

Problem 1C.1

Some consequences of the Maxwell-Boltzmann distribution. In the simplified kinetic theory in §1.4, several statements concerning the equilibrium behavior of a gas were made without proof. In this problem and the next, some of these statements are shown to be exact consequences of the Maxwell-Boltzmann velocity distribution.

The Maxwell-Boltzmann distribution of molecular velocities in an ideal gas at rest is

$$f(u_x, u_y, u_z) = n(m/2\pi kT)^{3/2} \exp(-mu^2/2kT) \quad (1C.1-1)$$

in which \mathbf{u} is the molecular velocity, n is the number density, and $f(u_x, u_y, u_z)du_x du_y du_z$ is the number of molecules per unit volume that is expected to have velocities between u_x and $u_x + du_x$, u_y and $u_y + du_y$, u_z and $u_z + du_z$. It follows from this equation that the distribution of the molecular speed u is

$$f(u) = 4\pi n u^2 (m/2\pi kT)^{3/2} \exp(-mu^2/2kT) \quad (1C.1-2)$$

(a) Verify Eq. 1.4-1 by obtaining the expression for the mean speed \bar{u} from

$$\bar{u} = \frac{\int_0^{\infty} u f(u) du}{\int_0^{\infty} f(u) du} \quad (1C.1-3)$$

(b) Obtain the mean values of the velocity components \bar{u}_x , \bar{u}_y , and \bar{u}_z . The first of these is obtained from

$$\bar{u}_x = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_x f(u_x, u_y, u_z) du_x du_y du_z}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(u_x, u_y, u_z) du_x du_y du_z} \quad (1C.1-4)$$

What can one conclude from these results?

(c) Obtain the mean kinetic energy per molecule from

$$\frac{1}{2} m \bar{u}^2 = \frac{\int_0^{\infty} \frac{1}{2} m u^2 f(u) du}{\int_0^{\infty} f(u) du} \quad (1C.1-5)$$

The correct result is $\frac{1}{2} m \bar{u}^2 = \frac{3}{2} kT$.

Solution

Part (a)

Substitute the formula for $f(u)$ in Equation 1C.1-2 into Equation 1C.1-3.

$$\bar{u} = \frac{\int_0^{\infty} u \cdot 4\pi n u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mu^2}{2kT}\right) du}{\int_0^{\infty} 4\pi n u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mu^2}{2kT}\right) du}$$

Bring the constants in front and cancel them.

$$\bar{u} = \frac{4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty u^3 \exp\left(-\frac{mu^2}{2kT}\right) du}{4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty u^2 \exp\left(-\frac{mu^2}{2kT}\right) du}$$

Let $a = m/2kT$ to make the integral easier to write. Then we have

$$\bar{u} = \frac{\int_0^\infty u^3 e^{-au^2} du}{\int_0^\infty u^2 e^{-au^2} du}$$

Integrate the numerator by parts as follows.

$$\begin{aligned} v &= u^2 & dw &= ue^{-au^2} du \\ dv &= 2u du & w &= -\frac{e^{-au^2}}{2a} \end{aligned}$$

Integrate the denominator by parts as follows.

$$\begin{aligned} v &= u & dw &= ue^{-au^2} du \\ dv &= du & w &= -\frac{e^{-au^2}}{2a} \end{aligned}$$

The formula being used is $\int v dw = vw - \int w dv$, so we have

$$\bar{u} = \frac{-\frac{u^2 e^{-au^2}}{2a} \Big|_0^\infty - \int_0^\infty \left(-\frac{ue^{-au^2}}{a}\right) du}{-\frac{ue^{-au^2}}{2a} \Big|_0^\infty - \int_0^\infty \left(-\frac{e^{-au^2}}{2a}\right) du}$$

The first term in the numerator and denominator is zero. Bring the constants in front of the remaining integrals.

$$\bar{u} = \frac{\frac{1}{a} \int_0^\infty ue^{-au^2} du}{\frac{1}{2a} \int_0^\infty e^{-au^2} du}$$

Cancel the common term and evaluate these integrals. The one in the denominator is known.

$$\begin{aligned} \bar{u} &= \frac{\frac{1}{a} \left(-\frac{e^{-au^2}}{2a}\right) \Big|_0^\infty}{\frac{1}{2a} \cdot \frac{1}{2} \sqrt{\frac{\pi}{a}}} \\ &= 4\sqrt{\frac{a}{\pi}} \left(\frac{1}{2a}\right) \\ &= \frac{2}{\sqrt{\pi a}} \end{aligned}$$

Now substitute the expression for a .

$$\bar{u} = \frac{2\sqrt{2kT}}{\sqrt{\pi m}}$$

Therefore,

$$\bar{u} = \sqrt{\frac{8kT}{\pi m}}.$$

Part (b)

Plug the formula for $f(u_x, u_y, u_z)$ in Equation 1C.1-1 into Equation 1C.1-4.

$$\bar{u}_x = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_x n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mu^2}{2kT}\right) du_x du_y du_z}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mu^2}{2kT}\right) du_x du_y du_z}$$

Bring the constants in front, cancel them, and then substitute $a = m/2kT$ and $u^2 = u_x^2 + u_y^2 + u_z^2$.

$$\bar{u}_x = \frac{n \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_x e^{-a(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z}{n \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-a(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z}$$

Split up the triple integrals into three single integrals each.

$$\bar{u}_x = \frac{\underbrace{\left(\int_{-\infty}^{+\infty} u_x e^{-au_x^2} du_x \right)}_{=0} \left(\int_{-\infty}^{+\infty} e^{-au_y^2} du_y \right) \left(\int_{-\infty}^{+\infty} e^{-au_z^2} du_z \right)}{\left(\int_{-\infty}^{+\infty} e^{-au_x^2} du_x \right) \left(\int_{-\infty}^{+\infty} e^{-au_y^2} du_y \right) \left(\int_{-\infty}^{+\infty} e^{-au_z^2} du_z \right)}$$

The integral of an odd function over a symmetric interval is zero, so the first integral in the numerator is zero. Therefore,

$$\boxed{\bar{u}_x = 0.}$$

Plug the formula for $f(u_x, u_y, u_z)$ in Equation 1C.1-1 into the analogous equation for \bar{u}_y .

$$\bar{u}_y = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_y n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mu^2}{2kT}\right) du_x du_y du_z}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mu^2}{2kT}\right) du_x du_y du_z}$$

Bring the constants in front, cancel them, and then substitute $a = m/2kT$ and $u^2 = u_x^2 + u_y^2 + u_z^2$.

$$\bar{u}_y = \frac{n \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_y e^{-a(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z}{n \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-a(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z}$$

Split up the triple integrals into three single integrals each.

$$\bar{u}_y = \frac{\left(\int_{-\infty}^{+\infty} e^{-au_x^2} du_x \right) \underbrace{\left(\int_{-\infty}^{+\infty} u_y e^{-au_y^2} du_y \right)}_{=0} \left(\int_{-\infty}^{+\infty} e^{-au_z^2} du_z \right)}{\left(\int_{-\infty}^{+\infty} e^{-au_x^2} du_x \right) \left(\int_{-\infty}^{+\infty} e^{-au_y^2} du_y \right) \left(\int_{-\infty}^{+\infty} e^{-au_z^2} du_z \right)}$$

The integral of an odd function over a symmetric interval is zero, so the second integral in the numerator is zero. Therefore,

$$\boxed{\bar{u}_y = 0.}$$

Plug the formula for $f(u_x, u_y, u_z)$ in Equation 1C.1-1 into the analogous equation for \bar{u}_z .

$$\bar{u}_z = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_z n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mu^2}{2kT} \right) du_x du_y du_z}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} n \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mu^2}{2kT} \right) du_x du_y du_z}$$

Bring the constants in front, cancel them, and then substitute $a = m/2kT$ and $u^2 = u_x^2 + u_y^2 + u_z^2$.

$$\bar{u}_z = \frac{n \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_z e^{-a(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z}{n \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-a(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z}$$

Split up the triple integrals into three single integrals each.

$$\bar{u}_z = \frac{\left(\int_{-\infty}^{+\infty} e^{-au_x^2} du_x \right) \left(\int_{-\infty}^{+\infty} e^{-au_y^2} du_y \right) \underbrace{\left(\int_{-\infty}^{+\infty} u_z e^{-au_z^2} du_z \right)}_{=0}}{\left(\int_{-\infty}^{+\infty} e^{-au_x^2} du_x \right) \left(\int_{-\infty}^{+\infty} e^{-au_y^2} du_y \right) \left(\int_{-\infty}^{+\infty} e^{-au_z^2} du_z \right)}$$

The integral of an odd function over a symmetric interval is zero, so the third integral in the numerator is zero. Therefore,

$$\boxed{\bar{u}_z = 0.}$$

From the boxed results it can be concluded that molecules in an ideal gas at rest have no preferred direction in their motion on average.

Part (c)

Substitute the formula for $f(u)$ in Equation 1C.1-2 into Equation 1C.1-5.

$$\frac{1}{2} \overline{mu^2} = \frac{\int_0^{\infty} \frac{1}{2} mu^2 \cdot 4\pi nu^2 \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mu^2}{2kT} \right) du}{\int_0^{\infty} 4\pi nu^2 \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mu^2}{2kT} \right) du}$$

Bring the constants in front and cancel them.

$$\frac{1}{2} \overline{mu^2} = \frac{1}{2} m \frac{4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty u^4 \exp\left(-\frac{mu^2}{2kT}\right) du}{4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty u^2 \exp\left(-\frac{mu^2}{2kT}\right) du}$$

Let $a = m/2kT$ to make the integral easier to write. Then we have

$$\frac{1}{2} \overline{mu^2} = \frac{1}{2} m \frac{\int_0^\infty u^4 e^{-au^2} du}{\int_0^\infty u^2 e^{-au^2} du}.$$

Integrate the numerator by parts as follows.

$$\begin{aligned} v &= u^3 & dw &= ue^{-au^2} du \\ dv &= 3u^2 du & w &= -\frac{e^{-au^2}}{2a} \end{aligned}$$

The formula being used is $\int v dw = vw - \int w dv$, so we have

$$\frac{1}{2} \overline{mu^2} = \frac{1}{2} m \frac{-\frac{u^3 e^{-au^2}}{2a} \Big|_0^\infty - \int_0^\infty \left(-\frac{3u^2 e^{-au^2}}{2a}\right) du}{\int_0^\infty u^2 e^{-au^2} du}.$$

The first term in the numerator is zero. Bring the constant in front of the remaining integral and cancel it with the one in the denominator.

$$\frac{1}{2} \overline{mu^2} = \frac{1}{2} m \frac{\frac{3}{2a} \int_0^\infty u^2 e^{-au^2} du}{\int_0^\infty u^2 e^{-au^2} du}$$

It's not necessary to evaluate the integrals because they cancel.

$$\frac{1}{2} \overline{mu^2} = \frac{3m}{4a}$$

Now substitute the expression for a .

$$\frac{1}{2} \overline{mu^2} = \frac{3m \cdot 2kT}{4m}$$

Therefore,

$$\frac{1}{2} \overline{mu^2} = \frac{3}{2} kT.$$