Multiplicity of a Monoatomic Ideal Gas, Entropy, and Pressure

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1 The Setup

Here we will put a somewhat familiar system into the language of statistical mechanics: the ideal gas. The one thing we know about this system is the ideal gas law: $PV = Nk_\mathrm{B}T$ (sometime written as $PV = nRT$, where $n = N/N_\mathrm{A}$ is the number of moles, $R = N_\mathrm{A}k_\mathrm{B}$ is the Universal gas constant, with $N_\mathrm{A} \approx 6 \times 10^{23}$ being Avogadro's number). Now, consider a simple monoatomic ideal gas with the following properties:

- **Particles:** N identical, indistinguishable particles.
- **Mass:** Each particle has mass m.
- **Volume:** The particles are confined to a physical volume V.
- **Energy:** The system has a fixed total energy E.
- **No interaction**: Gas particles do not interact with each other. This means that all particles are independent of each other. This assumption is valid for a dilute gas.

2 Defining the "Volume" of States

In the semi-classical phase space formulation, the state of the system is a single point in a $6N$-dimensional phase space ($3N$ position coordinates $\mathbf{x}$ and $3N$ momentum coordinates $\mathbf{p}$).

We define the multiplicity Ω as the total volume of the region in phase space accessible to the system, normalized by the phase space "volume" of a single quantum state:

$$\Omega = \frac{1}{\text{Normalization}} \int d^{3N}x \int d^{3N}p \tag{1}$$

3 The Quantum Corrections (Normalization)

To make this classical integral match quantum reality, we must apply two specific corrections:

- **Heisenberg Uncertainty Principle:** The smallest "cell" in phase space for one degree of freedom is Planck's constant h, that is, $\Delta x \Delta p = h$. This product could of course be larger than that, but we are interested in the best-case scenario here where we pack as many states as possible within our volume V. For $3N$ degrees of freedom, the fundamental volume unit is $(\Delta x)^{3N}(\Delta p)^{3N} = h^{3N}$.
- **Indistinguishability (Gibbs Paradox):** In quantum mechanics, swapping two identical atoms does not create a new state. Since the classical integral treats every particle as unique, we must divide by the number of permutations, $N!$.

The corrected formula is:

$$\Omega(N, V, E) = \frac{1}{N!h^{3N}} \underbrace{\left(\int d^{3N}x\right)}_{\text{Position}} \underbrace{\left(\int d^{3N}p\right)}_{\text{Momentum}} \tag{2}$$

4 Step 1: The Position Integral

The particles are non-interacting, so the position of one particle does not depend on the others. The limits of integration are simply the boundaries of the box V:

$$\int d^{3N}x = \prod_{i=1}^{N} \left(\int_V d^3x_i \right) = \prod_{i=1}^{N} V = V^N \tag{3}$$

5 Step 2: The Momentum Integral

The Hamiltonian for a monoatomic ideal gas is purely kinetic.

- The total energy is given by: $E = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$.
- Rearranging for momentum yields the equation of a hypersphere in $3N$-dimensions:

$$\sum_{i=1}^{3N} p_i^2 = 2mE \tag{4}$$

- This describes a hypersphere with radius $R = \sqrt{2mE}$.

Thus, when computing the momentum integral above, we are integrating over all momenta subject to the constraint that they all lie on the surface of this hypersphere. So the result is really the area of the hypersphere rather than its volume. However, the large N, there is little difference between the area and volume of a hypersphere since nearly all the volume lies near its surface. We calculate the volume of this hypersphere using the geometric formula for an n-sphere (where $n = 3N$):

$$\mathrm{Vol}_{3N} = \frac{\pi^{3N/2}}{(3N/2)!} R^{3N} \tag{5}$$

For comparison, the area of $3N$-sphere is

$$\mathrm{Area}_{3N} = \frac{2\pi^{3N/2}}{(3N/2-1)!} R^{3N-1}, \tag{6}$$

which for $N \gg 1$ reduces to the above, up to a small number (a factor of 2). Substituting $R = \sqrt{2mE}$:

$$\int d^{3N}p \approx \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2} \tag{7}$$

6 The Final Result

Combining the normalization, position, and momentum factors:

$$\Omega(N, V, E) = \frac{1}{N! h^{3N}} \cdot V^N \cdot \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2} \tag{8}$$

Grouping the constants gives the standard result:

$$\boxed{\Omega(N, V, E) = \frac{V^N}{N!} \left(\frac{2\pi m E}{h^2} \right)^{3N/2} \frac{1}{(\frac{3N}{2})!}} \tag{9}$$

7 Entropy

The entropy of an ideal gas $S(N, V, E)$ is given by

$$S = k_{\mathrm{B}} \ln \Omega(N, V, E) = N k_{\mathrm{B}} \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right], \tag{10}$$

where the last equation is known at the Sackur-Tetrode formula for the entropy of a monoatomic ideal gas. You will derive this in the worksheet. As expected, the entropy is proportional to $N k_{\mathrm{B}} \sim \mathcal{O}(1)\mathrm{J/K}$ if $N \sim 10^{23}$. This indicates that the physically relevant combination in everyday life is $N k_{\mathrm{B}}$, rather than N or k_{B} alone. Both numbers on their own reflects something fundamental: *atoms are very small* compared to the scales that we encounter everyday.

8 Pressure

The ideal gas allowed us to introduce another key external parameter controlling the properties of the system: the volume V. From our discussion last time, we know that the temperature is related to the derivative of the entropy with respect to the energy. But now, we have the option of taking a different derivative with respect to V. What does this give us? A quantity that we are all familiar with – the pressure P (well almost):

$$P \equiv T \frac{\partial S}{\partial V}. \tag{11}$$

To check that this is a reasonable definition, let's compute this for the ideal gas above

$$\begin{aligned} P &= T \frac{\partial}{\partial V} \left(N k_{\mathrm{B}} \left(\ln V + \text{terms independent of } V \right) \right) & (12) \\ &= \frac{N k_{\mathrm{B}} T}{V}, & (13) \end{aligned}$$

from which we recover the ideal gas law $PV = N k_{\mathrm{B}} T$, indicating that the above definition is very reasonable indeed.