Entropy and the Second Law

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I. MIRCO- AND MACROSTATES

Simple things can pose subtle questions. A bouncing ball quickly and surely comes to rest. Why doesn't a ball at rest start to bounce? There is nothing in Newton's law of motion that could prevent this; yet we have never seen it occur. Two flask connected by a hose. Initially, bromine gas is on one flask only. When the clamp is opened, the bromine diffuses almost instantly into the evacuated flask. The gas fills the two flasks about equally. The molecules seem never to rush back and all congregate in one flask.

The metaphoric images invoked for entropy include "disorder," "randomness," "smoothness," "dispersion," and "homogeneity."

Microscopic characterization: coordinates and momenta of all molecules. *Macroscopic* characterization: more or less uniform distribution [large scale]. **Macroscopic regularity**: When a physical system is allowed to evolve in isolation, some single macroscopic outcome is overwhelmingly more probable than others. Macroscopic state: pressure P, volume V, temperature T, and mass m. Some macrostates have many microstates that correspond to them: others just a few: the multiplicity of a macrostate equals the number of microstates that corresponds to the macrostate.

II. COMBINATORICS

100 coin toss. Macrostate with zero heads: $\Omega(0) = 1$. Macrostate with one head: $\Omega(1) = 100$. Macrostate with two heads: first head has 100 possible locations, the second one has 99 possible locations. Because the two heads are interchangable, we have

$$\Omega(2) = \frac{100 \cdot 99}{2}. \tag{1}$$

For three heads:

$$\Omega(3) = \frac{100 \cdot 99 \cdot 98}{3 \cdot 2 \cdot 1}. \tag{2}$$

For arbitrary n:

$$\begin{aligned} \Omega(n) &= \frac{100 \cdot 99 \cdot 98 \cdot \ldots (100-n+1)}{n \cdot (n-1) \cdot \ldots 2 \cdot 1} \\ &= \frac{100!}{n!(100-n)!} \equiv \begin{pmatrix} 100 \\ n \end{pmatrix}. \end{aligned} \tag{3}$$

Two state paramagnet: $N_\uparrow$ spins up and $N_\downarrow$ spins down. Total number of spins $N = N_\uparrow + N_\downarrow$. The multiplicity of a macrostate with $N_\uparrow$ spins up:

$$\Omega(N_\uparrow) = \frac{N!}{N_\uparrow ! N_\downarrow !}. \tag{4}$$

III. EINSTEIN SOLID

Consider a collection of microscopic systems that can each store any number of energy units, all of the same size. Question: in how many ways can we distribute the energy q among N oscillators? This number we call the *multiplicity* Ω. We represent each energy unit by a dot and the partition between oscillator by a line. The total number of symbols is $q + N - 1$. What is the number of ways of choosing q dots among $q + N - 1$ symbols:

$$\Omega(N, q) = \begin{pmatrix} q+N-1 \\ q \end{pmatrix} = \frac{(q+N-1)!}{q!(N-1)!}. \tag{5}$$

System made up of two solids "A" and "B",

$$N_A = N_B = 3, \tag{6}$$

and the total energy

$$q_{\rm tot} = q_A + q_B = 6. \tag{7}$$

A macrostate specifies the energy q_A, q_B in each subsystem. A microstaate would also specify the energy in each oscillator belonging either to solid A or B. We find

q_A	Ω_A	q_B	Ω_B	$\Omega = \Omega_A \cdot \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

(8)

This gives a total of

$$462 = \begin{pmatrix} 6+6-1 \\ 6 \end{pmatrix} \tag{9}$$

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possible arrangements.

How does the distribution depend on the size of the system [i.e., N, N_A, N_B]? Generally, we have for the variance $\sigma^2 \propto N$ [this is called the *law of large numbers*] so that a fluctuation follows

$$q_A - \langle q_A \rangle \propto \sqrt{N}. \tag{10}$$

This implies that the relative size of fluctuations scales with systemm size

$$\frac{q_A - \langle q_A \rangle}{\langle q_A \rangle} \sim \frac{1}{\sqrt{N}}. \tag{11}$$

Therefore, the distribution becomes infinitely narrow for macroscopic systems, and the energy of a macroscopic system has a well-defined meaning.

IV. SECOND LAW OF THERMODYANICS

Fundamental assumption of statistical mechanics: in an isolated system in thermal equilibrium, all possible microstates are equally possible. If we make the system larger and larger $N \to \infty$, the distribution becomes more and more narrow: most likely configuration. Second law of Thermodynamics: the spontaneous flow of energy stops when a system is at, or very near, its most likely macrostate, that is the state with the greatest multiplicity. This is the origin of irreversible behavior in nature.

Question: Could we build a rocket by pumping seawater, extract some energy, and then throw the water back as ice? First law: okay. But we go from one macrostate with high multiplicity to a macrostate with low multiplicity.

V. ENERGY TRANSFER BY HEATING

Consider an ideal gas and study how the multiplicity changes when we allow the gas to expand by a small amount. As we slowly out in energy by heating, we let the gas (slowly) expand and do work so that the temperature of the gas doesn't change: $\Delta U = 0$, or

$$q = -\Delta W. \tag{12}$$

The multiplicity of the system $\Omega \sim V^N$. Thus

$$\frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}} = \frac{V + \Delta V)^N}{V^N} = \left(1 + \frac{\Delta V}{V}\right)^N. \tag{13}$$

We have

$$q = P\Delta V = \frac{NkT}{V}\Delta V, \tag{14}$$

or,

$$\frac{q}{NkT} = \frac{\Delta V}{V}. \tag{15}$$

We then have for the ratio of multiplicities:

$$\frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}} = \left(1 + \frac{q}{NkT}\right)^N \sim \exp\left(\frac{q}{kT}\right) \quad N \to \infty. \tag{16}$$

We define *entropy*

$$S = k \ln \Omega. \tag{17}$$

We then have

$$S_{\text{final}} - S_{\text{intial}} = \frac{q}{T}. \tag{18}$$

Entropy is Greek and mean "the turning" or "the transformation." (Clausius 1865).

Generalization: If the expansion is fast and we do not put in energy as heat $q = 0$ but $\Delta S > 0$. In general, we then have

$$\Delta S \geq \frac{q}{T}. \tag{19}$$

But is the second law compatible with Newtonian mechanics? We can describe our system by a region in a multidimensional phase space. The increase in entropy then implies that the region in phase space is increasing. But this cannot be since the system obeys Newton's law of motion so that the phase volume of the system is constant [Liouville's theorem]. To resolve this puzzle, we note that the phase volume may spread out into fine filaments. The second law of thermodynamics thus makes only sense in a 'coarse-grained' picture and we can say that the phase volume has *effectively* grown larger: we are forced to say this if we are unable to distinguish the spaces between filaments. As an instructive analogue [due to Gibbs], consider the insertion of a small ink spot in a viscous fluid such as honey which is then stirred. The ink will spread out over the whole liquid, but when observed under a microscope, fine filaments of ink will be observed and the total volume of the ink drop has not changed. The volume of the ink drop is thus conserved but upon coarse observation one would say that the ink has "spread over" the whole volume of honey. [Irreversibility and the foundations of thermodynamics are topics of current research (and controversy): they are related to 'coarse graining' and ergodicity. Useful introductions are J. L. Lebowitz and O. Penrose, Physics Today, February 1973 and J. L. Lebowitz, September 1993]

VI. SOME EXAMPLES

Melting of ice: Suppose we slowly melt an ice cube at 0°C. By what factor does the multiplicity change? Latent heat of melting $L = 3.34 \times 10^5$J/kg. An ice cube is about 18 grams so that

$$Q = 6.01\,\text{kJ}. \tag{20}$$

The change in entropy follows:

$$\Delta S = \frac{Q}{T} = \frac{6.01\,\text{kJ}}{273\,\text{K}} = 22\,\text{JK}^{-1}. \tag{21}$$

We thus have for the ratio of multiplicities:

$$\ln\left(\frac{\Omega_{\text{liquid}}}{\Omega_{\text{ice}}}\right) = \frac{1}{k}\frac{Q}{T} = 1.6\times 10^{24}, \qquad (22)$$

or

$$\frac{\Omega_{\text{liquid}}}{\Omega_{\text{ice}}} = \exp\left(1.6\times 10^{24}\right). \qquad (23)$$

This is a staggering increase in multiplicity.

Slow adiabatic expansion: We allow the gas to expand slowly, but now specify *no heating* by an external source of energy. We have $q = 0$ so that $\Delta S = 0$ and thus the multiplicity of the gas does not change. Note that the momentum contributes to the multiplicity of the system. If the accessible configuration space increases then the momentum space must decrease: that is, the momenta of the particles must be smaller. Because the temperature is proportional to the kinetic energy, this implies that the gas is cooling down.

Mixing: Question: What is the change in entropy that occurs when two moles of helium and three moles of oxygen, bothh at s.t.p. and in adjacent volumes, are allowed to mix by removing the partition between them?
Solution: The number of microstates available to a system of N objects confined to a volume V is proportional to V^N [both classically and quantum-mechanically]. Initially there are $2N_A$ molecules of helium occupying $2V_0$ ($V_0 \simeq 0.0224\,\text{m}^3$), and $3N_A$ molecules of oxygen occupying $3V_0$. After the partition is removed, there are $5N_A$ molecules occupying $5V_0$. The ratio of the number of microsates [multiplicity] is:

$$\frac{W_{\text{f}}}{W_{\text{i}}} = \frac{(5V_0)^{2N_A}}{(2V_0)^{2N_A}} \times \frac{(5V_0)^{3N_A}}{(3V_0)^{3N_A}} = \frac{(5V_0)^{5N_A}}{(2V_0)^{2N_A}\,(3V_0)^{3N_A}}. \qquad (24)$$

Thus, the change in entropy follows

$$\Delta S = k\ln\frac{W_{\text{f}}}{W_{\text{i}}} = kN_A\left(5\ln 5 - 2\ln 2 - 3\ln 3\right) = 27.9\,\text{JK}^{-1}. \qquad (25)$$

Note: If we had investigated the mixing of two *identical* gases [e.g., two moles of helium and three moles of helium] both at s.t.p., the calculated entropy change would seem to be the same. However, it is obvious there can be no entropy change, because physically nothing is happening by inserting a partition. We have to include a so-called delabeling factor $N!$ reflects the fact that $N!$ different phase space points corresponds to the same physical system. These $N!$ points all represent N particles at N given locations and with corresponding given velocities, and differ only in the labels affixed to the various particles. On a more pragmatic vein, if the factor $N!$ were absent, then the resulting entropy would not be extensive, i.e., $S \propto N$. This is called the *Gibbs paradox* [see, e.g., D. Hestenes, Am. J. Phys. **38**, 840 (1970)].

Monatomic ideal gas: The multiplicity of a monatomic gas is difficult. We have the length of a box l so that $S \sim l^{3N} \sim V^N$. The maximum momentum is $p_{\max} \sim U^{1/2}$ so that $S \sim (U^{1/2})^{3N} = U^{3N/2}$. Combined we have

$$\Omega(U, V, N) = f(N)V^N U^{3N/2}. \qquad (26)$$

The entropy of a pure classical monatomic ideal gas as a function of energy E, volume V, and particle number N is given by the Sackur-Tetrode formula:

$$S(E, V, N) = kN\left[\frac{3}{2}\ln\left(\frac{4\pi mEV^{2/3}}{3h^2N^{5/3}}\right) + \frac{5}{2}\right]. \qquad (27)$$

Here h is Planck's constant. [In classical mechanics, h is an arbitrary constant with the dimensions of action]. Let's examine the qualitative behavior. If V increases then S increases: if the volume goes up, then each particle has more places where it can be, so the entropy ought to go up. If the E increases then S increases: if there is more energy, then there are more different ways to split up and share it among the particles. What about the dependence on m? Sackur-Tetrode tells us that the entropy increases with mass, but is there a way to understand this qualitatively? Two arguments: 1) We have $E = (1/2m)\sum_i p_i^2$ so for a given E, any individual particle may have a momentum between 0 and $\sqrt{2mE}$ so that a larger mass implies a wider range of possible momenta. This suggests more microstates and a greater entropy. 2) We write instead $E = (m/2)\sum_i v_i^2$, so far a given E, any individual particle may have sspeed ranging from 0 and $\sqrt{2E/m}$. A larger mass implies a narrowed range of possible speed. This suggests fewer microstates and a smaller entropy. [The resolution of this puzzle hinges on the fact that the propoer 'home' of statistical mechanics is phase space and not configuration space, see Liouville's theorem].

Lattice gas configurations: D. F. Styer, Am. J. Phys. **68**, 1090 (2000): distinction between a *typical* and an *average* configuration.

Entropy and Poker: Consider the hand

$$A\heartsuit, K\heartsuit, Q\heartsuit, J\heartsuit, 10\heartsuit \qquad (28)$$

which is the Royal flush, the most powerful hand in poker. Any poker player who has ever been dealt a royal flush will remember it for the rest of his/her life. By contrast, no one can remember whether he or she has been dealt the hand

$$4\diamondsuit, 3\diamondsuit, J\heartsuit, 2\spadesuit, 7\diamondsuit \qquad (29)$$

because this hand is a member of an enormous class of not-particularly valuable poker hands. But the probability of being dealt this hand is exactly the same as the probability of being dealt the royal flush. The reason why one hand is memorable and the other hand has to do with the size of the class if which that hand is a member. We may thus define *entropy as freedom*: if the class entropy is high, then there are many ways to satisfy the class membership criteria [eg, a invaluable hand in poker]. If the class entropy is low, then that class is very demanding [eq, only four royal flushes].