

Physics 415 - Lecture 7: Statistical Thermodynamics

February 5, 2025

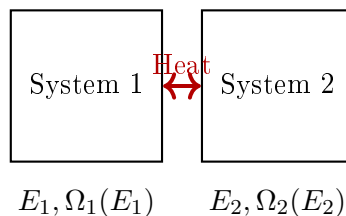
Connect statistical mechanics with general properties of macroscopic systems. Introduce important (purely statistical) notions of entropy & temperature.

Recap

- Isolated system with energy in range $(E, E + \delta E)$.
- $\Omega(E) = \#$ of accessible μ -states.
- Fundamental Postulate: In equilibrium, $\text{Prob}(\mu\text{-state}) = 1/\Omega(E)$.
- Equilibrium \implies probability distribution of μ -states is time-independent.

Interaction Between Macroscopic Systems: Thermal Contact

Consider two macroscopic systems, 1 and 2, which can exchange energy through heat transfer (thermal contact). Assume no work is done for now (e.g., volumes V_1, V_2 fixed).



- The combined system (1+2) is isolated. Total energy $E = E_1 + E_2 = \text{constant}$.
- Assume interaction between 1 & 2 is weak enough that energy is additive.
- Now, E is fixed, but E_1 and E_2 can vary ($E_2 = E - E_1$) due to energy exchange.
- In a statistical ensemble of such combined systems, there will be a distribution of values for E_1 (and E_2).

The number of accessible states of the combined system when system 1 has energy E_1 (and system 2 has $E_2 = E - E_1$) is $\Omega_1(E_1)\Omega_2(E - E_1)$. The total number of accessible states of the combined system is:

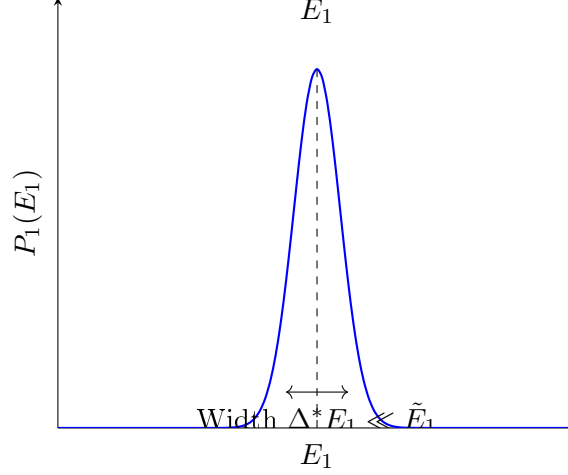
$$\Omega(E) = \sum_{E_1} \Omega_1(E_1)\Omega_2(E - E_1)$$

(The sum is over all possible energies E_1 of system 1).

The probability that system 1 has energy E_1 is:

$$P_1(E_1) = \frac{\# \text{ states where system 1 has } E_1}{\text{Total } \# \text{ states}} = \frac{\Omega_1(E_1)\Omega_2(E - E_1)}{\Omega(E)}$$

Now investigate how $P_1(E_1)$ behaves for a macroscopic system. Recall $\Omega(E) \sim E^{aN}$, where $N = \#$ of particles and $a \sim O(1)$ (e.g., $a = 3N/2$ for classical ideal gas). Ω grows extremely rapidly with E and N . Schematically: $\Omega_1(E_1) \sim E_1^{a_1 N_1}$ and $\Omega_2(E_2) = \Omega_2(E - E_1) \sim (E - E_1)^{a_2 N_2}$. The product $\Omega_1(E_1)\Omega_2(E - E_1)$ will be very sharply peaked around some value $E_1 = \tilde{E}_1$.



The probability $P_1(E_1)$ is narrowly peaked near the most probable value $E_1 = \tilde{E}_1$. The width $\Delta^* E_1$ of the peak is very small compared to \tilde{E}_1 for macroscopic systems.

Let's find the most probable value \tilde{E}_1 by finding the maximum of $P_1(E_1)$. It's easier to maximize $\ln P_1(E_1)$:

$$\ln P_1(E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E - E_1) - \ln \Omega(E)$$

Set the derivative with respect to E_1 to zero:

$$\frac{\partial}{\partial E_1}(\ln P_1(E_1)) = \frac{\partial(\ln \Omega_1)}{\partial E_1} + \frac{\partial(\ln \Omega_2)}{\partial E_1} - 0 = 0$$

Using the chain rule for the second term: $\frac{\partial}{\partial E_1} = \frac{\partial E_2}{\partial E_1} \frac{\partial}{\partial E_2} = (-1) \frac{\partial}{\partial E_2}$.

$$\begin{aligned} \frac{\partial(\ln \Omega_1)}{\partial E_1} - \frac{\partial(\ln \Omega_2)}{\partial E_2} &= 0 \\ \Rightarrow \frac{\partial(\ln \Omega_1)}{\partial E_1} \Big|_{E_1=\tilde{E}_1} &= \frac{\partial(\ln \Omega_2)}{\partial E_2} \Big|_{E_2=E-\tilde{E}_1} \quad (*) \end{aligned}$$

This condition determines the most probable energy distribution $(\tilde{E}_1, \tilde{E}_2)$.

Entropy and Temperature

We define the (statistical) "entropy" S as:

$$S \equiv \ln \Omega$$

(Note: We will discuss units involving Boltzmann's constant k_B later. For now, S is dimensionless).

The condition (*) for the most probable energy distribution becomes:

$$\frac{\partial S_1}{\partial E_1} \Big|_{\tilde{E}_1} = \frac{\partial S_2}{\partial E_2} \Big|_{\tilde{E}_2}$$

This is the condition that determines the energy sharing (\tilde{E}_1, \tilde{E}_2) when the systems are in thermal equilibrium.

Also note that maximizing $P_1(E_1)$ is equivalent to maximizing $\ln P_1(E_1) = S_1 + S_2 - \ln \Omega(E)$. Since $\Omega(E)$ is constant, this is equivalent to maximizing the total entropy $S = S_1 + S_2$. The condition of maximum probability = condition of maximum total entropy.

The quantity $\partial S / \partial E$ is clearly important. We define the "absolute temperature" T such that:

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E}$$

(Note: With $S = \ln \Omega$, T has units of energy). The condition for thermal equilibrium between systems 1 and 2 is then simply:

$$\frac{1}{T_1} = \frac{1}{T_2} \implies T_1 = T_2$$

Question: How do we identify $T = 1/(\partial S / \partial E)$ with the familiar notion of temperature? We'll show that this quantity T behaves qualitatively as you'd expect for temperature. Consider how systems 1 and 2 approach equilibrium.

Approach to Equilibrium

Consider the initial situation where 1 and 2 are thermally isolated with initial mean energies $\bar{E}_1^{(0)}$ and $\bar{E}_2^{(0)}$, and corresponding initial temperatures $T_1^{(0)}$ and $T_2^{(0)}$. Assume $T_1^{(0)} \neq T_2^{(0)}$. Now, suppose the insulating barrier is removed, so energy can be exchanged (heat transfer). We expect the mean energies to evolve in time toward the most probable state \tilde{E}_1, \tilde{E}_2 . Since $P_1(E_1)$ is sharply peaked, we can identify the final average energies with the most probable energies: $\bar{E}_1 \rightarrow \tilde{E}_1$ and $\bar{E}_2 \rightarrow \tilde{E}_2$. (Conservation holds: $E_1^{(0)} + E_2^{(0)} = \tilde{E}_1 + \tilde{E}_2 = E$).

Consider the rate of change of total entropy $S = S_1(E_1) + S_2(E_2)$ as the systems evolve (assume evolution is slow enough to define S_1, S_2 at each step, i.e., quasi-static approach):

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt} = \frac{\partial S_1}{\partial E_1} \frac{dE_1}{dt} + \frac{\partial S_2}{\partial E_2} \frac{dE_2}{dt}$$

Since $E_1 + E_2 = E = \text{const}$, $\frac{dE_2}{dt} = -\frac{dE_1}{dt}$.

$$\frac{dS}{dt} = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) \frac{dE_1}{dt}$$

Using the definition $1/T = \partial S / \partial E$:

$$\frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt}$$

Now, suppose initially $T_2^{(0)} > T_1^{(0)}$. We expect heat to flow from the hotter system (2) to the colder system (1). This means system 1 gains energy, so $\frac{dE_1}{dt} > 0$. In this case, since $T_2 > T_1 \implies 1/T_1 > 1/T_2$, the term $(1/T_1 - 1/T_2)$ is positive. Therefore, $\frac{dS}{dt} > 0$. The total entropy S increases until equilibrium is reached, where $T_1 = T_2$ and $dS/dt = 0$.

This demonstrates a key aspect of the Second Law of Thermodynamics: For an isolated system (1+2), the entropy tends to increase towards its maximum value, which corresponds to equilibrium. It also shows that energy passes (heat is transferred) from the system at higher T to that at lower T , consistent with our intuitive understanding of temperature.

Some Additional Properties of T

Since $\Omega(E) \sim E^{aN}$ (in general for large N), we have $S = \ln \Omega \sim aN \ln E$. Then $\frac{1}{T} = \frac{\partial S}{\partial E} \sim \frac{aN}{E}$.

$$\implies T \sim \frac{E}{aN}$$

We also expect E to be positive, and Ω increases with E , so $\partial S/\partial E > 0$, which means $T > 0$ (generally). The temperature T measures (roughly) the mean energy per degree of freedom (or per particle) for the system. When two systems are in thermal contact, the equilibrium condition $T_1 = T_2$ is therefore (roughly) the statement that the total energy $E = E_1 + E_2$ is shared between the systems such that the mean energy per DOF is the same for both systems.

Note on Units

We have defined T with units of energy (since $1/T = \partial S/\partial E$ and $S = \ln \Omega$ is dimensionless). Often, temperature is measured in degrees Kelvin (K). The conversion factor is Boltzmann's constant:

$$k_B \approx 1.38 \times 10^{-23} \text{ J/K} \quad (\text{or } 1.38 \times 10^{-16} \text{ erg/K})$$

$$T_{\text{energy}} = k_B \times T_{\text{Kelvin}}$$

If temperature T is measured in degrees (Kelvin), a factor of k_B is also conventionally included in the definition of entropy to make the argument of functions like $\exp(-E/(k_B T))$ dimensionless:

$$S_{\text{conventional}} = k_B \ln \Omega$$

This gives S units of Energy/Temperature (e.g., J/K). $\frac{\partial S_{\text{conv}}}{\partial E} = k_B \frac{\partial(\ln \Omega)}{\partial E} = k_B \left(\frac{1}{T_{\text{energy}}} \right) = \frac{k_B}{k_B T_{\text{Kelvin}}} = \frac{1}{T_{\text{Kelvin}}}$. The definition $1/T = \partial S/\partial E$ holds regardless of the units chosen for T , provided S is defined consistently.

We will often (unless specified otherwise) measure T in energy units and keep $S = \ln \Omega$ dimensionless. To convert results to conventional units, make the substitutions $T \rightarrow k_B T$ and $S \rightarrow S/k_B$.