

# Entropy and time

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The emergence of a direction of time in statistical mechanics from an underlying time-reversal-invariant dynamics is explained by examining a simple model. The manner in which time-reversal symmetry is preserved and the role of initial conditions are emphasized. An extension of the model to finite temperatures also is discussed. © 1999 American Association of Physics Teachers.

## I. INTRODUCTION

The second law of thermodynamics is usually stated as the inequality  $\Delta S \geq 0$  for an isolated system, where  $S$  is the entropy. Implicit in thermodynamics is thus a direction of time determined by the evolution toward equilibrium of a macroscopic system with no external influences. The extent to which this notion emerges from statistical mechanics based on an underlying time-reversal-invariant dynamics is the topic of this paper.

The point of view taken here is not controversial; it has been accepted since the work of Boltzmann<sup>1</sup> was understood. Including the topic in this special issue may thus seem unnecessary. However, our impression is that many undergraduate (and even many graduate) courses do not cover this thought-provoking topic adequately. The reason may be that the message can be lost in subtleties described by words such as *Stosszahlansatz*, *Umkehrinwand*, and *Wiederkehrinwand*, and by discussing the topic in the context of Boltzmann's equation, Liouville's theorem, and coarse graining. An alternative is to discuss simple concrete models. We will consider one that is easy to simulate and has a long history: the 1907 double-urn model of Paul and Tatiana Ehrenfest.<sup>2</sup> Our treatment is based in part on Chapter 10 of Ref. 3.

The outline of the paper is as follows. After a brief general discussion, the way in which a direction of time follows from the statistics of large numbers is illustrated using the Ehrenfest model (in its dog–flea version). The difference between time symmetric fluctuations and the time evolution of a macroscopically identifiable nonequilibrium initial condition is emphasized. Calculations are done for a single system and for an ensemble of systems, the latter being described by a Markovian equation. With the passage of time (no pun intended), the model has become more topical than its conceivers could have imagined. Here it is used to describe the approach to equilibrium of two-level quantum systems such as spins. Temperature is introduced into the model via a METROPOLIS algorithm, and the approach to equilibrium at constant temperature is discussed, including a population-inversion (negative temperature) initial condition. To our knowledge, the Ehrenfest model has not been used in this way, especially as regards the introduction of temperature.

## II. BACKGROUND

From the point of view of thermal physics, the state of an isolated physical system with many degrees of freedom is specified by its energy and other macroscopic parameters such as volume and magnetization. The assumption of many degrees of freedom implies a dense spectrum of excitations, and thus a very large number of microscopic states in a small

energy interval consistent with the given macroscopic parameters. The starting point of a statistical analysis of a mechanical system is the enumeration (allowed in principle by both quantum and classical mechanics) of these microscopic states. The fundamental postulate of equilibrium statistical mechanics is that each of them is equally probable in equilibrium; the logarithm of their number is the entropy associated with the thermodynamic equilibrium of the isolated system.

We are interested in how equilibrium is reached. A reasonable, but incorrect, expectation is that if the microscopic states are not equally likely at some instant, the evolution will be toward a situation in which they are. If the number of microstates explored by the system increased with time, its logarithm or entropy would also increase, giving a statistical underpinning to the rule that an increase of entropy characterizes spontaneous processes in isolated systems.

The trouble with this too simple idea is that not every one of the microscopic configurations consistent with a given macroscopic nonequilibrium state tends, under the action of the laws of mechanics, toward equilibrium, although most of them do. As a result the strict inequality in the second law has to be replaced by a statement of overwhelming likelihood in statistical mechanics, thereby allowing the latter to be consistent with the time-symmetric equations of motion. A tiny loophole now opens, with the consequence that there is no longer a strict logical connection between the direction of time and the increase of entropy: One can never rule out the overwhelmingly unlikely possibility that a low entropy initial condition is a time-symmetric giant fluctuation caught midway. To close the loophole, we have to make the extremely reasonable hypothesis that macroscopic deviations from equilibrium are due to externally imposed initial conditions.

The word “overwhelming” is not being used lightly. To illustrate its meaning, consider the ratio of the number of microscopic configurations for a gas filling all or 99.99% of a container. If we treat the  $N$  molecules of the gas as very weakly interacting, an estimate for this ratio is  $0.9999^{-N}$ , because each molecule has 0.01% fewer available states in the smaller volume. For a liter,  $N$  is order  $10^{22}$ , so that the *logarithm* of the ratio is  $10^{18}$ . The reciprocal of the ratio is thus very small indeed. Yet, this unimaginably tiny number is the probability that a gas in equilibrium in the entire container would be found to be occupying 99.99% of its volume, and thus to have undergone a small but macroscopic entropy-reducing spontaneous fluctuation.

## III. THE DOG–FLEA MODEL

Treating the evolution of a reasonably realistic statistical system is technically difficult. Even for a weakly interacting

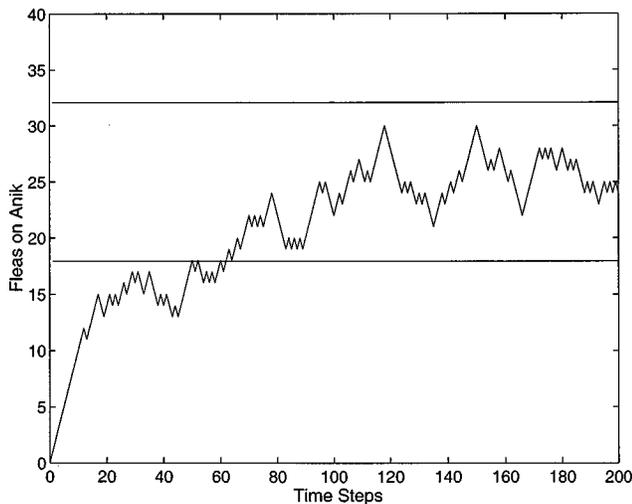


Fig. 1. Early time development of the number of fleas on Anik due to random jumps. The horizontal lines indicate two standard deviations above and below the mean.

gas, collisions cannot be ignored, because they are the mechanism that shuffles a particular molecule between its states of motion. The approach to equilibrium thus depends on the details of the motion, and is a less general phenomenon than equilibrium itself. In order not to lose the woods for the trees, it is useful to look for simple but illustrative examples. One such example is a collection of “two-level” systems, that is, systems described by two possible outcomes.

As a physical realization of this model, one could consider a collection of weakly interacting quantum spin  $\frac{1}{2}$  systems each of which has up and down states. A more whimsical illustration is based on the model proposed in Ref. 2: Consider a system consisting of a subsystem of 50 fleas whose “states” are residence on dog A or dog B, which we shall call Anik and Burnside, sleeping side by side. To simulate molecular agitation, we suppose that the fleas jump back and forth between the dogs. Now we need something that plays the role of the rest of the system. Let us suppose that the fleas are each equipped with a number, and have been trained to jump when their number is called. The “environment” agitating the fleas, which is like a heat reservoir, will be something that calls out numbers at random, and our closed system will be the fleas and the reservoir.

To simulate the approach to equilibrium, it is necessary to start from a configuration that almost never occurs in the maximally random state of affairs. Suppose that in the beginning Anik has no fleas at all. We agitate the fleas by having a computer generate random numbers between 1 and 50 and transferring the flea with this number from one dog to the other. At every step we record the total number (between 0 and 50) of fleas on Anik, but not their labels. This way has the practical advantage that we do not have to keep track of the  $2^{50}$  ways of assigning 50 labeled fleas to the two dogs. It also means that we are following only the “macrostate.”

A typical sequence is shown in Figs. 1 and 2. In the first step it is certain that the number called will belong to a flea on Burnside. In the second step the probability of this happening again is  $49/50$ . Thus, there initially seems to be a steady march toward an equal partition of the fleas between the dogs. The early time development is shown in Fig. 1.

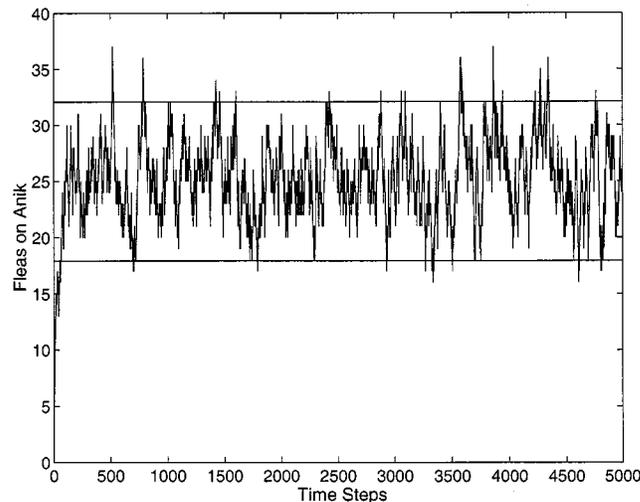


Fig. 2. Long time behavior of fleas on Anik showing fluctuations in equilibrium. The horizontal lines indicate two standard deviations above and below the mean.

After about 100 steps we reach a situation where sometimes Anik and sometimes Burnside has more fleas. In this region we would expect that every one of the  $2^{50}$  configurations mentioned above would be equally likely. This expectation translates into a binomial distribution corresponding to the repeatable random event of tossing 50 fair coins, namely

$$P(m) = \frac{1}{2^{50}} \binom{50}{m}, \quad (1)$$

where  $P(m)$  is the probability of the macrostate with  $m$  fleas on Anik, and  $\binom{50}{m}$  is the combinatorial coefficient.

An examination of Fig. 2 confirms this expectation. The horizontal lines have been drawn to include two standard deviations on either side of the mean, which corresponds approximately to the 95% range for the distribution Eq. (1). (The standard deviation is  $\sqrt{50/2} \approx 3.5$ .) Our eye tells us that, except for the initial transient, fluctuations outside this range are indeed rare.

We can be more quantitative. Figure 3 is a histogram of the relative durations of the possible outcomes, constructed from Fig. 2 with the first 100 steps omitted. Superimposed on the histogram is the binomial distribution. The agreement is very good.<sup>4</sup> The dance of the fleas in Fig. 2 has thus very quickly forgotten its unusual starting point and become the endless jitterbug of “equilibrium,” in which an event as unlikely as a flea-less dog simply never happens again without outside intervention.

Figure 2 also illustrates the role of motion reversal. The model is time-reversal invariant because a string of random numbers in reverse order is just as random. After the first 100 or so steps, the evolution has no sense of time. If we were to expand the region near one of the reasonably large fluctuations away from the mean, we would find that there is no characteristic feature of the buildup preceding the maximum deviation to distinguish it from the time reverse of the decay following the maximum. There is also no conclusive argument to rule out the possibility that the start of the trace shown in Fig. 1 has captured a truly giant fluctuation midway. Of course, we know that the figure was not produced in this way.

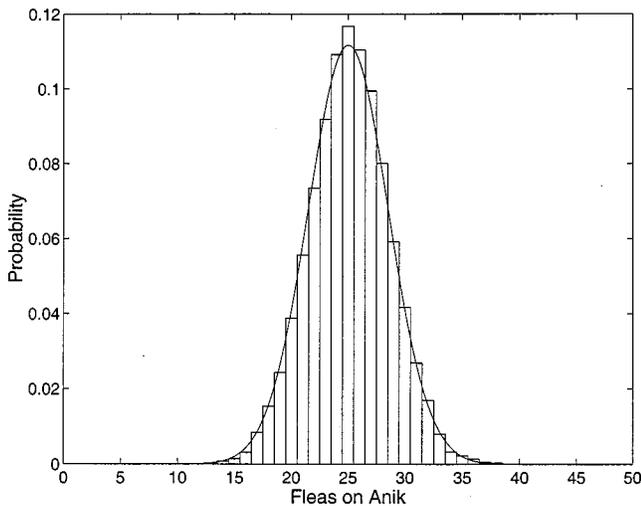


Fig. 3. Histogram generated from Fig. 2 with the first 100 time steps omitted.

The point of the previous paragraph is worth reemphasizing. The time asymmetry expressed in the second law is *not* simply the consequence of applying time-symmetric microscopic dynamics to systems having many degrees of freedom. Time-reversal symmetry is indeed preserved in our system. If at some instant the system is in a highly improbable state (that is, no fleas on Anik), it is overwhelmingly likely that it will be in a more evenly distributed state at some later time. However, *if* the improbable state were due to a giant fluctuation, precisely the same argument could be made regarding the prior history of the system—it would then be overwhelmingly likely that at earlier times the system was also in a more evenly distributed state. In this sense, there is perfect symmetry between past and future.

The notion of a statistical “arrow of time” thus depends on the added ingredient of imposed initial conditions. When we see a system in a highly unlikely state, we justifiably assume that this state is the result of a prepared starting condition, and not of an overwhelmingly improbable fluctuation from equilibrium. As has been particularly emphasized by Peierls,<sup>5</sup> this setting of initial conditions at some specified time breaks the symmetry between past and future.

In fact it is virtually impossible to wait long enough for the initial configuration in Figs. 1 and 2 to occur as a fluctuation in equilibrium, where it has a probability of  $2^{-50}$ . To have a reasonable chance of witnessing such a fluctuation, we would have to allow a number of time steps approximately equal to the reciprocal of this probability—about  $10^{15}$ —to elapse. Thus, to recover the unlikely configuration of a totally clean Anik by random shuffling of fleas between equally dirty dogs, even for this *very* small system of 50 fleas, we would need a plot roughly two hundred thousand million times as long as Fig. 2, which extends for only 5000 time steps. Because Fig. 2 is about 5 cm wide, the length of the required trace would be about 10 mil km. In comparison, the distance to the moon is only about 400 000 km. The law of large numbers is at work, here making an unlikely event overwhelmingly unlikely. Though not logically certain, it is roughly 99.999 999 999 999% probable that the time in Fig. 1 is running in the direction of increasing disorder.

Ehrenfest’s dogs bring into focus the essential characteristics of time in statistical mechanics. (i) A starting point

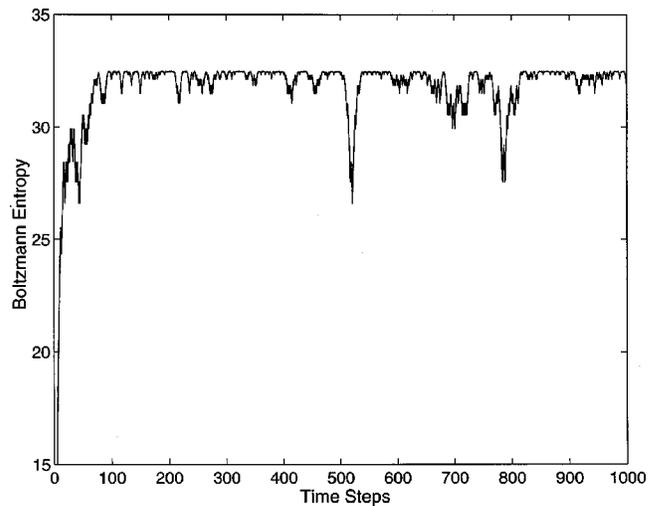


Fig. 4. The Boltzmann entropy associated with Fig. 2, showing fluctuations in equilibrium.

macroscopically distinct from equilibrium is overwhelmingly likely to evolve to greater disorder, that is, toward equilibrium. (ii) In equilibrium, fluctuations have no sense of time. (iii) Giant fluctuations from equilibrium to extremely unlikely states are extremely rare. (iv) A statistically determined direction of time follows from the assumption that a system in a highly unlikely ordered state has been so prepared by external influences. Even for the rather small system we considered, these uses of the words “overwhelmingly” and “extremely” are very conservative.

The word entropy has not appeared in this section. As a matter of fact, there is more than one way to introduce that notion here, as will be seen in more detail in Sec. IV. The essential point can be made by noting that the states with  $n$  fleas on Anik are “macrostates,” each allowing for  $\binom{50}{n}$  assignments of distinct fleas or “microstates.” We could simply call the logarithm of the latter number, the entropy, that is,  $S(n) = \ln \binom{50}{n}$ . The combinatorial coefficients have a maximum half way, at  $n=25$ , and become smaller in either direction. In Fig. 4, the values of  $n$  plotted in Fig. 2 have been converted to a plot of entropy versus time steps using this rule. As in Fig. 2,  $S$  starts from zero, because  $S(0) = \ln \binom{50}{0} = \ln 1 = 0$ , and has fluctuations.

This entropy, sometimes called the Boltzmann entropy, can be associated with a *single* time trace such as in Fig. 2. Although it fluctuates in equilibrium, the fluctuations diminish as the size of the system increases. In a sufficiently large system the Boltzmann entropy increases steadily as equilibrium is approached.

Note that we have ignored any contribution to the entropy of the closed system from the reservoir which is responsible for the hopping of the fleas. This assumption is justified here because energy has not entered into our considerations, making the model slightly artificial. It is probably best to think of the reservoir as having a very high temperature (in energy units) compared to the characteristic energies of the subsystem. As a result, heat exchanges with the subsystem occur with no change in the entropy of the reservoir, and only the flea entropy changes with time. The introduction of energy and temperature in Sec. V will lead to an interesting difference.

#### IV. GIBBS ENTROPY

The dog–flea model is simple enough to allow the solution of several other interesting problems in time-dependent statistical mechanics. We first reexamine the assignment of entropy to our subsystem of fleas. The usual expression for the entropy in statistical mechanics is

$$S = - \sum_i P_i \ln P_i, \quad (2)$$

where the sum is over microstates labeled by the index  $i$  and  $P_i$  is the probability of  $i$ . This entropy is associated with a distribution describing an ensemble of systems, whereas the Boltzmann entropy introduced earlier is defined for the macroscopic time development of a single system. If there are  $M$  equally likely microstates, each of the  $P_i$ s would equal  $1/M$ , and Eq. (2) reduces to  $\ln M$ . The Boltzmann entropy has exactly this form if the macrostate with  $n$  fleas has  $\binom{50}{n}$  equally likely microstates. As we saw, the equilibrium Boltzmann entropy fluctuates for the subsystem plus reservoir.

It is possible to assign a constant entropy to equilibrium. A system of 50 two-level systems at a temperature much higher than the level spacing is commonly assigned an entropy of  $50 \ln 2 = 34.657$ . Expression (2) gives this result if each of the  $2^{50}$  microstates is taken to be equally probable. As we saw from Fig. 3, the fluctuations in Figs. 1 and 2 are an expression of equal likelihood of all these microstates.

Even when the probabilities  $P(m)$  of the macrostates corresponding to  $m$  fleas on Anik are not given by Eq. (1), the probabilities of the equally likely  $\binom{50}{m}$  microstates  $i(m)$  associated with  $m$  are

$$P_{i(m)} = P(m) / \binom{50}{m}. \quad (3)$$

If we substitute Eq. (3) into Eq. (2) and do the sum over  $i(m)$ , we obtain

$$S = - \sum_{m=0}^{50} P(m) \ln P(m) + \sum_{m=0}^{50} P(m) \ln \binom{50}{m}. \quad (4)$$

The second term on the right-hand side of Eq. (4) arises, as was just shown, from the fact that a macrostate having  $m$  fleas on Anik has an additional contribution to the entropy coming from the equally likely microstates which make up the macrostate. If expression (1) is substituted into Eq. (4), the result is the previously mentioned  $50 \ln 2$ . We shall call this new entropy the Gibbs entropy, because it is analogous to the entropy in Gibbs's canonical ensemble.

To associate a Gibbs entropy with the early, and consequently nonequilibrium, part of the time development we have been discussing, we need more information than the single time trace we have been discussing. Because this entropy is a property of a distribution, we need to assign probabilities to every time step of the process, which means that we have to contemplate an ensemble of subsystems and define probabilities in terms of occurrences in the ensemble. One way to proceed would be to create a very large number of traces such as the one in Fig. 1, all of them starting with the same configuration. Because the sequence of random numbers would be different in each run, these traces would

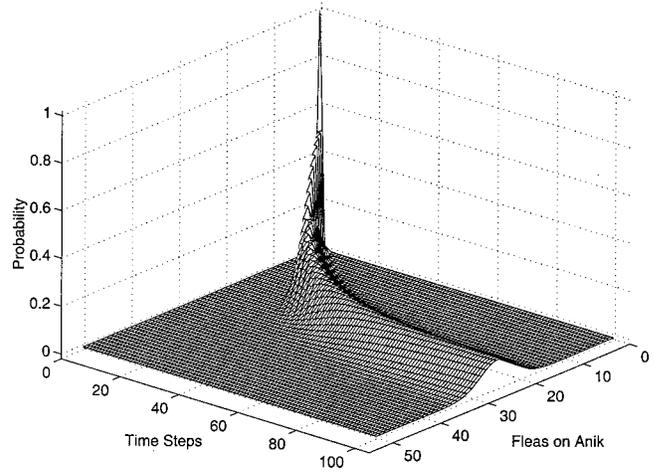


Fig. 5. The probabilities of fleas on Anik with the passage of time.

differ from one another. At any given time, we could calculate a histogram like Fig. 3.

Obtaining reliable distributions by this method would require a very large number of runs. Fortunately, there is a much simpler way of implementing the idea, which does not require a random number generator. Let us calculate a distribution function  $P(m)$ , with  $m$  running from 0 to 50, which changes from step to step, and reflects the random transfer of fleas from dog to dog. At the start of the process we know with certainty that there are no fleas on Anik. In the language of probability, the distribution at  $t=0$  is  $P_0(0)=1, P_0(1)=P_0(2)=\dots=P_0(50)=0$ . (To indicate the time we need another label, which we shall write as a subscript.) Now we argue that the probability distribution at time  $t$  determines the probability distribution at time  $t+1$ . The assumption that the fleas are being called at random implies that

$$P_{t+1}(m) = \frac{m+1}{50} P_t(m+1) + \frac{50-(m-1)}{50} P_t(m-1). \quad (5)$$

Equation (5) can be understood by saying it in words. Anik can have  $m$  fleas at time  $t+1$  either because she had  $m+1$  at time  $t$  and one jumped off, which has a probability proportional to  $m+1$ , or because she had  $m-1$  and one jumped on, which has a probability proportional to the  $50-(m-1) = 51-m$  fleas that were on Burnside at time  $t$ .

We can write a program to develop the distribution corresponding to the initial certainty forward in time using Eq. (5). However, there is one artificiality in this time evolution: At odd (even) times only odd (even) numbers of fleas can be on Anik. This artificiality can be remedied by averaging Eq. (5) over two forward steps. The resulting evolution is shown in Fig. 5.

The three-dimensional plot in Fig. 5 is obtained by stacking together the distributions at successive times. It very clearly shows the initial certainty evolving to a distribution—which, not surprisingly, can be shown to be the binomial in Eq. (1)—with the outer regions in the range of possibilities being extremely unlikely. At each step we can calculate an entropy using Eq. (4). The result, shown in Fig. 6, shows that the entropy rises steadily from zero to  $50 \ln 2$ .

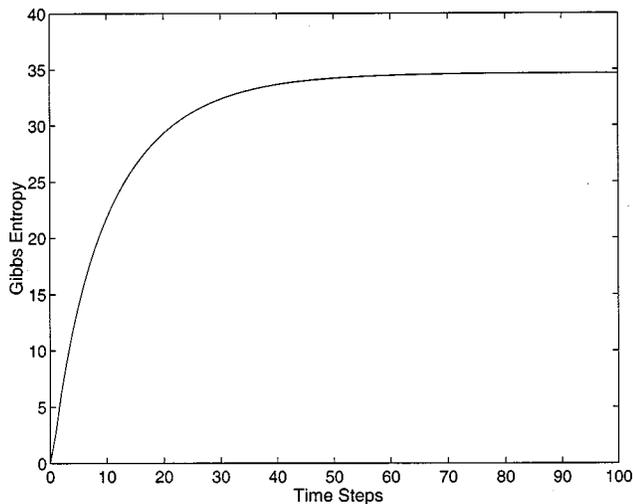


Fig. 6. Entropy of Anik's fleas computed by averaging over many trials, via the time-dependent probabilities generated via Eq. (5).

By imagining that the system can be restarted at will, we have, as in Sec. III, insisted on the possibility of the external imposition of an initial condition that is overwhelmingly unlikely in equilibrium. Time-symmetric dynamics applied to such an initial condition is overwhelmingly likely to evolve toward equilibrium.<sup>5</sup> If it were possible to repeatedly arrange for such a state to be a final condition, we could use a backwards-in-time evolution equation relating the distribution function at time  $t-1$  to the distribution function at time  $t$ . This equation would be identical to Eq. (5), except for the replacement of  $t+1$  by  $t-1$ :

$$P_{t-1}(m) = \frac{m+1}{50} P_t(m+1) + \frac{51-m}{50} P_t(m-1). \quad (6)$$

Equation (6) would predict the opposite of what is shown in Fig. 5—as one moved back in time through the history of the system, the entropy would increase monotonically. But such repeated occurrences of low entropy states as fluctuations in equilibrium are unimaginable. Such states do not typically arise in this fashion, nor can we arrange for them to do so. Time asymmetry in this context thus originates through our use of Eq. (5) and rejection of Eq. (6).<sup>5</sup>

## V. ENERGY AND TEMPERATURE

Up to now, the word temperature has only appeared at the end of Sec. III where it was argued that the standard Ehrenfest model describes equilibration at high temperature. We have confirmed this argument by showing that the entropy evolves to the situation in which all microscopic configurations are equally likely. It is, however, not difficult to introduce temperature in this context. Suppose that Anik is cleaner than Burnside, providing a less friendly environment for fleas. We may model this environment by assuming an energy cost  $\epsilon$  to be paid by a flea jumping from Burnside to Anik. Let the fleas be at an effective temperature  $T$  (in energy units), and define  $\Delta = \epsilon/T$ . We argue that Eq. (5) should be changed to

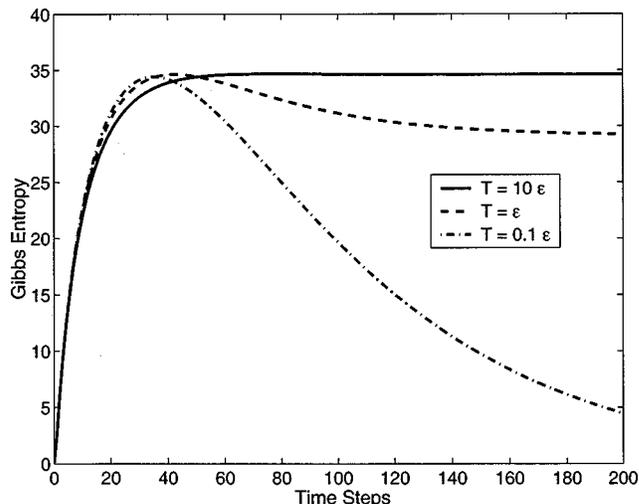


Fig. 7. Evolution of the Gibbs entropy for various temperatures, starting from a state where all fleas are on the "clean" dog Anik.

$$P_{t+1}(m) = \frac{m+1}{50} P_t(m+1) + \frac{50-m}{50} [1 - e^{-\Delta}] P_t(m) + \frac{50-(m-1)}{50} e^{-\Delta} P_t(m-1). \quad (7)$$

For the new conditions, we expect that in equilibrium any particular flea will spend more time on (dirty) Burnside than on (clean) Anik. This expectation is implemented in Eq. (7), which implies that when the number of one of the fleas on Anik is called, it jumps to Burnside with probability unity (term 1), but if one of the fleas on Burnside is called, it either stays put with probability  $1 - e^{-\Delta}$  (term 2), or jumps with probability  $e^{-\Delta}$  (term 3).

Making the jump-probability from Burnside to Anik smaller than the reverse process by the factor  $e^{-\Delta}$  does in fact achieve equilibrium in the steady state. In equilibrium, at temperature  $T$ , the probability  $p$  of a flea being on Anik, and the probability  $1-p$  of one being on Burnside should be given by the Gibbs distribution

$$p = \frac{e^{-\Delta}}{1 + e^{-\Delta}}, \quad 1 - p = \frac{1}{1 + e^{-\Delta}}. \quad (8)$$

For 50 fleas the equilibrium probability distribution should be the binomial corresponding to 50 tosses of an unfair coin with outcome probabilities  $p$  and  $1-p$ :

$$P_{\text{eq}}(m) = \binom{50}{m} p^m (1-p)^{50-m}. \quad (9)$$

It can be verified that Eqs. (8) and (9) are a stationary solution of Eq. (7), namely that substituting this form on the right reproduces it on the left. In short, the effective temperature of the fleas determines how many are willing to put up with Anik's cleanliness. In the high temperature limit,  $\Delta \ll 1$ , Eq. (5) is recovered. At very low temperatures,  $\Delta \gg 1$  and few fleas leave the snug comfort of Burnside.

Several interesting and informative computations can be performed with the evolution equation—Eq. (7). We will focus on one which we find particularly illuminating. Shown in Fig. 7 are three entropy versus time traces, each at a different temperature but with the same initial condition of all

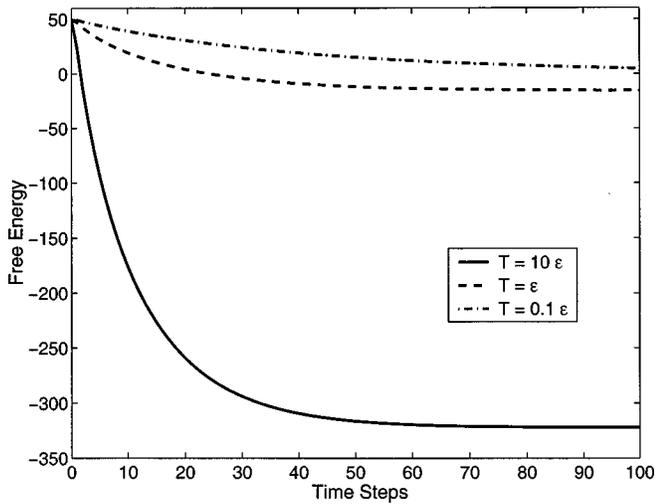


Fig. 8. Evolution of the free energy  $F$  (in units of  $\epsilon$ ) for various temperatures, starting from a state where all fleas are on the “clean” dog Anik.

50 fleas on the “clean” (energetically unfavorable) dog Anik. The curves have been generated by computing the Gibbs entropy (4) at successive time steps. We observe that at low temperatures, the entropy of the system does not increase monotonically in time—after a certain critical time, it actually starts to *decrease*. Have we managed to violate the second law?

A little thought shows that there is no violation. The second law requires only that the *total* entropy of the dog–flea system plus reservoir increase with time. The entropy of the reservoir is insensitive to changes in the configuration of the fleas only at temperatures much greater than the energy cost  $\epsilon$ . In general, changes in entropy and energy of the reservoir at temperature  $T$  are related by

$$dS_{\text{res}} = \frac{dU_{\text{res}}}{T} = -\frac{dU}{T}, \quad (10)$$

where the last equality is the result of conservation of energy, and  $U$  is  $\epsilon$  times the number of fleas on Anik. (Note that the energy transfer is at fixed  $\epsilon$ , which implies that no work is done.<sup>3,6</sup>) Using Eq. (10), an increase of the total entropy translates as usual into a decrease of the Helmholtz free energy  $F$  of the flea subsystem, defined by  $F = U - TS$ , where  $T$  is the temperature of the reservoir and  $S$  is the entropy defined in Eq. (4). In Fig. 8, we plot the time evolution of the free energy for the same initial conditions and temperatures used in Fig. 7. We see that in all cases, the free energy decreases monotonically with time.

Note that the initial condition for Figs. 7 and 8 (all fleas on Anik) corresponds to having a negative temperature for the dog–flea system. Consequently, reducing the internal energy (moving fleas from Anik to Burnside) initially increases the entropy above its equilibrium low temperature value.

## VI. CONCLUSION

We have demonstrated that an understanding of time in statistical mechanics can be obtained by carefully examining the simple Ehrenfest dog–flea model. The model has the virtues of offering qualitative insights and yielding easily to quantitative analysis. Our study has emphasized the manner in which time-reversal invariance is maintained in the model, and the role of initial conditions in establishing a direction of time. We have also shown that the model can be extended to finite temperatures, where it may be used to explore interesting issues.

Finally, we list some suggestions for further reading. Excellent elementary discussions are to be found in Ref. 7. The subject is also treated in many textbooks accessible to advanced undergraduates.<sup>8</sup> Whereas the topic is often underplayed in courses on thermal physics, the opposite may be true in specialized books. Several thought-provoking articles as well as discussions of the deep implications of the ideas presented here are to be found in Ref. 9.

*Note added in proof.* Our colleague Ben Widom remarks that there are “purists”—among whom he does not include himself—who think that the Ehrenfest model is not a first-principles explanation of irreversibility because there is a “stochastic element” in the model, which makes it “not deterministic, as real dynamics is...” To any such purists among our readers, we point out that our implementation of the model uses computer generated pseudo-random numbers which are completely deterministic. (See Chapter 11 of Ref. 3 for an elementary introduction to deterministic chaos.)

## ACKNOWLEDGMENT

This work has been partially supported by the National Science Foundation under Grant No. DMR-9805613.

<sup>1</sup>L. Boltzmann, “On Certain Questions of the Theory of Gases,” *Nature* (London) **51**, 413–415 (1895).

<sup>2</sup>P. and T. Ehrenfest, “Über zwei bekannte Einwände gegen das Boltzmannsche H-Theorem,” *Phys. Z.* **8**, 311–314 (1907).

<sup>3</sup>V. Ambegaokar, *Reasoning about Luck: Probability and Its Uses in Physics* (Cambridge U.P., Cambridge, 1996).

<sup>4</sup>But not perfect. How reasonable the disagreement is, given the number of trials, is a question we desist from asking, because ultimately that would include among other things a test of the random number generator.

<sup>5</sup>R. E. Peierls, *Surprises in Theoretical Physics* (Princeton U.P., Princeton, NJ, 1979), p. 73.

<sup>6</sup>F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw–Hill, New York, 1965).

<sup>7</sup>R. P. Feynman, *The Character of Physical Law* (MIT, Cambridge, MA, 1967), pp. 108–126; A. J. Leggett, *The Problems of Physics* (Oxford U.P., New York, 1987), pp. 148–157; J. L. Lebowitz, “Boltzmann’s entropy and time’s arrow,” *Phys. Today* **46**, September 32–38 (1993).

<sup>8</sup>K. Huang, *Statistical Mechanics* (Wiley, New York, 1987); G. Wannier, *Statistical Physics* (Wiley, New York, 1966); C. J. Thompson, *Mathematical Statistical Mechanics* (Macmillan, New York, 1972); J. D. Walecka, *Fundamentals of Statistical Mechanics* (Stanford U.P., Stanford, 1989); J. Waldram, *Theory of Thermodynamics* (Cambridge U.P., Cambridge, 1985).

<sup>9</sup>P. T. Landsberg, ed., *The Enigma of Time* (Hilger, London, 1982); J. J. Halliwell *et al.*, eds., *Physical Origins of Time Asymmetry* (Cambridge U.P., Cambridge, 1994).