

obtain  $T_{\text{kinetic}}$ . Choose units such that  $m$  and Boltzmann's constant  $k$  are unity. How is  $T_{\text{kinetic}}$  related to the mean demon energy? How do your results compare to the relation given in introductory physics textbooks that the total energy of an ideal gas of  $N$  particles in three dimensions is  $E = \frac{3}{2}NkT$ ? (In one dimension the analogous relation is  $E = \frac{1}{2}NkT$ .)

- (e) A limitation of most simulations is the finite number of particles. Is the relation between the mean demon energy and mean kinetic energy per particle the same for  $N = 2$  and  $N = 10$  as it is for  $N = 40$ ? If there is no statistically significant difference between your results for the three values of  $N$ , explain why finite  $N$  might not be an important limitation for the ideal gas in this simulation. ■

### Problem 15.3 Demon energy distribution

- (a) Add a method to class `IdealDemon` to compute the probability  $P(E_d)\Delta E_d$  that the demon has energy between  $E_d$  and  $E_d + \Delta E_d$ . Choose the same parameters as in Problem 15.2 and be sure to determine  $P(E_d)$  only after equilibrium has been obtained.
- (b) Plot the natural logarithm of  $P(E_d)$  and verify that  $\ln P(E_d)$  depends linearly on  $E_d$  with a negative slope. What is the absolute value of the slope? How does the inverse of this value correspond to the mean energy of the demon and  $T_{\text{kinetic}}$  as determined in Problem 15.2?
- (c) Generalize the `IdealDemon` class and determine the relation between the mean demon energy, the mean energy per particle of the system, and the inverse of the slope of  $\ln P(E_d)$  for an ideal gas in two and three dimensions. It is straightforward to write the class so that it is valid for any spatial dimension. ■

## 15.4 ■ THE DEMON AS A THERMOMETER

We found in Problem 15.3 that the form of  $P(E_d)$  is given by

$$P(E_d) \propto e^{-E_d/kT}. \quad (15.3)$$

We also found that the parameter  $T$  in (15.3) is related to the kinetic temperature of an ideal gas.

In Problem 15.4 we will do some further simulations to determine the generality of the form (15.3).

### Problem 15.4 The Boltzmann probability distribution

Modify your simulation of an ideal gas so that the kinetic energy of a particle is proportional to the absolute value of its momentum instead of the square of its momentum. Such a dependence would hold for a relativistic gas where the particles are moving at velocities close to the speed of light. Choose various values of the total energy  $E$  and number of particles  $N$ . Is the form of  $P(E_d)$  the same as in (15.3)? How does the inverse slope of  $\ln P(E_d)$  versus  $E_d$  compare to the mean energy per particle of the system in this case? ■

According to the equipartition theorem of statistical mechanics, each quadratic degree of freedom contributes  $\frac{1}{2}kT$  to the energy per particle. Problem 15.4 shows that the equipartition theorem is not applicable for other dependencies of the particle energy.

Although the microcanonical ensemble is conceptually simple, it does not represent the situation usually found in nature. Most systems are not isolated but are in thermal contact with their environment. This thermal contact allows energy to be exchanged between the laboratory system and its environment. The laboratory system is usually small relative to its environment. The larger system with many more degrees of freedom is commonly referred to as the *heat reservoir* or *heat bath*. The term heat refers to energy transferred from one body to another due to a difference in temperature. A heat bath is a system for which such energy transfer causes a negligible change in its temperature.

A system that is in equilibrium with a heat bath is characterized by the temperature of the latter. If we are interested in the equilibrium properties of such a system, we need to know the probability  $P_s$  of finding the system in microstate  $s$  with energy  $E_s$ . The ensemble that describes the probability distribution of a system in thermal equilibrium with a heat bath is known as the *canonical ensemble*. In general, the canonical ensemble is characterized by the temperature  $T$ , the number of particles  $N$ , and the volume  $V$ , in contrast to the microcanonical ensemble which is characterized by the energy  $E$ ,  $N$ , and  $V$ .

We have already discussed an example of a system in equilibrium with a heat bath, the demon! In Problems 15.2–15.4, the system of interest was an ideal gas and the demon was an auxiliary (special) particle that facilitated the exchange of energy between the particles of the system. If we take the demon to be the system of interest, we see that the demon exchanges energy with a much bigger system (the ideal gas), which we can take to be the heat bath. We conclude that the probability distribution of the microstates of a system in equilibrium with a heat bath has the same form as the probability distribution of the energy of the demon. (Note that the microstate of the demon is characterized by its energy.) Hence, the probability that a system in equilibrium with a heat bath at temperature  $T$  is in microstate  $s$  with energy  $E_s$  has the form given by (15.3):

$$P_s = \frac{1}{Z} e^{-\beta E_s} \quad (\text{canonical distribution}), \quad (15.4)$$

where  $\beta = 1/kT$  and  $Z$  is a normalization constant. Because  $\sum P_s = 1$ ,  $Z$  is given by

$$Z = \sum_s e^{-E_s/kT}. \quad (15.5)$$

The sum in (15.5) is over the microstates of the system for a given  $N$  and  $V$ . The quantity  $Z$  is the *partition function* of the system. The ensemble defined by (15.4) is known as the *canonical ensemble*, and the probability distribution (15.4) is the *Boltzmann* or the *canonical distribution*. The derivation of the Boltzmann distribution is given in textbooks on statistical mechanics. We will simulate systems in equilibrium with a heat bath in Section 15.6.

The partition function plays a key role in statistical mechanics, because the (Helmholtz) free energy  $F$  of a system is defined as

$$F = -kT \ln Z. \quad (15.6)$$

All thermodynamic quantities can be found from various derivatives of  $F$ . In equilibrium the system will be in the state of minimum  $F$  for given values of  $T$ ,  $V$ , and  $N$ . (This result