

Comparison between the Maxwellian Velocity and Energy Distributions

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(Dated: 20 December 2017)

Density distributions are used throughout physics to describe the profile and range of physical quantities related to particles in the course of their motion. The first density distribution encountered by most physics students is the Maxwellian velocity distribution. In many cases, it is soon followed with an introduction to the Maxwellian energy distribution. Afterwards, comparisons are made in the course of describing these *density* distributions. One misperception is that the “peak of one distribution” corresponds to the “peak of the other distribution,” and this is certainly not the case when comparing density functions. In the course of this paper it is shown that the peak of the Maxwellian *velocity* distribution does not correspond to the peak of the *energy* distribution by the simple relationship $\epsilon = \frac{1}{2}mv^2$. The paper continues with a simple example describing how the peaks are related and how the probabilities are preserved between the 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 and “strongly suggest” that a correction be made. The first equation (18.32) is the Maxwellian velocity distribution which is correct. However, the second equation (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.

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

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

$$\int_0^\infty f(v)dv = 1 \quad (2)$$

Also $f(v)$ has the correct physical units **prob./unit velocity**.

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

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

First of all, the normalization is:

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

which means the function $f^*(\epsilon)$ is not properly normalized. Furthermore, the units of $f^*(\epsilon)$ are

probability/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 erroneous result:

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

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,

$$f(v) dv = f(\epsilon) d\epsilon \quad (6)$$

This is a subtle but important point because probabilities must be conserved between the *velocity* and the *energy* distributions. 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:

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

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

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

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 incorrect result shown in Eq. 5.

The key feature missing from Eq. 18.33 from University Physics is the the Jacobian of transformation, $v dv = d\epsilon/m$. It was not included when changing between independent variables, namely *velocity* \rightarrow *energy*.

III. COMPARING VELOCITY AND ENERGY

Both 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 the University Physics textbook, the text goes on to say that, “You can prove that the *peak* of each curve occurs where $\epsilon = kT$,” however, this is an incorrect statement. The peak of $f(v)$ occurs at:

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

while the peak of $f(\epsilon)$ occurs at:

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

and these peak values correspond to different kinetic energies, kT and $\frac{1}{2}kT$ respectively. This difference is illustrated in Figs. 1 and 2.

A certain amount of care must be taken when interpreting density functions because the casual observer typically looks at $f(v)$ and presumes that the largest fraction of molecules are moving at the peak velocity $v_{\text{mp}} = \sqrt{2kT/m}$. Indeed they are; however, the observer has tacitly assumed that the velocities are measured in equal velocity bins dv .

Let’s investigate how these fixed velocity bins transform to the *energy* representation $f(\epsilon)$. When the velocity bins (*a*, *b*, and *c*) are transformed to the energy distribution as show in Fig. 2, we observe three things.

First, the peak value of $f(v)$ ($v_{\text{mp}} = \sqrt{2kT/m}$) has a corresponding kinetic energy that does not coincide with the peak value of $f(\epsilon)$, $\epsilon_{\text{peak}} = \frac{1}{2}kT$. Instead, its corresponding energy is kT . Second, the probabilities are equal to the areas (*a*, *b*, and *c*) and the individual areas are preserved between Figs. 1 and 2. While it may not be obvious, bin “*b*” has the largest area in both the velocity and the energy distributions, thus preserving the notion that particles with velocities near v_{mp} appear with the

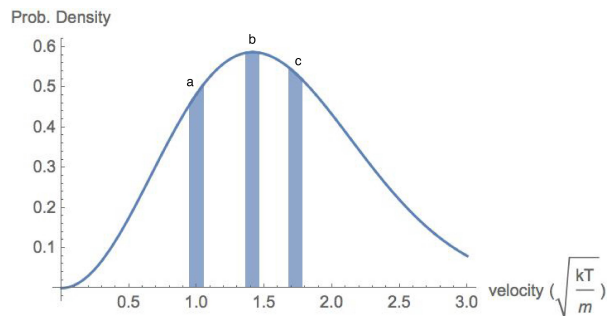


FIG. 1. Maxwellian velocity distribution $f(v)$ with probabilities (i.e., areas) centered at three velocities (1, $\sqrt{2}$ and $\sqrt{3}$) times $\sqrt{kT/m}$. The width of each bin is fixed to 0.1 units with the most-probable velocity occurring at $\sqrt{2kT/m}$.

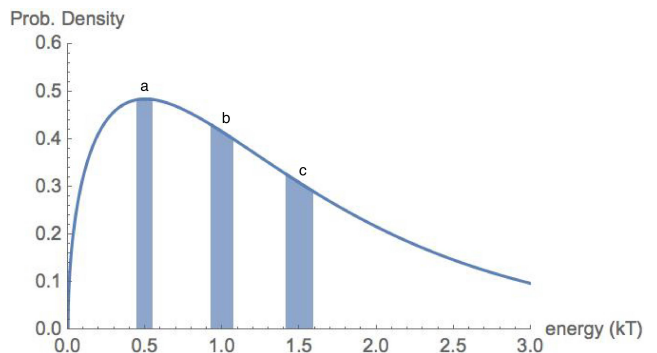


FIG. 2. Maxwellian energy distribution with probabilities (i.e., areas) mapped from the three velocity bins shown in Fig. 1. The “mapped” energies are located at ($\frac{1}{2}$, 1, and $\frac{3}{2}$) times kT . The width of each bin varies due to the Jacobian of transformation $d\epsilon = mv dv$, with the most-probable energy occurring at $kT/2$.

largest fraction of energy in the energy distribution—but not at the peak. Third, while the width of the bins in Fig. 2 are monotonically increasing (due to the Jacobian), their areas (i.e., their probabilities) are also monotonically decreasing for energies $\epsilon > kT$ on the energy scale.

IV. CONCLUSIONS

Both of these distributions have their respective applications. If the velocity of a gas is measured in the lab, and the velocity “bites” over which the velocities are sampled are identical (i.e., the bin widths are the same), then one will produce the velocity distribution shown in Fig. 1. However, if the measuring device is measuring the *kinetic energy* of the gas and the energy “bites” over which the energies are sampled have the same energy width, then one will reproduce the distribution shown in Fig. 2.

This same technique of changing variables occurs frequently in modern physics, for example, when transforming the Planck blackbody spectrum between wavelengths

(λ), and frequencies (ν). Once again, the peak wavelength in the spectral intensity $I(\lambda, T)$ does not correspond to the peak frequency in the spectral intensity

$I(\nu, T)$. It depends on whether the device making the measurement is recording the data in equal units of wavelength, or equal units of frequency.