Application of the Partition Function and Boltzmann Distribution: The Monoatomic Ideal Gas

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1 Introduction

The partition function for a system in the canonical ensemble is defined as the sum over all microstates:

$$Z = \sum_n e^{-\beta E_n} \tag{1}$$

where $\beta \equiv \frac{1}{k_B T}$. We will calculate this for a monoatomic ideal gas, starting with a single particle in a 1D box of length L, and then generalizing to N particles in 3D.

We can approach this calculation in two ways: using the quantized momentum states from quantum mechanics, or using a phase space integral from classical mechanics.

2 Approach 1: Quantum Particle in a 1D Box

For a particle of mass m confined to a 1D box of length L, the de Broglie wavelength is restricted to standing waves:

$$\lambda_n = \frac{2L}{n}, \quad n = 1, 2, 3, \ldots \tag{2}$$

The momentum of the particle is quantized as $p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$. Since the gas is monoatomic, its energy is entirely kinetic ($E = \frac{p^2}{2m}$):

$$E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2} \tag{3}$$

The partition function is the sum over all states n:

$$Z_{1D} = \sum_{n=1}^{\infty} e^{-\beta E_n} = \sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8mL^2}\right) \tag{4}$$

For a macroscopic box, the energy levels are incredibly close together, so we can approximate the discrete sum as a continuous integral over n:

$$Z_{1D} \simeq \int_0^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8mL^2}\right) dn \tag{5}$$

To evaluate this Gaussian integral, we use a substitution. Let $x^2 = \frac{\beta h^2 n^2}{8mL^2}$, which means $x = \frac{\sqrt{\beta} h n}{\sqrt{8m} L}$. Taking the differential gives $dx = \frac{\sqrt{\beta} h}{\sqrt{8m} L} dn$, or $dn = \frac{\sqrt{8m} L}{\sqrt{\beta} h} dx$.

$$Z_{1D} \simeq \frac{\sqrt{8m} L}{\sqrt{\beta} h} \int_0^{\infty} e^{-x^2} dx$$

Using the standard result for the half-Gaussian integral $\int_0^\infty e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$:

$$Z_{1D} \simeq \frac{\sqrt{8m}L}{\sqrt{\beta}h} \frac{\sqrt{\pi}}{2} = \frac{\sqrt{2\pi m}L}{\sqrt{\beta}h} = \frac{L\sqrt{2\pi m k_B T}}{h}$$

2.1 The Thermal de Broglie Wavelength

We define a characteristic length scale called the **thermal de Broglie wavelength**, λ_Q:

$$\lambda_Q \equiv \frac{h}{\sqrt{2\pi m k_B T}} \tag{6}$$

This allows us to write the 1D partition function very compactly:

$$Z_{1D} = \frac{L}{\lambda_Q} \tag{7}$$

3 Approach 2: Classical Phase Space Integral

Alternatively, we can compute Z_{1D} using a semi-classical integration over continuous phase space (position x and momentum p). We must divide by h to account for the fundamental volume of a quantum state:

$$Z_{1D} = \frac{1}{h} \int_0^L dx \int_{-\infty}^{\infty} dp\, e^{-\beta p^2/2m} \tag{8}$$

The position integral trivially evaluates to L:

$$Z_{1D} = \frac{L}{h} \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}p^2} dp \tag{9}$$

Using the full Gaussian integral formula $\int_{-\infty}^{\infty} e^{-\alpha p^2} dp = \sqrt{\frac{\pi}{\alpha}}$ with $\alpha = \frac{\beta}{2m}$:

$$Z_{1D} = \frac{L}{h}\sqrt{\frac{2\pi m}{\beta}} = \frac{L\sqrt{2\pi m k_B T}}{h} = \frac{L}{\lambda_Q} \tag{10}$$

Both approaches yield the exact same result!

4 Generalizing to 3D and N Particles

For a single particle moving in 3 dimensions ($V = L^3$), the partition function is simply the product of three independent 1D partition functions:

$$Z_{3D} = (Z_{1D})^3 = \frac{L^3}{\lambda_Q^3} = \frac{V}{\lambda_Q^3} \tag{11}$$

Now, consider an ideal gas of N *indistinguishable* and non-interacting particles. The total partition function is the product of N single-particle partition functions, but we must divide by $N!$ to avoid overcounting all permutations of identical particles:

$$Z_{N,3D} = \frac{(Z_{3D})^N}{N!} = \frac{V^N}{N!\lambda_Q^{3N}} \tag{12}$$

5 Average Energy

We can now find the average energy using the fundamental relation $\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z$. First, take the natural log of the N-particle partition function:

$$\begin{aligned}\ln Z_{N,3D} &= \ln\left(\frac{V^N}{N!\lambda_Q^{3N}}\right)\\ &= N\ln V - \ln N! - 3N\ln\lambda_Q\end{aligned}$$

Taking the derivative with respect to β, note that V and N are constants. The only temperature dependence is inside λ_Q:

$$\langle E\rangle = -\frac{\partial}{\partial\beta}(-3N\ln\lambda_Q) = \frac{3N}{\lambda_Q}\frac{\partial\lambda_Q}{\partial\beta} \tag{13}$$

Recall that $\lambda_Q = \frac{h}{\sqrt{2\pi m}}\beta^{1/2}$. Thus, its derivative is:

$$\frac{\partial\lambda_Q}{\partial\beta} = \frac{h}{\sqrt{2\pi m}}\left(\frac{1}{2}\beta^{-1/2}\right) = \frac{1}{2\beta}\left(\frac{h}{\sqrt{2\pi m}}\beta^{1/2}\right) = \frac{\lambda_Q}{2\beta} \tag{14}$$

Substituting this back into the energy equation:

$$\langle E\rangle = \frac{3N}{\lambda_Q}\left(\frac{\lambda_Q}{2\beta}\right) = \frac{3N}{2\beta} \tag{15}$$

Since $\beta = \frac{1}{k_B T}$, we recover the famous equipartition theorem result for a monoatomic ideal gas:

$$\boxed{\langle E\rangle = \frac{3}{2}Nk_BT} \tag{16}$$

6 Entropy and the Sackur-Tetrode Equation

What about the entropy? We can compute S using the formula we derived previously:

$$S = \frac{\langle E\rangle}{T} + k_B\ln Z_{N,3D} \tag{17}$$

Substitute $\frac{\langle E\rangle}{T} = \frac{3}{2}Nk_B$:

$$S = \frac{3}{2}Nk_B + k_B(N\ln V - \ln N! - 3N\ln\lambda_Q) \tag{18}$$

To evaluate $\ln N!$ for a macroscopic system, we apply Stirling's approximation ($\ln N! \approx N\ln N - N$):

$$\begin{aligned}S &\approx \frac{3}{2}Nk_B + k_B(N\ln V - (N\ln N - N) - 3N\ln\lambda_Q)\\ &= \frac{3}{2}Nk_B + k_B(N\ln V - N\ln N + N - N\ln(\lambda_Q^3))\\ &= \frac{3}{2}Nk_B + Nk_B + Nk_B(\ln V - \ln N - \ln\lambda_Q^3)\\ &= \frac{5}{2}Nk_B + Nk_B\ln\left(\frac{V}{N\lambda_Q^3}\right)\end{aligned}$$

Factoring out Nk_B, we arrive at the **Sackur-Tetrode equation** for the entropy of an ideal monoatomic gas:

$$\boxed{S = Nk_B \left[\ln\left(\frac{V}{N\lambda_Q^3}\right) + \frac{5}{2} \right]} \tag{19}$$

7 Application of the Boltzmann Factor to atomic levels

Let's consider hydrogen atoms in the atmosphere of the sun, where the temperature is about 5800 K. When neglecting fine and hyperfine splitting, the energy levels of the different states of the hydrogen atom are simply given by

$$E_n = -\frac{13.6}{n^2}\,\mathrm{eV}, \tag{20}$$

where the energy is negative because this corresponds to the binding energy of the electron forming the atom (that is, I have to supply positive energy to unbound (ionize) the electron from the atom). As a simple example, let's consider the relative probability of finding an atom in the first excited state ($n = 2$) relative to finding one in the ground state ($n = 1$). Remember that the probability of finding an atom in a specific state is given by the Boltzmann distribution

$$p(n) = \frac{e^{-\beta E_n}}{Z}. \tag{21}$$

One important thing to remember is that the $n = 2$ state has four degenerate states (the one $2s$ and the three $2p$ states). Using this, the relative probability of the $n = 2$ and $n = 1$ states is

$$\begin{aligned} \frac{p(n=2)}{p(n=1)} &= \frac{4e^{-\beta E_2}}{e^{-\beta E_1}} \\ &= 4e^{-\beta(E_2 - E_1)}, \end{aligned} \tag{22}$$

where the partition function has canceled out in the ratio. Now the difference in energy is $E_2 - E_1 = 10.2$ eV. Meanwhile

$$\beta = \frac{1}{8.62\times10^{-5}\,\mathrm{eV/K}\,5800\,\mathrm{K}} \approx 2.0\,\mathrm{eV}^{-1}. \tag{23}$$

Therefore

$$\frac{p(n=2)}{p(n=1)} \approx 4e^{-20.4} \tag{24}$$

$$\approx 5.5\times10^{-9}. \tag{25}$$

This means that for every billion hydrogen atoms in the ground state in the sun's atmosphere, there are about 5 atoms in the first excited state. What about the next excited state ($n = 3$)? Repeating the above argument, and remembering that there are nine (3^2) degenerate states with $n = 3$, we have

$$\frac{p(n=3)}{p(n=1)} \approx 9e^{-24.2} \tag{26}$$

$$\approx 2.8\times10^{-10}, \tag{27}$$

more than an order of magnitude smaller. The higher excited states have even smaller probability. This should convince you that most hydrogen atoms in the sun's atmosphere are in the ground state.