# PHYS 301: Temperature and Heat Capacity

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## 1 Review: Boltzmann Entropy

So far, the main physical concept we have introduced is the Boltzmann entropy:

$$S = k_B \ln \Omega \tag{1}$$

where $\Omega$ is the multiplicity (number of microstates).

For a combined system with total energy $E_{\rm tot}$, the total multiplicity is the sum over all possible energy partitions:

$$\Omega(E_{\rm tot}) = \sum_{\{E_i\}} \Omega_1(E_i)\Omega_2(E_{\rm tot} - E_i) = \sum_{\{E_i\}} \exp\left[\frac{S_1(E_i)}{k_B} + \frac{S_2(E_{\rm tot} - E_i)}{k_B}\right] \tag{2}$$

## 2 Thermal Equilibrium and Temperature

### 2.1 The Most Likely State

We argued (and saw with the Einstein solid examples) that $\Omega(E_{\rm tot})$ is sharply peaked for large systems around a specific value $E_1 = E_*$. This value $E_*$ corresponds to the most likely state.

To find $E_*$, we maximize the term inside the sum, which leads to the condition:

$$\left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=E_*} = \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2=E_{\rm tot}-E_*} \tag{3}$$

From the fundamental assumption of statistical mechanics, all microstates are equally likely. However, there are vastly more microstates with $E_1 \approx E_*$ than any other configuration. Therefore, if we observe the system, we are extremely likely to find it with energy near $E_*$. Once the system reaches this configuration, it stops evolving macroscopically because there are no other states with higher multiplicity.

### 2.2 Defining Temperature

We now introduce the statistical mechanical definition of temperature:

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} \tag{4}$$

Does this match our intuitive understanding of temperature?

1. **Units:** This definition gives the correct units for temperature. 2. **Equilibrium Condition:** The condition for the most likely state ($\frac{\partial S_1}{\partial E} = \frac{\partial S_2}{\partial E}$) becomes $T_1 = T_2$. This implies that two systems in equilibrium have the same temperature, which is very reasonable.

## 3 Heat Flow and the Second Law

Suppose two systems $S_1$ and $S_2$ are initially at slightly different temperatures. When brought into contact, they exchange energy, but the total energy is fixed ($\delta E_1 = -\delta E_2$).

The total change in entropy is:

$$\begin{aligned}\delta S &= \frac{\partial S_1}{\partial E_1}\delta E_1 + \frac{\partial S_2}{\partial E_2}\delta E_2 \\ &= \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)\delta E_1 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta E_1 \end{aligned} \tag{5}$$

By the Second Law of Thermodynamics, we must have $\delta S \geq 0$. If $T_1 > T_2$, then $(1/T_1 - 1/T_2)$ is negative. To ensure $\delta S \geq 0$, we must have $\delta E_1 < 0$. This means energy flows out of system 1 and into system 2. Thus, energy flows from the hotter system to the colder one, which matches our physical intuition.

To confirm that our definition matches reality, we need to calculate it for a known system (like an ideal gas). We will do this next lecture.

# 4 Heat Capacity

Counting microstates directly is often very difficult for macroscopic systems. Instead, we can use the definition of temperature to compute changes in entropy using quantities measurable in a lab.

$$\frac{\partial S}{\partial T} = \frac{\partial S}{\partial E}\frac{\partial E}{\partial T} = \frac{1}{T}C \tag{6}$$

where $C = \frac{\partial E}{\partial T}$ is the **Heat Capacity**.

We can integrate this to find the change in entropy:

$$\Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T} dT \tag{7}$$

$C(T)$ describes how the energy of a system changes as we change its temperature. It serves as the closest link between theory and experiment.

## 4.1 Stability and Negative Heat Capacity

Consider the derivative of temperature with respect to energy:

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{\partial T}{\partial E} = -\frac{1}{T^2 C} \tag{8}$$

Since $T^2 > 0$, if the heat capacity $C > 0$, then $\frac{\partial^2 S}{\partial E^2} < 0$. This confirms that the entropy is indeed a maximum at equilibrium.

Most systems have $C > 0$. However, self-gravitating systems (like star clusters or black holes) can have negative heat capacity.

# 5 Example: System of N Spins

Let us apply this to a system of $N$ spins. Previously, we derived the entropy using Stirling's approximation:

$$S = k_B[N \ln N - N_\uparrow \ln N_\uparrow - N_\downarrow \ln N_\downarrow] \tag{9}$$

Assume spin down has 0 energy and spin up has energy $\epsilon$. The total energy is $E = N_\uparrow \epsilon$. We can express the populations as:

$$N_\uparrow = \frac{E}{\epsilon}, \quad N_\downarrow = N - \frac{E}{\epsilon} \tag{10}$$

Substituting these into the entropy equation:

$$S = k_B\left[N \ln N - \frac{E}{\epsilon}\ln\left(\frac{E}{\epsilon}\right) - \left(N - \frac{E}{\epsilon}\right)\ln\left(N - \frac{E}{\epsilon}\right)\right] \tag{11}$$

## 5.1 Computing Temperature

We calculate $1/T = \partial S/\partial E$:

$$\frac{1}{T} = k_B \left[ -\frac{1}{\epsilon} \ln\left(\frac{E}{\epsilon}\right) - \frac{E}{\epsilon}\left(\frac{\epsilon}{E}\right)\frac{1}{\epsilon} + \frac{1}{\epsilon}\ln\left(N - \frac{E}{\epsilon}\right) - \left(N - \frac{E}{\epsilon}\right)\frac{1}{(N - E/\epsilon)}\left(-\frac{1}{\epsilon}\right)\right]$$
$$= \frac{k_B}{\epsilon}\ln\left(\frac{N - E/\epsilon}{E/\epsilon}\right) = \frac{k_B}{\epsilon}\ln\left[\frac{N\epsilon}{E} - 1\right] \tag{12}$$

In the microcanonical ensemble, $E$ is fixed and $T$ is an emergent quantity. For instance, at $E = 0$, we have $T = 0$. At $E = N\epsilon/2$ (for which entropy is maximized), we have $T \to \infty$. With all spins up ($E = N\epsilon$), we have $T \to -\infty$, that is, a **negative temperature**. Negative temperature occurs in the microcanonical ensemble when we drive the system to energies higher than the value of $E$ maximizing entropy (here $E > N\epsilon/2$). Negative temperatures should be understood at higher than infinite temperature. It is actually easier to visualize this in term of the inverse temperature $\beta$

$$\beta \equiv \frac{1}{k_\mathrm{B}T}. \tag{13}$$

With this definition, $T = 0$ corresponds to $\beta \to \infty$, $T \to \infty$ corresponds to $\beta = 0$, and $T < 0$ corresponds to $\beta < 0$. $\beta$ is thus continuous between $-\infty$ and $+\infty$, making it a nicer variable to play with instead of having this strange jump from infinite temperature to negative temperatures as we go through the state with maximum entropy.

## 5.2 Occupancy at fixed temperature

Moving away from the microcanonical ensemble for a moment, we can invert this expression to solve for the occupancy $N_\uparrow/N$ (where $N_\uparrow = E/\epsilon$):

$$\frac{\epsilon}{k_BT} = \ln\left[\frac{N}{N_\uparrow} - 1\right] \implies e^{\epsilon/k_BT} = \frac{N}{N_\uparrow} - 1 \tag{14}$$

$$\frac{N_\uparrow}{N} = \frac{1}{e^{\epsilon/k_BT} + 1} \tag{15}$$

This is one example of the **Fermi-Dirac distribution**. We will derive it more formally later in the course. But for now, it suffices to say that it tells us about the occupancy of the spin-up states for different temperatures. For instance,

- As $T \to 0$, occupancy $N_\uparrow/N \to 0$ (Ground state).
- As $T \to \infty$, occupancy $N_\uparrow/N \to 1/2$ (Max entropy state).

What happens when $N_\uparrow/N > 1/2$? We already know this is the regime of negative temperature: If we pump enough energy such that $N_\uparrow/N > 1/2$, the slope of the entropy curve ($\partial S/\partial E$) becomes negative. Since $1/T =$ slope, this region corresponds to **negative temperature**.