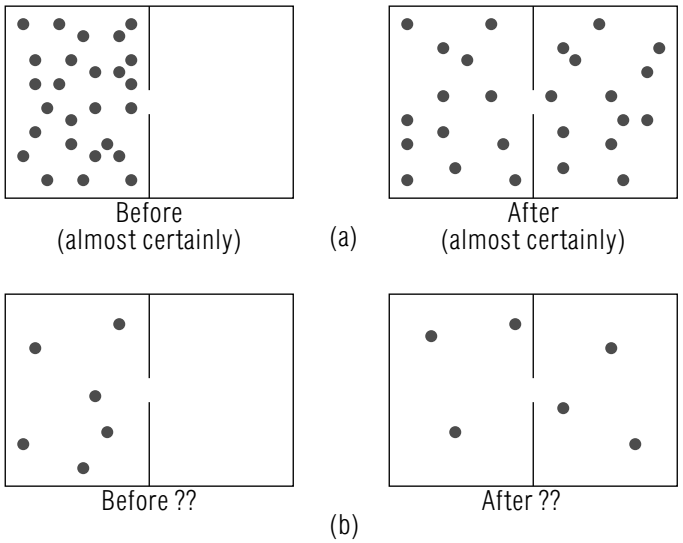
PHYSNET

MISN-0-357

THE APPROACH TO EQUILIBRIUM



Project PHYSNET Physics Bldg. Michigan State University East Lansing, MI

THE APPROACH TO EQUILIBRIUM

by

Robert Ehrlich

Title: **The Approach to Equilibrium**

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Length: 2 hr; 16 pages

Input Skills:

1. Vocabulary: half-life, simulation (MISN-0-356), entropy (MISN-0-160).
2. Enter and use a computer program which simulates a random physical process (MISN-0-356).

Output Skills (Project):

P1. Enter and run a program which uses the Monte Carlo method to simulate a coin flipping model of the approach to equilibrium.

P2. Modify the program in P1 to simulate the disintegration of a sample of radioactive nuclei, obtain the half-life of the nucleus and compare the half-life so obtained to the theoretical half-life.

External Resources (Required):

1. A computer with FORTRAN or BASIC.

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1. The Second Law of Thermodynamics

1a. Introduction. This module uses a computer simulation applicable to several physical systems. The simulations involve the second law of thermodynamics, also known as the entropy law. It will be of particular interest to examine how well this law applies to systems of very small numbers of particles.

1b. The Entropy Law: An Arrow of Time. One version of the second law of thermodynamics states that the entropy of an isolated system must either stay constant or increase. In other words, when things are left alone, they either "coast" or "run down," i.e., they tend to approach a steady equilibrium state. This principle, which conforms to our everyday observations of complex systems, appears to be contradicted by the behavior of simple systems which contain a small number of particles. To illustrate the difficulty, let us consider a box partitioned in the middle with a number of gas molecules all initially to the left of the partition. If a small hole is made in the partition, some molecules enter the right half of the box. If the number of molecules is very large, as is ordinarily the case with a gas in a macroscopic box, then within the limits of accuracy of our instruments, we always find that the system tends to approach equilibrium, which in this case means equal pressures, or equal numbers of molecules in each half of the box. (see Fig. 9) The reverse process (starting with equal numbers of molecules in each half and later finding all in one half) is never observed. Thus, we can infer with (near) certainty the time sequence of the pictures in Fig. 1a from the pictures themselves. It is in this sense that we speak of the entropy law as singling out a particular direction (arrow) in time.

1c. The Entropy Law: Dependence on N. The entropy law which seems to establish a direction in time for complex systems (involving large numbers of particles), fails to do so when the number of particles, N, is small. Consider, for example, the same two compartment box now containing a small number of molecules (Fig. 1b). If the left half of the box initially contains six gas molecules, then due to their random motion we would find that at some future time after the hole is made, the system

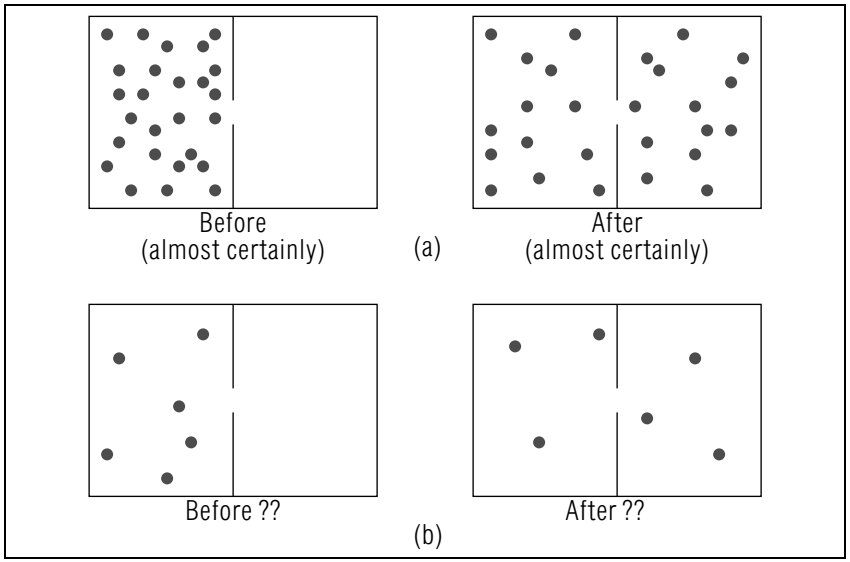

Figure 1. Gas molecules in a partitioned box with two compartments.

has reached the equilibrium state of three molecules in each half of the box. However, it is not at all unlikely that at some still later time, due to the random molecular motion, the initial state of all six molecules in the left half of the box will recur, making it impossible to infer the time sequence of the pictures in Fig. 1b from the pictures themselves. In fact, using statistics we could determine how long, on the average, we would have to wait for such a recurrence of the initial state. If a large number of molecules are in the box, such a recurrence of the initial state is still expected, but only after a fantastically long time. Over any observable time (say one human lifetime), large departures from the equilibrium state, once it is reached occur with vanishingly small probability. Thus, the thermodynamic principle that the entropy of an isolated system does not decrease, or that the system can approach equilibrium but not depart from it, must be understood on a statistical basis: this is what (almost) always happens to systems of very many particles over an observable period of time. Over a very long period of time, however, an isolated system can depart from its equilibrium state by an arbitrarily large amount, the magnitude of the departures from equilibrium being more readily observable the longer the time period, and the fewer the system. For a large number of molecules, N, we can meaningfully describe the process as an

approach to equilibrium, as the molecules initially in one half gradually spread through out the box. For small N, however, the "arrow of time" defined by the entropy law is not well defined, and we no longer can speak of an approach to equilibrium.

2. A Simulation Using Coins

2a. Overview. It is difficult to make directly the observations described in the previous section because normally the number of gas molecules in a box is so huge. In addition, the fluctuations for the case of a small number of molecules in each half would require keeping track of the motion of each molecule. We shall, therefore, describe an alternative system involving coins which would be expected to behave in virtually the same manner as the molecules in the box.

2b. A Coin Model of Molecules in a Box. Suppose we have N coins on a tray. A coin which is face up (heads) represents a particle in the left half of the box, and one which is face down (tails) a particle in the right half. To represent a particle going through the hole in the partition we turn over a coin selected at random. This assumes that it is purely a matter of chance which of the particles, numbered $1, 2, ..., N$, goes through the hole. Starting with all coins heads (all particles in the left half of the box), we can follow the evolution of the N-particle gas by repeatedly choosing a coin at random and turning it over. Since all the coins are initially heads, if N is large, it is likely that the first few turns will result in an increase in the number of tails. In general, on any turn of a randomly chosen coin, the chances of an increase in the number of tails depends only on the fraction of all coins that are heads. Thus, the tendency for the system to reach the equilibrium state of equal numbers of heads and tails (equal numbers of particles in the two halves of the box), is simply a consequence of the laws of statistics.

2c. Mathematics of the Coin Model. Let us use statistical considerations to determine the manner in which this system approaches equilibrium. We let n designate the number of tails after x randomly chosen coins have been turned over. On the next turn, the probability p_h of a coin being turned from tails to heads is just the fraction of all coins that are tails: $p_h = f = n/N$. The probability of a coin being turned from heads to tails is therefore $p_t = 1 - p_h$. Hence, on the average, the

change in the number of tails on the next turn is given by

$$\Delta n = p_t - p_h = 1 - \frac{2n}{N}.$$

If Δx randomly chosen coins are turned over at one time, instead of just one, we have

$$\Delta n = \left(1 - \frac{2n}{N}\right) \Delta x. \tag{1}$$

Treating n and x as continuous variables, and using differentials instead of finite differences, we divide both sides of Eq. 1 by the factor $(1 - 2n/N)$ to obtain

$$\frac{dn}{\left(1 - \frac{2n}{N}\right)} = dx,$$

which can be integrated to give

$$-\frac{N}{2} ln(N - 2n) = x + C.$$

We choose the constant of integration C equal to $-(N/2)lnN$, in order to conform to the assumed initial condition $n = 0$ for $x = 0$ (all coins initially heads). Solving for the fraction $f = n/N$, we obtain

$$f = n/N = \frac{1}{2}\left(1 - e^{-2x/N}\right). \tag{2}$$

According to Eq. 2, the fraction of coins which are tails, on the average, after x coins have been turned over is an exponential function of x which approaches the equilibrium value of 1/2 for $x \to \infty$. If we were to plot the fraction of coins that are tails, $f = n/N$ versus x, based on the results of an actual coin turning experiment, we would find an irregular curve resembling, on the average, an exponential function with random statistical fluctuation superimposed. The magnitude of the fluctuations decrease as the number of coins increases. For a small number of coins (or molecules) the relatively large fluctuations may completely obscure any exponential approach to equilibrium, and in fact make the concept somewhat meaningless.

2d. Simulation of Radioactive Decay. The same model using N coins can be used to simulate the disintegration of a large number of nuclei. Let a coin which is heads represent a nucleus that has not yet disintegrated. The probability that any one nucleus disintegrates in any

short time interval Δt is a constant p_0, independent of how long the nucleus has been in existence. To simulate the disintegration process, we start with all coins heads (no nucleus yet disintegrated). We set up a loop to step the time: $t = 0, \Delta t, 2\Delta t, ..., n\Delta t$. For each value of the time, we set up a loop over the N nuclei, $j = 1, 2, ..., N$. For each nucleus, we test whether it has already disintegrated (j^{th} coin tails), and if so, we skip this one and go on to the next. If the j^{th} nucleus has not yet disintegrated, we "give it a chance" to disintegrate by generating a random number r, uniformly distributed from zero to one, and having the nucleus disintegrate if r is less than p_0. When the nucleus disintegrates, we turn the j^{th} coin over. After giving all N nuclei a chance to disintegrate for a particular time interval, we compute the fraction of nuclei that have not yet disintegrated f, and print out both its numerical value, along with a line of characters for a plot of f versus time. We repeat the process for each time interval, until all n time intervals have been treated (or until all N nuclei have disintegrated).

3. Program for the Coin Model

3a. Introduction. The coin model is particularly easy to simulate on a computer. The array $U_1, ..., U_1000$, is used to record the state of each of up to 1000 coins according to the convention:

U_j = +1 means the j^{th} coin is heads,
U_j = -1 means the j^{th} coin is tails.

To flip a random coin we need only generate a random number j and then change the sign of the array element U_j.

3b. Input. The program begins by reading numerical values for `COINS` and `TURNS`, where

`COINS`	=	number of coins
`TURNS`	=	number of times to turn over coins selected at random.

The program initially sets all the elements of the array U equal to +1 (all coins initially heads). Then in a loop over $k = 1, 2, ...,$ `TURNS`, an integer j is chosen at random between 1 and `COINS`, and the j^{th} coin is turned over by simply reversing the sign of U_j. The number of tails is stored in the variable `TAILS`, so that by subtracting U_j from `TAILS` each time a coin is turned the program correctly accounts for changes in the number of tails.

(It increases the number of tails by one if the coin is turned from heads to tails and decreases it by one in the opposite case). The program computes the fraction of coins that are tails, prints and plots the results provided that this turn is one of 50 selected turns evenly interspersed between 1 and `TURNS`. The reason for only printing the results at 50 selected turns is to get a single-page plot. Because of this, you should choose values for `TURNS` that are integral multiples of 50. Once the loop over the specified number of turns is complete, the program goes on to read another data set if any remain to be read.

3c. Output. The output shown in Figs. 2 and 3 was produced using these numerical values for the parameters:

	`COINS`	`TURNS`
1^{st} set	25.00	50.00
2^{nd} set	1000.00	3000.00

The random statistical fluctuations are much more pronounced when the number of coins is small, as in the first case. Note that when a large value for `COINS` is used, it is also necessary to use a large value for `TURNS` if we wish to reach the equilibrium state. The value used for `COINS` on the second data card (1000) is the largest allowed value due to the size of the array U. While there is no such upper limit on the value of `TURNS`, the amount of computation time will depend on this value. Recall that the value chosen for `TURNS` should be an integral multiple of 50.

4. Procedures

4a. The Approach to Equilibrium. Run the program using values for `COINS` in the range 25 to 1000, with appropriate values for `TURNS`. You might try the following six pairs:

RUN	`COINS`	`TURNS`
1	25	50
2	25	50
3	100	200
4	100	200
5	1000	2000
6	1000	2000

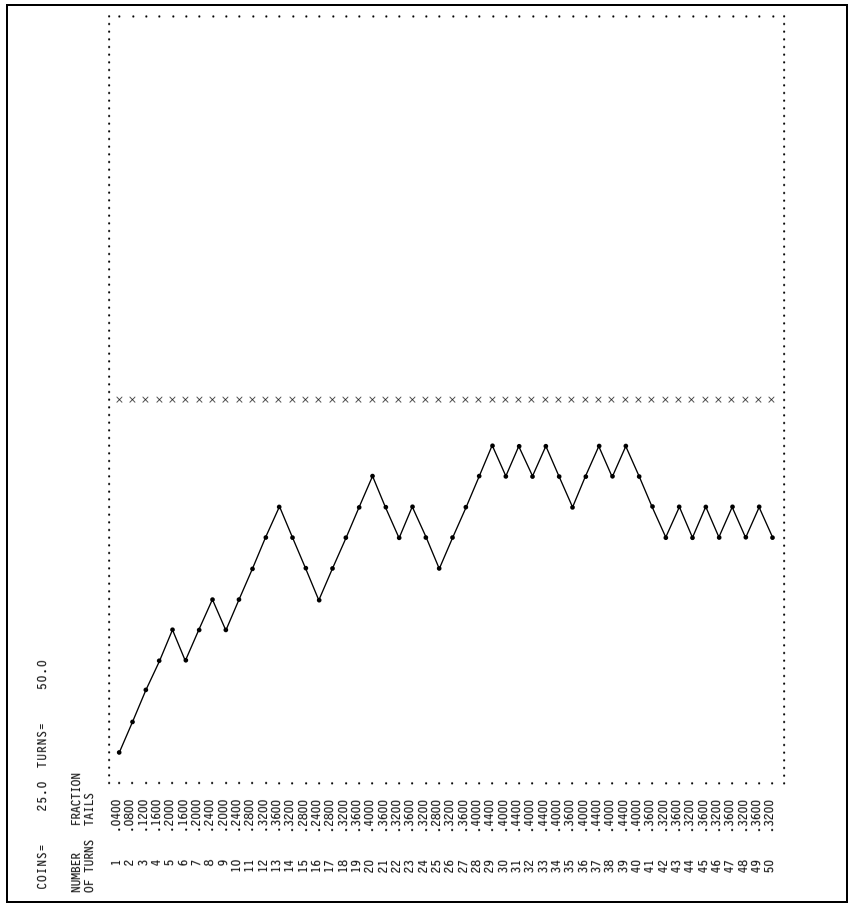

Figure 2. Output for 25 coins.

The reason for two runs with each pair of identical values is that any one run uses different random numbers. With two runs we can observe different statistical fluctuations by using the same input variables twice. When you obtain your output, you can check the predicted exponential approach to equilibrium (Eq. 2), which should hold on the average (i.e., apart from statistical fluctuations). One simple check to make is that according to Eq. 2, for $x = (1/2)N$, we should have $f = (1/2)(1 - e^{-1}) \approx 0.316$.

4b. Recurrence of the Initial State. Run the program using values for `COINS` of 3, 4, 5 and 6, and `TURNS`=50. For numbers of coins this

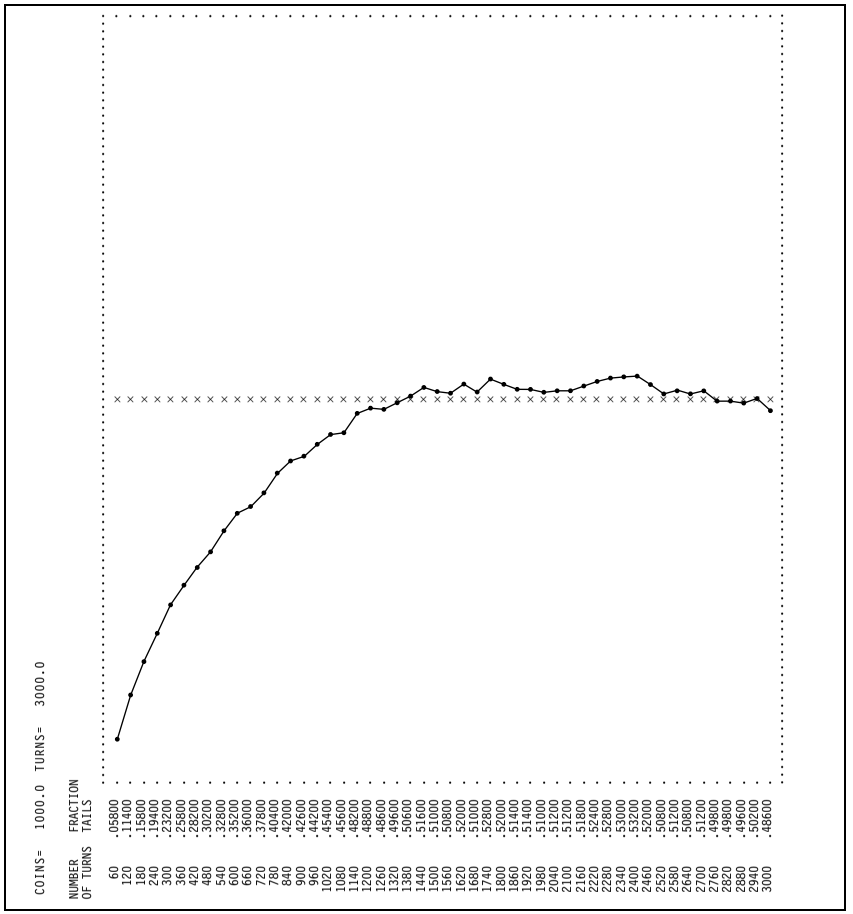

Figure 3. Output for 1000 coins.

small, the large random statistical fluctuations make it meaningless to speak of an approach to equilibrium. According to the laws of statistics, the initial state (all coins heads) should recur, on the average, at intervals of 2^N turns, where $N =$ `COINS`. Check this prediction for the cases of 3, 4, 5 and 6 coins. (Note that when the number of coins is reasonably large, say $N = 100$, a recurrence of the initial state is still predicted, but only on the average of once every 2^{100} turns. The size of this number is so great that if we could turn random coins over a billion times a second, we would have to wait, on the average, ten thousand times the present age of the universe (about ten billion year) before seeing a recurrence of

the initial state, after equilibrium has been reached.)

4c. Radioactive Decay Simulation. Modify the original (approach to equilibrium) program, so that it uses the procedure outlined above to simulate the process of radioactive decay. Run the program using a number of values for the parameters:

$$\begin{array}{rcl} N_0 & = & \text{Number of nuclei present at time } t = 0 \\ \Delta t & = & \text{time step} \\ n & = & \text{number of time steps} \\ p_0 & = & \text{probability that a nucleus disintegrates in time interval } \Delta t. \end{array}$$

Note that the probability p_0 is related to the nuclear mean life, T, which appears in the formula for the predicted exponential time dependence of f versus time:

$$N(t) = N_0 e^{-t/T} \tag{3}$$

which should hold for large values of N. According to this formula after a time t equal to the lifetime T, the fraction of nuclei which have not yet disintegrated is $1/e$. The relation between the probability p_0 and the mean life T is

$$p_0 = \frac{\Delta t}{T}. \tag{4}$$

Another useful quantity is the half-life, $T_{1/2}$. This is the time t for which $N(t) = 1/2(N_0)$. Using

$$N = \frac{1}{2}N_0 = N_0 e^{-t/T}\,,$$

we easily find that:

$$T_{1/2} = T\,ln2 \tag{5}$$

The exponential dependence of $N(t)$ on time only holds for large values of N_0, the number of original nuclei. For small values of N_0, we would expect a curve that shows many statistical fluctuations. After you modify the program in the manner described try running it using the following input parameters:

$$\begin{array}{rcl} N_0 & = & 50 \\ \Delta t & = & 1.0 \text{ hr} \\ n & = & 50 \\ p_0 & = & .0277 \end{array}$$

These values should result in a half-life $T_{1/2} = 25.0\,hr$, according to Eqs. 4 and 5. See if that is what is found when the simulation is run. Remember that several runs of a random process will give different values for each run. Try 5 runs using the specified input parameters and empirically determine the half-life for each, and compare with the expected value.

A. Fortran, Basic, C++ Programs

All programs are at

`http://www.physnet.org/home/modules/support_programs`

which can be navigated to from the home page at

`http://www.physnet.org`

by following the links: → `modules` → `support programs`, where the programs are:

`m357p1f.for`, Fortran;
`m357p1b.bas`, Basic;
`m357p1c.cpp`, C++;
`lib351.h`, needed Library for C++ program;

MODEL EXAM

Examinee:
On your computer output sheet(s):

(i) Mark page numbers in the upper right corners of all sheets.

(ii) Label all output, including all axes on all graphs.

On your Exam Answer Sheet(s), for each of the following parts of items (below this box), show:

(i) a reference to your annotated output; and

(ii) a blank area for grader comments.

When finished, staple together your sheets as usual, but include the original of your annotated output sheets just behind the Exam Answer Sheet.

1. Submit your hand-annotated output that illustrates the coin-flipping model of the approach to equilibrium. Be sure that it shows:
   a. at least three values, in the range 25 to 100, for the number of coins; the number of flips about twice that; and each run being done twice with independent quasi-randomness.
   b. (graphically) the extent to which the results check with an exponential approach to equilibrium.
2. Submit your hand-annotated output that applies the coin-flipping model to radioactive decay. Be sure that it shows:
   a. that you made 5 runs with the parameter values: initial number of systems, 50; time step, 1.0 hr; number of time steps, 50; probability for each one of the undecayed nuclei to decay in 1.0 hr, 0.0277.
   b. your deduction of the half life from the output in a), and its comparison with the expected value.

INSTRUCTIONS TO GRADER

If the student has submitted copies rather than originals of the computer output, state that on the exam answer sheet and **immediately stop grading the exam and give it a grade of zero.**