## Chapter 3

## The Boltzmann, Normal and <br> Maxwell Distributions

## Topics

The heart of the matter, numerical simulation of the Boltzmann distribution. The two-dimensional Maxwell distribution. The isothermal atmosphere. Degeneracies. The complete answer.

### 3.1 The Heart of the Matter

It may come as a surprise, but we have actually come remarkably close to some of the most important results in statistical physics. Rather than spend a lot of time grinding through mathematics, we will use the power to computers to demonstrate directly some of the most important aspects of statistical and thermal physics. We will then relate these statistical ideas to the properties of real gases, liquids and solids.

Let me give you the answer we are seeking straightaway. The probability that a state of energy $E_{i}$ is occupied in thermal equilibrium is

$$
\begin{equation*}
p\left(E_{i}\right) \propto g\left(E_{i}\right) \exp \left(-E_{i} / k T\right) \tag{3.1}
\end{equation*}
$$

where $T$ is the temperature and $g\left(E_{i}\right)$ is the degeneracy of the state of energy $E_{i}$ - by degeneracy, we
mean the number of states of energy $E_{i}$ which are accessible to the particle. For continuous probability distributions, (3.1) becomes

$$
\begin{equation*}
p(E) \mathrm{d} E \propto g(E) \exp (-E / k T) \mathrm{d} E \tag{3.2}
\end{equation*}
$$

It might look as though this must be a simple function to derive, but it is not all that easy to do this rigorously. The quickest route is to use the calculus of variations which you will meet in the Mathematics course next year. Rather, let us look at some illustrative examples.

### 3.2 A Numerical Simulation of the Approach to Statistical Equilibrium

The key idea is that the particles of the system are in thermal equilibrium. By this we mean that all the processes by which the particles can exchange energy are perfectly balanced. If, for example, a particle $i$ exchanges energy with another particle $j$, the opposite process by which a particle $j$ transfers the same energy to the particle $i$ are in exact balance statistically. These exchanges of energy go on all the time and, although they might get slightly out of balance for a short while, over a long period they all balance out. This long term average is the equilibrium energy distribution, but equally we recognise that there must be fluctuations about the equilibrium distribution. These are key ideas in statistical physics.

Let us demonstrate how such a system evolves towards equilibrium through a simple simulation. Here are the rules of the simulation.

- Begin with an array of cells and suppose that energy comes in unit packets which we can allocate to each cell. We need not be specific about the system, or about the nature of the interactions between the elements.
- Allow the cells to interact with each other at random by some unspecified process. The rules of exchange are as follows.

1. Choose a cell $i$ of the array at random.
2. Choose another cell $j$ of the array at random,

For the enthusiast, I have given a simple derivation using the calculus of variations in Theoretical Concepts in Physics, Cambridge University Press, 2003.
3. Give one unit of energy from $i$ to $j$, unless there is no energy in the element $i$,

- Start off with all the elements having the same energy, so that the initial histogram of energy has a single peak.
- After many thousands of interactions, equilibrium is reached when the interchanges between each energy element of the array and every other have come into statistical equilibrium.

Two versions of the simulation are shown in Figures 3.1 and 3.2.

In the first case, we watch the evolution of the array in slow motion. We start off with an array of 100 cells and allocate 5 energy elements to each of them, as shown in Figure 3.1 (first panel). The energy distribution among the cells is shown in the panels on the right. The second panel shows the energy distribution after 100 random exchanges. The energy distribution begins to spread out and resemble a normal or gaussian distribution. After about 200 exchanges, the low energy side of the distribution hits the origin, but there are no negative energy states and the distribution begins to pile up at $E=0$, as shown by the evolution after 300 exchanges. After 1000 exchanges, the shape of the distribution begins to stabilise. The distribution is roughly exponential, but there are significant fluctuations about the mean distribution. The result is that the distribution is very different from the initial monoenergetic distribution of energies. The numbers are small and so we cannot say precisely what the distribution is, but it is roughly an exponential.

In the second case, we deal with a very much larger array and allow very large numbers of exchanges to take place in each time step, without displaying the evolution. In this simulation, we begin with an array of 10,000 cells and each cell has initially 20 quanta. The initial energy distribution is shown in the top diagram of Figure 3.2. We again allow the random exchange of energy units between pairs of cells. The second diagram shows the energy distribution after 300,000 random exchanges of energy

| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |


| 5 | 5 | 8 | 7 | 8 | 6 | 6 | 5 | 5 | 6 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 3 | 2 | 4 | 4 | 6 | 5 | 5 | 2 | 3 | 5 |
| 6 | 5 | 4 | 3 | 4 | 4 | 7 | 3 | 3 | 6 |
| 5 | 5 | 3 | 6 | 7 | 5 | 5 | 6 | 5 | 4 |
| 2 | 4 | 8 | 8 | 6 | 4 | 5 | 5 | 5 | 5 |
| 5 | 6 | 2 | 6 | 3 | 5 | 4 | 4 | 7 | 4 |
| 4 | 4 | 6 | 5 | 4 | 4 | 6 | 6 | 8 | 4 |
| 7 | 4 | 3 | 4 | 3 | 6 | 6 | 5 | 7 | 5 |
| 6 | 5 | 5 | 3 | 6 | 9 | 4 | 5 | 6 | 5 |
| 5 | 7 | 4 | 5 | 5 | 5 | 5 | 4 | 6 | 5 |


| 4 | 8 | 4 | 5 | 12 | 7 | 7 | 6 | 2 | 4 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 9 | 4 | 0 | 3 | 6 | 2 | 8 | 6 | 7 |
| 6 | 3 | 1 | 4 | 6 | 4 | 6 | 3 | 5 | 6 |
| 4 | 5 | 6 | 7 | 3 | 0 | 3 | 6 | 3 | 3 |
| 3 | 6 | 6 | 5 | 5 | 4 | 7 | 4 | 8 | 7 |
| 7 | 10 | 3 | 6 | 2 | 5 | 10 | 1 | 9 | 3 |
| 2 | 2 | 7 | 2 | 2 | 5 | 9 | 5 | 0 | 7 |
| 2 | 4 | 9 | 10 | 2 | 1 | 7 | 4 | 7 | 6 |
| 6 | 8 | 9 | 0 | 6 | 14 | 3 | 6 | 2 | 8 |
| 3 | 8 | 8 | 2 | 1 | 8 | 5 | 5 | 1 | 4 |


| 0 | 10 | 2 | 4 | 15 | 11 | 2 | 13 | 2 | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 5 | 8 | 2 | 0 | 0 | 12 | 15 | 18 | 2 | 6 |
| 8 | 7 | 2 | 6 | 12 | 6 | 0 | 1 | 9 | 0 |
| 0 | 4 | 3 | 8 | 5 | 1 | 0 | 4 | 0 | 5 |
| 7 | 4 | 1 | 1 | 2 | 9 | 9 | 2 | 20 | 9 |
| 9 | 3 | 8 | 5 | 3 | 5 | 23 | 1 | 8 | 0 |
| 3 | 1 | 5 | 6 | 6 | 2 | 7 | 0 | 5 | 5 |
| 3 | 3 | 5 | 3 | 4 | 7 | 5 | 0 | 1 | 1 |
| 0 | 7 | 2 | 0 | 4 | 13 | 0 | 5 | 4 | 2 |
| 5 | 15 | 3 | 1 | 0 | 1 | 6 | 11 | 4 | 7 |



Figure 3.1: The evolution of the distribution of quanta between cells. The initial distribution has 5 quanta per cell (top). Pairs of cells are selected at random and one quantum exchanged between them; after approximately 100 exchanges the distribution approaches a gaussian distribution (middle upper). After approximately 300 exchanges a significant number of cells have zero or one quanta and the distribution now departs from a gaussian since we cannot have negative numbers of quanta per cell (middle lower). After approximately 1000 exchanges the final form of the distribution is reached; given the small number of cells large fluctuations are observed.


Figure 3.2: The evolution of a system of $10^{4}$ cells. The initial distribution has 20 quanta in every cell (top). After $3 \times 10^{5}$ exchanges of quanta between pairs of cells, the distribution function approximates a gaussian (middle upper). After $1.8 \times 10^{6}$ exchanges a significant number of cells have zero quanta and the distribution function begins to broaden. Finally, after approximately $4 \times 10^{6}$ exchanges, a steady-state is reached; the distribution function is accurately described by an exponential function, shown by the solid line.
quanta. Again, the energy distribution begins to spread out to roughly a gaussian or normal distribution, but again it hits the origin and begins to climb the $y$-axis. The third diagram shows the distribution after 1.8 million exchanges. There are now a number of cells with zero energy. Finally, after 4 million exchanges, an exponential distribution is reached, as is illustrated by the solid line in the final panel of Figure 3.2. If we continue to run the simulation, we find that the exponential shape does not change, although the energy of an individual cell can vary very widely. In this state, the system is said to have reached a state of statistical equilibrium.

The final distribution is of exponential form,

$$
\begin{equation*}
p\left(E_{i}\right) \propto \exp \left(-\alpha E_{i}\right) \tag{3.3}
\end{equation*}
$$

This is the primitive form of the exponential Boltzmann distribution.

Notice a key feature of these simulations. There are fluctuations about the mean and some cells can have very large energies relative to the average. These features are crucial in understanding the evolution of many different types of system in physics, chemistry and biology. The evolution of biological systems depends upon these fluctuations and the fact that spontaneously the properties of cells can far exceeding the average. The statistics are governed by the Boltzmann distribution.

### 3.3 The Two-dimensional Maxwell Distribution

Let us now work out the velocity or, equally important, the momentum distribution of the particles in a two-dimensional gas, assuming they all have the same mass $m$. Let us demonstrate this using a numerical simulation similar to that of the last section, but now we follow the velocities, or momenta, of the particles as they exchange energy and momentum in collisions, as we illustrated on the air-table.

Suppose the colliding particles have momenta $\boldsymbol{p}_{1}$ and $\boldsymbol{p}_{2}$. In two dimensions, these vectors are

$$
\begin{equation*}
\boldsymbol{p}_{1} \equiv\left[p_{1 x}, p_{1 y}\right] \quad \boldsymbol{p}_{2} \equiv\left[p_{2 x}, p_{2 y}\right] \tag{3.4}
\end{equation*}
$$

We leave it as an optional exercise to work out the momenta with which the particles leave the elastic collision. We carry out exactly the same calculation as in Section 1.2, but now allow both particles to be moving.

Example: First find the velocity $\boldsymbol{V} \equiv\left[V_{x}, V_{y}\right]$ of the centre of momentum frame of reference. The components of this frame are found as usual by adding $\boldsymbol{V}$ to the components of the momentum vectors so that

$$
\begin{align*}
\left(p_{1 x}+m V_{x}\right)+\left(p_{2 x}+m V_{x}\right) & =0  \tag{3.5}\\
\left(p_{1 y}+m V_{y}\right)+\left(p_{2 y}+m V_{y}\right) & =0 \tag{3.6}
\end{align*}
$$

Therefore,

$$
\begin{equation*}
V \equiv\left[V_{x}, V_{y}\right]=-\frac{1}{2 m}\left[p_{1 x}+p_{2 x}, p_{1 y}+p_{2 y}\right] \tag{3.7}
\end{equation*}
$$

In this frame of reference, the momenta of the particles are

$$
\begin{aligned}
& \text { 1. }\left[\frac{1}{2}\left(p_{1 x}-p_{2 x}\right), \frac{1}{2}\left(p_{1 y}-p_{2 y}\right)\right] \text {, } \\
& \text { 2. }\left[\frac{1}{2}\left(p_{2 x}-p_{1 x}\right), \frac{1}{2}\left(p_{2 y}-p_{1 y}\right)\right] .
\end{aligned}
$$

In this frame of reference, the total momentum is zero, the particles have equal and opposite momenta and so after the collision, conserving energy, the particles are sent out in opposite directions with velocities of the same magnitude, but at some angle $\theta$ with respect to the original axis of the collision. To rotate the momentum vectors, we use the rotation formulae (see Mathematics Handbook):

$$
\begin{align*}
& A_{x}^{\prime}=A_{x} \cos \theta+A_{y} \sin \theta  \tag{3.8}\\
& A_{y}^{\prime}=-A_{x} \sin \theta+A_{y} \cos \theta \tag{3.9}
\end{align*}
$$

Therefore, for particle 1, we find

$$
\begin{aligned}
p_{1 x}^{\prime} & =\frac{1}{2}\left(p_{1 x}-p_{2 x}\right) \cos \theta+\frac{1}{2}\left(p_{1 y}-p_{2 y}\right) \sin \theta \\
p_{1 y}^{\prime} & =-\frac{1}{2}\left(p_{1 x}-p_{2 x}\right) \sin \theta+\frac{1}{2}\left(p_{1 y}-p_{2 y}\right) \cos \theta
\end{aligned}
$$

Figure 3.5. Elastic collision in the centre of momentum frame of reference.

In centre of momentum frame $S^{\prime}$

Similarly for particle 2, we obtain

$$
\begin{aligned}
p_{2 x}^{\prime} & \left.=\frac{1}{2}\left(p_{2 x}-p_{1 x}\right) \cos \theta+\frac{1}{2}\left(p_{2 y}-p_{1 y}\right) \sin \theta\right] \\
p_{2 y}^{\prime} & \left.=-\frac{1}{2}\left(p_{2 x}-p_{1 x}\right) \sin \theta+\frac{1}{2}\left(p_{2 y}-p_{1 y}\right) \cos \theta\right]
\end{aligned}
$$

The value of $\theta$ can be chosen at random. Finally, we return to the laboratory frame of reference by adding the

Figure 3.3. Elastic collision of two point masses with momenta $\boldsymbol{p}_{1}$ and $\boldsymbol{p}_{2}$.

In laboratory frame $S$


Figure 3.4. Elastic collision in the centre of momentum frame of reference.

In centre of momentum frame $S^{\prime}$

centre of momentum velocity to both particles. Therefore, the final answer for particle 1 is,
$p_{1 x}^{\prime \prime}=\frac{1}{2}\left[\left(p_{1 x}-p_{2 x}\right) \cos \theta+\left(p_{1 y}-p_{2 y}\right) \sin \theta+\left(p_{1 x}+p_{2 x}\right)\right]$,
$p_{1 y}^{\prime \prime}=\frac{1}{2}\left[-\left(p_{1 x}-p_{2 x}\right) \sin \theta+\left(p_{1 y}-p_{2 y}\right) \cos \theta+\left(p_{1 y}+p_{2 y}\right)\right]$.

Similarly, for particle 2,
$p_{2 x}^{\prime \prime}=\frac{1}{2}\left[\left(p_{2 x}-p_{1 x}\right) \cos \theta+\left(p_{2 y}-p_{1 y}\right) \sin \theta+\left(p_{1 x}+p_{2 x}\right)\right.$,
$p_{2 y}^{\prime \prime}=\frac{1}{2}\left[-\left(p_{2 x}-p_{1 x}\right) \sin \theta+\left(p_{2 y}-p_{1 y}\right) \cos \theta+\left(p_{1 y}+p_{2 y}\right)\right.$.

The expressions (3.10) to (3.13) are the key relations. Notice that the new components of the momenta depend only upon $\theta$, the rotation angle of the collision. Therefore, we can set up the same array of cells as in the previous simulation, but each box now has $p_{x}$ and $p_{y}$ components. We need to ensure that the system has no net momentum and so we arrange the initial state of the molecules of the gas so that

$$
\begin{equation*}
\sum_{i} p_{x i}=0, \quad \sum_{i} p_{y i}=0 . \tag{3.14}
\end{equation*}
$$

An arbitrary example of such an array is shown in Table 3.1, where the momenta are given integral values.

The simulation proceeds as follows:

1. Choose an element $i$ of the array at random.
2. Choose another element of the array at random $j$.
3. Allow $i$ and $j$ to collide and choose the angle $\theta$ at random.
4. Determine the values of $\left[p_{1 x}^{\prime \prime}, p_{1 y}^{\prime \prime}\right]$ and $\left[p_{2 x}^{\prime \prime}, p_{2 y}^{\prime \prime}\right]$ using the expressions (3.10) to (3.13).
5. Replace the original values of the $\left[p_{1 x}, p_{1 y,}\right]$ and $\left[p_{2 x}, p_{2 y}\right]$ by the new $\left[p_{1 x}^{\prime \prime}, p_{1 y}^{\prime \prime}\right]$ and $\left[p_{2 x}^{\prime \prime}, p_{2 y}^{\prime \prime}\right]$.
6. Choose a new pair of cells at random and repeat the process.

| Table 3.1. An array of $p_{x i}, p_{y i}$ values. |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $-12,12$ | $-11,7$ | $-10,2$ | $-9,-3$ | $-8,-8$ |
| $-7,11$ | $-6,6$ | $-5,1$ | $-4,-4$ | $-3,-9$ |
| $-2,10$ | $-1,5$ | 0,0 | $1,-5$ | $2,-10$ |
| 3,9 | 4,4 | $5,-1$ | $6,-6$ | $7,-11$ |
| 8,8 | 9,3 | $10,-2$ | $11,-7$ | $12,-12$ |

Figure 3.6. Outcome of elastic collision in the laboratory frame of reference.

In laboratory frame $S$

7. Repeat this procedure thousands of times.

The outcomes of these simulations are shown in Figure 3.6. We can set the system up with any distribution of momentum we like. For illustrative purposes, we show an example in which there are 10,000 particles and the momentum distribution of these particles is flat in the $x$ and $y$ directions between $\pm 10$ units in both directions.

The second panel shows the change in the momentum distribution after 1000 collisions. It can be seen that already the momentum distribution is becoming bell-shaped. After 25,000 random collisions, the momentum distribution has already settled down to a gaussian, or normal, distribution in both the $x$ and $y$ directions. Furthermore, the widths of the distribution, or more precisely, their standard deviations are identical in the two orthogonal directions. Again, as we leave the simulation running, notice that the momentum distributions are stationary in the $x$ and $y$ directions - the system has reached a state of statistical equilibrium, but now in 'momentum space'.

Therefore, writing the distributions in terms of the velocities in the $x$ and $y$ directions,

$$
\begin{align*}
& f_{1}\left(v_{x}\right) \mathrm{d} v_{x} \propto \exp \left(-\frac{v_{x}^{2}}{2 \sigma^{2}}\right) \mathrm{d} v_{x},  \tag{3.15}\\
& f_{1}\left(v_{y}\right) \mathrm{d} v_{y} \propto \exp \left(-\frac{v_{y}^{2}}{2 \sigma^{2}}\right) \mathrm{d} v_{y} . \tag{3.16}
\end{align*}
$$

But we notice that the $v_{x}^{2}$ and $v_{y}^{2}$ are just proportional to the kinetic energies of the particles in the $x$ and $y$ directions and so the probability distributions for the energies of the particles in each coordinate are

$$
\begin{equation*}
f_{1}\left(E_{x}\right) \propto \exp \left(-\alpha E_{x}\right) \quad f_{1}\left(E_{y}\right) \propto \exp \left(-\alpha E_{y}\right) . \tag{3.1}
\end{equation*}
$$

Again we have recovered a version of the Boltzmann distribution.

### 3.4 The isothermal atmosphere

We have not yet worked out what the constant $\alpha$ is in the Boltzmann distribution. Let us find it



Figure 3.6: The evolution of a two-dimensional gas of $10^{4}$ particles. The initial distribution of momenta is flat between $\pm 10$ units (top). After only $\sim 10^{3}$ collisions the distribution function becomes bell-shaped (middle). After $\sim 25 \times 10^{3}$ collisions, a gaussian distribution (shown by the solid curve) is obtained in both the $x$ and $y$ directions with the same standard deviation.
by a calculation in classical physics. An isothermal atmosphere is an atmosphere in a gravitational field in which the temperature is the same everywhere. We assume that the gravitational acceleration is uniform locally for heights $h$ small compared with the radius of the Earth $r_{\mathrm{E}}$ and so we approximate the gravitational potential as follows:

$$
\begin{align*}
\phi(h) & =-\frac{G M_{\mathrm{E}}}{r_{\mathrm{E}}+h}=-\frac{G M_{\mathrm{E}}}{r_{\mathrm{E}}}\left(1+\frac{h}{r_{\mathrm{E}}}\right)^{-1}  \tag{3.18}\\
& =-\frac{G M_{\mathrm{E}}}{r_{\mathrm{E}}}+\frac{G M_{\mathrm{E}} h}{r_{\mathrm{E}}^{2}} \tag{3.19}
\end{align*}
$$

If we measure the gravitational potential relative to the value at the surface of the Earth $\phi(0)=$ $-G M_{\mathrm{E}} / r_{\mathrm{E}}$, we can write

$$
\begin{equation*}
\phi(h)=\frac{G M_{\mathrm{E}} h}{r_{\mathrm{E}}^{2}}=|\boldsymbol{g}| h=g h \tag{3.20}
\end{equation*}
$$

Let us now solve the problem of the pressure distribution in a uniform gravitational field. We consider the equilibrium of an element of the atmosphere of thickness $\mathrm{d} h$ at height $h$ above the surface of the Earth, as illustrated in the diagram. The density of the atmosphere is $\rho$.

The pressure on the cylindrical element is isotropic at each point, meaning the same in all directions at that point, and so we can write the pressure at the top surface as $p+\mathrm{d} p$ and that on the bottom as $p$. The weight of the element of atmosphere $\rho A \mathrm{~d} h \times g$ is balanced by the pressure difference between the top and bottom surfaces. Therefore, taking account of the directions of the forces shown in Figure 3.7,

$$
\begin{gather*}
A(p+\mathrm{d} p)+\rho A g \mathrm{~d} h=A p \\
A\left(p+\frac{\mathrm{d} p}{\mathrm{~d} h} \mathrm{~d} h\right)+\rho A g \mathrm{~d} h=A p \\
\frac{\mathrm{~d} p}{\mathrm{~d} h}=-\rho g \tag{3.21}
\end{gather*}
$$

Now, the equation of state of the gas, which relates the pressure to its density and temperature in thermal equilibrium is $p=n k T$, where $n$ is the number density of molecules. Therefore, if $m$ is the average mass of the molecules of the atmosphere, its density

Figure 3.7. Variation of atmospheric pressure with depth

is $\rho=m n$. Substituting into (3.21), we find

$$
\begin{align*}
\mathrm{d} p=-\rho g \mathrm{~d} h & =-n m g \mathrm{~d} h=-\frac{m g p}{k T} \mathrm{~d} h \\
\frac{\mathrm{~d} p}{p} & =-\frac{m g}{k T} \mathrm{~d} h \tag{3.22}
\end{align*}
$$

Integrating from 0 to $h$, we find

$$
\begin{align*}
\int_{p(0)}^{p(h)} \frac{\mathrm{d} p}{p} & =-\int_{0}^{h} \frac{m g}{k T} \mathrm{~d} h \\
p & =p_{0} \exp \left(-\frac{m g h}{k T}\right) \tag{3.23}
\end{align*}
$$

Thus, the pressure and density of an isothermal atmosphere decrease exponentially with increasing height above the surface of the Earth. This is actually quite a good approximation for the pressure distribution in the Earth's atmosphere, which is given in Table 3.2.

Certainly when I have been observing on the summit of Mauna Kea in Hawaii at 4.2 km altitude, you really feel the effects of the decreased atmospheric pressure. Notice that the scale height of the atmosphere, meaning the height at which the pressure is only $1 / \mathrm{e}=0.368$ of its value at sea level is about 8 km . You can understand the problems of scaling $8,000 \mathrm{~m}$ peaks in the Himalayas.

There are all sorts of other consequences. You can measure altitude by measuring local atmospheric pressure. Provided you calibrate the pressure gauge at a known altitude, you can get accuracies of about 5 metres. You notice the difference in performance of propeller-driven aircraft at high altitude - helicopters really have problems in the Himalayas. Water boils at a lower temperature at high altitude, as we will demonstrate in Chapter 7.

Let us now rewrite the expression for the pressure at height $h$ in terms of the number density of particles using $p=n k T$. Then,

$$
\begin{equation*}
n=n_{0} \exp \left(-\frac{m g h}{k T}\right) \tag{3.24}
\end{equation*}
$$

We recognise that the quantity $m g h$ represents the potential energy of a molecule of mass $m$ at height $h$ above the ground. If we set the energy equal to zero

| Table 3.2 |  |  |  |
| :---: | :---: | :---: | :---: |
| Height <br> $(h / \mathrm{km})$ | Pressure <br> $\left(p /\right.$ millibar* $\left.^{*}\right)$ | Relative <br> pressure | Isothermal <br> atmosphere |
| 0.0 | 1013 | 1 | 1 |
| 1.5 | 840 | 0.83 | 0.83 |
| 2.4 | 752 | 0.74 | 0.74 |
| 3.0 | 697 | 0.69 | 0.69 |
| 6.1 | 465 | 0.46 | 0.47 |
| 8.5 | 333 | 0.33 | 0.35 |

* 1 millibar $=100$ Pascal $=100 \mathrm{~Pa}=0.75$ mm of mercury. Normal atmospheric pressure is $1,013.2$ millibar.
at the ground, we can write $E=m g h$. Therefore, we can also write

$$
\begin{equation*}
n=n_{0} \exp \left(-\frac{E}{k T}\right) \tag{3.25}
\end{equation*}
$$

This is a highly suggestive result. We could equally well interpret it as meaning that, if the system is in equilibrium at temperature $T$, the probability $p_{i}(E)$ of finding a molecule $i$ in a state of energy $E$ above zero energy is
$p_{i}(E)=p_{i}(0) \exp \left(-\frac{E}{k T}\right) \quad$ or $\quad p_{i} \propto \exp \left(-\frac{E}{k T}\right)$
We see that the constant $\alpha$ which appears in the exponential is just $1 / k T$, where $T$ is the temperature.

This is, in fact, a special case of the very general result which we quoted in the introduction. To repeat it somewhat more formally,

> If a system, or element of a system, can exist in one of a number of different states, each with a different energy, then, in thermal equilibrium, the probability $p_{i}$ of finding it in the ith state $_{\text {with energy } E_{i} \text { is }}$

$$
\begin{equation*}
p_{i} \propto \exp \left(-\frac{E_{i}}{k T}\right) \tag{3.27}
\end{equation*}
$$

This is $50 \%$ of the content of the Boltzmann distribution.

### 3.5 Degeneracies

The other $50 \%$ of the Boltzmann distribution involves how many states there are available to particles with energy $E_{i}$. If we are dealing with discrete states of energy $E_{i}$, as we will find in quantum systems, the answer is straightforward. If there are $g_{i}\left(E_{i}\right)$ states, all with the same energy $E_{i}$, we say that the degeneracy of the state is $g_{i}\left(E_{i}\right)$. Then, the probability of a particle being found in any state of energy $E_{i}$ is

$$
\begin{equation*}
p_{i} \propto g_{i}\left(E_{i}\right) \exp \left(-\frac{E_{i}}{k T}\right) \tag{3.28}
\end{equation*}
$$

This is the complete expression for the Boltzmann distribution.

We will find a similar result when we deal with a continuous distribution of energy, or momentum, states,

$$
\begin{equation*}
p(E) \mathrm{d} E \propto g(E) \exp \left(-\frac{E}{k T}\right) \mathrm{d} E \tag{3.29}
\end{equation*}
$$

The simplest example we will deal with will be the three-dimensional Maxwellian velocity distribution, which we will discuss in Section 4.4.2.

### 3.6 Conclusion

These arguments make it entirely plausible that the equilibrium distribution contains two factors:

- the Boltzmann factor which describes the probability that a state of energy $E_{i}$ is occupied in thermal equilibrium at temperature $T, p_{i} \propto$ $\exp \left(-E_{i} / k T\right)$.
- the number of states of energy $E_{i}$ which can be occupied by the particles, what we have called the degeneracy $g_{i}$ of the energy state $E_{i}$.

These are the principles which we will develop in the following chapters.

