium,

$$\tfrac{1}{2}m_1\overline{v_{x1}^2} = \tfrac{1}{2}m_1\overline{v_{y1}^2} = \tfrac{1}{2}m_1\overline{v_{z1}^2}$$

$$= \tfrac{1}{2}m_2\overline{v_{x2}^2} = \tfrac{1}{2}m_2\overline{v_{y2}^2} = \tfrac{1}{2}m_2\overline{v_{z2}^2} = \tfrac{1}{2}kT. \tag{8.3}$$

This is the first example of the *equipartition theorem*. It states that:

> In thermal equilibrium, each independent mode in which energy can be stored is awarded $\tfrac{1}{2}kT$ of energy.

This principle clearly works for the energy stored in the kinetic energy of the particles. The theorem is, however, much more widely applicable. Let us next consider the case of the one-dimensional harmonic oscillator.

8.2 The One-dimensional Harmonic Oscillator

Let us revise some of the important ideas expounded in the *Fields, Oscillations and Waves* course. Consider the motion of a one-dimensional harmonic oscillator, such as a mass m on the end of a spring. The equation of motion is

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = m\frac{\mathrm{d}v_x}{\mathrm{d}t} = -\alpha x,$$

meaning that the acceleration of the mass m is due to the restoring force $-\alpha x$. The solution of this

equation is simple harmonic motion

$$x = x_0 \sin \omega t \quad \text{and} \quad v_x = \frac{\mathrm{d}x}{\mathrm{d}t} = x_0 \omega \cos \omega t, \quad (8.4)$$

where $\omega = \sqrt{\alpha/m}$.

We find the energy of the oscillator by multiplying through by v_x and integrating with respect to time. Thus,

$$\int m v_x \frac{\mathrm{d}v_x}{\mathrm{d}t}\,\mathrm{d}t + \int \alpha x v_x\,\mathrm{d}t = 0,$$

$$m \int v_x \frac{\mathrm{d}v_x}{\mathrm{d}t}\,\mathrm{d}t + \int \alpha x \frac{\mathrm{d}x}{\mathrm{d}t}\,\mathrm{d}t = 0,$$

$$\tfrac{1}{2}m \int \frac{\mathrm{d}(v_x)^2}{\mathrm{d}t}\,\mathrm{d}t + \tfrac{1}{2}\alpha \int \frac{\mathrm{d}(x^2)}{\mathrm{d}t}\,\mathrm{d}t = 0,$$

$$\tfrac{1}{2}m v_x^2 + \tfrac{1}{2}\alpha x^2 = \text{constant}.$$

> **Revision**
>
> Recall that the total work done is
>
> $$\text{Work done} = \int_0^r \boldsymbol{f} \cdot \mathrm{d}\boldsymbol{r} = \int_0^x f_x\,\mathrm{d}x,$$
>
> $$= \int_0^t f_x \frac{\mathrm{d}x}{\mathrm{d}t}\,\mathrm{d}t,$$
>
> $$= \int_0^t v_x f_x\,\mathrm{d}t.$$

The first term represents the *kinetic energy* of the mass and the second term the *potential energy* stored in the spring. As the mass oscillates, the sum of the two energies is constant and energy is passed back and forth between the kinetic energy of motion and the potential energy of the compressed or extended spring.

We can now work out the average kinetic and potential energies in the spring. Taking averages over one period of the oscillation, $T = 2\pi/\omega$, we find:

Mean kinetic energy

$$= \frac{1}{T}\int_0^T \tfrac{1}{2}m v_x^2\,\mathrm{d}t,$$

$$= \frac{1}{T}\int_0^T \tfrac{1}{2}m x_0^2 \omega^2 \cos^2 \omega t\,\mathrm{d}t,$$

$$= \frac{1}{T}\tfrac{1}{2}m x_0^2 \omega^2 \frac{T}{2},$$

$$= \tfrac{1}{4}m x_0^2 \omega^2,$$

Mean potential energy

$$= \frac{1}{T}\int_0^T \tfrac{1}{2}\alpha x^2\,\mathrm{d}t,$$

$$= \frac{1}{T}\int_0^T \tfrac{1}{2}\alpha x_0^2 \sin^2 \omega t\,\mathrm{d}t,$$

$$= \frac{1}{T}\tfrac{1}{2}\alpha x_0^2 \frac{T}{2},$$

$$= \tfrac{1}{4}\alpha x_0^2,$$

where we have used the relations

$$\int_0^T \cos^2 \omega t\,\mathrm{d}t = \int_0^T \sin^2 \omega t\,\mathrm{d}t = \frac{T}{2}. \quad (8.5)$$

But $\omega^2 = \alpha/m$ and so the *mean kinetic energy is equal to the mean potential energy.*

Now, in thermal equilibrium, we know that the mean kinetic energy of the one-dimensional oscillator is $\frac{1}{2}kT$ and so the potential energy term must also be awarded $\frac{1}{2}kT$ in thermal equilibrium. Therefore, the mean energy of a one-dimensional oscillator in thermal equilibrium at temperature T is

$$\overline{E} = kT. \qquad (8.6)$$

This is a very important and fundamental result for any oscillator in thermal equilibrium according to classical physics.

8.3 Degrees of Freedom and the Equipartition Theorem

Notice an important aspect of this calculation. We have associated the mean energy $\frac{1}{2}kT$ with each of the squared terms in the expression for the mean energy of the oscillator, $\frac{1}{2}m\overline{v_x^2}$ and $\frac{1}{2}\alpha\overline{x^2}$. This is part of a more general way of looking at the law of equipartition of energy. The factor $\frac{1}{2}kT$ arises from the form of the integral performed over the Boltzmann distribution. Consider what happens if there is a term in the energy which is proportional to some quantity squared $E = \frac{1}{2}az^2$ – in the case of kinetic energy $a = m$ and $z = v_x$. Recalling that the Boltzmann factor has the form $\exp(-E/kT)$, the expression for the mean energy associated with the quantity z is:

$$\overline{E} = \frac{\displaystyle\int_{-\infty}^{\infty} \frac{1}{2}az^2 \exp\left(-\frac{az^2}{2kT}\right)\,\mathrm{d}z}{\displaystyle\int_{-\infty}^{\infty} \exp\left(-\frac{az^2}{2kT}\right)\,\mathrm{d}z}$$

Making the usual substitution $x^2 = az^2/2kT$, we find

$$\overline{E} = \frac{a}{2}\,\frac{\left(\dfrac{2kT}{a}\right)^{3/2} \displaystyle\int_{-\infty}^{\infty} x^2 \exp(-x^2)\,\mathrm{d}x}{\left(\dfrac{2kT}{a}\right)^{1/2} \displaystyle\int_{-\infty}^{\infty} \exp(-x^2)\,\mathrm{d}x},$$

$$= kT\,\frac{\pi^{1/2}/2}{\pi^{1/2}} = \tfrac{1}{2}kT. \qquad (8.7)$$

Thermal Fluctuations of a Spring
There is an important consequence of this calculation. Any spring in thermal equilibrium at temperature T possesses an *average energy* $\overline{E} = kT$ but the spring fluctuates randomly about the mean position because of these thermal motions. The typical displacement of the spring is

$$\tfrac{1}{2}kT = \tfrac{1}{2}\alpha\overline{x^2} \qquad \overline{x^2} = \frac{kT}{\alpha}$$

This is the mean square random variation in the position of the mass, by virtue of being in thermal equilibrium at temperature T. This sets an important limitation to the precision of instruments such as an atomic force microscope.

This is an extremely important result. The average energy is independent of the form of the motion and is always equal to $\frac{1}{2}kT$. For the translational motion of a particle we associated $\frac{1}{2}kT$ with the motion in each of the x, y and z directions because they were independent – the details of this calculation were given in chapter 4.

Generalising this result, in thermal equilibrium, we award $\frac{1}{2}kT$ of energy to each independent part of the motion associated with an energy which depends upon the square of some independent variable. We define the *number of degrees of freedom* as the number of independent squared terms that enter into the total energy.

This is the final version of the classical *theorem of the equipartition of energy*:

> In thermal equilibrium, each degree of freedom is awarded $\frac{1}{2}kT$ of energy.

Degrees of freedom
The number of independent squared terms that enter into the total energy

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Equipartition theorem
In thermal equilibrium, each degree of freedom is awarded $\frac{1}{2}kT$ of energy

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8.4 Rotating Particles in Thermal Equilibrium

We can apply the equipartition theorem to the rotation of a rigid body about a fixed axis. In this case the kinetic energy is $\frac{1}{2}I\omega^2$, where I is the moment of inertia about the fixed axis and ω its angular velocity. The mean energy associated with this rotational motion in thermal equilibrium is therefore

$$\overline{E}_{\mathrm{rot}} = \tfrac{1}{2}I\overline{\omega^2} = \tfrac{1}{2}kT. \qquad (8.8)$$

We now need to generalise this result to rigid particles which both move and rotate in three dimensions without any fixed axis of rotation. We have already seen in the Mechanics and Relativity course that we can describe the motion of a rigid body of mass m as the translational motion of the centre of mass with a velocity v together with rotation about the centre of mass. Furthermore the total kinetic energy is the sum of the kinetic energy associated with the translational motion plus the kinetic energy of rotation about the centre of mass,

$$E = \tfrac{1}{2}m\boldsymbol{v}^2 + \tfrac{1}{2}I\omega^2. \qquad (8.9)$$

The translational motion has three degrees of freedom

$$E_{\text{trans}} = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2.$$

In three dimensions the rotational motion also has three degrees of freedom associated with rotation about three distinct axes. These axes however are not the x, y and z axes which are fixed in space, but instead the rotational motion is best described in terms of axes fixed with respect to the rigid body.

It can be shown that for any rigid body we can define three axes about which the rotational motion is independent. We shall call these axes 1, 2 and 3 and associated with each there is a moment of inertia I_1, I_2 and I_3 and an angular velocity ω_1, ω_2 and ω_3 respectively. ω_1, ω_2 and ω_3 form the components of a vector and the total rotational kinetic energy is given by:

$$E_{\text{rot}} = \tfrac{1}{2}I_1\omega_1^2 + \tfrac{1}{2}I_2\omega_2^2 + \tfrac{1}{2}I_3\omega_3^2. \qquad (8.10)$$

In thermal equilibrium, since these axes are independent, there are three degrees of freedom associated with the rotational motion:

$$\begin{aligned}\overline{E}_{\text{rot}} &= \tfrac{1}{2}I_1\overline{\omega_1^2} + \tfrac{1}{2}I_2\overline{\omega_2^2} + \tfrac{1}{2}I_3\overline{\omega_3^2} \\ &= \tfrac{1}{2}kT + \tfrac{1}{2}kT + \tfrac{1}{2}kT \\ &= \tfrac{3}{2}kT \end{aligned} \qquad (8.11)$$

For completeness a table of equivalences between translational and rotational motion is given below including the vector nature of the rotation in three dimensions. We recall that:

- The *linear displacement* dr corresponds to the *angular displacement* dθ;

- The *linear velocity* dv corresponds to the *angular velocity* dω;

- The *mass m* corresponds to the *moment of inertia I* ;

- The *linear momentum p* corresponds to the *angular momentum* $L = I\omega = (I_1\omega_1, I_2\omega_2, I_3\omega_3)$;

The motion of the body in space is complicated since rotation about an axis fixed with respect to the body rotates the *axes* of the body with respect to fixed axes in space. The average behaviour can still be described with respect to the axes fixed with respect to the body.

Rotational motion in thermal equilibrium
For a rigid body there are three independent rotation axes giving three rotational degrees of freedom:

$$\overline{E}_{\text{rot}} = \tfrac{1}{2}I_1\overline{\omega_1^2} + \tfrac{1}{2}I_2\overline{\omega_2^2} + \tfrac{1}{2}I_3\overline{\omega_3^2}$$
$$= \tfrac{3}{2}kT$$

- The *linear kinetic energy* $= \frac{1}{2}m\boldsymbol{v}^2 = \boldsymbol{p}^2/2m$ corresponds to the *rotational kinetic energy* $\frac{1}{2}I\boldsymbol{\omega}^2 = \boldsymbol{L}^2/2I$.

Description	Linear Motion	Rotational Motion
Small displacement	$\mathrm{d}\boldsymbol{r}$	$\mathrm{d}\boldsymbol{\theta}$
Velocity	$\boldsymbol{v} = \dfrac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t}$ $= (v_x, v_y, v_z)$	$\boldsymbol{\omega} = \dfrac{\mathrm{d}\boldsymbol{\theta}}{\mathrm{d}t}$ $= (\omega_1, \omega_2, \omega_3)$
Inertia	Mass m	Moment of Inertia $I = \sum mr^2$
Momentum	$\boldsymbol{p} = (p_x, p_y, p_z)$ $= m\boldsymbol{v} = (mv_x, mv_y, mv_z)$	$\boldsymbol{L} = (L_1, L_2, L_3)$ $= I\boldsymbol{\omega} = (I_1\omega_1, I_2\omega_2, I_3\omega_3)$
Magnitude of Momentum	$\lvert\boldsymbol{p}\rvert^2 = p_x^2 + p_y^2 + p_z^2$	$\lvert\boldsymbol{L}\rvert^2 = L_1^2 + L_2^2 + L_3^2$ $= \lvert I\boldsymbol{\omega}\rvert^2 = (I_x\omega_1)^2 + (I_y\omega_2)^2 + (I_z\omega_3)^2$
Energy	Kinetic $= \frac{1}{2}m\boldsymbol{v}^2 = \dfrac{\boldsymbol{p}^2}{2m}$	Kinetic $= \frac{1}{2}I\boldsymbol{\omega}^2 = \dfrac{\boldsymbol{L}^2}{2I}$

The model for the rotating particles is exactly the same as that which we adopted for the case of linear velocity, but now the collisions between the particles cause them to exchange angular velocity and rotational energy rather than linear velocity and linear kinetic energy.

Finally, we note that we can apply Boltzmann's statistics to the rotational motion and so obtain the distribution function for rotational motion about any of the axes of the body. Using the equivalences given in the above table, we see that

$$f_1(v_x)\,\mathrm{d}v_x = \sqrt{\frac{m}{2\pi kT}}\, e^{-mv_x^2/2kT}\,\mathrm{d}v_x$$

$$\downarrow$$

$$f_1(\omega_1)\,\mathrm{d}\omega_1 = \sqrt{\frac{I_1}{2\pi kT}}\, e^{-I_1\omega_1^2/2kT}\,\mathrm{d}\omega_1.$$

As an exercise, or using the general result (8.7), we see that the average kinetic energy of rotation is

$$\overline{E_1} = \overline{\tfrac{1}{2}I_1\omega_1^2} = \tfrac{1}{2}kT.$$

8.5 Summary

The important lesson of this chapter is that, according to classical statistical mechanics, we award $\frac{1}{2}kT$ of energy to each degree of freedom of the system. This was the result which caused so much grief for Maxwell and Boltzmann. As was mentioned in Section 6.4.2, we expect the internal kinetic energy of a gas of particles, which have both linear and rotational motion, to be $U = N_A \times 6 \times \frac{1}{2}kT = 3RT$ per mole. Hence, $C_V = (\mathrm{d}U/\mathrm{d}T) = 3R$ and so the ratio of specific heats should be

$$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 4/3 = 1.333.$$

Diatomic gases have $\gamma = 1.4$. This result greatly depressed Maxwell. In the last sentence of his great paper, in which he first derived the Maxwell distribution, he wrote:

> 'Finally, by establishing a necessary relation between the motions of translation and rotation of all particles not spherical, we proved that a system of such particles could not possibly satisfy the known relation between the two specific heats of all gases'.

In his report to the British Association for the Advancement of Science of 1860, Maxwell stated that this discrepancy 'overturned the whole hypothesis'.

We will see that quite new concepts were needed to resolve this nasty problem, which threatened to overturn the principle of equipartition of energy and consequently the kinetic theory of gases itself.