The Canonical Ensemble and the Partition Function

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1 Introduction

So far, we have mostly considered systems with fixed total energy E, and from this we deduced the equilibrium temperature via:

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

But this is a little backward: It is much easier to fix the temperature of a system by e.g. putting it in contact with a large reservoir.

For example, a glass of water left on the counter will eventually reach the same temperature as the room (here acting as the reservoir).

2 The Canonical Ensemble

Consider a system S in contact with a large reservoir R, which has temperature T.

- The reservoir R has temperature T.
- The energy of S is negligible compared to R.
- The combined system has fixed total energy E_{tot}.
- S can exchange energy with the reservoir without changing its temperature.

Question: How are the energy levels of S populated? Assume that system S had enough time to equilibrate to temperature T.

2.1 Derivation

Label the microstates of the system as $|n\rangle$, each with energy $E_n \ll E_{\text{tot}}$. The number of microstates of the combined system (S and R) is given by the sum over *all possible microstates* of S:

$$\Omega(E_{\text{tot}}) = \sum_n \Omega_R(E_{\text{tot}} - E_n) \cdot 1 \tag{2}$$

where Ω_R is the multiplicity of the reservoir, and where we have used the fact that every microstate of S has multiplicity 1. I emphasize again that the above sum is over the microstates of S, and not the energy states of S.

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

$$\Omega(E_{\text{tot}}) = \sum_n \exp\left[\frac{S_R(E_{\text{tot}} - E_n)}{k_B}\right] \tag{3}$$

Since $E_n \ll E_{\text{tot}}$, we can Taylor expand the entropy of the reservoir around E_{tot}:

$$S_R(E_{\text{tot}} - E_n) \approx S_R(E_{\text{tot}}) - E_n \frac{\partial S_R}{\partial E} + \dots \tag{4}$$

Recall that $\frac{\partial S_R}{\partial E} = \frac{1}{T}$.

$$S_R(E_{\text{tot}} - E_n) \approx S_R(E_{\text{tot}}) - \frac{E_n}{T} \tag{5}$$

Substituting this back into the sum:

$$\Omega(E_{\text{tot}}) \approx \sum_n \exp\left[\frac{S_R(E_{\text{tot}})}{k_B} - \frac{E_n}{k_B T}\right] \tag{6}$$

$$\Omega(E_{\text{tot}}) = e^{S_R(E_{\text{tot}})/k_B} \sum_n e^{-E_n/k_B T} \tag{7}$$

The above is the total number of accessible states for the combined $R+S$ systems. Using the fundamental assumption of statistical mechanics, all of these states are equally probable.

3 The Boltzmann Factor

The probability $p(n)$ of finding the system S in a specific microstate $|n\rangle$ is equal to the number of reservoir states available when S is in that state, divided by the total number of states $\Omega(E_{\text{tot}})$. The former is just one of the term in the sum in Eq. (7), $e^{S_R(E_{\text{tot}})/k_B} e^{-E_n/k_B T}$.

$$p(n) = \frac{e^{S_R(E_{\text{tot}})/k_B} e^{-E_n/k_B T}}{e^{S_R(E_{\text{tot}})/k_B} \sum_m e^{-E_m/k_B T}} = \frac{e^{-E_n/k_B T}}{\sum_m e^{-E_m/k_B T}}, \tag{8}$$

where we see that the reference to the reservoir has dropped out of the problem. It only enters through the temperature T. Here, m is just a dummy index of summation. Note that $\sum_n p(n) = 1$ so our probability distribution is properly normalized. The term in the numerator is called the **Boltzmann Factor**:

$$\text{Boltzmann Factor} = e^{-\beta E_n} \tag{9}$$

where $\beta \equiv \frac{1}{k_B T}$ (the inverse temperature).

3.1 Physical Implications

- The exponential suppression of the Boltzmann factor means that states with $E_n \gg k_B T$ are very unlikely to be populated.
- States with $E_n \lesssim k_B T$ have a decent chance of being populated.
- As $T \to 0$ ($\beta \to \infty$), only the ground state (lowest energy) will be populated.

4 The Partition Function

The normalization of the probability distribution $\sum_n e^{-E_n/k_B T}$ is very important. We define the **Partition Function** with the notation Z:

$$Z = \sum_n e^{-\beta E_n} \tag{10}$$

Z should be seen as a function of the inverse temperature β. With this notation, the probability of being in state n is then:

$$p(n) = \frac{e^{-\beta E_n}}{Z} \tag{11}$$

Z is the most important quantity in statistical mechanics. It encodes all information about the system.

4.1 Example: Quantum Harmonic Oscillator

Consider a quantum harmonic oscillator with frequency ω. The quantized energy levels for one oscillator are:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \ldots \tag{12}$$

The partition function is:

$$Z = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega} \tag{13}$$

Factor out the zero-point energy term:

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} x^n \tag{14}$$

where $x = e^{-\beta\hbar\omega} < 1$ (for $\beta \neq 0$).

Using the geometric series sum formula $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ (valid when $x < 1$):

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \tag{15}$$

Multiplying numerator and denominator by $e^{\beta\hbar\omega/2}$:

$$Z = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2\sinh(\frac{\beta\hbar\omega}{2})} \tag{16}$$

5 The Einstein Solid Model

The Einstein solid model treats a crystal of N atoms as a collection of independent quantum harmonic oscillators.

- The atoms are located at fixed lattice sites, making them **distinguishable**.
- Each atom can vibrate in 3 spatial dimensions (x, y, z).
- Therefore, a system of N atoms is mathematically equivalent to a system of $3N$ independent, distinguishable 1D harmonic oscillators, all with the same frequency ω. Each of these oscillators has the partition function we derived above

$$Z_{1D} = \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}. \tag{17}$$

5.1 Total Partition Function (Z)

Since the $3N$ oscillators are independent and distinguishable, the total partition function is the product of the individual partition functions:

$$Z = (Z_{1D})^{3N} = \left[\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}\right]^{3N} = \frac{1}{2^{3N}} \operatorname{csch}^{3N}\left(\frac{\beta\hbar\omega}{2}\right) \tag{18}$$

5.2 Average Energy ($\langle E\rangle$)

The average energy is calculated using the relation $\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta}$. First, calculate $\ln Z$:

$$\ln Z = 3N \ln\left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}\right) = 3N\left[-\frac{\beta\hbar\omega}{2} - \ln(1 - e^{-\beta\hbar\omega})\right] \tag{19}$$

Now, take the derivative with respect to β:

$$\begin{aligned}
\langle E\rangle &= -\frac{\partial}{\partial\beta}\left(3N\left[-\frac{\beta\hbar\omega}{2} - \ln(1 - e^{-\beta\hbar\omega})\right]\right) \\
&= -3N\left[-\frac{\hbar\omega}{2} - \frac{1}{1 - e^{-\beta\hbar\omega}} \cdot (-e^{-\beta\hbar\omega}) \cdot (-\hbar\omega)\right] \\
&= 3N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}\right]
\end{aligned}$$

Multiplying the second term by $e^{\beta\hbar\omega}/e^{\beta\hbar\omega}$:

$$\boxed{\langle E\rangle = 3N\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)} \tag{20}$$

This corresponds to the Zero Point Energy plus the energy from thermal excitations (Planck distribution).

5.3 Heat Capacity (C_V)

The heat capacity is defined as $C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V$. Using the chain rule $\frac{\partial}{\partial T} = \frac{d\beta}{dT}\frac{\partial}{\partial \beta} = -\frac{1}{k_B T^2}\frac{\partial}{\partial \beta}$:

$$C_V = \frac{d}{dT}\left[\frac{3N\hbar\omega}{e^{\hbar\omega/k_B T} - 1}\right] \tag{21}$$

Let $x = \frac{\hbar\omega}{k_B T}$. The derivative yields:

$$\boxed{C_V = 3Nk_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2}} \tag{22}$$

5.4 High-Temperature Limit (Dulong-Petit Law)

In the limit of high temperature, $k_B T \gg \hbar\omega$, so $x \ll 1$. We approximate $e^x \approx 1 + x$.

$$\langle E \rangle \approx 3N\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{1 + \beta\hbar\omega - 1}\right) \approx 3N\left(\frac{1}{\beta}\right) = 3Nk_B T \tag{23}$$

Consequently, the heat capacity becomes:

$$C_V \approx \frac{\partial}{\partial T}(3Nk_B T) = 3Nk_B \tag{24}$$

This recovers the classical **Dulong-Petit law**z