

6.1: Distribution Functions for Gas-velocity Components

In Chapter 2, we assume that all of the molecules in a gas move with the same speed and use a simplified argument to conclude that this speed depends only on temperature. We now recognize that the individual molecules in a gas sample have a wide range of speeds; the velocities of gas molecules must be described by a distribution function. It is true, however, that the average speed depends only on temperature.

James Clerk Maxwell was the first to derive the distribution function for gas velocities. He did it about 1860. We follow Maxwell's argument. For a molecule moving in three dimensions, there are three velocity components. Maxwell's argument uses only one assumption: the speed of a gas molecule is independent of the direction in which it is moving. Equivalently, we can say that the components of the velocity of a gas molecule are independent of one another; knowing the value of one component of a molecule's velocity does not enable us to infer anything about the values of the other two components. When we use Cartesian coordinates, Maxwell's assumption means also that the same mathematical model must describe the distribution of each of the velocity components.

Since the velocity of a gas molecule has three components, we must treat the velocity distribution as a function of three random variables. To understand how this can be done, let us consider how we might find probability distribution functions for velocity components. We need to consider both spherical and Cartesian coordinate systems.

Let us suppose that we are able to measure the Cartesian-coordinate components v_x , v_y , and v_z of the velocities of a large number of randomly selected gas molecules in a particular constant-temperature sample. Then we can transform each set of Cartesian components to spherical-coordinate velocity components v , θ , and φ . We imagine accumulating the results of these measurements in a table like Table 1. As a practical matter, of course, we cannot make the measurements to complete such a table. However, there is no doubt that, at every instant, every gas molecule can be characterized by a set of such velocity components; the values exist, even if we cannot measure them. We imagine that we have such data only as a way to clarify the properties of the distribution functions that we need.

Table 1. Molecular Velocity Components

| Molecule Number | v_x | v_y | v_z | v | θ | φ |
|-----------------|----------|----------|----------|--------|-------------|--------------|
| 1 | $v_x(1)$ | $v_y(1)$ | $v_z(1)$ | $v(1)$ | $\theta(1)$ | $\varphi(1)$ |
| 2 | $v_x(2)$ | $v_y(2)$ | $v_z(2)$ | $v(2)$ | $\theta(2)$ | $\varphi(2)$ |
| 3 | $v_x(3)$ | $v_y(3)$ | $v_z(3)$ | $v(3)$ | $\theta(3)$ | $\varphi(3)$ |
| 4 | $v_x(4)$ | $v_y(4)$ | $v_z(4)$ | $v(4)$ | $\theta(4)$ | $\varphi(4)$ |
| ... | ... | ... | ... | ... | ... | ... |
| N | $v_x(N)$ | $v_y(N)$ | $v_z(N)$ | $v(N)$ | $\theta(N)$ | $\varphi(N)$ |

These data have several important features. The scalar velocity, v , ranges from 0 to $+\infty$; v_x , v_y , and v_z range from $-\infty$ to $+\infty$. In §2, we see that θ varies from 0 to π ; and φ ranges from 0 to 2π . Each column represents data sampled from the distribution of the corresponding random variable. In Chapter 3, we find that we can use such data to find mathematical models for such distributions. Here, we can find mathematical models for the cumulative distribution functions $f_x(v_x)$, $f_y(v_y)$, and $f_z(v_z)$. We can approximate the graph of $f_x(v_x)$ by plotting the rank probability of v_x versus v_x . We expect this plot to be sigmoid; at any v_x , the slope of this plot is the probability-density function, $df_x(v_x)/dv_x$. The probability density function for v_x depends only on v_x , because the value measured for v_x is independent of the values measured for v_y and v_z . However, by Maxwell's assumption, the functions describing the distribution of v_y and v_z are the same as those describing the distribution of v_x . While redundant, it is convenient to introduce additional symbols to represent these probability density functions. We define $\rho_x(v_x) = df_x(v_x)/dv_x$, $\rho_y(v_y) = df_y(v_y)/dv_y$, and $\rho_z(v_z) = df_z(v_z)/dv_z$.

When we find these one-dimensional distribution functions by modeling the experimental data in this way, each v_x datum that we use in our analysis comes from an observation on a molecule and is associated with particular v_y and v_z values. These values of v_y and v_z can be anything from $-\infty$ to $+\infty$. This is a significant point. The functions $f_x(v_x)$ and $df_x(v_x)/dv_x$ are independent of

v_y and v_z . We can also say that $df_x(v_x)/dv_x$ describes the distribution of v_x when v_y and v_z are averaged over all the values it is possible for them to have.

To clarify this, let us consider another cumulative probability distribution function, $f_{xyz}(v_x, v_y, v_z)$, which is just the fraction of all molecules whose respective Cartesian velocity components are less than v_x, v_y, v_z . Since $f_x(v_x)$, $f_y(v_y)$, and $f_z(v_z)$ are the fractions whose components are less than v_x, v_y , and v_z , respectively, their product is equal to $f_{xyz}(v_x, v_y, v_z)$. We have $f_{xyz}(v_x, v_y, v_z) = f_x(v_x) f_y(v_y) f_z(v_z)$. For the velocity of a randomly selected molecule, (v_x^*, v_y^*, v_z^*) , to be included in the fraction represented by $f_{xyz}(v_x, v_y, v_z)$, the velocity must be in the particular range $+\infty < v_x^* < v_x$, $+\infty < v_y^* < v_y$, and $+\infty < v_z^* < v_z$.

However, for a velocity v_x^* to be included in $f_x(v_x)$, we must have $v_x^* < v_x$, $v_y^* < \infty$, and $v_z^* < \infty$; that is, the components v_y^* and v_z^* can have any values. Since the probability that v_x, v_y , and v_z satisfy $v_x^* < v_x$, $v_y^* < v_y$, and $v_z^* < v_z$ is

$$P(v_x^* < v_x, v_y^* < v_y, v_z^* < v_z) = f_{xyz}(v_x, v_y, v_z) \\ = f_x(v_x) f_y(v_y) f_z(v_z)$$

the probability that v_x^* is included in $f_x(v_x)$ becomes

$$P(v_x^* < v_x, v_y^* < \infty, v_z^* < \infty) = f_{xyz}(v_x, \infty, \infty) \\ = f_x(v_x) f_y(\infty) f_z(\infty) \\ = f_x(v_x)$$

For our purposes, we need to be able to express the probability that the velocity lies within any range of velocities. Let us use υ to designate a particular "volume" region in velocity space and use $P(\upsilon)$ to designate the probability that the velocity of a randomly selected molecule is in this region. When we let υ be the region in velocity space in which x -components lie between v_x

and $v_x + dv_x$, y -components lie between v_y , and $v_y + dv_y$, and z -components lie between v_z and $v_z + dv_z$, $dP(\upsilon)$ denotes the probability that the velocity of a randomly chosen molecule, (v_x^*, v_y^*, v_z^*) , satisfies the conditions $v_x < v_x^* < v_x + dv_x$, $v_y < v_y^* < v_y + dv_y$, and $v_z < v_z^* < v_z + dv_z$.

$dP(\upsilon)$ is an increment of probability. The dependence of $dP(\upsilon)$ on $v_x, v_y, v_z, dv_x, dv_y$, and dv_z can be made explicit by introducing a new function, $\rho(v_x, v_y, v_z)$, defined by

$$dP(\upsilon) = \rho(v_x, v_y, v_z) dv_x dv_y dv_z$$

Since $dv_x dv_y dv_z$ is the volume available in velocity space for velocities whose x -components are between v_x and $v_x + dv_x$, whose y -components are between v_y , and $v_y + dv_y$, and whose z -components are between v_z and $v_z + dz$, we see that $\rho(v_x, v_y, v_z)$ is a probability density function in three dimensions. The value of $\rho(v_x, v_y, v_z)$ is the probability, per unit volume in velocity space, that a molecule has the velocity (v_x, v_y, v_z) . For any velocity, (v_x, v_y, v_z) , there is a value of $\rho(v_x, v_y, v_z)$; this value is just a number. If we want the probability of finding a velocity within some small volume of velocity space around (v_x, v_y, v_z) , we can find it by multiplying $\rho(v_x, v_y, v_z)$ by this volume.

From the one-dimensional probability-density functions, the probability that the x -component of a molecular velocity lies between v_x and $v_x + dv_x$, is just $(df_x(v_x)/dv_x) dv_x$, whatever the values of v_y and v_z . The probability that the y -component lies between v_y and $v_y + dv_y$, is just $(df_y(v_y)/dv_y) dv_y$, whatever the values of v_x and v_z . The probability that the z -component lies between v_z and $v_z + dv_z$, is just $(df_z(v_z)/dv_z) dv_z$, whatever the values of v_x and v_y . When we interpret Maxwell's assumption to mean that these are independent probabilities, the probability that all three conditions are realized simultaneously is

$$dP(\upsilon) = \left(\frac{df_x(v_x)}{dv_x} \right) \left(\frac{df_y(v_y)}{dv_y} \right) \left(\frac{df_z(v_z)}{dv_z} \right) dv_x dv_y dv_z = \rho(v_x, v_y, v_z) dv_x dv_y dv_z$$

Evidently, the product of these three one-dimensional probability densities is the three-dimensional probability density. We have

$$\rho(v_x, v_y, v_z) = \left(\frac{df_x(v_x)}{dv_x} \right) \left(\frac{df_y(v_y)}{dv_y} \right) \left(\frac{df_z(v_z)}{dv_z} \right) = \rho_x(v_x) \rho_y(v_y) \rho_z(v_z)$$

From Maxwell's assumption, we have derived the conclusion that $\rho(v_x, v_y, v_z)$ can be expressed as a product of the one-dimensional probability densities $(df(v_x)/dv_x) dv_x$, $(df(v_y)/dv_y) dv_y$, and $(df(v_z)/dv_z) dv_z$. Since these are probability densities, we have

$$\int_{-\infty}^{\infty} \left(\frac{df_x(v_x)}{dv_x} \right) dv_x = \int_{-\infty}^{\infty} \left(\frac{df_y(v_y)}{dv_y} \right) dv_y = \int_{-\infty}^{\infty} \left(\frac{df_z(v_z)}{dv_z} \right) dv_z = 1$$

and

$$\iiint_{-\infty}^{\infty} \rho(v_x, v_y, v_z) dv_x dv_y dv_z = 1$$

Moreover, because the Cartesian coordinates differ from one another only in orientation, $(df(v_x)/dv_x) dv_x$, $(df(v_y)/dv_y) dv_y$, and $(df(v_z)/dv_z) dv_z$ must all be the same function.

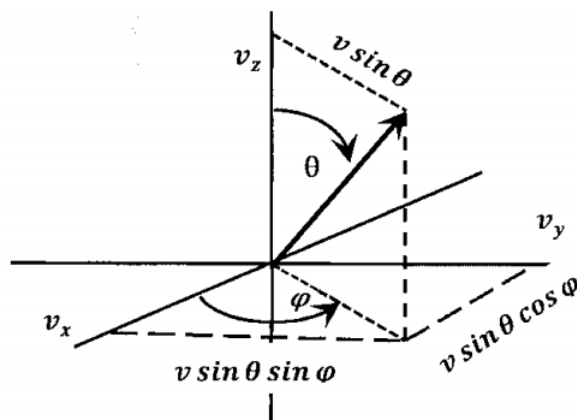


Figure 1. Transformation from Cartesian to spherical coordinates.

To summarize the development above, we define $\rho(v_x, v_y, v_z)$ independently of $df_x(v_x)/dv_x$, $df_y(v_y)/dv_y$, and $df_z(v_z)/dv_z$. Then, from Maxwell's assumption that the three one-dimensional probabilities are independent, we find

$$\begin{aligned} \rho(v_x, v_y, v_z) &= \left(\frac{df_x(v_x)}{dv_x} \right) \left(\frac{df_y(v_y)}{dv_y} \right) \left(\frac{df_z(v_z)}{dv_z} \right) \\ &= \rho_x(v_x) \rho_y(v_y) \rho_z(v_z) \end{aligned}$$

Alternatively, we could take Maxwell's assumption to be that the three-dimensional probability density function is expressible as a product of three one-dimensional probability densities:

$$\rho(v_x, v_y, v_z) = \rho_x(v_x) \rho_y(v_y) \rho_z(v_z)$$

In this case, the relationships of $\rho_x(v_x)$, $\rho_y(v_y)$, and $\rho_z(v_z)$, to the one-dimensional cumulative probabilities ($f_x(v_x)$, etc.) must be deduced from the properties of $\rho(v_x, v_y, v_z)$. As emphasized above, our deduction of $f_x(v_x)$ from experimental data uses v_x values that are associated with all possible values of v_y and v_z . That is, what we determine in our (hypothetical) experiment is

$$\begin{aligned} f_x(v_x) &= \int_{v_x=-\infty}^{v_x} \iint_{v_y, v_z=-\infty}^{\infty} \rho(v_x, v_y, v_z) dv_y dv_z \\ &= \int_{-\infty}^{v_x} \rho_x(v_x) dv_x \int_{-\infty}^{\infty} \rho_y(v_y) dv_y \int_{-\infty}^{\infty} \rho_z(v_z) dv_z \\ &= \int_{-\infty}^{v_x} \rho_x(v_x) dv_x \end{aligned}$$

from which it follows that

$$\frac{df_x(v_x)}{dv_x} = \rho_x(v_x)$$

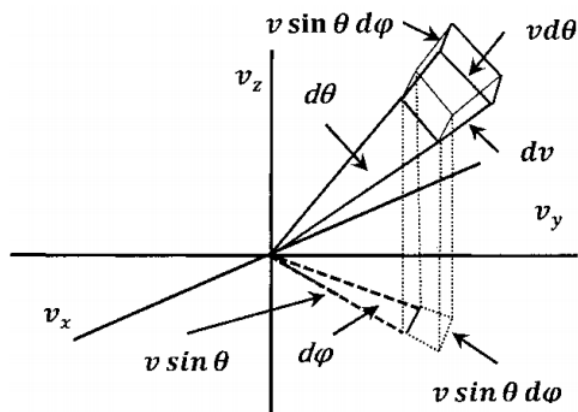


Figure 2. The differential volume element in spherical coordinates.

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