2.3.1 Bath-and-plate system

To familiarize ourselves with the concept of pressure, we consider a box filled with hard disks and closed off by a piston, at position $x = L$. A spring pushes the piston to the left with constant force, independent of x (see Fig. 2.31). The particles and the piston have kinetic energy. The piston has also potential energy, which is stored in the spring. The sum of the two energies is constant. If the piston is far to the right, the particles have little kinetic energy, because potential energy is stored in the spring. In contrast, at small L, the particles are compressed and they have a higher kinetic energy. As the average kinetic energy is identified with the temperature (see Subsection 2.2.4), the disks are not only at variable volume but also at nonconstant temperature.

It is preferable to keep the piston–box system at constant temperature. We thus couple it to a large bath of disks through a loose elastic plate, which can move along the x-direction over a very small distance Δ (see Fig. 2.34). By zigzagging in this interval, the plate responds to hits from both the bath and the system. For concreteness, we suppose that the particles in the system and in the bath, and also the plate, all have a mass $m = 1$ (the spring itself is massless). All components are perfectly elastic. Head-on collisions between elastic particles of the same mass exchange the velocities (see Fig. 2.33), and the plate, once hit by a bath particle with an x-component of its velocity v_x will start vibrating with a velocity $\pm v_x$ inside its small interval (over the small distance Δ) until it eventually transfers this velocity to another particle, either in the box or in the bath.

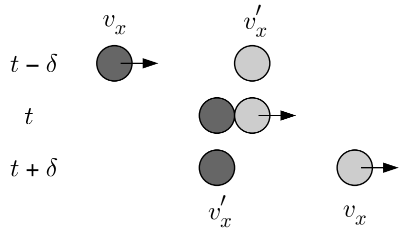

Fig. 2.33 Elastic head-on collision between equal-mass objects (case $v'_x = 0$ shown).

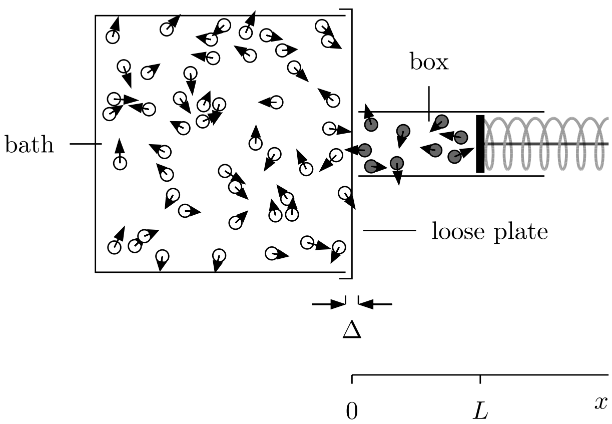

Fig. 2.34 The box containing particles shown in Fig. 2.31, coupled to an infinite bath through a loose plate.

The plate's velocity distribution—the fraction of time it spends at velocity v_x—is not the same as the Maxwell distribution of one velocity component for the particles. This is most easily seen for a bath of Maxwell-distributed noninteracting point particles (hard disks with zero radius): fast particles zigzag more often between the plate and the left boundary of the bath than slow particles, biasing the distribution by a factor $|v_x|$:

$$\pi(v_x)\,\mathrm{d}v_x \propto |v_x| \exp\left(-\beta v_x^2/2\right) \mathrm{d}v_x. \tag{2.12}$$

We note that the Maxwell distribution for one velocity component lacks the $|v_x|$ term of eqn (2.12), and it is finite at $v_x = 0$. The biased distribution, however, must vanish at $v_x = 0$: to acquire zero velocity, the plate must be hit by a bath particle which itself has velocity zero (see Fig. 2.33). However, these particles do not move, and cannot get to the plate. This argument for a biased Maxwell distribution can be applied to a small layer of finite-size hard disks close to the plate, and eqn (2.12) remains valid.

The relatively infrequent collisions of the plate with box particles play no role in establishing the probability distribution of the plate velocity, and we may replace the bath and the plate exactly by a generator of biased Gaussian random velocities (with $v_x > 0$; see Fig. 2.33). The distribution in eqn (2.12) is formally equivalent to the Maxwell distribution for the absolute velocity in two dimensions, and so we can sample it with two independent Gaussians as follows:

$$\begin{aligned} \{\Upsilon_1, \Upsilon_2\} &\leftarrow \{\texttt{gauss}\,(1/\sqrt{\beta})\,, \texttt{gauss}\,(1/\sqrt{\beta})\}, \\ v_x &\leftarrow \sqrt{\Upsilon_1^2 + \Upsilon_2^2}. \end{aligned} \tag{2.13}$$

Alternatively, the sample transformation of Subsection 1.2.4 can also be applied to this problem:

$$\int_0^1 \mathrm{d}\Upsilon = c \int_0^\infty \mathrm{d}u\ \exp(-u) = c' \int_0^\infty \mathrm{d}v_x\ v_x \exp\left(-\beta v_x^2/2\right).$$

The leftmost integral is sampled by $\Upsilon = \texttt{ran}\,(0,1)$. The substitutions $\exp(-u) = \Upsilon$ and $\beta v_x^2/2 = u$ yield

$$v_x \leftarrow \sqrt{\frac{-2\log\left[\texttt{ran}\,(0,1)\right]}{\beta}}.$$

Maxwell boundary

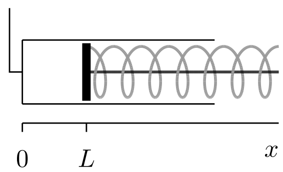

Fig. 2.35 A piston with Maxwell boundary conditions at $x = 0$.

This routine is implemented in Alg. 2.10 (`maxwell-boundary`). It exactly replaces—integrates out—the infinite bath.

procedure `maxwell-boundary`
input $\{v_x, v_y\}$ (disk in contact with plate)
$\Upsilon \leftarrow \texttt{ran}\,(0,1)$
$v_x \leftarrow \sqrt{-2\texttt{log}\,(\Upsilon)\,/\beta}$
output $\{v_x, v_y\}$
——

Algorithm 2.10 `maxwell-boundary`. Implementing Maxwell boundary conditions.

In conclusion, to study the box–bath–piston system, we need not set up a gigantic molecular dynamics simulation with particles on either