EHRENFEST'S LOTTERY — TIME AND ENTROPY MAXIMIZATION

"Why don't you call it entropy? ... no one understands entropy very well, so in any discussion you will be in a position of advantage."

– John von Neumann's name suggestion to Claude Shannon for missing information in information theory.[1]

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The conservation of energy dictated by the First Law of Thermodynamics is an intuitively appealing concept. Simply put, energy is neither created nor destroyed, but is just transformed from one form to another—kinetic energy transformed into potential energy, electrostatic energy transformed into gravitational energy, etc. The challenge of applying the First Law of Thermodynamics then reduces to an accountant's job, maintaining a balance sheet for energy in its different forms. Tracking down apparent discrepancies in the First Law can serve as a tool for scientific discovery, having played a vital role in the development of relativity, quantum mechanics, and particle physics. Despite the power of the First Law, it does not tell us how systems change with time when they are freely allowed to evolve (*e.g.*, a locking pin is removed from a piston or an ice cube is placed in a hot cup of coffee) and what the final state is, despite our intuitions (the piston moves to equate pressures and the ice cube melts). Simply put, the First Law of Thermodynamics is insufficient to determine equilibrium.

Thermodynamic equilibrium is determined by the introduction of the concept of entropy, which unlike the energy is not a conserved property but obeys a maximization principle encapsulated by the Second Law of Thermodynamics. According to this law, the entropy change of an isolated system is greater than or equal to zero for any spontaneous process, and the entropy is maximized at thermodynamic equilibrium. The Second Law of Thermodynamics identifies a time direction by equating time spontaneously moving forward as the direction in which entropy increases. In difference to other natural laws which are time reversible, like Newton's laws of motion, the arrow of time is unique to the Second Law of Thermodynamics. Indeed, it has been asserted that all phenomena that behave differently in one time direction can ultimately be linked to the Second Law of Thermodynamics.[2]

It is usually at this point in an introductory thermodynamics class that reversible and irreversible processes are introduced, and the differential change in entropy (dS) is equated with the reversible heat that crosses a closed system's boundaries (dQ_{rev}) divided by the absolute temperature (T),

$$dS = \frac{dQ_{rev}}{T}, \tag{1}$$

following Clausius' historical development. While this classical statement of the entropy change is true, the connection between an idealized reversible process that takes an infinite amount of time to complete and real observable changes in properties that occur over finite time scales is somewhat abstract. To help solidify this concept, it is helpful to provide physically motivated examples of the entropy in action and the approach to equilibrium.

From his studies of gas dynamics and equilibrium, Ludwig Boltzmann proposed an alternate entropy formulation that draws connections between macroscopic observables and the

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molecular nature of matter. Boltzmann's entropy formula,

$$S = k \ln \Omega, \qquad (2)$$

is famously engraved above his bust at his grave marker in Vienna.[3] The macroscopic entropy in this expression is identified as proportional to the logarithm of the number of available molecular states of a system, Ω, where the constant of proportionality $k = R/N_A$ is Boltzmann's constant, and is equal to the ratio of the ideal gas constant to Avagodro's number. Interestingly from a historical point of view, Planck was the first to articulate Eq. (2) in resolving the black body radiation problem, building upon Boltzmann's earlier work on the connections between entropy and probability.[4, 5] Following Eq. (1), Boltzmann's entropy formula directly links the addition of heat to an increase in the number of accessible molecular states. Boltzmann's entropy formula underlies the popular conceptualization of entropy as disorder or randomness. A literal interpretation of entropy as disorder can be problematic, however, due to gut feelings of what constitutes disorder,[6, 7] and alternate interpretations that equate entropy with energy dispersal.[8] Adding to the confusion, a first principles derivation of Eq. (2) is unavailable and its justification is ultimately empirical, resting on its predictive power.

A better understanding of the Second Law of Thermodynamics necessarily requires students to work through examples and thought experiments. To familiarize students with the connections between their personal expectations for equilibrium and maximization of the entropy with increasing time, I describe a series of games that can be played out in class or on a computer. The student assumes the role of a Bingo-like caller transferring numbered marbles between urns based on the outcomes of spins of a lottery wheel. The relationships between entropy, time (*i.e.*, spins of the wheel), and increases in the number of states are shown to be applicable to engineering concepts like diffusion and the derivation of equations-of-state. By establishing entropy maximization in terms of familiar concepts, I hope to form a stronger foundation for explaining the connection between the Second Law of Thermodynamics and equilibrium, and show how this principle pervades problems outside the traditional thermodynamics curriculum.

EHRENFEST'S LOTTERY

Paul and Tatiana Ehrenfest proposed a simple thought experiment to explore the connections between probability, entropy, and time.[9] The experiment is played out as a lottery obeying the following rules (Figure 1): You are given two urns and N **sequentially numbered** marbles. Initially, the first urn is filled with n_1 marbles, while the second urn is filled with the remaining n_2 marbles. At regular time intervals, Δt, a lottery wheel is spun, randomly producing a number between 1 and N. The randomly selected marble is then located, taken from the urn it is in, and placed into the other urn. The wheel is then spun again and the process is repeated *ad infinitum*. On the molecular level the marbles can be thought of as representing individual gas molecules, while the urns correspond to discrete volume units. While the correspondence between the lottery's random-transfer dynamics and molecular motions may appear tenuous, this model has been shown to provide an accurate description of gas mixing.[10]

After describing the lottery, the class may already have a number of intuitive expectations about the evolution of urn occupancy trends, including:

1) *After playing the game for a sufficiently long time, the number of marbles in both urns will average N/2.*
2) *The relative time sequence of different occupational states can be, roughly, worked out given the number of marbles in each urn. For example, say you are told $N = n_1 = 100$ marbles, and that at one point in the spin sequence there are $n_1 = 47$ and $n_2 = 53$ marbles distributed between the urns, while at another point there are $n_1 = 84$ and $n_2 = 16$ marbles in the two urns. It is most reasonable to expect then that the second instance occurred before the first in the sequence.*

The first expectation reflects the limiting probability for a fair game so that each marble has a 50/50 chance of being in either urn. The second expectation, while perfectly reasonable, is not as easy to justify based only on gut feelings. In the long time limit, the probability distribution of urn occupational probabilities approaches a binomial distribution. For large N, the binomial distribution is sharply peaked about the 50/50 occupational probability, but it does not rule out the observation of a heavily skewed distribution such as 84 and 16 marbles. The probability of observing this configuration for a well-mixed system is approximately 10^{-12}, small but finite. These skewed distributions become exceedingly rare with increasing N, so that in practice they can be neglected. We note that this omission provides a potential entry for Maxwell's demon to wreak havoc, getting usable work by waiting for unlikely events. While outside the scope of this article, it may be useful to segue into a discussion of Maxwell's demon after introducing Ehrenfest's lottery.[11]

The relationship between Boltzmann's entropy and the urn occupational states can be evaluated by counting the number of ways of randomly choosing n_1 marbles to be placed in urn 1 and n_2 marbles in urn 2 independent of the specific numbering of the individual marbles. To calculate the number of ways of divvying up the marbles between the two urns we draw a hypothetical random sequence of all the marbles, and then place the first n_1 marbles in urn 1 and the remaining n_2 marbles in urn 2. The number of ways of arranging all the marbles in a random sequence is N! following standard combinatorial arguments. The order in which the first n_1 marbles are placed in urn 1, however, does not change the final state of the system, which is only specified by the number of marbles in each urn but not their identities. The number of ways of choosing n_1 marbles to be placed in urn 1 is therefore over counted by the number of ways of randomly selecting this subset of marbles, $n_1!$. A similar over counting holds for the marbles designated for urn 2. The number of ways of randomly dividing n_1 and n_2 marbles between the two urns is then

$$\Omega = \frac{N!}{n_1!n_2!}. \qquad (3)$$

A perceptive student may notice that Eq. (3) implies that each marble is indistinguishable from one another, but in fact we have indicated that the marbles are numbered from 1 to N. When the marbles are distinguishable the number of ways of putting specified marbles in each urn is exactly one. For example for a 4-marble system we could specify that marbles 1 and 4 are in the first urn and marbles 2 and 3 are in the second, and there is only one way to achieve this distribution. The numbering scheme, however, is only a matter of convenience for the purpose of choosing a marble to move, and we are free after each spin to renumber the marbles for the next spin without changing the probabilistic distribution of marbles in the lottery. So, returning to our 4-marble example we could renumber the marbles 1 and 2 in the first urn and 3 and 4 in the second without changing the equilibrium outcome of the game. From the game's point of view, only the number of ways of distributing the n_1 and n_2 marbles matters, not the numbered identities of the individual marbles. The same can be said for mixing identical molecules in a volume, where only separations of chemical species, rather than specified individual molecules, can be achieved by manipulating the vastly smaller number of macroscopic thermodynamic state variables like temperature and pressure.[12]

The entropy of a configuration of indistinguishable marbles can be evaluated by substituting Eq. (3) into Boltzmann's entropy formula, yielding

$$S = k\ln\left[\frac{N!}{n_1!N_2!}\right] \approx -k\left[n_1\ln\frac{n_1}{N} + n_2\ln\frac{n_2}{N}\right]. \qquad (4)$$

In this expression the factorial terms were simplified by applying Stirling's approximation, *i.e.*, $\ln X! \approx X\ln X - X$.[13] When all the marbles reside entirely in either urn 1 or 2 ($n_1 = N$ or 0) there is only one way to generate this configuration and the entropy is zero. When the marbles are evenly distributed between the urns ($n_1 = n_2 = N/2$) the entropy is a maximum and equal to that $S_{max} = kN\ln 2$. Between the two extremes, the entropy is a monotonically increasing function.

The expectation that the entropy of the system increases on average with each spin of the lottery wheel can be verified by considering the marble transfer probabilities. The average change in the entropy as the result of a lottery spin is determined by summing over all possible transfer moves the probability of choosing to transfer a marble from one urn to the other (*i.e.*, $p(\text{urn1} \to \text{urn 2})$ or $p(\text{urn 2} \to \text{urn 1})$ multiplied by the change in the entropy associated with each move (*i.e.*, $\Delta S(\text{urn1} \to \text{urn 2})$ or $(\text{urn 2} \to \text{urn 1})$)

$$\langle \Delta S \rangle = p(\text{urn1} \to \text{urn2})\Delta S(\text{urn1} \to \text{urn2}) + p(\text{urn2} \to \text{urn1})\Delta S(\text{urn2} \to \text{urn1}). \qquad (5)$$

The angled brackets, $\langle \ldots \rangle$, denote an average. The probability of choosing to move a marble from an urn is equal to the number of marbles in that urn divided by the total number of marbles, *e.g.*, $p(\text{urn 1} \to \text{urn 2}) = n_1/N$. Expanding Eq. (4) in terms of n_1 and substituting into Eq. (5), an accurate expression for the average change in the entropy between successive spins of the wheel can be derived,

$$\langle \Delta S \rangle = k\frac{n_1 - n_2}{N}\ln\left(\frac{n_1}{n_2}\right) \geq 0. \qquad (6)$$

This average entropy change is positive when the occupation numbers differ and approaches zero as the occupations of each urn approach one another. As shown below, however, this expression does not preclude fleeting, instantaneous, entropy decreases due to random fluctuations in the urn occupational state about the equilibrium average.

Starting with $n_1 = N = 100$ marbles in urn 1, Figure 2 (next page) shows the outcomes for two independent, random lotteries simulated using MATLAB®. As the game plays out, the number of marbles in urn 1 decreases for the first ~150 spins of the lottery wheel, and then fluctuates about the 50/50 occupational state (Figure 2a). The entropy concurrently increases as the marbles become more evenly distributed between the urns (Figure 2b). The occupational fluctuations about the 50/50 marble distribution are a result of the stochastic nature of Ehrenfest's lottery. The relative magnitude of these occupational fluctuations decreases as $N^{-1/2}$ in accordance with the central

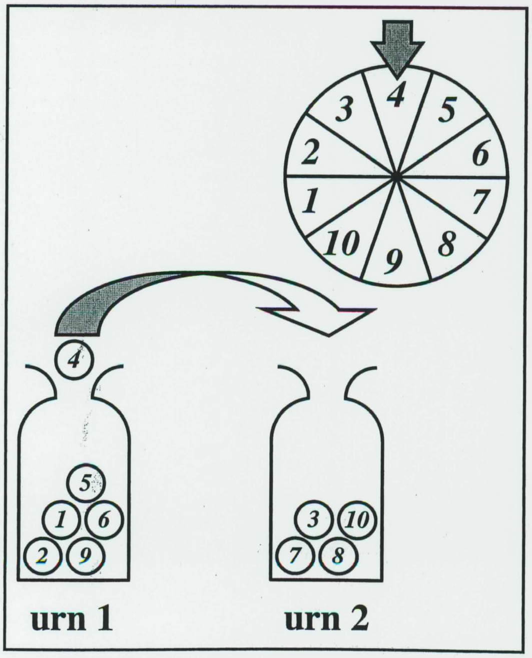


Figure 1. *Schematic illustration of the two-urn lottery with 10 marbles.*

limit theorem, so that on a per-marble basis excursions from the average diminish as the number of marbles increases (Figure 3). For a macroscopic number of molecules/marbles these fluctuations would appear insignificant, although they are manifested experimentally in measurable quantities like the heat capacity and isothermal compressibility.[14] While the occupation fluctuations are above and below the equilibrium 50/50 state, these deviations are manifested as spontaneous decreases in the entropy below the maximum value (Figure 2b). These downward fluctuations away from the maximal entropy point to the statistical nature of the Second Law of Thermodynamics. In particular, the Second Law of Thermodynamics is more appropriately thought of as a statement about the equilibrium distribution rather than a property of a single snapshot of molecular positions.[15]

The average urn occupancy can be solved analytically from a master equation for the discrete lottery spin dynamics. Given an average of $\langle n_1(s)\rangle$ marbles are in urn 1 for spin s, the probability a marble in urn 1 is chosen to be moved into urn 2 is the number of marbles in urn 1 divided by the total number of marbles. Similarly, given $\langle n_2(s)\rangle$ marbles are in urn 2, the probability a marble in urn 2 is chosen to be moved into urn 1 is $\langle n_2(s)\rangle/N$. The change in the average occupancy of urn 1 between spin s and s+1 is the probability a marble is added to urn 1 less the probability one is taken away,

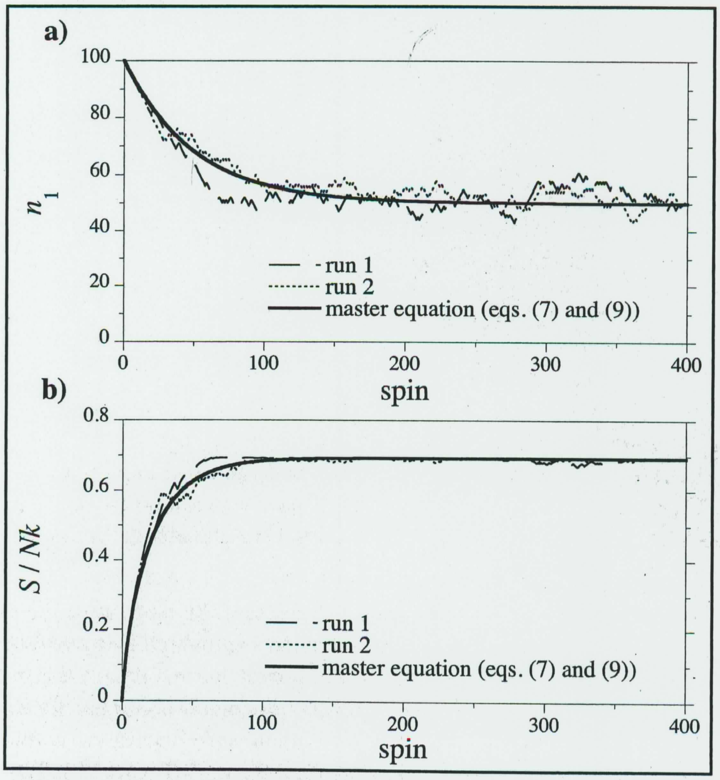


***Figure 2.** Outcomes of two random simulations of the two-urn lottery with 100 marbles and the master equation description of the mean behavior. Plots a and b show the occupation of urn 1 and the entropy, respectively.*

$$\langle n_1(s+1)\rangle - \langle n_1(s)\rangle = \frac{\langle n_2(s)\rangle}{N} - \frac{\langle n_1(s)\rangle}{N} = 1 - 2\frac{\langle n_1(s)\rangle}{N}. \quad (7)$$

The long time equilibrium state for which the average occupancy does not change between successive spins, $\langle n_1(s+1)\rangle - \langle n_1(s)\rangle = 0$, is

$$\langle n_1(s)\rangle = \frac{N}{2}, \quad (8)$$

as expected for a fair lottery. Conservation of the number of marbles dictates the average occupation of urn 2. For an initial occupation of $0 \le n_1(0) \le N$ in urn 1, the solution of Eq. (7) yields

$$\langle n_1(s)\rangle = \frac{N}{2} + \left(n_1(0) - \frac{N}{2}\right)\left(1 - \frac{2}{N}\right)^s. \quad (9)$$

It is straightforward to verify that Eq. (9) satisfies Eq. (7) by back substitution. The occupation dynamics and entropy evolution described by Eq. (9) are compared to the simulated example discussed in Figure 2. The agreement between the random lotteries and master equation results is excellent, although the fluctuations are suppressed by the master equation since it only describes the mean behavior.

APPLICATION TO MULTIPLE URNS – A MODEL FOR DIFFUSION

Ehrenfest's lottery can be extended to an arbitrary number of urns numbered from 1 to i_{max}. In difference to the two-urn lottery, the marbles are moved following the spins of two lottery wheels. The first spin chooses the marble to be moved as in the two-urn game. The second wheel chooses whether the marble is moved to the urn above or below the starting urn in the sequence, *i.e.*, from urn i to either urn i+1 or i–1. When a marble is chosen to move to an urn outside the sequence, *i.e.*, from urn 1 to urn 0 or from urn i_{max} to urn $i_{max}+1$, the marble is returned to its starting urn.

The combinatorial counting of states described by Eq. (3) can be extended by replacing the denominator with the product of factorials of the occupancy of each urn. The entropy in this case is

$$S = k \ln \frac{N!}{\prod_{i=1}^{i_{max}} n_i!} \approx -k \sum_{i=1}^{i_{max}} n_i \ln \frac{n_i}{N}, \quad (10)$$

where Stirling's approximation has again been used to simplify the factorials. It is worthwhile to consider the limits of Eq. (10) to assure ourselves the entropy follows intuitive expectations for the marble distribution as the lottery is played out. When all the marbles sit in urn j, substituting $n_j = N$ and $n_{i\neq j} = 0$ into Eq. (10) there is only one way to achieve this distribution and the entropy is zero. In the other extreme, the entropy is maximized when the occupancies of each urn are the same and equal to N/i_{max}.[16] The entropy maximum in this case is $S_{max} = kN\ln i_{max}$, which is a generalization of the entropy maximum obtained for the two-urn lottery where $i_{max} = 2$.

While a derivation of the mean change in the entropy, $\langle \Delta S \rangle$, following each spin is more involved for the multi-urn lottery, each spin of the lottery wheel results in an exchange between only two urns. The mean entropy change is then expected to follow an equation comparable to Eq. (6). The entropy of the multi-urn lottery should therefore increase as the game is played out following the same logic as for the two-urn lottery.

Figure 4 shows the outcome of a multi-urn game with $i_{max} = 10$ urns and $N = 100$ marbles all initially placed in the first urn. The occupancy of the first urn decreases as the lottery is played out, and the marbles disperse among the remaining urns (Figure 4a). After approximately 10,000 spins, the distribution of marbles is essentially uniform and equilibrium is attained within the statistical fluctuations. As in the two-urn game, the relative fluctuations about the occupation averages decrease as the number of marbles in the game increases. The entropy of the lottery increases as the game is played, and appears to asymptotically approach the equilibrium value of $S_{max}/kN = \ln 10 = 2.3$ (Figure 4c).

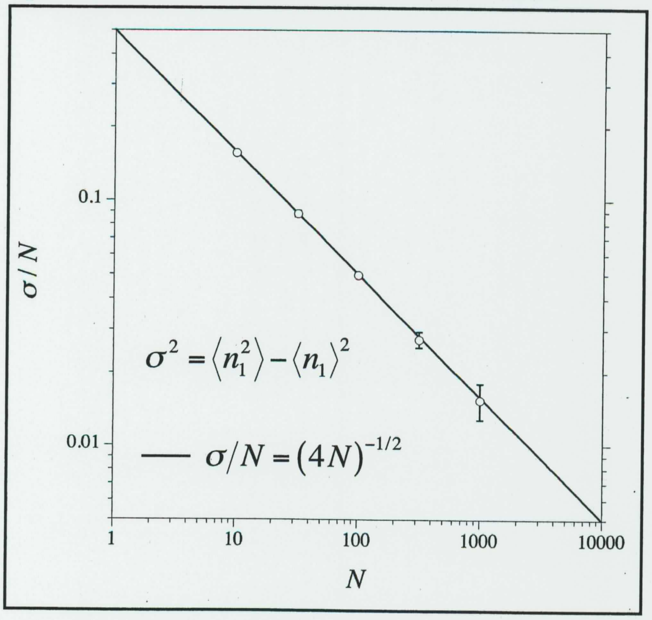
As in the two-urn game, statistical fluctuations about the equilibrium occupational state where all urns have equal numbers of marbles results in downward fluctuations in the entropy. Indeed these fluctuations appear more prominent in the 10-urn lottery than in the two-urn lottery. For a fixed number of marbles (*e.g.*, $N = 100$), the probability of observing the marbles to be evenly distributed between all the urns is lower for the multi-urn case than compared to the two-urn lottery, resulting in entropies below the maximum when each urn has equal numbers of marbles. Moreover, for a fixed number of marbles fluctuations about the mean occupational state have a larger relative effect on the fractional occupations used to calculate the entropy [Eq. (10)] as the number of urns increases. These spurious deviations from the monotonic increase in the entropy dictated by the Second Law diminish as the number of marbles increases, in agreement with the two-urn lottery.

A discrete master equation for the mean multi-urn occupation dynamics can be developed analogous to the two-urn equation [Eq. (7)]. In the present case, the change in the number of marbles in urn i as the result of a lottery spin is equal to the probability a marble from either urn i-1 or i+1 is chosen to be added to $\left[\langle n_{i+1}(s)\rangle + \langle n_{i-1}(s)\rangle\right]/2N$, less the probability a marble from urn i is removed,

$$\langle n_i(s+1)\rangle - \langle n_i(s)\rangle = \frac{\left[\langle n_{i+1}(s)\rangle + \langle n_{i-1}(s)\rangle\right]}{2N} - \frac{\langle n_i(s)\rangle}{N}. \qquad (11)$$

When a marble is chosen to move to an urn outside the sequence, the marble return boundary condition applied to urns $i = 1$ and i_{max} reduces Eq. (11) to

$$\langle n_{i\text{ or }i_{max}}(s+1)\rangle - \langle n_{i\text{ or }i_{max}}(s)\rangle = \frac{\langle n_{2\text{ or }(i_{max}-1)}(s)\rangle}{2N} - \frac{\langle n_{i\text{ or }i_{max}}(s)\rangle}{2N}. \qquad (12)$$



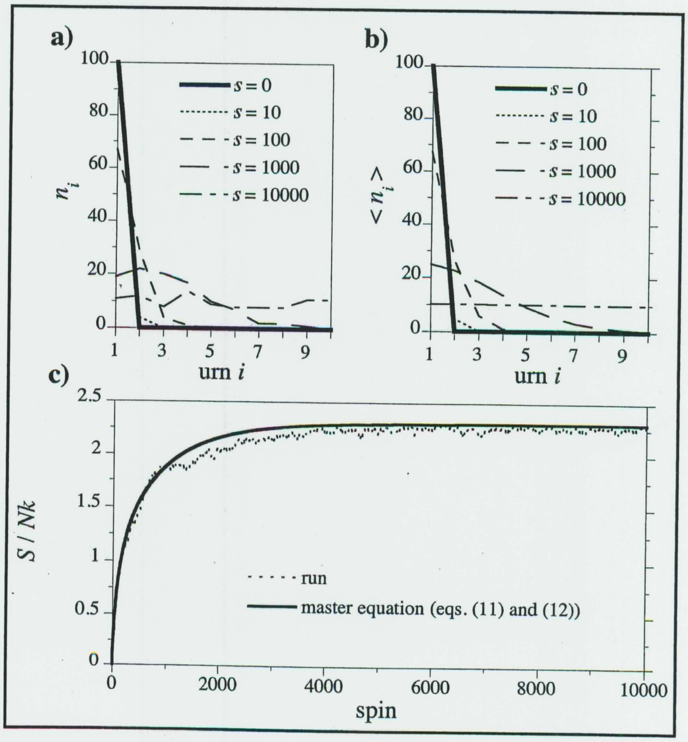


Figure 3 (above). *Relative fluctuation, σ / N, in the occupation number of urn 1 in the two-urn lottery as a function of the total number of marbles.* ***Figure 4 (right).*** *Results for a 10-urn lottery with all 100 marbles initially placed in the first urn. Occupational distributions after s spins for a random lottery and by numerical solution of the master equation description are plotted in a and b, respectively. The calculated entropies are plotted in c.*

By establishing entropy maximization in terms of familiar concepts, I hope to form a stronger foundation for explaining the connection between the Second Law of Thermodynamics and equilibrium, and show how this principle pervades problems outside the traditional thermodynamics curriculum.

If the urns are considered as being evenly spaced apart from one another by Δx, this lottery can be thought of as a model for diffusion with no flux boundary conditions. Comparing Eq. (11) with Fick's Second Law in one dimension, $\partial n/\partial t = D\partial^2 n/\partial x^2$, the change in the average occupation of urn i after the spin on the left-hand sign of the equals sign corresponds to a dimensionless time derivative, while the difference in mean urn occupations between neighboring urns on the right-hand side corresponds to a dimensionless spatial second derivative. The effective diffusion coefficient is

$$D = \frac{\Delta x^2}{2N\Delta t}. \qquad (13)$$

It should be noted that the diffusion coefficient decreases as the number of marbles increases since the marbles are moved only one at a time, while molecules truly move simultaneously. Equilibrium is achieved for Eqs. (11) and (12) when the mean occupation of all the urns is the same, at which point the entropy [Eq. (10)] is maximized. This lottery can be readily generalized to multi-dimensional diffusion depending on the spatial arrangement of urns. The occupational distribution evolution predicted by Eqs. (11) and (12) and corresponding entropies are shown in Figure 4. The agreement with the random lottery is excellent.

A TECHNICAL ISSUE REGARDING THE CONVERGENCE OF THE TWO-URN LOTTERY

It was recently pointed out that Ehrenfest's two-urn lottery technically does not converge to the binomial distribution in the limit of an infinite number of spins, but rather oscillates between two distributions whose average is the binomial distribution.[17] Perhaps the simplest demonstration of this non-convergence is if we consider a two-urn lottery with a single marble placed in urn 1. After the first spin the marble will be moved to urn 2, and subsequently relocated to urn 1 after the second spin. As the lottery progresses, the marble will oscillate back an forth between the urns, occupying urn 1 after even numbers of spins and urn 2 after odd numbers of spins. After an even number of spins then, the marble will occupy urn 1 with a probability of one and urn 2 with a probability of zero. Similarly, after an odd number of spins the marble will occupy urns 1 and 2 with probabilities of zero and one, respectively. The occupational probability distribution then has not converged to a single distribution, but vacillates between two distinct distributions. If the even and odd spin probability distributions are averaged, however, we obtain a 50/50 probability distribution as dictated by the binomial distribution for a single marble.

The nonconvergence of the two-urn probability distribution can be alleviated by breaking the even/odd symmetry by introducing spin outcomes where no marbles are moved, thereby opening up the possibility of the marble in the example above of being found in urn 1 (2) after an odd (even) number of spins. The no-flux boundary condition for the multi-urn lottery breaks the even/odd symmetry of the two-urn lottery, allowing the occupational probability distribution to converge. The two-urn lottery could converge to a single distribution, rather than an average of even and odd distributions, by enforcing the no-flux boundary condition of the multi-urn lottery after performing a second move direction determining spin. In practice, however, the nonconvergence of the two-urn lottery does not have any practical consequences on the results presented in Figures 2 and 3, since they track the evolution of states of individual spin sequences.[17]

RELATIONSHIP TO THE IDEAL GAS LAW

The long-time equilibrium of the multi-urn lottery provides an inroad for deriving the ideal gas law as an outcome of entropy maximization. From standard thermodynamic relationships, the equation of state follows from the derivative of the equilibrium entropy with respect to volume at constant internal energy and number of marbles (molecules), *i.e.*, $P = T\left(\partial S_{max}/\partial V\right)_{U,N}$. As pointed out above, the equilibrium entropy of the multi-urn lottery is $S_{max} = kN\ln i_{max}$. Based on the lottery rules, the marbles do not interact and an infinite number of marbles could potentially be placed in an urn, making the energy effectively constant. If each urn has the same volume, v_{urn}, the total volume of the system is given by the product of the number of urns and their volumes $V = i_{max} v_{urn}$. To this point I have not discussed the temperature, T, within the context of the lottery. Since the temperature is directly related to the average molecular velocity, $\Delta x/N\Delta t$, we can surmise the temperature is inversely related to the time between spins.

Based on these considerations, the pressure is given by the increase in the equilibrium entropy associated with adding another urn (volume) increment to the lottery while keeping the number of marbles constant,

$$P \approx T\frac{\Delta S_{max}}{\Delta V} = T\frac{S_{max}\left(i_{max}+1\right)-S_{max}\left(i_{max}\right)}{\left(i_{max}+1\right)v_{urn}-i_{max}v_{urn}} = kNT\frac{\ln\left(\frac{V+v_{urn}}{v_{urn}}\right)-\ln\left(\frac{V}{v_{urn}}\right)}{v_{urn}}$$

$$= kNT\frac{\ln\left(\frac{V+v_{urn}}{V}\right)}{v_{urn}} \approx \frac{kNT}{V} = \frac{nRT}{V}. \qquad (14)$$

In the final equality, $n = N/N_A$ is the number of marbles/molecules in mole units. Thus, the ideal gas law follows from the dispersal of marbles among a collection of urns. Non-ideal contributions to the equation-of-state arise from the introduction of energetic interactions between marbles, *e.g.*, excluded volume and dispersion interactions, which temper the urn occupancies.

PROGRAM AVAILABILITY

The lottery results reported in Figures 2 – 4 were generated using a MATLAB® simulation. I have uploaded the MATLAB® program, sample input files, and run instructions to the MathWorks file exchange website for free distribution.[18] This program simulates the two- and multi-urn lotteries, solves the master equation spin dynamics, calculates entropies, and plots the results.

DISCUSSION

Ehrenfest's Lottery can be used at multiple points throughout the thermodynamics curriculum to reinforce the role of the Second Law of Thermodynamics in determining equilibrium and to highlight the molecular nature of substances. In practice, I have used the two-urn lottery at the beginning of our discussions of the Second Law during the first semester thermodynamics class at Tulane University. The multi-urn lottery and the connection to the ideal gas law are introduced further along in the semester once thermodynamic partial derivative relationships have been discussed. I return to the multi-urn lottery in our second-semester thermodynamics class after our students have had transport phenomena to connect diffusion processes to the Second Law. This model can be readily extended to ideal mixing and the van der Waals equation of state by introducing additional rules into the game, like adding colors to the marbles (mixing) or finite marble volumes and attractive interactions between marbles in neighboring urns (van der Waals). An alternate formulation of this model, referred to as the Dog and Flea model, has also been developed to further explore transport phenomena for small systems and chemical reactions.[19] While not a panacea, Ehrenfest's lottery provides a simple model that, when used in conjunction with other illustrative examples like the Carnot cycle, can shore up student appreciation of the Second Law of Thermodynamics.

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