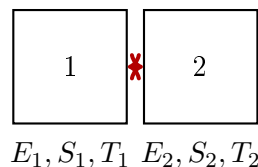


Physics 415 - Lecture 8: Entropy and Equilibrium

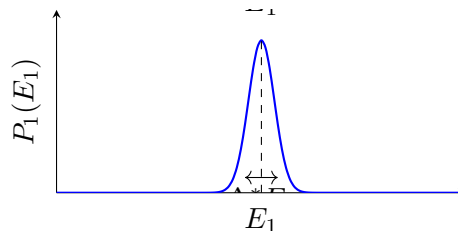
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Summary of Lecture 7

- $\Omega(E) = \#$ accessible states with energy $(E, E + \delta E)$.
- Entropy: $S = \ln \Omega$. (Dimensionless definition for now).
- Temperature: $\frac{1}{T} = \frac{\partial S}{\partial E}$. (T has units of energy).
- S and T are functions of the macrostate of the system.
- Thermal interaction between systems 1 and 2 (isolated together, $E = E_1 + E_2 = \text{const}$):



- Probability $P_1(E_1)$ is sharply peaked at $E_1 = \tilde{E}_1$. Width $\Delta^* E_1 \ll \tilde{E}_1$.



- Condition for maximum probability ($E_1 = \tilde{E}_1$) is $S_{tot} = S_1 + S_2 = \text{max}$.
- This implies the equilibrium condition: $T_1 = T_2$. The most probable state has equal temperatures.
- If initially $E_1 = E_1^{(0)} \neq \tilde{E}_1$ and $E_2 = E_2^{(0)} \neq \tilde{E}_2$, the system evolves towards the most probable state $(\tilde{E}_1, \tilde{E}_2)$.
- During this spontaneous process for an isolated system (1+2), the total entropy increases:

$$\Delta S_{tot} = S_{tot}(\text{final}) - S_{tot}(\text{initial}) = [S_1(\tilde{E}_1) + S_2(\tilde{E}_2)] - [S_1(E_1^{(0)}) + S_2(E_2^{(0)})] \geq 0$$

Tying up Loose Ends

Dependence of Entropy S on Energy Range δE

We defined $S = \ln \Omega(E)$. Since $\Omega(E) = \omega(E)\delta E$, where $\omega(E)$ is the density of states (independent of δE), we have:

$$S = \ln(\omega(E)\delta E) = \ln \omega(E) + \ln \delta E$$

So the entropy S formally depends on the choice of δE . If we choose a different subdivision $\delta E'$, the entropy would be $S' = \ln(\omega(E)\delta E')$. The difference is $S - S' = \ln(\delta E/\delta E')$.

However, for macroscopic systems, $S \sim N$ (# of DOF or particles, $N \sim 10^{23}$). The term $\ln(\delta E/\delta E')$ is just a constant, independent of N , and utterly negligible compared to $S \sim N$. Even if $\delta E' \sim N\delta E$, $\ln(1/N) \sim -\ln N \ll N$. Conclusion: For $N \gg 1$, the choice of δE does not affect macroscopic results. $S \approx S'$ for all practical purposes.

Note also that the temperature T is independent of δE :

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial}{\partial E}(\ln \omega(E) + \ln \delta E) = \frac{\partial(\ln \omega(E))}{\partial E}$$

Additivity Property of Entropy

Consider the combined system 1+2 in thermal equilibrium ($T_1 = T_2$). The total number of states is $\Omega(E) = \sum_{E_1} \Omega_1(E_1)\Omega_2(E - E_1)$. Let $S = \ln \Omega$, $S_1 = \ln \Omega_1$, $S_2 = \ln \Omega_2$.

As discussed, the probability $P_1(E_1) = \Omega_1(E_1)\Omega_2(E - E_1)/\Omega(E)$ is sharply peaked around $E_1 = \tilde{E}_1$ with width Δ^*E_1 . The sum for $\Omega(E)$ is dominated by terms near the peak:

$$\Omega(E) \approx \sum_{E_1 \in (\tilde{E}_1 \pm \Delta^*E_1)} \Omega_1(E_1)\Omega_2(E - E_1)$$

Approximating the term $\Omega_1(E_1)\Omega_2(E - E_1)$ by its maximum value $\Omega_1(\tilde{E}_1)\Omega_2(\tilde{E}_2)$ over the width of the peak Δ^*E_1 . The number of terms in the sum is roughly $\Delta^*E_1/\delta E$ (where δE is the energy step size, related to the cell size used for Ω).

$$\Omega(E) \approx [\Omega_1(\tilde{E}_1)\Omega_2(\tilde{E}_2)] \times (\# \text{ of states in peak}) \approx [\Omega_1(\tilde{E}_1)\Omega_2(\tilde{E}_2)] \times \frac{\Delta^*E_1}{\delta E}$$

Taking the logarithm:

$$S = \ln \Omega \approx \ln \Omega_1(\tilde{E}_1) + \ln \Omega_2(\tilde{E}_2) + \ln \left(\frac{\Delta^*E_1}{\delta E} \right)$$

$$S \approx S_1(\tilde{E}_1) + S_2(\tilde{E}_2) + \ln \left(\frac{\Delta^*E_1}{\delta E} \right)$$

The first two terms S_1, S_2 scale with N_1, N_2 respectively ($\sim N$). The last term involves the width $\Delta^*E_1 \sim \tilde{E}_1/\sqrt{N_1}$ and δE . The ratio $\Delta^*E_1/\delta E$ might be large, but its logarithm $\ln(\dots)$ scales at most as $\ln N$ or is independent of N . This logarithmic term will always be negligible compared to $S_1 + S_2$ (which scale as N) for macroscopic systems ($N \gg 1$).

Therefore, for macroscopic systems ($N \gg 1$):

$$S \approx S_1 + S_2$$

The entropy of the combined system (at equilibrium) is the sum of the individual entropies (evaluated at the most probable energies \tilde{E}_1, \tilde{E}_2). Entropy is additive (extensive). This is similar to the total energy $E = E_1 + E_2$.

Sharpness of the Probability Distribution

Let's analyze $P_1(E_1)$ near its maximum \tilde{E}_1 . Write $E_1 = \tilde{E}_1 + \eta$, where η is small. We expand $\ln P_1(E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E_2) - \ln \Omega(E)$ around $\eta = 0$. Recall $E_2 = E - E_1 = (E - \tilde{E}_1) - \eta = \tilde{E}_2 - \eta$. Using Taylor expansion for $S = \ln \Omega$:

$$S_1(\tilde{E}_1 + \eta) = S_1(\tilde{E}_1) + \left. \frac{\partial S_1}{\partial E_1} \right|_{\tilde{E}_1} \eta + \frac{1}{2} \left. \frac{\partial^2 S_1}{\partial E_1^2} \right|_{\tilde{E}_1} \eta^2 + \dots$$

$$S_2(\tilde{E}_2 - \eta) = S_2(\tilde{E}_2) + \left. \frac{\partial S_2}{\partial E_2} \right|_{\tilde{E}_2} (-\eta) + \frac{1}{2} \left. \frac{\partial^2 S_2}{\partial E_2^2} \right|_{\tilde{E}_2} (-\eta)^2 + \dots$$

Let $1/T_1 = (\partial S_1 / \partial E_1)|_{\tilde{E}_1}$ and $1/T_2 = (\partial S_2 / \partial E_2)|_{\tilde{E}_2}$. At equilibrium, $T_1 = T_2 = T$. Define curvature parameters:

$$\lambda_1 \equiv - \left. \frac{\partial^2 S_1}{\partial E_1^2} \right|_{\tilde{E}_1} = - \left. \frac{\partial(1/T_1)}{\partial E_1} \right|_{\tilde{E}_1}$$

$$\lambda_2 \equiv - \left. \frac{\partial^2 S_2}{\partial E_2^2} \right|_{\tilde{E}_2} = - \left. \frac{\partial(1/T_2)}{\partial E_2} \right|_{\tilde{E}_2}$$

For the sum $S_1 + S_2$ to be maximum at $\eta = 0$, we need the second derivative to be negative, so $\lambda_1 > 0$ and $\lambda_2 > 0$. Then:

$$S_1(\tilde{E}_1 + \eta) + S_2(\tilde{E}_2 - \eta) \approx S_1(\tilde{E}_1) + S_2(\tilde{E}_2) + \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \eta - \frac{1}{2} (\lambda_1 + \lambda_2) \eta^2$$

Since $T_1 = T_2 = T$ at the maximum (equilibrium):

$$S_1(E_1) + S_2(E_2) \approx S_1(\tilde{E}_1) + S_2(\tilde{E}_2) - \frac{1}{2} \lambda \eta^2$$

where $\lambda = \lambda_1 + \lambda_2 > 0$. Now, $\ln P_1(E_1) = (S_1(E_1) + S_2(E_2)) - \ln \Omega(E)$. Since $\ln P_1(\tilde{E}_1) = (S_1(\tilde{E}_1) + S_2(\tilde{E}_2)) - \ln \Omega(E)$, we have:

$$\ln P_1(E_1) \approx \ln P_1(\tilde{E}_1) - \frac{1}{2} \lambda \eta^2$$

$$\implies P_1(E_1) \approx P_1(\tilde{E}_1) e^{-\frac{1}{2} \lambda \eta^2} = P_1(\tilde{E}_1) e^{-(E_1 - \tilde{E}_1)^2 / (2\lambda^{-1})}$$

This is a Gaussian distribution for the energy E_1 around its most probable (and mean) value \tilde{E}_1 . The width of the distribution (standard deviation) is:

$$\Delta^* E_1 \equiv \frac{1}{\sqrt{\lambda}} = \frac{1}{\sqrt{\lambda_1 + \lambda_2}}$$

For $|E_1 - \tilde{E}_1| > \Delta^* E_1$, the probability is negligible.

Estimate of the width $\Delta^* E_1$: We had $S_1 \sim a_1 N_1 \ln E_1$. $\frac{\partial S_1}{\partial E_1} \sim \frac{a_1 N_1}{E_1} = \frac{1}{T_1}$. $\frac{\partial^2 S_1}{\partial E_1^2} \sim -\frac{a_1 N_1}{E_1^2} = -\lambda_1$. So $\lambda_1 \sim N_1 / E_1^2$ (since $a_1 \sim O(1)$). The width $\Delta^* E_1 = (\lambda_1 + \lambda_2)^{-1/2}$. If system 1 is much smaller than system 2 ($N_1 \ll N_2$), then typically $\lambda_1 \gg \lambda_2$, or consider combined system. Let's assume $\lambda \sim N / E^2$ where $N = N_1 + N_2$ and $E = E_1 + E_2$. Then $\Delta^* E_1 \sim \sqrt{E^2 / N} = E / \sqrt{N}$. Let's refine using $\lambda_1 \sim N_1 / E_1^2$. If $N_1 \sim N$, $E_1 \sim E$, then $\lambda \sim N / E^2$. The width scales as $\Delta^* E_1 \sim E / \sqrt{N}$. The relative width is:

$$\frac{\Delta^* E_1}{\tilde{E}_1} \sim \frac{E / \sqrt{N}}{E / N} \sim \frac{1}{\sqrt{N}}$$

(Assuming $E_1 \propto N_1 \propto N$). Since N is macroscopic ($N \sim 10^{23}$), $\sqrt{N} \sim 10^{11.5}$. The relative width $1/\sqrt{N}$ is extremely small. Fluctuations about the mean (most probable) value are utterly negligible.

Conclusion: This behavior is generic for macroscopic quantities (energy, pressure, etc.). They are essentially equal to their most probable (=mean) values. Even though our μ -scopic description is statistical, the predictions for macroscopic behavior are essentially deterministic because statistical fluctuations are so insignificant.

Also note: $\lambda = -\partial^2 S / \partial E^2 = -\partial(1/T) / \partial E = -(-\frac{1}{T^2}) \frac{\partial T}{\partial E} = \frac{1}{T^2} \frac{\partial T}{\partial E}$. Since $\lambda > 0$ (for stability/maximum) and $T^2 > 0$, we must have $\frac{\partial T}{\partial E} > 0$. The temperature T of a typical macroscopic system is an increasing function of its energy E .

Reversible and Irreversible Processes

Entropy leads to the concept of "reversible" and "irreversible" processes.

- For systems in thermal contact (isolated together), the total entropy increases as equilibrium is approached: $\Delta S_{tot} = \Delta S_1 + \Delta S_2 \geq 0$.
- In general, when a constraint on a closed/isolated system is removed, the entropy can only increase or stay the same. $\Delta S_{isolated} \geq 0$. (This is the Second Law of Thermodynamics).
- A process is "irreversible" if the total entropy of the isolated system involved increases ($\Delta S > 0$). **Example:** Heat transfer between two bodies initially at different temperatures $T_1^{(0)} \neq T_2^{(0)}$. When they reach equilibrium at $T_f = T_1 = T_2$, the final total entropy $S_f = S_1(\tilde{E}_1) + S_2(\tilde{E}_2)$ is greater than the initial total entropy $S^{(0)} = S_1(E_1^{(0)}) + S_2(E_2^{(0)})$.
- A process is "reversible" if the total entropy of the isolated system involved remains constant ($\Delta S = 0$). These processes must proceed quasi-statically through a sequence of equilibrium states. (Examples later).