Theo. 4. Statistical Physics.

Lecture 7.

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November 12, 2023.

Last time: Microstates & macrostates.
Statistical definition of temperature.
Boltzmann distribution.

Today: Kinetic theory of gases
Maxwell-Boltzmann distribution
Equipartition theorem.

From last time, we saw that a statistical approach to a closed system of two subsystems that can exchange energy led to an equality condition of

$$\frac{d \ln \Omega_1}{dE_1} = \frac{d \ln \Omega_2}{dE_2} \equiv \frac{1}{k_B T}$$

Here, $\Omega_1(E_1)$ is the number of microstates given the subsystem energy E_1. Counting Ω_1 explicitly is subject to a measure problem when individual microstates are continuous with respect to their individual energy contributions, so we will have to eventually introduce the concept of the partition function to regulate this complication.

In the meantime, it is sufficient to understand that as the subsystem energy E_1 is raised or lowered, the number of ~~me~~microstates accessible by the subsystem increases or decreases, respectively, since the existence of one microstate with max energy E_1 in one dof becomes multiply-defined with more $\tilde{E}_1 > E_1$.

From considering E_1 as a "small" subsystem compared to a "large" reservoir with energy $E_2 = E_{tot} - E_1$, we saw that the ~~was~~ number of microstates in subsystem E_1 follows a Boltzmann distribution:

$$\Omega(E_1 - \epsilon) \approx \Omega(E_1)\, e^{-\epsilon/k_B T}$$

Remark: recall $k_B = 1.3807 \cdot 10^{-23}\ J/K$ is a tiny number.

For $T = 300\ K$, room temperature, $k_B T \sim 4 \cdot 10^{-21}\ J$, so even small changes in energies lead to exponential changes in the number of microstates.

The Boltzmann distribution is centrally responsible for the velocity distribution of gas particles in thermal equilibrium. This begins our study of the kinetic theory of gases.

Kinetic theory of gases:

We recall that classical kinetic energy is $\frac{1}{2} m |\vec{v}_i|^2$ for any velocity vector. What impact does the Boltzmann distribution make on the velocity distribution?

For v_x, define the density of states with velocities v_x and $v_x + dv_x$ as $g(v_x)\, dv_x$. This density of states is proportional to the Boltzmann factor for the corresponding kinetic energy associated with the velocity magnitude v_x:

$$g(v_x) \propto e^{-\frac{1}{2} m v_x^2 / k_B T}.$$

Addendum:

The concept of a density of states is familiar wherever you change from a probability over a set of discrete outcomes to a probability over a continuous set of outcomes. Imagine trying to select |velocity| (speed) of exactly 10 m/s: this is not meaningful since |velocity| can be 10.0001 m/s but not exactly 10 m/s, and so enumerating each possible velocity is not possible.

In contrast, enumerating possible outcomes is possible when outcomes are discrete (i.e. heads or tails).

So, for continuous distributions, we instead ask for a finite range of outcomes: speeds between 10 m/s and 10.1 m/s, and we have a probabilistic weight for this spread in speeds. The probabilistic weight is called the density of states, and the integral over the density of states needs to be 1 in order to think of it as a probabilistic weight. (Just like the sum of discrete outcomes would give the overall rescaling in order for the total probability of all outcomes to equal 100%).

As usual, we impose a normalization condition on $g(v_x)$:

We want $\int_{-\infty}^{\infty} g(v_x)\,dv_x = 1$

so calculate $\int_{-\infty}^{\infty} e^{-\frac{1}{2}mv_x^2/k_BT}\,dv_x = N$

We recognize this is a Gaussian integral.

Standard solution:

$$I = \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv_x^2/k_BT}\,dv_x = \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv_y^2/k_BT}\,dv_y$$

$$I^2 = \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv_x^2/k_BT}\,dv_x \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv_y^2/k_BT}\,dv_x\,dv_y$$

Change to polar $= \int_0^{\infty} v_r\,dv_r \int_0^{2\pi} d\theta\; e^{-\frac{1}{2}mv_r^2/k_BT}$

$$= 2\pi \int_0^{\infty} v_r\,dv_r\, e^{-\frac{1}{2}mv_r^2/k_BT}$$

Use $u \equiv v_r^2$, $du = 2v_r\,dr$

$$= 2\pi \int_0^{\infty} \frac{du}{2}\, e^{-\frac{1}{2}mu/k_BT}$$

$$= \frac{2\pi}{2} \cdot \frac{e^{-\frac{1}{2}mu/k_BT}}{\left(-\frac{1}{2}\frac{m}{k_BT}\right)}\Bigg|_{u=0}^{\infty}$$

$$= \pi\left(0 + \frac{1}{\frac{1}{2}\frac{m}{k_BT}}\right) = \frac{2\pi\,k_BT}{m}$$

So $I^2 = N^2 = \frac{2\pi k_BT}{m} \Rightarrow N = \sqrt{\frac{2\pi k_BT}{m}}$

and $g(v_x)\,dv_x = \sqrt{\frac{m}{2\pi k_BT}}\; e^{-\frac{1}{2}mv_x^2/k_BT}\,dv_x$

is a properly normalized velocity distribution obeying the Boltzmann distribution.

Clearly, each component of velocity (Cartesian) is equivalent, so we have density of states in a cube of (v_x, v_y, v_z) to $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ as

$$g(v_x)\, g(v_y)\, g(v_z)\, dv_x\, dv_y\, dv_z = e^{-\frac{1}{2}mv^2/k_BT}\, dv_x\, dv_y\, dv_z.$$

Note, this Cartesian volume element is not as useful because changing the total kinetic energy changes the integration variables in a <u>constrained</u> way. Therefore, it is better to use spherical coordinates, with $dv_x\, dv_y\, dv_z = v_r^2\, dv_r\, d\Omega = v_r^2\, dv_r\, d\cos\theta\, d\varphi$, and $\int d\Omega = 4\pi$ is the total solid angle.

We thus have the density of states for particles with velocities between v_r and $v_r + dv_r$ as

$$f(v)\, dv \propto v^2\, dv\, e^{-\frac{1}{2}mv^2/k_BT}.$$

We again normalize this fcn. & calculate

$$\int_0^\infty v^2 e^{-\frac{1}{2}mv^2/k_BT}\, dv = \frac{1}{4}\sqrt{\frac{\pi}{(m/(2k_BT))^3}}$$

so

$$f(v)\, dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_BT}\right)^{3/2} v^2\, dv\, e^{-\frac{1}{2}mv^2/k_BT}$$

This is the <u>Maxwell-Boltzmann</u> distribution, which simply stems from the Boltzmann factor applied to kinetic energy!

It is important to make the connection between thermodynamic coordinates and the microscopic / constituent variables and parameters.

We recall that temperature is a macroscopic quantity, while an individual gas molecule follows the Maxwell-Boltzmann velocity distribution. Given T fixed, what is $\langle v \rangle$ and $\langle v^2 \rangle$? We can calculate the expectation values by calculating the convolution against the probability distribution:

$$\langle v \rangle = \int_0^\infty v \cdot f(v)\, dv = \int_0^\infty \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{3/2} v^3\, dv\, e^{-\frac{1}{2}mv^2/k_B T}$$

Exercise: Show $\langle v \rangle = \sqrt{\frac{8 k_B T}{\pi m}}$.

Should use integration by parts, $a \equiv v^2$, $db \equiv v^{-1/2 mv^2/k_B T}\, dv$.

Can use $\int_0^\infty v\, e^{-1/2 mv^2/k_B T}\, dv = \frac{k_B T}{m}$.

Also, $\langle v^2 \rangle = \int_0^\infty v^2 f(v)\, dv = \underline{\frac{3 k_B T}{m}}$.

So as T increases, the average speed increases as $\sqrt{T}$ while the average speed squared increases linearly.

It is important to note that the Maxwell-Boltzmann distribution resulted by assigning kinetic energy into a Boltzmann distribution for a given degree of freedom. In fact, we see that the three dofs are reflected in the fact that

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{k_B T}{m} \quad +$$

$$\langle v^2 \rangle = \frac{3 k_B T}{m}.$$

If we consider the kinetic energy, and every gas molecule has mass m, then

$\langle E_{kin} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$, and each component of velocity contributed $\frac{1}{2} k_B T$.

Thinking about this from the macroscopic viewpoint, we consider a system of many identical particles with some number of internal dofs. If we change the temperature of the system, how does the temperature scale with the average kinetic energy associated with each dof?

The answer is a generalization of the above result & is known as the equipartition of energy theorem. In fact, it applies to both kinetic & potential energy & is essentially a consequence of harmonic motion around an average that is governed by a Boltzmann distribution. The equipartition theorem states that

~~For any energy dependence on~~ a dof that has quadratic dependence on a variable for internal energy (kinetic or potential), the mean energy for this dof is $\frac{1}{2} k_B T$.

(Examples of quadratic dependence include springs: $E = \frac{1}{2} k x^2$ & velocities: $E = \frac{1}{2} m v^2$.)

This scaling also requires that the mean energy of a system sums up each independent dof., so the mean energy of a system w/ n dofs. at temp T is $n \cdot \frac{1}{2} k_B T$.

This is a very powerful result since it emphasizes the intensive nature of temperature and how the Boltzmann distribution, generated via a differential relation regarding energy exchange, works on all subsystem scales for a given sized system.

We will discuss the consequences & intuition provided by the equipartition theorem in the next lecture.