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Course 565/665 Lecture Number ______ Date 3/25/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Problem Set #5 - Chapter 10

Problem: 10.1, 10.7, 10.8, 10.11

Last Time

$$P_j = \frac{e^{-E_j/kT}}{\sum_{j=1}^{t} e^{-E_j/kT}}$$

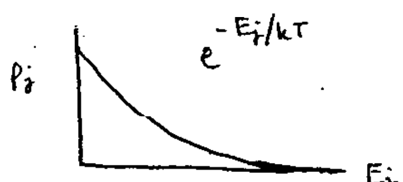
β in this case is $\frac{1}{kT}$ where k is Boltzmann's constant.

- j denotes a particular microstate.
- The denominator $\sum_{j=1}^{t} e^{-E_j/kT} = Q$, the partition fn.

Given i and j microstates, (*at equilibrium),

$$\frac{P_i^*}{P_j^*} = \frac{e^{-E_i/kT}}{Q} \cdot \frac{Q}{e^{-E_j/kT}} = e^{-(E_i - E_j)/kT} = e^{-\Delta E/kT}$$

$P_j \Rightarrow$ probabilities,
populations (fraction of population) in a given microstate.



Implication of Boltzmann Energy Distribution.

- Lower E – Higher Populatede
- Higher E – Lower Populations.

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By preferentially occupying lower E levels by a given particle, we allow other particles to maximize the multiplicity by which populating the ~~remaining~~ remaining energy levels at a given total energy.

⟶ Read example 10.1 on your own.

Example | Distribution of gas velocities:

Integrals to Remember:

① $$\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

② $$\int_{-\infty}^{+\infty} x^2 e^{-ax^2}\, dx = \frac{2}{4a}\sqrt{\frac{\pi}{a}}$$

Given a gas, each particle has m, v, and ε. These particles are noninteracting (no potential energy). Thus, ε is the kinetic energy.

$$\varepsilon(v) = \frac{1}{2} m v^2$$

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$$p(v_x) = \frac{e^{-\varepsilon(v_x)/kT}}{\int_{-\infty}^{+\infty} e^{-\varepsilon(v_x)/kT}\, dv_x} = \frac{e^{-mv^2/2kT}}{\int_{-\infty}^{\infty} e^{-mv_x^2/2kT}\, dv_x}$$

This is a continuous probability distribution fn. Thus, we integrate over all $e^{-\varepsilon(v_x)/kT}$ instead of sum. But it's the same idea. It is continuous because velocities of gas particles are not quantized. (or at least not that we can tell). Thus, the energy levels are infinitesimally separated, making a continuous distribution function.

$$p(v_x) = \sqrt{\frac{m}{2\pi kT}}\; e^{-mv_x^2/2kT}$$

For unbiased motion, it is arbitrary which direction the above development was done for. It could just as easily be in the y or z direction.

Thus,

$$V_x = V_y = V_z$$

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Can Show That

$$\vec{v} = v_x \vec{x} + v_y \vec{y} + v_z \vec{z}$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Thus,

$$p(v) = \left(\sqrt{\frac{m}{2\pi kT}}\right)^3 e^{-mv^2/2kT} \quad \text{where } v^2$$

$$\boxed{p(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mv^2/2kT}}$$

because $p(v) = p(v_x)\,p(v_y)\,p(v_z)$

Width of distribution $\langle v^2 \rangle$

$$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} v_x^2 \, p(v_x)\, dv_x = \frac{kT}{m}$$

mean square velocity

$$\frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} kT$$

Average kinetic energy in x direction.

$$\frac{m}{2}\langle v^2 \rangle = \frac{3}{2} kT = \frac{1}{2} m \left(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \right)$$

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More on Q (Partition Function)

Q → Linking macroscopic to microscopic worlds.

For $E_1 = 0$

$$Q = \sum_{j=1}^{t} e^{-E_j/kT} = 1 + e^{-E_2/kT} + \dots + e^{-E_t/kT}$$

In the Low T Limit $(T \to 0)$

$$\lim_{T\to 0};\quad \frac{E_j}{kT} \longrightarrow \infty,\quad e^{-E_j/kT} = e^{-\infty} = 0$$

But $E_1 = 0$ and $e^{-E_1/kT} = e^{-0/kT} = 1$

$$Q = 1 + 0 + \dots + 0.$$

As $T \to 0$, $Q \longrightarrow 1$.