Comparison between the Maxwellian Velocity and Energy Distributions

Darrel Smith[1]

Embry-Riddle Aeronautical University
Prescott, AZ 86301

(Dated: 15 December 2023)

In the course of investigating molecular speeds of gases in thermodynamic equilibrium, it is common to express the probability in terms of the Maxwellian velocity distribution. It is also possible to represent the probability in terms of an energy distribution, derived from the Maxwellian velocity distribution. The relationship between these two distributions is described in this paper, in particular, the peak velocity and the peak energy of these two distributions.

The purpose of this paper is to examine equations 18.32 and 18.33 in the 14th edition of University Physics by Young and Freedman[1] and "strongly suggest" that a correction be made. The first equation (18.32) is the Maxwellian velocity distribution which is correct. However, the second question (18.33) is presented as the Maxwellian (kinetic) energy distribution, which is incorrect for the reasons shown below. The correct energy distribution is derived and verified during the course of this examination.

I. MAXWELLIAN VELOCITY DISTRIBUTION

The Maxwellian velocity distribution is correctly shown in Eq. 18.32.

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} \tag{1}$$

It has all the "right" properties. For example, it is normalized.

$$\int_0^\infty f(v)dv = 1 \tag{2}$$

Also the physical units of $f(v)$ are `prob./unit velocity`, as it should be.

When examining the Maxwellian energy distribution shown in Eq. 18.33 from University Physics, we encounter some major incongruities.

$$f^*(\epsilon) = \frac{8\pi}{m} \left(\frac{m}{2\pi kT}\right)^{3/2} \epsilon \, e^{-\epsilon/kT} \tag{3}$$

First of all, the normalization is:

$$\int_0^\infty f^*(\epsilon) \, d\epsilon = 2\sqrt{\frac{2kTm}{\pi}} \neq 1 \tag{4}$$

which means the function $f^*(\epsilon)$ is not properly normalized. Furthermore, the units of $f^*(\epsilon)$ are `energy`^{2}`/unit velocity` which is obviously incorrect. The units of $f(\epsilon)$ should be `probability/energy`. If the function $f^*(\epsilon)$

is used to calculate the mean energy of a molecule, we encounter another incorrect result:

$$\int_0^\infty f^*(\epsilon) \, \epsilon \, d\epsilon = 4 \, (kT)^{3/2} \sqrt{\frac{2m}{\pi}} \neq \frac{3}{2}kT \tag{5}$$

So, obviously there is something wrong with the Maxwellian energy distribution $f^*(\epsilon)$ as presented in University Physics Eq. 18.33.

II. MAXWELLIAN ENERGY DISTRIBUTION

The correct procedure for generating $f(\epsilon)$ from $f(v)$ is to equate *probabilities* and not *probability densities*. In other words,

$$f(v) \, dv = f(\epsilon) \, d\epsilon \tag{6}$$

This is a subtle but important point because probabilities must be conserved between the *veloicty* distribution and the *energy* distribution. In order to calculate the "correct" $f(\epsilon)$ we start with Eq. 6 and use the following relationships: $\epsilon = \frac{1}{2}mv^2$, $d\epsilon = mv \, dv$, and $v = \sqrt{2E/m}$. Making these substitutions to Eq. 6, we find that:

$$f(v) \, dv = \sqrt{\frac{2}{\pi}} \frac{1}{(kT)^{3/2}} \epsilon^{1/2} \, e^{-\epsilon/kT} \, d\epsilon \tag{7}$$

where we can now extract $f(\epsilon)$:

$$f(\epsilon) = \sqrt{\frac{2}{\pi}} \frac{1}{(kT)^{3/2}} \epsilon^{1/2} \, e^{-\epsilon/kT} \tag{8}$$

One can easily check the normalization:

$$\int_0^\infty f(\epsilon) \, d\epsilon = 1$$

and find it is indeed properly normalized. One can also check the units of $f(\epsilon)$ and show that they are `probability/unit energy`, as they should be. Furthermore, if one calculates the mean kinetic energy of a gas molecule one correctly obtains:

$$\int_0^\infty \epsilon \, f(\epsilon) \, d\epsilon = \frac{3}{2}kT$$

and not the erroneous result shown in Eq. 5.

III. CONCLUSION

Each of the Maxwellian distributions have their merits. The velocity distribution $f(v)$ gives the reader a sense of the range of speeds for the molecules in thermodynamic equilibrium at a temperature T. Meanwhile, the energy distribution $f(\epsilon)$ is a universal curve for all species of molecules occupying the same volume at temperature T, independent of mass.

In University Physics, the book goes on to say that, "You can prove that the *peak* of each curve occurs where $\epsilon = kT$," however, this is an <u>incorrect</u> statement. The peak of $f(\epsilon)$ occurs at:

$$\epsilon_{\mathrm{peak}} \ = \ \frac{1}{2}kT$$

while the peak of $f(v)$ occurs at:

$$v_{\mathrm{mp}} \ = \ \sqrt{\frac{2kT}{m}}$$

and these peak values correspond to different kinetic energies.

[1]H. D. Young and R. A. Freedman, *University Physics, 2*nd *Ed.* (Pearson, 2016).