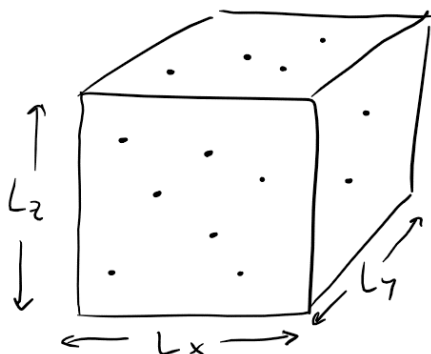


Lecture 4 – Entropy of an ideal gas

LAST TIME: we determined the multiplicity for an Einstein solid and a paramagnet

TODAY: the ideal gas – free, independent, and indistinguishable particles (for now, assume monatomic particles)



Closed 3-D system of volume $V = L_x L_y L_z$ with N atoms

The one tool we have so far is the multiplicity $\Omega(U, N)$

How do we count microstates of the system?

Treat gas as particles in a box

Review of “particle in a box” problem in undergraduate quantum mechanics:

The Hamiltonian for a free particle contains a kinetic energy term only

$$H\psi(\vec{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) = \varepsilon \psi(\vec{r}, t)$$

This is solved by the following wavefunction, which has energy

$$\psi(\vec{r}, t) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r} - i\omega t}, \quad \varepsilon = \frac{p^2}{2m} = \frac{\hbar^2}{2m} |\vec{k}|^2 = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

The walls of the box impose reflecting boundary conditions that constrain the values of the wavevector \vec{k}

$$k_x = \frac{\pi n_x}{L_x}, \quad k_y = \frac{\pi n_y}{L_y}, \quad k_z = \frac{\pi n_z}{L_z}, \quad \text{with } n_{x,y,z} = 1, 2, 3, \dots$$

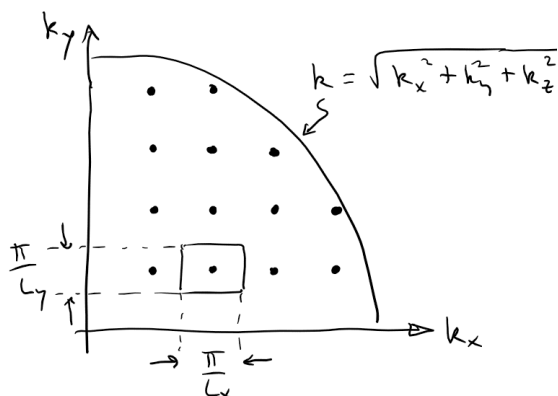
so the energy is quantized according to:

$$\varepsilon = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right), \quad \text{with } n_{x,y,z} = 1, 2, 3, \dots$$

(Compare this to energy quantization for harmonic oscillator)

Calculating Ω involves finding all the microstates of this particle (i.e. the sets of integers $\{n_x, n_y, n_z\}$) that give the same macrostate (i.e. energy ε). Unlike the harmonic oscillators in the Einstein solid, there is no simple formula for this.

How do we proceed? Look at this graphically:



In k -space, each quantum state of the particle is represented by a point on a lattice.

Microstates with the same energy sit on a sphere in k -space with radius $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$

$\Omega(\varepsilon)$ is given by the number of lattice points that intersect the surface of the sphere. There is no simple analytical solution for this. (See Fig. 1.2 in K & K)

Let's solve a simpler problem first: how many microstates are there with energy $\leq \varepsilon$?

Each state occupies a box in k -space of volume: $\frac{\pi}{L_x} \frac{\pi}{L_y} \frac{\pi}{L_z} = \frac{\pi^3}{V}$, so

$$\# \text{ of microstates with energy } \leq \varepsilon \approx \frac{\text{volume of sphere in } k\text{-space with radius } k = \sqrt{\frac{2m}{\hbar^2} \varepsilon}}{\text{volume in } k\text{-space per state}}$$

$$\Phi(\varepsilon) \approx \frac{\frac{4\pi}{3} k^3 / 8}{\pi^3 / V} = \frac{V}{6\pi^2} k^3 = \frac{V}{6\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{3/2}$$

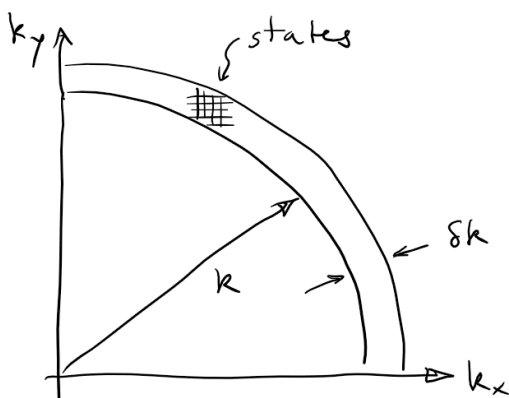
(The factor of 1/8 arises because $k_x, k_y, k_z > 0$, i.e. volume in k -space is 1/8 that of a sphere.)

This is an excellent approximation when the radius of the sphere is much larger than the spacing between lattice points, $k \gg \Delta k = \pi/L$ or $\varepsilon \gg \Delta \varepsilon = \pi^2 \hbar^2 / 2mV^{2/3}$, i.e. when the energy of the particle is much larger than the average spacing between energy levels.

Next, instead of calculating the # of microstates at one energy ε , let's find the # of microstates in a narrow range of energies $\varepsilon, \varepsilon + \delta \varepsilon$:

$$\Omega(\varepsilon, \varepsilon + \delta \varepsilon) = \Phi(\varepsilon + \delta \varepsilon) - \Phi(\varepsilon) \approx \frac{\partial \Phi}{\partial \varepsilon} \delta \varepsilon = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} \delta \varepsilon$$

This is an also excellent approximation, provided $\varepsilon \gg \delta \varepsilon \gg \Delta \varepsilon$.



$\Omega(\varepsilon, \varepsilon + \delta\varepsilon)$ corresponds to integrating over a shell in k -space with volume $\frac{4\pi}{8} k^2 \delta k$:

$$\begin{aligned}\Omega(\varepsilon, \varepsilon + \delta\varepsilon) &= \frac{V}{\pi^3} \frac{4\pi}{8} k^2 \delta k = \frac{V}{2\pi^2} k^2 \delta k \\ &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon \frac{\delta\varepsilon}{2\varepsilon^{1/2}} \\ &= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} \delta\varepsilon\end{aligned}$$

Question 1: Imagine a 2-D ideal gas in a box of area A . How many single-particle microstates are there with energy $\leq \varepsilon$, and in an energy band $\varepsilon, \varepsilon + \delta\varepsilon$?

Each state occupies a box in k -space of area $\frac{\pi}{L_x} \frac{\pi}{L_y} = \frac{\pi^2}{A}$, and the states with energy $\leq \varepsilon$ occupy an area of $\frac{1}{4}$ of a circle in k -space, so

$$\Phi(\varepsilon) = \frac{A}{\pi^2} \frac{1}{4} \pi k^2 = \frac{A}{4\pi} k^2 = \frac{A}{4\pi} \left(\frac{2m}{\hbar^2} \right) \varepsilon, \quad \text{and} \quad \Omega(\varepsilon, \varepsilon + \delta\varepsilon) = \frac{\partial\Phi}{\partial\varepsilon} \delta\varepsilon = \frac{A}{4\pi} \left(\frac{2m}{\hbar^2} \right) \delta\varepsilon$$

Note: we define the density of states, $D(\varepsilon)$, as the number of states per energy interval:

$$D(\varepsilon) = \frac{\partial\Phi}{\partial\varepsilon} \quad \text{or} \quad \int_0^\varepsilon d\varepsilon' D(\varepsilon') = \Phi(\varepsilon)$$

and $\Omega(\varepsilon, \varepsilon + \delta\varepsilon) = D(\varepsilon) \delta\varepsilon$. We will use this concept many times in this class.

That was all for 1 particle in a box. How do we extend this to 2, 3, ... N particle?

With 2 particles, we have double the number of variables:

$$U = \varepsilon_1 + \varepsilon_2 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} = \frac{\hbar^2 k^2}{2m}, \quad \text{with } k = \sqrt{k_{x1}^2 + k_{y1}^2 + k_{x2}^2 + k_{y2}^2}$$

with each wavenumber quantized as before.

Now, states are represented as points on a lattice in a $2 \times 3 = 6$ -dimensional k -space

Each 2-particle quantum state occupies a box in k -space of volume: $\left(\frac{\pi^3}{V}\right)^2$

States with energy $\leq U$ occupy a volume $= 1/8^2 = 1/2^6$ of a hypersphere in 6-D k -space

States with energy in range $U, U+\delta U$ occupy a volume $= 1/2^6$ of a hypershell in 6-D k -space

\vdots

With N particles, states are represented as points on a lattice in a $3N$ -dimensional k -space

Each N -particle quantum state occupies a box in k -space of volume: $\left(\frac{\pi^3}{V}\right)^N$

States with energy $\leq U$ occupy a volume $= 1/2^{3N}$ of a hypersphere in $3N$ -D k -space

States with energy in range $U, U+\delta U$ occupy a volume $= 1/2^{3N}$ of a hypershell in $3N$ -D k -space

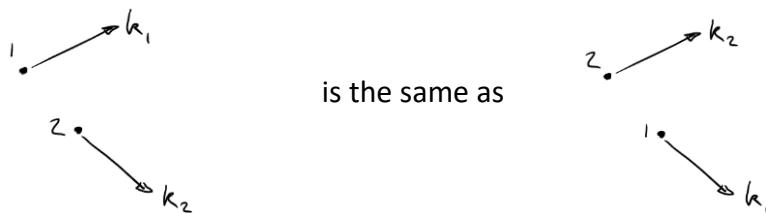
Question 2: Using dimensional arguments, derive how Φ_N and Ω_N should scale with total energy U and volume V for arbitrary N

Follow the pattern, using the fact that $k \propto \sqrt{U}$:

$N = 1:$	$\Phi_1(U) \propto V k^3 \propto V U^{3/2}$	$\Omega_1(U, U + \delta U) \propto V k^2 \delta k \propto V U^{1/2} \delta U$
$N = 2:$	$\Phi_2(U) \propto V^2 k^6 \propto V^2 U^3$	$\Omega_2(U, U + \delta U) \propto V^2 k^5 \delta k \propto V^2 U^2 \delta U$
\vdots		
$N:$	$\Phi_N(U) \propto V^N k^{3N} \propto V^N U^{3N/2}$	$\Omega_N(U, U + \delta U) \propto V^N k^{3N-1} \delta k \propto V^N U^{3N/2-1} \delta U$

What is left out of these expressions are constants like $2m/\hbar^2$ and a numerical factor that accounts for the integration over the solid angle of the hypershell in $3N$ -dimensional k -space

Also, we want to avoid overcounting states because particles are indistinguishable. For 2 particles:



So we should divide Ω_2 by 2, i.e. the number of ways to interchange the particles.

For N particles, we should divide Ω_N by $N!$

If we write everything out explicitly:

$$\Omega_N(U, U + \delta U) = \frac{g_{3N}}{2^{3N} N!} \left(\frac{V}{\pi^3} \right)^N \left(\frac{2m}{\hbar^2} \right)^{3N/2} \frac{U^{3N/2-1}}{2} \delta U$$

where g_D is the solid angle of a hypershell in D dimensions (e.g. $g_3 = 4\pi$). A formula for g_D can be derived but we'll leave this aside for now.

Note: If you are worried about units, a nice way to rewrite this expression using $\Delta\epsilon = \frac{\hbar^2 \pi^2}{2mV^{2/3}}$,

roughly the average spacing between energy levels, is:

$$\Omega_N(U, U + \delta U) = \frac{g_{3N}}{2^{3N+1} N!} \left(\frac{U}{\Delta\epsilon} \right)^{3N/2-1} \frac{\delta U}{\Delta\epsilon}$$

which is dimensionless, as expected.

Since N is a very large number ($\sim 10^{20}$), the multiplicity is a very rapidly increasing function of the total energy of the system U , similarly to the Einstein solid. Unlike the Einstein solid, Ω_N also depends on the system volume V . This makes sense: the larger V is, the more microstates there are available for each particle.

Let's explore the consequences by calculating the entropy from Ω_N

$$S(U, U + \delta U; V) = k_B \ln \Omega_N = Nk_B \ln V + \left(\frac{3}{2}N - 1 \right) k_B \ln U + k_B \ln \delta U + k_B \ln f(N)$$

where the last term is a function of N and constants only.

First consider the energy-dependent terms:

- Notice that the 1 can be neglected compared to $N \gg 1$, and that the $\ln \delta U$ term is insignificant compared to the other term. $U \gg \delta U$, so $N \ln U \gg \ln U > \ln \delta U$ by many orders of magnitude!
- So, we are completely justified in neglecting these small terms:

$$S(U, V) \approx Nk_B \ln V + \frac{3}{2} Nk_B \ln U + k_B \ln f(N)$$

S , to a very good approximation, is independent of the range of energies δU we choose, so long as it is greater than the spacing between energy levels and $N \gg 1$

Calculating the temperature

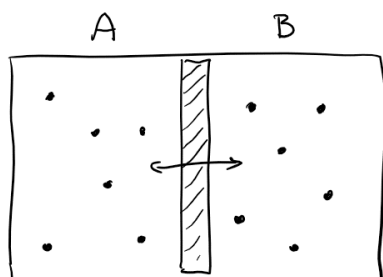
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N} = \frac{3Nk_B}{2U}, \text{ so } U = \frac{3}{2} Nk_B T$$

i.e. each particle carries an average energy of $3/2 k_B T$. (We'll re-derive this result using a powerful approach called the equipartition theorem later in the semester)

Next consider the volume-dependent term:

KEY CONCEPT: Mechanical equilibrium

Consider two gases A, B in thermal equilibrium with each other in an isolated box of constant volume with a moveable piston between the two



$$V_{tot} = V_A + V_B \text{ is fixed}$$

but V_A and V_B can vary

Just like in derivation of thermal equilibrium, S_{tot} of total closed system A + B is maximized

$$\begin{aligned} S_{tot} &= S_A + S_B \\ \frac{\partial S_{tot}}{\partial V_A} &= \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = 0 \\ &= \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_B} \frac{\partial V_B}{\partial V_A} = 0 \end{aligned} \quad \text{Therefore, at equilibrium } \frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$$

Define pressure as $p = T \left(\frac{\partial S}{\partial V} \right)_{U,N}$

At thermal equilibrium $T_A = T_B$, so $p_A = p_B$. This is called mechanical equilibrium.

Question 3: Calculate the pressure generated by an ideal gas

$$p = T \left(\frac{\partial S}{\partial V} \right)_{U,N} \quad \text{and} \quad S(U, V) = Nk_B \ln V + \text{terms independent of } V$$

$$\text{So, } p = T \frac{\partial}{\partial V} Nk_B \ln V = \frac{Nk_B T}{V} \quad \text{and} \quad pV = Nk_B T, \text{ the ideal gas law!}$$

KEY CONCEPT: The thermodynamic identity

$S = S(U, V)$ so

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV \\ &= \frac{1}{T} dU + \frac{p}{T} dV \end{aligned}$$

Or, in terms of dU :

$$dU = \underbrace{T dS}_{\text{“Heat”}} - \underbrace{p dV}_{\text{“Work”}}$$

This is called the thermodynamic identity (it is a statement of the 1st law of thermodynamics)

Note regarding energy scales: When is it valid to write $\varepsilon \gg \delta\varepsilon \gg \Delta\varepsilon$?

Consider a cube of volume 1 cm^3 filled with He gas ($m = 6.6 \times 10^{-27} \text{ kg}$). The spacing between energy levels is:

$$\Delta\varepsilon = \frac{\hbar^2 \pi^2}{2mV^{2/3}} \sim 10^{-19} \text{ eV}$$

On the other hand the average energy per particle at temperature T is:

$$\langle \varepsilon \rangle = \frac{3}{2} k_B T \sim 10^{-2} \text{ eV (at room temperature) or } 10^{-4} \text{ eV (at 1K)}$$

so usually $\varepsilon \gg \Delta\varepsilon$ by many, many orders of magnitude!

Therefore, the range in energy $\delta\varepsilon$ we consider in $\Omega(\varepsilon, \varepsilon + \delta\varepsilon)$ can be much larger than $\Delta\varepsilon$ and still many orders of magnitude smaller than $\langle \varepsilon \rangle$. The exact value for $\delta\varepsilon$ is determined by the precision with which the energy of the system is defined, whether determined by the instrument used to measure energy or the Heisenberg Uncertainty Principle. For example:

$$\delta\varepsilon \delta t \geq \hbar/2 = 3.3 \times 10^{-16} \text{ eV} \cdot \text{s}$$

for a measurement of energy several seconds in duration, the minimum achievable uncertainty $\delta\varepsilon$ is still several orders of magnitude larger than the spacing between energy levels, i.e. $\varepsilon \gg \delta\varepsilon \gg \Delta\varepsilon$. Ultimately, the choice of $\delta\varepsilon$ has such an insignificant effect on the entropy that its exact value does not really matter.