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Thermodynamics using coins

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Abstract. Students often have difficulty understanding the concepts of entropy and irreversibility, and to a lesser extent, temperature. This is partially due to the statistical nature of these concepts and the abstract connection between probability and energy. The example of a large collection of coins is used to elucidate the basic concepts of probability (in particular, the law of large numbers), and uses them in the same setting to disentangle the more difficult notions of temperature, entropy, and irreversibility.

1. A review of the statistics of coins

The probability $P_n(m)$ of m 'heads' (H) turning up in a throw of n coins, for very large n and m with m very close to $n/2$, is given (see appendix A.1) by

$$P_n(m) \approx \sqrt{\frac{2}{n\pi}} \exp\left(-\frac{(n-2m)^2}{2n}\right) = P_n(n/2) \exp\left(-\frac{(n-2m)^2}{2n}\right). \qquad (1)$$

Here $P_n(m)$ is a typical Gaussian bell-shaped curve with a maximum of $\sqrt{2/n\pi}$ at $m = n/2$ (see figure 1). The *relative width* (see below for a definition) of this curve determines how quickly the probability drops to 'negligible' values as m moves away from $n/2$. For us, negligible means small compared with the *most probable*. So, let us consider the ratio $r \equiv P_n(m)/P_n(n/2)$, and agree that if r is less than some small number 10^{-2x} we call the corresponding probability negligible. The value we assign to x depends on how demanding we wish to be. We can thus define $m_\pm$ by the following relation:

$$r = \exp\left(-\frac{(n-2m_\pm)^2}{2n}\right) = 10^{-2x} \quad \Rightarrow \quad m_\pm = \frac{n}{2} \pm \sqrt{nx \ln 10}. \qquad (2)$$

We expect the probability to be concentrated between the two values of m_- and m_+ if we take x in (2) sufficiently large. In appendix A.1 we calculate this probability and denote it by $P_\pm(x)$. If we take x to be 3, so that $m_\pm$ is a millionth of the maximum, then $P_\pm(3) = 0.999\,999\,86$. In terms of coins, this means that for large n, say a million coins, for which $m_\pm = 500\,000 \pm 2628$, the probability of getting a number of heads larger than 502 628 or smaller than 497 372 is only 1.4 parts in 10 million! For larger values of x the probability is considerably smaller.

Note that although the absolute width $m_+ - m_-$ of the curve increases as $\sqrt{n}$, the *relative* width $(m_+ - m_-)/n$ shrinks as $1/\sqrt{n}$. Since we are comparing outcomes with the maximum at $n/2$, it is the relative width that is the true measure of the sharpness of the peak. This is reflected in figure 1.

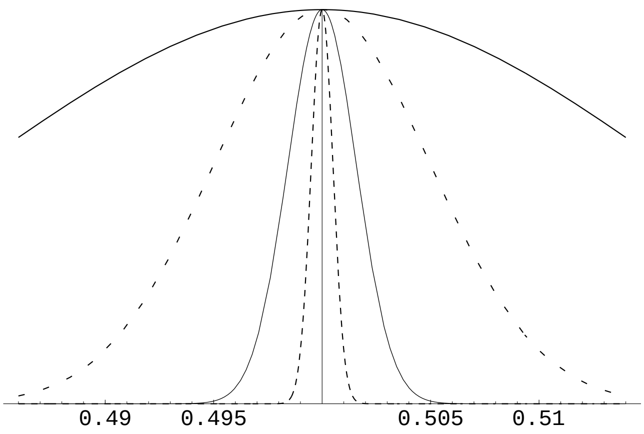

Figure 1. The ratio r for 1000 (the outermost curve), 10 000, 100 000, and a million (the innermost curve) coins. The number of heads (horizontal axis) has been normalized to one. It can clearly be seen that the *relative* peak becomes narrower and narrower as the number of coins increases.

1.1. The law of large numbers

To appreciate the counter-intuitive character of probability theory, let us describe a thought experiment in which we toss a large number of coins, say a trillion, and 'count' the number of 'heads' that turn up in each toss. A detailed enumeration of the coins is out of the question. A slightly more convenient alternative is to paint the 'tail' of each coin white and the 'head' black, load them on cargo planes, drop the coins over a flat desert, and check for 'grayness'. Assume we are so far above the ground that the area covered with black and white coins appears as one square foot. Then if exactly half of the coins were head and half tail, we would see a shade of gray which we call *perfect*.

We now ask the important question: what are the odds of seeing anything *but* a perfect gray? An imperfect gray would have a shade of black or white indicating an imbalance between the number of heads and the number of tails. Let us concentrate on the shade of black, and ask the question: how many more black sides (than white sides) should turn up before the eye can distinguish the shade of black? The following analogy helps clarify this question.

The resolution of the eye in distinguishing various shades of gray varies from person to person. Assume that we can find somebody whose eyes are sharp enough to distinguish between perfect gray and the shade obtained when one drop of black paint is added to a gallon of perfect gray. What is the ratio of black to white? There is half a gallon plus one drop of black and exactly half a gallon of white. There are approximately 100 000 drops in a gallon. Out of these, 50 000 are black and 50 000 are white when the paint is perfect gray. Adding one black drop changes the ratio to $50\,001/50\,000 = 1.000\,02$.

Going back to the coins, we conclude that, for this pair of 'super' eyes to be able to distinguish the shade of black, the ratio of the number of black coins to white coins must be at least 1.000 02. Since the total number of coins is one trillion, the actual number of black heads must be 500 005 000 000 leaving 499 995 000 000 white tails.

What are the odds that in a random throw of a trillion coins, the number of heads is larger than 500 005 000 000 or smaller than 499 995 000 000? With $m_+ = 500\,005\,000\,000$, we get $x = 10.857$ and a value of $P_\pm$ which is extremely close to 1. In fact the probability $P = 1 - P_\pm(10.857)$ of obtaining a number of heads which is fewer than m_- and larger than m_+ is approximately 1.5×10^{-23}.

This is an astonishingly small number. To get a better understanding of how small this number is, suppose that we construct microscopic black and white pennies so that each trial consists of shaking them in a can and throwing them on a flat table-top, and suppose that we have a machine that can do this a hundred thousand times per second. To see an occurrence of non-perfect gray, we need (on average) to throw the coins 10^{23} times, or wait 10^{18} s, i.e. over 30 billion years, or almost twice the age of the Universe!

The upshot of the above discussion is that as the number of coins (events) increases, the probability of getting anything but the average (expected, mean) value becomes smaller and smaller. For extremely large numbers of events, such as 10^{12} in the above experiment or 10^{24} for the number of atoms or molecules in a typical sample of matter, the probability of any measurable deviation from the mean is hopelessly small. This is the *law of large numbers*. This law is responsible for the predictive power of both the second law of thermodynamics and the entire quantum theory. Both of these disciplines are utterly useless when predicting *individual* microscopic events, but become indispensable when dealing with a macroscopic collection of these events. Fortunately, we rarely deal with a single microscopic phenomenon, so both the second law of thermodynamics and quantum theory are as predictive as the deterministic laws of classical mechanics.

2. The statistical origin of temperature

In our preceding analysis of coins, we placed no constraint on 'energy'. there was an unlimited supply of energy that could be added to the system. This energy was simply the effort of the tosser of the coins. How would the analysis change if energy conservation were taken into account? Let us assign the values of energy $+\epsilon$ to the head and $-\epsilon$ to the tail of a coin. Conservation of energy then does not allow any configuration whose total energy does not add up to the given fixed numerical value of energy. Thus, if we have 10 coins, and the total energy is $+6\epsilon$, any combination of the 10 coins resulting in 8 heads (H) and 2 tails (T) (and *only* 8 H and 2 T) is allowed. The allowed configurations, i.e. those that respect the energy conservation law are called *accessible states*.

Isolated systems are not interesting, because they neither affect nor are affected by the outside world; in particular, one cannot observe them, as observation requires interaction and contact. So, we let our system come in contact with another system. By contact we mean to imply the possibility of *energy exchange* between the two systems. Of course, conservation of energy does not allow the total energy of the two systems to change. However, because of the exchange of energy, the system of interest has more freedom of movement. In particular, many more accessible states are available to it.

As a concrete numerical example, imagine that the system above (call it system A) interacts with system B with 20 coins. Let us assume again that the total energy of the combined system is $+6\epsilon$. Because of its interaction with system B, system A has many more possibilities open to it. For instance, while in the discussion above the coins of our system could not have been all $+\epsilon$ or all $-\epsilon$, this possibility now exists because the 10 coins can borrow energy from the other system and all flip to head or to tail. In fact the only constraint is that the total number of positive coins outnumber the total number of negative coins by 6. This means that out of 30 coins, we must have 18 positive coins and 12 negative coins. How these positive or negative coins distribute themselves in the two systems is irrelevant.

In what states are we most likely find our system when we allow it to interact with another system? Suppose that the first system has n coins, m of which are positive, the second system N coins, M of which are positive, and the total energy of the two systems is $\mathcal{E}$. In appendix A.2 we show that the result can be expressed as

$$\frac{e_{\max}}{n} = \frac{E_{\max}}{N} = \frac{\mathcal{E}}{N+n} \tag{3}$$

where $e_{\max}$ is the energy of the first system that maximizes the probability, and $E_{\max} = \mathcal{E} - e_{\max}$ is the corresponding energy for the other system. Noting that $e_{\max}/n$ is the most probable *average* energy per coin of the system (with corresponding interpretation for the other ratios), equation (3) states:

> The most probable configuration of one system in contact with another is that for which the *average energy* per coin of both systems are equal, and both have the common value of the average energy of the two systems combined.

This statement connects statistical mechanics with thermodynamics. Two systems in contact will eventually attain the same final *temperature*. On the other hand, any macroscopic system in equilibrium is always in the most probable state (recall the example of perfect gray and how improbable it was to get anything but perfect gray). It follows that the balance of temperature is attained at the same time that the balance of average energies are achieved. It is, therefore, natural to conclude that *temperature is proportional to the average energy of the coins*:

$$e_{\mathrm{avg}} = kT = \frac{e_{\max}}{n}. \tag{4}$$

When two systems are in the most probable (combined) configuration, we say they are in *thermal equilibrium*. Regardless of their initial states, the final (most probable) configuration is marked by the equality of their temperatures, or average energy per molecule.

3. Entropy and irreversibility

A paradigm of irreversibility and a situation in which the concept of entropy is usually introduced is the transfer of heat (energy) from a hot object to a cold object. Consider bringing two systems A and B, with initial temperatures T_{A} and T_{B}, in contact with one another. First let us look at what happens to the temperatures of the two systems. The average energy in the final equilibrium of the combined system, i.e. the final temperature T_{f}, can be obtained by using equations (3) and (4):

$$T_{\mathrm{f}} = \frac{\mathcal{E}}{k(n_{\mathrm{A}} + n_{\mathrm{B}})} = \frac{e_{\mathrm{A}\max} + e_{\mathrm{B}\max}}{k(n_{\mathrm{A}} + n_{\mathrm{B}})} = \frac{n_{\mathrm{A}}T_{\mathrm{A}} + n_{\mathrm{B}}T_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}}. \tag{5}$$

Thus, the final temperature lies somewhere between the initial temperatures of the two systems. If one of the systems is much larger than the other, say $n_{\mathrm{B}} \gg n_{\mathrm{A}}$, then $T_{\mathrm{f}} \approx T_{\mathrm{B}}$. Consequently, the temperature of a very large system in contact with a much smaller system does not change. It is common to call such a large system a *reservoir*.

Next we ask how likely it is for each system in contact to attain a temperature that is different from T_{f}, and therefore (by conservation of energy), different from the other system's temperature. Appendix A.3 gives the answer as

$$\frac{P(T_{\mathrm{A}})}{P(T_{\mathrm{f}})} = \exp\left(-(\Delta T/\tau)^2\right) \qquad \text{where} \;\; \tau = \frac{\epsilon}{k}\sqrt{2\left(\frac{1}{n_{\mathrm{A}}} + \frac{1}{n_{\mathrm{B}}}\right)}.$$

For typical values of $\epsilon = 10^{-19}$, $k = 10^{-23}$, and $n_{\mathrm{A}} \approx n_{\mathrm{B}} \approx 10^{24}$, we get $\tau \approx 10^{-8}$. Thus, for any reasonable finite value of ΔT, the ratio is completely negligible. For example, the odds of the occurrence of as small a temperature difference as a millionth of a degree is 10^{4343} to 1! Therefore, unless $T_{\mathrm{A}} = T_{\mathrm{B}}$ already, retention of (or subsequent return to) the initial configuration is extremely unlikely. The process of the exchange of energy (heat) between systems A and B and their achievement of thermal equilibrium is *irreversible*, and this irreversibility is completely statistical.

The above discussion illustrates the connection between the number of accessible states and the entropy for a 'gas' of coins as follows. If two systems that are not in thermal equilibrium are brought together and allowed to exchange energy, the final equilibrium configuration will be *both* the most probable configuration *and* a configuration in which the temperatures are equal. However, the most probable configuration is precisely that configuration which has the largest number of accessible states as discussed in section 2. Since entropy is simply (proportional to the natural logarithm of) the number of accessible states, we conclude that *when two systems, initially not in thermal equilibrium, are brought in contact, their total entropy will increase*. This is the law of increasing entropy, the most common version of the second law of thermodynamics.

4. Conclusion

We have presented a discussion of the abstract thermodynamical concepts using the concrete statistical system of a large number of coins. In the presentation, we demonstrated the law of large numbers and the fact that the second law of thermodynamics, whether stated as the law of increase of entropy or as irreversibility, is completely statistical in nature, and that the same laws that govern the toss of coins also predict such inherently physical processes as the transfer of heat or the attainment of equilibrium temperatures.

Appendix

A.1. Probability

The frequency of m heads (H) turning up in a throw of n identical coins is denoted by $f_n(m)$ and is given [1, pp 10–15] by

$$f_n(m) = \frac{n!}{m!(n-m)!} \tag{A1}$$

and the probability is simply the ratio of the frequency to the total number of outcomes 2^n. So, writing $P_n(m)$ for this probability, we have

$$P_n(m) = \frac{f_n(m)}{2^n} = \frac{n!}{m!(n-m)!2^n}. \tag{A2}$$

A convenient approximation to this equation is obtained when n and m are very large and m is very close to $n/2$, the average number of H's. For such a situation, we can use the *Stirling approximation* for factorials, i.e. (see [1, pp 441–4] or [2, p 316])

$$N! \approx \sqrt{2\pi}\mathrm{e}^{-N} N^{N+\frac{1}{2}}.$$

This yields

$$P_n(m) \approx \frac{\sqrt{2\pi}\mathrm{e}^{-n} n^{n+\frac{1}{2}}}{2^n \sqrt{2\pi} \exp\left(-(\frac{1}{2}n+k)\right)(\frac{1}{2}n+k)^{\frac{1}{2}n+k+\frac{1}{2}} \sqrt{2\pi} \exp\left(-(\frac{1}{2}n-k)\right)(\frac{1}{2}n-k)^{\frac{1}{2}n-k+\frac{1}{2}}}$$

where we defined $k \equiv m - \frac{1}{2}n \ll \frac{1}{2}n$. The equation above simplifies to

$$\begin{aligned} P_n(m) &\approx \sqrt{\frac{n}{2\pi}} \frac{(\frac{1}{2}n)^n}{(\frac{1}{2}n)^{\frac{1}{2}n+k+\frac{1}{2}}(1+2k/n)^{\frac{1}{2}n+k+\frac{1}{2}}(\frac{1}{2}n)^{\frac{1}{2}n-k+\frac{1}{2}}(1-2k/n)^{\frac{1}{2}n-k+\frac{1}{2}}} \\ &= \sqrt{\frac{n}{2\pi}} \frac{1}{(\frac{1}{2}n)(1+2k/n)^{\frac{1}{2}n+k+\frac{1}{2}}(\frac{1}{2}n)^{\frac{1}{2}n-k+\frac{1}{2}}(1-2k/n)^{\frac{1}{2}n-k+\frac{1}{2}}} \end{aligned} \tag{A3}$$

Using $\ln[(1+x)^m] = m\ln(1+x) = m(x - x^2/2)$, we can show that up to order $1/n$

$$\left(1 \pm \frac{2k}{n}\right)^{\frac{1}{2}n\pm k+\frac{1}{2}} \approx \exp\left(\pm k + \frac{k^2}{n} \pm \frac{k}{n}\right).$$

Substituting this result in the denominator of equation (A3) yields equation (1).

We shall be interested in very large (10^{12}) values of n and m, but even for modest values, the approximation is in very good agreement with the exact formula. For example,

$P_{100}(51) = 0.078\,2087$ using the exact formula, and $P_{100}(51) = 0.078\,2085$ using the approximate formula.

Now we add the probabilities between the two values m_- and m_+ defined in the text. Instead of summing equation (A2), we integrate equation (1):

$$P_\pm(x) = \int_{m_-}^{m_+} \sqrt{\frac{2}{n\pi}} \exp\left(-\frac{(n-2m)^2}{2n}\right) \mathrm{d}m = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{2x \ln 10}} \mathrm{e}^{-t^2}\,\mathrm{d}t \qquad \text{(A4)}$$

where we changed the integration variable from m to $t = (2m - n)/\sqrt{2n}$.

A.2. Temperature

The total number of configurations available for the two systems is the *product of the numbers of configurations for the two systems*. Denoting the total number of possibilities by $F(m)$, we can write

$$F(m) = \left\{\frac{n!}{m!(n-m)!}\right\}\left\{\frac{N!}{M!(N-M)!}\right\}$$
$$\approx 2^{N+n}\sqrt{\frac{2}{n\pi}}\sqrt{\frac{2}{N\pi}} \exp\left(-\left[\frac{(n-2m)^2}{2n} + \frac{(N-2M)^2}{2N}\right]\right). \qquad \text{(A5)}$$

The function F depends only on m because M can be calculated in terms of m. To see this, we note that the energies e and E of the systems with n and N coins, respectively, can be written as

$$e = m\epsilon - (n-m)\epsilon = (2m-n)\epsilon \qquad \text{and} \qquad E = (2M - N)\epsilon. \qquad \text{(A6)}$$

Since the total energy of the combined system $\mathcal{E}$ is fixed, we have

$$\mathcal{E} = e + E = [2(M+m) - N - n]\epsilon \qquad \text{(A7)}$$

and

$$M = \tfrac{1}{2}[(\mathcal{E}/\epsilon) + N + n] - m. \qquad \text{(A8)}$$

The most probable configuration occurs at a value of m, denoted by $m_{\max}$, which maximizes the function $F(m)$. This maximum can be readily obtained by extremizing (the exponent of) equation (A5) subject to equation (A8). The result can be expressed as

$$\frac{m_{\max}}{n} = \frac{M_{\max}}{N} = \frac{M_{\max} + m_{\max}}{N+n} \qquad \text{(A9)}$$

with the second equality following from the first. Using equation (A6) in (A9), with $m_{\max}$ and $M_{\max}$ replacing m and M, gives the condition (3) of maximum probability in terms of energy.

An interesting consequence of equation (A8) is that $M + m$ is fixed. In particular, one can replace $M_{\max} + m_{\max}$ with $M + m$ in equation (A9) and obtain

$$m_{\max} = \frac{n}{N+n}(M+m). \qquad \text{(A10)}$$

We shall use this result shortly.

A.3. Irreversibility

In equation (A5), let

$$\alpha(m) \equiv \frac{(n-2m)^2}{2n} + \frac{(N-2M)^2}{2N}$$
$$= \frac{N+n}{2} - 2(M+m) + 2\left(\frac{m^2}{n} + \frac{M^2}{N}\right). \qquad \text{(A11)}$$

We are interested in the ratio $P(m)/P(m_{\rm max})$, which is the same as

$$\frac{F(m)}{F(m_{\rm max})} = \exp\left(\alpha(m_{\rm max}) - \alpha(m)\right)$$

Since $N + n$ and $M + m$ are fixed, evaluating equation (A11) at $m_{\rm max}$ and subtracting yields

$$\alpha(m_{\rm max}) - \alpha(m) = 2\frac{m_{\rm max}^2 - m^2}{n} + 2\frac{M_{\rm max}^2 - M^2}{N}.$$

Expressing $M_{\rm max}$ in terms of $m_{\rm max}$ using equation (A9), and M in terms of m and $m_{\rm max}$ using equation (A10), and substituting the result in the last equation, after a little algebra we obtain

$$\alpha(m_{\rm max}) - \alpha(m) = -\left(\frac{2}{n} + \frac{2}{N}\right)(m_{\rm max} - m)^2.$$

It now follows that

$$\frac{P(m)}{P(m_{\rm max})} = \frac{F(m)}{F(m_{\rm max})} = \exp\left(-\left(\frac{2}{n} + \frac{2}{N}\right)(m_{\rm max} - m)^2\right) \qquad \text{(A12)}$$

which, using equation (A10), can also be written as

$$\frac{P(m)}{P(m_{\rm max})} = \exp\left\{-\left(\frac{2}{n} + \frac{2}{N}\right)\left(\frac{Mn - mN}{n + N}\right)^2\right\}. \qquad \text{(A13)}$$

We now want to measure the probability of the two systems attaining two different temperatures (while still in contact). To do this, we express the exponent of equation (A13) in terms of temperatures. The specification of the temperature means that m is the most probable value of the system corresponding to a temperature T_m and M is the most probable value of the second system corresponding to a temperature T_M. Then equation (A6) yields

$$m = \frac{1}{2}\left(\frac{e}{\epsilon} + n\right) = \frac{1}{2}n\left(\frac{kT_m}{\epsilon} + 1\right) \qquad \text{and} \qquad M = \frac{N}{2}\left(\frac{kT_M}{\epsilon} + 1\right)$$

so that

$$\frac{Mn - mN}{n + N} = \frac{nNk(T_M - T_m)}{2\epsilon(N + n)} = \frac{(k/\epsilon)(T_M - T_m)}{2(1/N + 1/n)}.$$

Thus the ratio of the probability of finding the system away from its equilibrium state (with temperature $T_{\rm f}$ given by equation (5)) to the probability of finding it at its final equilibrium state is

$$\frac{P(T_m)}{P(T_{\rm f})} = \frac{P(m)}{P(m_{\rm max})} = \exp\left[-\frac{k^2(T_M - T_m)^2/\epsilon^2}{2(1/N + 1/n)}\right] \equiv \exp\left(-(\Delta T/\tau)^2\right) \quad \text{(A14)}$$

where

$$\tau = \frac{\epsilon}{k}\sqrt{2\left(\frac{1}{N} + \frac{1}{n}\right)}.$$

References

[1] Kittel P and Kroemer H 1980 *Thermal Physics* 2nd edn (San Francisco: Freeman)
[2] Hassani S 1999 *Mathematical Physics: A Modern Introduction to its Foundations* (Berlin: Springer)