

# Time asymmetry in a dynamical model of the one-dimensional ideal gas

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We present a simple dynamical model of the one-dimensional ideal gas and show how it can be used to introduce a number of fundamental ideas in statistical mechanics. We use the model to illustrate the role of initial conditions in explaining time asymmetry and show that although the dynamical model is time-reversal invariant, the macroscopic behavior of the gas can be time-asymmetric if the initial conditions are chosen properly. © 2008 American Association of Physics Teachers.  
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## I. INTRODUCTION

In this paper we present a simple dynamical model of the one-dimensional ideal gas and show how it can be used to illustrate a number of fundamental ideas in statistical mechanics. Statistical mechanics allows us to understand the equilibrium behavior of a complicated dynamical system by averaging over all the possible states that the system can occupy. For our model we can both evolve the system in time and perform the statistical averaging, so we can show that it does evolve toward an equilibrium state with the properties predicted by statistical mechanics. We use the model to help clarify the role of initial conditions in explaining thermodynamic time-asymmetry; that is, the tendency of thermodynamic systems to evolve toward an equilibrium state, and not away from it.<sup>1,2</sup> We show that although the model is time-reversal invariant, the macroscopic behavior of the gas can be time-asymmetric if the initial conditions are chosen properly. The paper should be accessible to advanced undergraduates, and is intended to supplement an introductory course in statistical mechanics.

## II. DYNAMICAL MODEL

The model that we consider describes a collection of  $N$  atoms which bounce back and forth between a fixed wall and a movable piston. The atoms collide only with the wall and piston, and not with one another. A constant force  $F$  is applied to the piston, pushing it inward toward the wall and counterbalancing the outward pressure that results from collisions with the atoms. We define  $m$  to be the mass of a single atom,  $M$  to be the mass of the piston, and  $r \equiv M/m$  to be the ratio of the piston mass to the atom mass. We denote the position and velocity of the piston by  $\{X, V\}$ , and the positions and velocities of the atoms by  $\{\vec{x}, \vec{v}\}$  (each component of the vectors  $\{\vec{x}, \vec{v}\}$  denotes a different atom). The coordinate system is chosen such that the wall is at the origin. The total energy of the system is  $E_{\text{tot}} = E_a + E_p$ , where  $E_a = m\vec{v} \cdot \vec{v}/2$  is the total energy of the atoms and  $E_p = MV^2/2 + FX$  is the energy of the piston. The system is conservative, so the total energy is a constant of the motion.

The time evolution of the system can be understood by first considering the case of a single atom (see Fig. 1). Suppose that at time  $t_i$  we start the system in the initial state  $\{x_0, v_0, X_0, V_0\}$ , and we evolve the system until the atom collides with either the piston or the wall. Let  $\{x_1, v_1, X_1, V_1\}$  and  $\{x_2, v_2, X_2, V_2\}$  denote the state of the system just before and just after the collision, and let  $t_c = t_i + \tau$  denote the time at which the collision occurs. Note that

$$\{x_1, v_1, X_1, V_1\} = \{x_0 + v_0\tau, v_0, X_0 + V_0\tau - a\tau^2/2, V_0 - a\tau\}, \quad (1)$$

where  $a \equiv F/M$  is the acceleration that results from the constant force applied to the piston.

We can determine whether the atom collides with the piston or the wall as follows. If we ignore the wall, then the atom collides with the piston at time  $t_c = t_i + \tau_p$ , where  $\tau_p = (V_0 - v_0 + ((V_0 - v_0)^2 + 2a(X_0 - x_0))^{1/2})/a$ . If we ignore the piston, then for  $v_0 \geq 0$  the atom never collides with the wall, and for  $v_0 < 0$  the atom collides with the wall at time  $t_c = t_i + \tau_w$ , where  $\tau_w = -x_0/v_0$ . Thus, for  $v_0 \geq 0$  the atom always collides with the piston, and for  $v_0 < 0$  the atom collides with the piston if  $\tau_p < \tau_w$  and with the wall if  $\tau_p > \tau_w$ .

If the atom collides with the piston, then the state of the system just before the collision is given by substituting  $\tau = \tau_p$  into Eq. (1), and the state of the system just after the collision can be obtained by applying the conservation laws of energy and momentum

$$v_1^2 + rV_1^2 = v_2^2 + rV_2^2, \quad (2)$$

$$v_1 + rV_1 = v_2 + rV_2. \quad (3)$$

The solution for  $v_2$  and  $V_2$  is

$$v_2 = (r + 1)^{-1}(2rV_1 - (r - 1)v_1), \quad (4)$$

$$V_2 = (r + 1)^{-1}((r - 1)V_1 + 2v_1). \quad (5)$$

The positions of the atom and piston do not change during the collision, so  $x_2 = X_2 = x_1 = X_1$ .

If the atom collides with the wall, then the state of the system just before the collision is given by substituting  $\tau = \tau_w$  into Eq. (1), and the state of the system just after the collision can be obtained by reversing the velocity of the atom:  $\{x_2, v_2, X_2, V_2\} = \{x_1, -v_1, X_1, V_1\}$ .

These results allow us to evolve an arbitrary initial state into the state of the system just after the next collision:  $\{x_0, v_0, X_0, V_0\} \rightarrow \{x_2, v_2, X_2, V_2\}$ . If we take the time-evolved state as the new initial state, this mapping can be iterated to evolve the system through as many collisions as we like. Although we have only considered a single atom, it is straightforward to generalize to  $N$  atoms: we calculate the time until the next collision for each atom, select the atom that collides first, and then proceed as for the one-atom case. (Note that when we evolve the system from time  $t_i$  to time  $t_c$ , the positions of the  $N - 1$  unselected atoms must also be updated.)

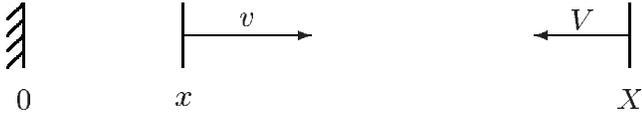


Fig. 1. Schematic of the system for a single atom: shown are the wall, atom, and piston at positions 0,  $x$ , and  $X$ . The velocities of the atom and piston are  $v$  and  $V$ .

### III. STATISTICAL MECHANICS

Before investigating the dynamical model, let us first review the statistical mechanics of an ideal gas. Consider an ideal gas of  $N$  atoms of mass  $m$ , which are confined to a region of fixed length  $L$ . The state of the gas is uniquely determined by specifying the positions  $\vec{x}$  and momenta  $\vec{p}$  of the atoms, and these quantities serve as coordinates  $\{\vec{x}, \vec{p}\}$  for the  $2N$ -dimensional phase space of the system. We will assume that the gas is thermally isolated, so the total energy  $E = |\vec{p}|^2/2m$  is conserved. Thus, the points in phase space that correspond to physically possible states lie on a  $(2N-1)$ -dimensional constant-energy surface, which is called the state space of the system.

For a given state in state space we can plot the position and momentum of each of the  $N$  atoms as a point in the  $x-p$  plane. Because we hold  $L$  and  $E$  fixed, these points will lie within a rectangular region defined by  $0 \leq x \leq L$ ,  $|p| \leq (2mE)^{1/2}$ . Let us partition this region into  $K$  cells of area  $\Lambda$ , and define  $n_k$  to be the number of points in cell  $k$ . Thus, for each state we obtain a corresponding list  $\{n_k\}$ . These lists give us a partial description of the state of the gas: they tell us how the position and momentum values of the atoms are distributed, but not which pair of values corresponds to which atom. Many different states can correspond to the same distribution list, so each list  $\{n_k\}$  defines a subspace  $\Sigma[\{n_k\}]$  consisting of states corresponding to that list. Let us define  $\Omega[\{n_k\}]$  to be the volume of the subspace  $\Sigma[\{n_k\}]$ . This volume is proportional to the number of ways that  $N$  distinguishable atoms can be distributed among  $K$  cells such that there are  $n_k$  atoms in cell  $k$ :

$$\Omega[\{n_k\}] = \left( \frac{N!}{n_1! n_2! \cdots n_K!} \right) \Omega_0, \quad (6)$$

where  $\Omega_0$  is a volume that is set by the cell size  $\Lambda$ . We can obtain a dimensionless measure of the volume by dividing  $\Omega[\{n_k\}]$  by  $N! \Omega_0$ , and we will define the entropy of the distribution list  $\{n_k\}$  to be the logarithm of this quantity:<sup>3</sup>

$$S[\{n_k\}] = \ln \frac{\Omega[\{n_k\}]}{N! \Omega_0} \simeq - \sum_k n_k \ln n_k, \quad (7)$$

where we used Stirling's approximation  $\ln n! \simeq n \ln n$ .

The distribution lists are discrete and rely on an arbitrary partitioning of the  $x-p$  plane into cells, but if  $N$  and  $K$  are large enough, we can approximate a list  $\{n_k\}$  by a continuous distribution  $f(x, p)$ , defined such that  $f(x, p) \simeq n_k / \Lambda$  if  $(x, p)$  lies in cell  $k$ . For small  $\delta x$  and  $\delta p$  the quantity  $f(x, p) \delta x \delta p$  gives the number of atoms with coordinates within  $\delta x/2$  of  $x$  and momenta within  $\delta p/2$  of  $p$ . We can obtain an expression for the entropy of a distribution  $f(x, p)$  by replacing the sum in Eq. (7) with integrals over position and momentum:

$$S[f(x, p)] = - \int \int f(x, p) \ln(\Lambda f(x, p)) dx dp. \quad (8)$$

We are interested in the entropy because it allows us to assign probabilities to distributions. The assignment relies on the ergodic hypothesis, which asserts that for extremely long time scales,<sup>4</sup> the amount of time the system spends in a given region of state space is proportional to the volume of the region. Because the probability that the system occupies a given region is the fraction of time that it spends there, the ergodic hypothesis gives a probability measure on state space. In our case, we want to know the probability that the distribution of the gas is  $f(x, p)$ ; this probability is proportional to the volume  $\Omega[f(x, p)]$  of the subspace  $\Sigma[f(x, p)]$ , and the volume  $\Omega[f(x, p)]$  is proportional to  $\exp(S[f(x, p)])$ .

A distribution of particular importance is the Maxwell distribution

$$f_M(x, p) = n \theta(x) \theta(L-x) (2\pi \bar{p}^2)^{-1/2} e^{-p^2/2\bar{p}^2}, \quad (9)$$

where  $n \equiv N/L$  is the number density and  $\bar{p} \equiv (2mE/N)^{1/2}$  is the root-mean-square momentum. In the limit of large  $N$  the Maxwell distribution is the unique distribution that maximizes the entropy.<sup>5</sup> If we substitute the Maxwell distribution into Eq. (8), we find that the maximum possible entropy is

$$S_M = S[f_M(x, p)] = N(\ln(\sqrt{2\pi} \bar{p} / \Lambda n) + 1/2). \quad (10)$$

Also, for large  $N$  almost all the states in state space have distributions that are very close to the Maxwell distribution.<sup>6</sup> As we shall see, these properties of the Maxwell distribution have important implications for the evolution of an ideal gas.

### IV. DYNAMICAL EVOLUTION

The evolution of a system is governed by a set of equations of motion for the phase space coordinates. For many systems, including our dynamical model, the equations of motion are invariant under time-reversal, by which we mean the following. Let us define a motion-reversal operator  $\mathcal{R}$  that acts on states by flipping the signs of the momenta:

$$\mathcal{R}\{\vec{x}(t), \vec{p}(t)\} = \{\vec{x}(t), -\vec{p}(t)\}. \quad (11)$$

Also, let us define an operator  $\mathcal{E}_\tau$  that evolves states by integrating the equations of motion:

$$\mathcal{E}_\tau\{\vec{x}(t), \vec{p}(t)\} = \{\vec{x}(t + \tau), \vec{p}(t + \tau)\}. \quad (12)$$

When we say that the equations of motion are time-reversal invariant, we mean that reversing the motion and then evolving the system forward in time is equivalent to evolving the system backward in time and then reversing the motion.<sup>7</sup>  $\mathcal{E}_\tau \mathcal{R} = \mathcal{R} \mathcal{E}_{-\tau}$ . For example, the equations of motion for a harmonic oscillator are time-reversal invariant, while the equations of motion for a damped harmonic oscillator are not time-reversal invariant.

Although the equations of motion for a gas are time-reversal invariant, the macroscopic behavior of gases is often time-asymmetric. For example, suppose a gas is initially confined to a bottle, and we release the gas by opening the bottle in a sealed room. The gas will rapidly expand until it fills the entire room, but the reverse evolution, in which the gas moves from the room to the bottle, never occurs. The expansion of the gas is an example of an irreversible process. We say that a process is irreversible if the process could

plausibly occur in the real world, but the equivalent time-reversed process could not occur. Many thermodynamic processes are irreversible in this sense. In addition to the example of the expanding gas, consider the flow of energy from a hot object to a cold object, or the evolution of a gas toward the Maxwell distribution. As a counterexample, consider an elastic collision between two atoms: the process is reversible, because time-reversing the collision yields a collision that is just as plausible.<sup>8</sup>

Whereas time-reversal invariance is a property of the equations of motion, reversibility is a property of the solutions to these equations. Also, time-reversal invariance is a clearly defined property that the equations of motion either do or do not possess, but reversibility is a less well-defined concept. Consider again the example of the expanding gas, but now imagine that the gas consists of only a few atoms and that the room and bottle are comparable in volume. If the atoms were initially dispersed throughout the room, we would not be surprised if they all spontaneously returned to the bottle. But as we increase the number of atoms and decrease the volume of the bottle, such an event becomes less and less likely. At some point we would say that the expansion of the gas constitutes an irreversible process, but there is not a clear-cut boundary.<sup>9</sup>

The time-reversal invariance of the equations of motion might appear to be inconsistent with the existence of irreversible processes,<sup>10</sup> but there is no real contradiction: the behavior of a gas is determined not only by the equations of motion, but also by the choice of the initial state. It is the choice of the initial state that is responsible for the existence of irreversible processes.

Perhaps the most natural way to choose the initial state is to pick a state at random from the state space using the probability measure provided by the ergodic hypothesis. Because the vast majority of states have distributions that are very close to  $f_M(x,p)$  and entropies that are very close to  $S_M$ , this procedure almost always yields a state with these properties. If we evolve such a state in time, either forward or backward, its entropy is unlikely to deviate significantly from  $S_M$ . In other words, the system we obtain is near thermal equilibrium, and does not deviate significantly from thermal equilibrium when evolved forward or backward in time. The macroscopic behavior of such a system is time-symmetric, and there are no irreversible processes.

If we want to obtain a nonequilibrium system, we cannot randomly pick the initial state from the entire state space. One way to obtain a nonequilibrium system is to randomly pick a state from the subspace of states whose entropy is equal to some specified value  $S_0$ , where  $S_0 < S_M$ . Note that for  $S_0 < S_M$ , the constraint  $S[f(x,p)] = S_0$  does not specify a unique distribution  $f(x,p)$ ; there are many distributions that satisfy this requirement. Thus, another way of obtaining a nonequilibrium system is to choose a particular distribution  $f_0(x,p)$  such that  $S[f_0(x,p)] = S_0$ , and then randomly pick a state from the subspace  $\Sigma[f_0(x,p)]$ . For either of these selection procedures it is very likely that as we evolve the resulting state in time, either forward or backward, the entropy will monotonically increase from  $S_0$  to  $S_M$ , and the distribution will approach the Maxwell distribution. The reason we expect this type of evolution is that almost all the states in state space have distributions close to the Maxwell distribu-

tion, so in the absence of any constraints the initial state will tend to evolve into a state whose distribution is close to the Maxwell distribution.

As an example, consider the distribution

$$f_0(x,p) = \frac{n}{2p_0} \theta(x) \theta(L-x) \theta(p_0 - |p|), \quad (13)$$

where  $p_0 \equiv \sqrt{3\bar{p}} = (6mE/N)^{1/2}$ . This distribution describes states in which the atoms are uniformly spread throughout a rectangular region in  $x-p$  space, and has entropy

$$S_0 = S[f_0(x,p)] = N \ln(\sqrt{12\bar{p}}/\Lambda n). \quad (14)$$

## V. COMPUTER SIMULATION

To illustrate these ideas we will use the dynamical model presented in Sec. II to simulate the evolution of an ideal gas. First we need to relate the dynamical model to the statistical mechanical description given in Sec. III.

In Sec. III we considered a gas in which we held fixed the number of atoms  $N$ , the length  $L$ , and the energy  $E$ . In our dynamical model we also fix the number of atoms, but because the atoms can push against the piston, the length  $X(t)$  and the energy  $E_a(t)$  may vary. For our dynamical model to give the same equilibrium behavior as a gas with fixed  $N$ ,  $L$ , and  $E$ , we want to choose the parameters of the model such that the number of atoms is  $N$ , the equilibrium value of  $X(t)$  is  $L$ , and the equilibrium value of  $E_a(t)$  is  $E$ . Thus, given  $N$ ,  $L$ , and  $E$ , we need to choose the force  $F$  and the initial state  $\{\vec{x}_0, \vec{v}_0, X_0, V_0\}$  so that these conditions are met.

To determine the force we note that in equilibrium the force  $F$  balances the pressure  $P$  of the gas ( $F=P$ ), the system obeys the ideal gas law ( $PL=NT$ , where  $T$  is the temperature), and the total energy is  $E=NT/2$ . From these conditions we find that  $F=2E/L$ . To choose the initial state we take  $X_0=L$ ,  $V_0=0$ , and we randomly choose  $\{\vec{x}_0, \vec{v}_0\}$  from the state space with energy  $E$ . To obtain an equilibrium system we choose from the entire state space,<sup>11</sup> and to obtain a nonequilibrium system we choose from the subspace  $\Sigma[f_0(x,p)]$ .

We also need to express Eq. (8) for the entropy in a form that can be applied to the simulations. Let us introduce a small momentum interval  $\delta p$ , where  $\delta p \ll \bar{p}$ , and define  $n_k$  to be the number of atoms with momentum between  $(k-1/2)\delta p$  and  $(k+1/2)\delta p$ . If we assume that the atoms are uniformly distributed in space,<sup>12</sup> then  $n_k = f(x, k\delta p)X\delta p$ , and we can approximate Eq. (8) by

$$S = - \sum_k n_k \ln((\Lambda/X\delta p)n_k), \quad (15)$$

where the sum is over all values  $k$  such that  $n_k \neq 0$ . The value of the entropy depends on the cell size  $\Lambda$ ; a convenient choice for this quantity is  $\Lambda = \bar{p}/n$ . If we substitute  $\Lambda = \bar{p}/n$  into Eqs. (10) and (14) for the entropies of  $f_M(x,p)$  and  $f_0(x,p)$ , we find that  $S_M = (N/2)(1 + \ln 2\pi) \approx 1.419N$  and  $S_0 = (N/2)(\ln 12) \approx 1.242N$ .

Once we have chosen an initial state at  $t=0$ , we can evolve the system forward and backward<sup>13</sup> in time using the method described in Sec. II. In Fig. 2 we plot the entropy per atom as a function of time. Curves are shown for two initial states: initial state  $A$  was chosen at random from the entire state space to obtain an equilibrium system, and initial state  $B$  was

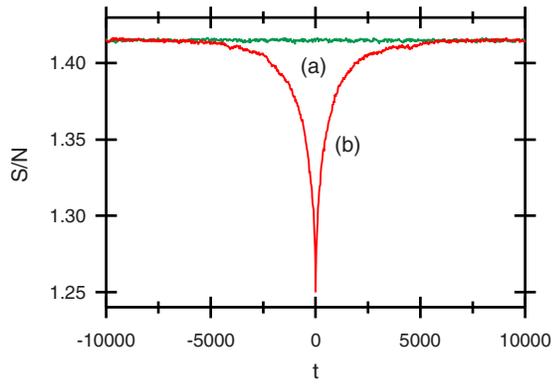


Fig. 2. Entropy per atom  $S/N$  versus the time  $t$ : (a) initial state  $A$  randomly chosen from the entire state space; (b) initial state  $B$  randomly chosen from the subspace  $\Sigma[f_0(x,p)]$ .

chosen at random from the subspace  $\Sigma[f_0(x,p)]$  to obtain a nonequilibrium system.<sup>14</sup> For these simulations  $N=10^4$  and  $r=10^3$ , and we have chosen units for distance and time such that  $a=\bar{p}/m=1$ . To calculate the entropy, we have chosen  $\delta p=\bar{p}/10$ .

As we predicted in Sec. IV, if we evolve the system starting from state  $A$ , then the entropy remains near the maximum possible value  $S_M$ , and if we evolve the system starting from state  $B$ , the entropy monotonically increases from  $S_0$  until it reaches  $S_M$ , after which it stays nearly constant. From Fig. 2, we see that for state  $B$  the entropy reaches  $S_M$  at time  $t_E \approx 6 \times 10^3$ . Note that during the interval  $[0, t_E]$  the entropy increases as the system is evolved forward in time, and during  $[-t_E, 0]$  the entropy increases as the system is evolved backward in time, so during  $[-t_E, t_E]$  the behavior of the system is time-asymmetric.

It might appear that the system violates the second law of thermodynamics during the interval  $[-t_E, 0]$ , but no such violation occurs. The second law of thermodynamics, as applied to this system, does not state that the entropy increases with increasing  $t$ , but rather that the entropy increases as we evolve the system away from the initial state  $B$  that we imposed at  $t=0$ .<sup>15</sup> The second law expresses the fact that because almost all the states in state space have entropy near  $S_M$ , almost all the states in  $\Sigma[f_0(x,p)]$  will evolve into states with entropy near  $S_M$ , and they will tend to do so whether we evolve the states forward or backward in time.<sup>16</sup>

In Sec. IV we also predicted that if we evolve the system in time starting from state  $B$ , the distribution should evolve from  $f_0(x,p)$  to  $f_M(x,p)$ . To check this prediction we start the system in state  $B$ , evolve it to time  $t$ , and then plot the momentum distribution of the atoms. Figure 3 shows momentum histograms for different values of  $t$ , where as before  $N=10^4$  and  $r=10^3$ . We see that the momentum distribution of the atoms evolves toward the Maxwell distribution, again confirming that the equilibrium behavior of the dynamical model agrees with the predictions of statistical mechanics.<sup>17</sup>

## VI. ADDITIONAL APPLICATIONS

Although our primary focus has been on using the dynamical model to clarify the origin of thermodynamic time-asymmetry, it has many other applications. As an illustration we will use the model to simulate the quasistatic expansion and contraction of an ideal gas.

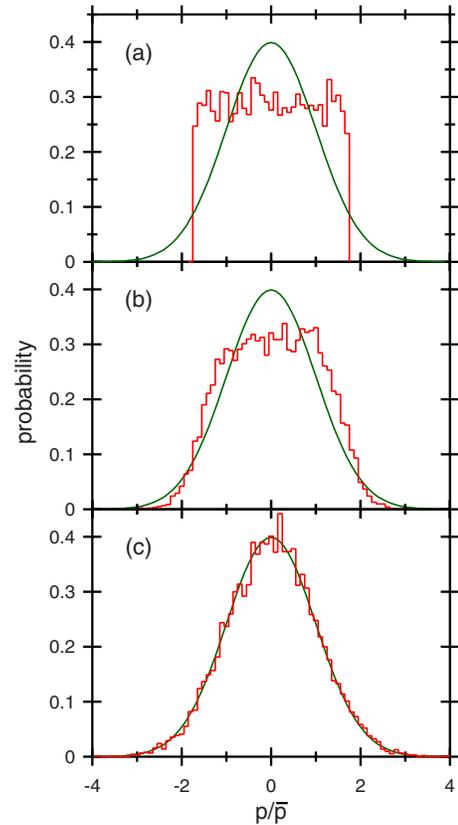


Fig. 3. Momentum distribution of the atoms after starting in state  $B$  and evolving the system to time  $t$ : (a)  $t=0$ , (b)  $t=10^3$ , and (c)  $t=10^4$ . For comparison, the Maxwell distribution is also plotted on each graph.

Suppose we start the system in an equilibrium state, and then give the piston a small momentum kick. The piston will begin to oscillate about its equilibrium position, causing the gas to expand and contract. If we assume that the expansion and contraction are quasistatic, then it is straightforward to show<sup>18</sup> that the frequency of these oscillations is  $\omega=(3F/ML)^{1/2}$ . The quasistatic assumption is justified if the maximum velocity of the piston is small compared to the root-mean-square velocity of the atoms. The root-mean-square velocity of the atoms is  $\bar{v}=(2E/mN)^{1/2}=(FL/mN)^{1/2}$ , where we have used the relation  $F=2E/L$  derived in Sec. V. If the amplitude of the oscillations is  $\delta X$ , then the maximum velocity of the piston is  $V_{\max}=\omega\delta X$ . Thus, the quasistatic assumption is justified when  $(\delta X/L)^2 \ll r/N$ . In Fig. 4 we

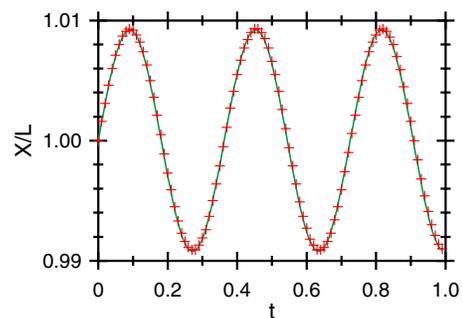


Fig. 4. Periodic oscillations of the piston: shown is  $X/L$  versus the time  $t$ . The points are from a simulation of the model; the solid line is the theoretical prediction.

show the results of a simulation of the oscillations. For this simulation  $N=10^4$  and  $r=10^6$ , so the quasistatic assumption is justified.

## ACKNOWLEDGMENT

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<sup>1</sup>Thermodynamic time-asymmetry can also be demonstrated using simple toy models. See P.-M. Binder, J. M. Pedraza, and S. Garzón, “An invertibility paradox,” *Am. J. Phys.* **67**(12), 1091–1093 (1999), which uses a chaotic mapping; V. Ambegaokar and A. A. Clerk, “Entropy and time,” *ibid.* **67**(12), 1068–1073 (1999), which uses Ehrenfest’s double-urn model; and G. R. Fowles, “Time’s arrow: A numerical experiment,” *ibid.* **62**(4), 321–328 (1994), which uses a toy model involving plane waves.

<sup>2</sup>The computer program used to perform these simulations will be provided upon request.

<sup>3</sup>Here we are only considering entropy in the context of the ideal gas. An overview of entropy in other contexts is given in K. Andrew, “Entropy,” *Am. J. Phys.* **52**(6), 492–496 (1984). A qualitative discussion of entropy is given in D. F. Styer, “Insight into entropy,” *ibid.* **68**(12), 1090–1096 (2000). The concept of entropy can also be introduced by explicitly counting microstates in discrete toy models; this approach is discussed in T. A. Moore and D. V. Schroeder, “A different approach to introducing statistical mechanics,” *ibid.* **65**(1), 26–36 (1997); M. I. Sobel, “A model for introducing the concept of entropy,” *ibid.* **61**(10), 941–942 (1993).

<sup>4</sup>By “extremely long” we mean long compared to the Poincaré recurrence time; that is, long enough that the system has a chance to sample the entire state space. By looking over such time scales, we ensure that the fraction of time that the system spends in a given region is independent of the initial conditions.

<sup>5</sup>See L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1*, 3rd ed. (Pergamon, Tarrytown, 1980), Sec. 40.

<sup>6</sup>For a given distribution  $f(x,p)$ , we can define a quantity  $P(x,p) = (\delta x \delta p / N) f(x,p)$  that gives the probability that an atom is within  $(\delta x/2, \delta p/2)$  of  $(x,p)$ ; for the Maxwell distribution  $P_M(x,p) = (\delta x \delta p / N) f_M(x,p)$ . We can show that if we average over the entire state space, the root-mean-square deviation of  $P(x,p)$  from  $P_M(x,p)$  is proportional to  $1/\sqrt{N}$  in the limit of large  $N$ . See K. Huang, *Statistical Mechanics*, 2nd ed. (Wiley, New York, 1987), Sec. 4.3.

<sup>7</sup>Time-reversal invariance is discussed in J. J. Sakurai, *Modern Quantum Mechanics* (Addison-Wesley, Reading, MA, 1994), Sec. 4.4

<sup>8</sup>There are also reversible thermodynamic processes such as the quasistatic process that we consider in Sec. VI. See M. Samiullah, “What is a reversible process?” *Am. J. Phys.* **75**(7), 608–609 (2007).

<sup>9</sup>For a more extensive discussion of irreversibility see R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, 1963), Vol. 1, Chap. 46.

<sup>10</sup>This apparent inconsistency was pointed out by Loschmidt in a 1876 paper that criticized Boltzmann’s derivation of the  $H$ -theorem, and is known as Loschmidt’s paradox. The historical development of the paradox is discussed in S. G. Brush, *The Kind of Motion We Call Heat* (North-Holland, Amsterdam, 1976).

<sup>11</sup>In the limit of large  $N$ , randomly choosing from the entire state space is equivalent to randomly choosing from the subspace  $\Sigma[f_M(x,p)]$ , because in this limit almost all the states in state space have distributions close to  $f_M(x,p)$ .

<sup>12</sup>The atoms are uniformly distributed in space for the initial states that we will consider, and will tend to remain uniformly distributed as the system evolves in time. Hence, this assumption is justified.

<sup>13</sup>To evolve the system backward in time, we motion-reverse the initial state, evolve it forward in time, and then motion-reverse the time-evolved state.

<sup>14</sup>To obtain state  $B$  we choose position and momentum values for each of the  $N$  atoms by randomly sampling the distribution  $f_0(x,p)$ . From Eq. (13), it follows that randomly sampling  $f_0(x,p)$  amounts to taking  $x = r_1 L$  and  $p = (2r_2 - 1)p_0$ , where  $r_1$  and  $r_2$  are randomly chosen from the interval  $[0,1]$  using a uniform probability distribution.

<sup>15</sup>This statement is only probabilistically true: it is possible, though unlikely, that the entropy will decrease when the system is evolved away from initial state  $B$ . The probability of such an entropy decrease is quantified by the fluctuation theorem, which was first proposed in D. J. Evans, E. G. D. Cohen, and G. P. Morriss, “Probability of second law violations in shearing steady states,” *Phys. Rev. Lett.* **71**, 2401–2404 (1993).

<sup>16</sup>Note that the second law does not say that the entropy increases when the system is evolved away from any low entropy state. For example, we can define a low entropy state  $C$  by evolving state  $B$  to  $t = 2 \times 10^3$ ; for state  $C$  the entropy increases when evolved forward, but decreases when evolved backward.

<sup>17</sup>A simulation of the evolution of the velocity distribution for the two-dimensional ideal gas is discussed in J. Novak and A. B. Bortz, “The evolution of the two-dimensional Maxwell-Boltzmann distribution,” *Am. J. Phys.* **38**(12), 1402–1406 (1970).

<sup>18</sup>The derivation of this result is left as an exercise for students; note that the equation of motion for the piston is  $M\ddot{X} = P - F$ , and that for quasistatic expansion and contraction  $PX^3$  is a constant, so  $PX^3 = FL^3$ .