

Unit 4: Ideal gases

22 Feb.

4.1 Volume, energy levels, and partition function

We now apply the canonical ensemble to investigate non-relativistic, classical, ideal gases. Using statistical physics we will explore how the large-scale behaviours of such gases emerge from the properties of the particles that compose them. The key particle properties are specified by the adjectives listed above:

- **Classical** systems are those for which we can ignore the effects of quantum mechanics. Among other things, this allows us to simultaneously define both the position (x, y, z) and the momentum $\vec{p} = (p_x, p_y, p_z)$ of each particle with arbitrary precision.
- **Non-relativistic** particles move with speeds small compared to the speed of light, which allows us to ignore small effects due to special relativity. The particles are therefore governed by the laws Isaac Newton published all the way back in 1687. In particular, the energy of each particle of mass m is

$$E_n = \frac{1}{2m} p_n^2,$$

where $p_n^2 = \vec{p}_n \cdot \vec{p}_n = (p_x)_n^2 + (p_y)_n^2 + (p_z)_n^2$ is the inner (or 'dot') product of the momentum vector for the n th particle in the micro-state of interest.

- **Ideal** gases are those whose constituent particles don't interact with each other. As a result, the total energy of the gas is simply the sum of the energies of the N individual particles,

$$E = \frac{1}{2m} \sum_{i=1}^N p_i^2. \quad (46)$$

As usual for the canonical ensemble, we consider the gas to be in thermodynamic equilibrium, and in thermal contact with a large external thermal reservoir with which it can exchange energy but not particles. To prevent particle exchange, we can specify that the gas is enclosed in a cubic box with volume $V = L^3$. The thermal reservoir fixes the temperature T of the gas.

The starting point for our analysis is to compute the partition function

$$Z = \sum_i e^{-E_i/T}.$$

Unfortunately there is a challenge confronting this sum over all possible micro-states ω_i of the N -particle system. These micro-states depend on the momenta \vec{p}_n for all N particles, and it's intuitive to suppose that each component of $(p_x, p_y, p_z)_n$ is a continuously varying real number that can (in principle) be distinguished with arbitrary precision. This implies an uncountably infinite set of distinct momenta and hence an uncountably infinite set of micro-states, making the summation above ill-defined.

To proceed, we need to regulate the system so that there are a countable number of micro-states we can sum over to define the partition function. We do this by positing that the particles' momentum components can take only discrete (or 'quantized') values that depend on the volume of the box. Specifically, we declare that the possible momenta are

$$\vec{p} = (p_x, p_y, p_z) = \frac{\hbar\pi}{L}(k_x, k_y, k_z) \quad k_{x,y,z} = 0, 1, 2, \dots \quad (47)$$

Each component of the non-negative-integer vector $\vec{k} = (k_x, k_y, k_z)$ is independent. The constant factor \hbar ("h-bar"), known as the (reduced) Planck constant (named after Max Planck), simply converts units from inverse-length ($\frac{1}{L}$) to momentum (p). Very similar discrete momenta turn out to be realized in nature, thanks to quantum mechanics—if you have previously studied quantum physics, you may recognize the momenta for a particle in a box, but for the purposes of this module we can just adopt this result as an ansatz.

What are the energies that correspond to these discretized momenta?

$$E_k = \frac{p^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} (k_x^2 + k_y^2 + k_z^2) = \mathcal{E} (k_x^2 + k_y^2 + k_z^2) \quad \mathcal{E} = \frac{\hbar^2 \pi^2}{2mL^2}$$

$$E = \mathcal{E} \{0, 1, 2, 3, 4, 5, 6, 8, \dots, 10, 11, 12, 13, 14, 17, \dots\}$$

Not 7, 15, 16

You should find energies that fall into discrete energy levels, somewhat similar to the spin system considered in Section 3.4. Unlike the spin system, in this case the energy gaps between subsequent energy levels are not constant.

Even though there are still an infinite number of possible momenta and energy levels for each particle in the gas, these are now countable, making our partition function well-defined. Let's start by considering the partition function Z_1 for a single particle in the box. The micro-states for this single-particle system are completely specified by that particle's momentum \vec{p} ,

$$Z_1 = \sum_i \exp\left[-\frac{E_i}{T}\right] = \sum_{\vec{p}} \exp\left[-\frac{p^2}{2mT}\right] = \sum_{k_{x,y,z}=0}^{\infty} \exp\left[-\frac{\hbar^2 \pi^2}{2mTL^2} (k_x^2 + k_y^2 + k_z^2)\right].$$

We can separately sum over each of the independent (k_x, k_y, k_z) , and recognize that all three summations are identical:

$$Z_1 = \sum_{k_x=0}^{\infty} \exp\left[-\frac{\hbar^2 \pi^2}{2mTL^2} k_x^2\right] \sum_{k_y=0}^{\infty} \exp\left[-\frac{\hbar^2 \pi^2}{2mTL^2} k_y^2\right] \sum_{k_z=0}^{\infty} \exp\left[-\frac{\hbar^2 \pi^2}{2mTL^2} k_z^2\right]$$

$$= \left(\sum_{k_i=0}^{\infty} \exp\left[-\frac{\hbar^2 \pi^2}{2mTL^2} k_i^2\right] \right)^3.$$

For non-relativistic ~~classical~~ ^{non-rel.} gases we can assume that Planck's constant \hbar is extremely small compared to $L\sqrt{mT}$,⁷ so that

$$\frac{\hbar^2 \pi^2}{2mTL^2} \ll 1.$$

This means that the function being summed varies very smoothly as the integer k_i increases, for any k_i small enough to leave the exponential factor non-negligible. We can therefore accurately approximate each sum by an integral over continuous real \hat{k}_i , so that

$$\sum_{k_i=0}^{\infty} \exp\left[-\frac{\hbar^2 \pi^2 k_i^2}{2mTL^2}\right] \approx \int_0^{\infty} \underline{d\hat{k}_i} \exp\left[-\frac{\hbar^2 \pi^2 \hat{k}_i^2}{2mTL^2}\right] = \frac{1}{2} \int_{-\infty}^{\infty} \underline{d\hat{k}_i} \exp\left[-\frac{\hbar^2 \pi^2 \hat{k}_i^2}{2mTL^2}\right].$$

The final equality simply notes that the integrand is an even function of \hat{k}_i , as it depends only on \hat{k}_i^2 .

Since we're back to working with continuous real variables, we may as well use Eq. 47 to return to the original momenta $dp_i = \hbar \frac{\pi}{L} d\hat{k}_i$,

$$\sum_{k_i=0}^{\infty} \exp\left[-\frac{\hbar^2 \pi^2 k_i^2}{2mTL^2}\right] = \frac{1}{2} \int \left(\frac{L}{\pi \hbar} dp_i\right) \exp\left[-\frac{p_i^2}{2mT}\right].$$

So we end up with the single-particle partition function

$$Z_1 = \left(\frac{L}{2\pi \hbar}\right)^3 \int \underline{d^3 p} \exp\left[-\frac{p^2}{2mT}\right],$$

again with $p^2 = p_x^2 + p_y^2 + p_z^2$. We can now account for all N particles in the ideal gas, which are completely independent and don't interact with each other. Assuming we can distinguish these particles from each other, then each of them simply contributes an independent factor of Z_1 to the overall partition function

$$Z_D = \left(\frac{L}{2\pi \hbar}\right)^{3N} \int \underline{d^{3N} p} \exp\left[-\sum_{i=1}^N \frac{p_i^2}{2mT}\right], \quad (48)$$

where the subscript reminds us of the particles' distinguishability. We will consider the indistinguishable case below.

We can recognize that each of the $3N$ independent integrations in Eq. 48 is a gaussian integral,

$$\frac{L}{2\pi \hbar} \int \underline{dp_i} \exp\left[-\frac{p_i^2}{2mT}\right] = \frac{L}{2\pi \hbar} \sqrt{2\pi mT} = \sqrt{\frac{mTL^2}{2\pi \hbar^2}} \equiv \underline{\lambda_{th}(T)}.$$

In the last step we have made the notation more compact by defining the thermal de Broglie wavelength (named after Louis de Broglie),

$$\lambda_{th}(T) = \sqrt{\frac{2\pi \hbar^2}{mT}}. \quad (49)$$

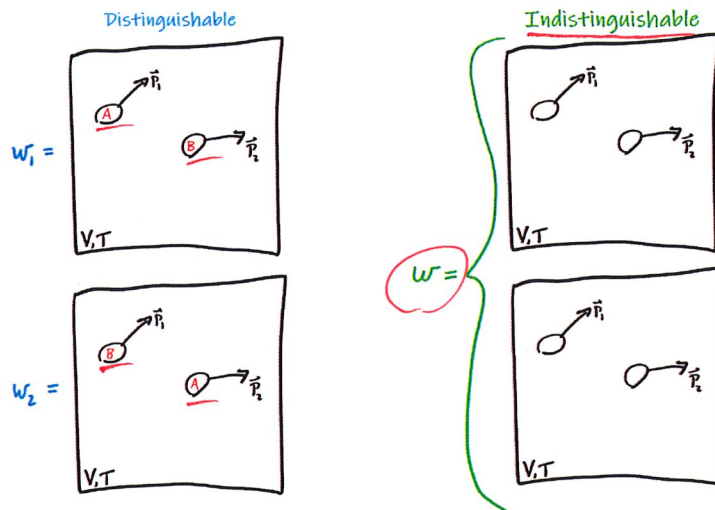
⁷If m is too small, effects due to special relativity become non-negligible. If T is too small, effects due to quantum physics become non-negligible. If L is too small, we don't have a sufficiently large-scale (*macroscopic*) system to justify analysis via statistical ensembles in the first place.

Performing all $3N$ gaussian integrals,

$$Z_D = \left(\frac{mTL^2}{2\pi\hbar^2} \right)^{3N/2} = \left(\frac{L}{\lambda_{th}} \right)^{3N} = \left(\frac{V}{\lambda_{th}^3} \right)^N, \quad (50)$$

since the volume of the box is $V = L^3$. It is worth emphasizing here that the partition function *depends on the volume of the gas*, in addition to the fixed temperature T and conserved particle number N . This dependence may persist in other quantities derived from the partition function, which we will consider in the next section.

First, let's determine what we would have with indistinguishable particles. For a classical gas, distinguishability means that we can label the particles and use those labels to tell them apart as they bounce around inside the box. In the simple two-particle example illustrated below, these labels mean we have a different micro-state ω_1 when particle A has momentum \vec{p}_1 while particle B has momentum \vec{p}_2 , compared to micro-state ω_2 in which particle A has momentum \vec{p}_2 while particle B has momentum \vec{p}_1 .



If the particles are indistinguishable, no such labeling is possible, and there is only one micro-state for these $\{\vec{p}_1, \vec{p}_2\}$, rather than two. This factor of 2 is not accidental, as you can explore by counting how many micro-states there are for three distinguishable particles with momenta $\{\vec{p}_1, \vec{p}_2, \vec{p}_3\}$, compared to the single micro-state for the indistinguishable case:

\vec{p}_1	A	A	B	B	C	C	} $6 = 3!$
\vec{p}_2	B	C	A	C	B	A	
\vec{p}_3	C	B	C	A	A	B	

Generalizing to N particles, we find that ideal gases with distinguishable particles have $N!$ times more micro-states compared to otherwise-identical ideal gases with indistinguishable particles: There are N possible ways to label the particle with momentum \vec{p}_1 , then $N-1$ possible labels for \vec{p}_2 , and so on.⁸ The partition function sums over these micro-states, but depends only on their energies, which are independent of any labeling. Therefore this factor of $N!$ is the only difference between Eq. 50 and the partition function for indistinguishable particles,

$$Z_I = \frac{1}{N!} \left(\frac{mTL^2}{2\pi\hbar^2} \right)^{3N/2} = \frac{1}{N!} \left(\frac{L}{\lambda_{\text{th}}} \right)^{3N} = \frac{1}{N!} \left(\frac{V}{\lambda_{\text{th}}^3} \right)^N. \quad (51)$$

$$Z_D = Z_I^N = N! Z_I$$

4.2 Internal energy, and entropy

Now that we have the canonical partition function, let's apply our work from Unit 3 to predict the large-scale behaviour of the ideal gas it describes. Our first targets are the average internal energy $\langle E \rangle$ and entropy S for the gas, as functions of its fixed temperature T , conserved particle number N , and the volume $V = L^3$ of the box in which it is contained. Let's begin with the slightly more complicated case of indistinguishable particles, Eq. 51. Recalling the derivatives in Eqs. 38–39, we should keep the temperature dependence explicit in our workings, rather than hidden inside the thermal de Broglie wavelength $\lambda_{\text{th}}(T)$.

Starting by writing down the Helmholtz free energy,

$$F_I = -T \log Z_I = -\frac{3NT}{2} \log \left(\frac{mTL^2}{2\pi\hbar^2} \right) + T \log(N!),$$

we can quickly extract the internal energy,

$$\langle E \rangle_I = -T^2 \frac{\partial}{\partial T} \left(\frac{F_I}{T} \right) = -T^2 \frac{\partial}{\partial T} \left(-\frac{3N}{2} \log T + T\text{-independent} \right) = \frac{3}{2} NT.$$

This in turn provides the entropy

$$S_I = \frac{\langle E \rangle_I - F_I}{T} = \frac{3}{2} N + \frac{3N}{2} \log \left(\frac{mTL^2}{2\pi\hbar^2} \right) - \log(N!).$$

We can clean this up by reintroducing the thermal de Broglie wavelength,

$$\frac{3N}{2} \log \left(\frac{mTL^2}{2\pi\hbar^2} \right) = \frac{3N}{2} \log \left(\frac{L^2}{\lambda_{\text{th}}^2} \right) = N \log \left(\frac{V}{\lambda_{\text{th}}^3} \right),$$

$$\log(N!) \approx N \log N - N$$

and by applying Stirling's formula to find

$$S_I = \frac{3}{2} N + N \log \left(\frac{V}{\lambda_{\text{th}}^3} \right) - \underline{N \log N} + N = \frac{5}{2} N + N \log \left(\frac{V}{N \lambda_{\text{th}}^3} \right).$$

We can interpret $N \lambda_{\text{th}}^3$ as the volume 'occupied' by the N particles.

⁸This argument assumes the momenta themselves are distinguishable, $\vec{p}_i \neq \vec{p}_k$ for any $i \neq k$. This is a reliable assumption for classical gases with $L\sqrt{mT} \gg \hbar$, but will need to be revisited when we consider quantum statistics.