Entropy and the Second Law of Thermodynamics

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1 Boltzmann Entropy

In the microcanonical ensemble, macrostates are labeled by their total energy E. We use $\Omega(E)$ to denote the multiplicity of that macrostate (the number of microstates).

We define the **Boltzmann Entropy** as:

$$S(E) \equiv k_B \ln \Omega(E) \tag{1}$$

where k_B is the Boltzmann constant:

$$k_B \approx 1.381 \times 10^{-23}\,\mathrm{J/K} \tag{2}$$

1.1 Why the Logarithm?

There are two main reasons for defining entropy with a natural logarithm:

1. **Tractability:** Multiplicities are often astronomically large numbers (e.g., if $\Omega(E) \sim e^N$, then $S(E) \sim N$). The logarithm makes these numbers manageable.

2. **Additivity:** The logarithm makes entropy an additive quantity. Consider two non-interacting systems with energies E_1 and E_2. The total number of states is the product of their individual multiplicities:

   $$\Omega(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2) \tag{3}$$

   Taking the logarithm gives:

   $$S(E_1, E_2) = k_B \ln(\Omega_1 \Omega_2) = S_1(E_1) + S_2(E_2) \tag{4}$$

2 The Second Law of Thermodynamics

Consider two initially isolated systems brought together so they can exchange energy (thermal contact). We assume the energy levels of each system remain unchanged by the interaction. In practice, this means that the interaction term in the joint Hamiltonian is small.

2.1 Energy Conservation and Multiplicity

The energy of the combined system is fixed:

$$E_{\text{tot}} = E_1 + E_2 \tag{5}$$

After contact, system 1 can have any energy $E_1 \leq E_{\text{tot}}$, and system 2 must have the remainder $E_2 = E_{\text{tot}} - E_1$.

In a quantum system, energy is discrete. The total multiplicity of the combined system is the sum over all possible partitions of energy:

$$\Omega(E_{\text{tot}}) = \sum_{\{E_i\}} \Omega_1(E_i)\Omega_2(E_{\text{tot}} - E_i) \tag{6}$$

Expressing this in terms of entropy ($\Omega = e^{S/k_B}$):

$$\Omega(E_{\text{tot}}) = \sum_{\{E_i\}} \exp\left[\frac{S_1(E_i) + S_2(E_{\text{tot}} - E_i)}{k_B}\right] \tag{7}$$

The entropy of the combined system is $S(E_{\text{tot}}) = k_B \ln(\Omega(E_{\text{tot}}))$. Since the new total multiplicity includes all possible partitions, it is strictly greater than the multiplicity of the separated systems:

$$S(E_{\text{tot}}) > S_1(E_1) + S_2(E_2) = k_B \ln(\Omega_1(E_1)\Omega_2(E_2)) \tag{8}$$

The entropy has increased because the number of available microstates has increased dramatically.

2.2 The Dominant Term

The sum of exponentials in $\Omega(E_{\text{tot}})$ above is dominated by its largest term. Let E_* be the energy for system 1 that maximizes the argument $S_1(E) + S_2(E_{\text{tot}} - E)$.

- For one choice of E, the term might be e^N.
- For the optimal choice E_*, the term might be e^{2N}.

Since $e^{2N} \gg e^N$ (e.g., if $N = 100$, $10^{86} \gg 10^{43}$), we can approximate the sum by just the largest term:

$$S(E_{\text{tot}}) \approx S_1(E_*) + S_2(E_{\text{tot}} - E_*) \tag{9}$$

The condition for this maximum (the extremum) is found where the derivatives with respect to energy are equal:

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=E_*} = \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2=E_{\text{tot}}-E_*} \tag{10}$$

2.3 Irreversibility

Once the system reaches the energy distribution E_* (which maximizes the number of states), it is extremely unlikely to ever return to a state with different energy partitioning. This statistical probability is responsible for the **irreversibility** we observe in nature.

The Second Law: Entropy always increases. Equivalently, when constraints on a system are removed, the total number of available states is vastly enlarged.

Note: While the 2nd Law is probabilistic, deviations are so improbable for macroscopic systems ($N \sim 10^{23}$) that they are effectively impossible. The law is "protected" by numbers so large they are "silly."

3 Example: The Einstein Solid

An Einstein solid is a collection of N quantum harmonic oscillators.

3.1 Energy Levels

The energy of a single oscillator is:

$$E_i = \left(n_i + \frac{1}{2}\right)\hbar\omega, \quad n_i \in \{0, 1, 2, \dots\} \tag{11}$$

In the microcanonical ensemble, we fix the total energy:

$$E_{\text{tot}} = \sum_{i=1}^{N} \left(n_i + \frac{1}{2}\right)\hbar\omega = \left(q + \frac{N}{2}\right)\hbar\omega \tag{12}$$

Here, $q = \sum n_i$ represents the total number of energy quanta distributed among the N oscillators. Macrostates are labeled by q.

3.2 Multiplicity Calculation (Stars and Bars)

To find the number of microstates for a given N and q, we use combinatorics. We must distribute q indistinguishable quanta (dots) among N distinguishable oscillators (bins). This requires $N-1$ dividers (bars).

The total number of arrangements of q dots and $N-1$ bars is $(q+N-1)!$. However, we must correct for the indistinguishability of the dots and the bars. The multiplicity is:

$$\Omega(N,q) = \frac{(q+N-1)!}{q!(N-1)!} = \binom{q+N-1}{q} \tag{13}$$

3.3 Two Interacting Einstein Solids

Consider two solids, A and B, brought into thermal contact.

- Solid A: N_A oscillators, q_A quanta.
- Solid B: N_B oscillators, q_B quanta.
- The total quanta are fixed: $q_{\text{tot}} = q_A + q_B$.

Numerical Example: Let $N_A = 3$, $N_B = 3$, and $q_{\text{tot}} = 6$. We calculate the multiplicity for each macrostate (defined by q_A).

The multiplicity for one solid ($N = 3$) is $\Omega(3,q) = \frac{(q+2)!}{q!2!} = \frac{(q+2)(q+1)}{2}$.

q_A	$\Omega_A(3,q_A)$	q_B $(6-q_A)$	$\Omega_B(3,q_B)$	$\Omega_{\text{tot}} = \Omega_A\Omega_B$
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

Conclusion: The macrostate with $q_A = q_B = 3$ (equipartition of energy) has the largest multiplicity ($\Omega_{\text{tot}} = 100$). This corresponds to the highest entropy and is the most likely state for the combined system to be in at equilibrium.