1 The Kinetic Theory of Gases

From McQuarrie and Simon (n.d.).

Chapter 27

27-5. Arrange the following gases in order of increasing root-mean-square speed at the same temperature: O_2, N_2, H_2O, CO_2, NO_2, $^{235}UF_6$, $^{238}UF_6$.

Answer. The root mean square speed is given by

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Thus, since the temperature is constant by hypothesis, the root mean square speed ordering will be entirely a function of the molar mass (and inversely proportional to it at that). It follows since

$$\begin{aligned}
M(\mathrm{O_2}) &= 32.00\,\mathrm{g/mol} \\
M(\mathrm{N_2}) &= 38.02\,\mathrm{g/mol} \\
M(\mathrm{H_2O}) &= 18.02\,\mathrm{g/mol} \\
M(\mathrm{CO_2}) &= 44.01\,\mathrm{g/mol} \\
M(\mathrm{NO_2}) &= 46.01\,\mathrm{g/mol} \\
M(^{235}\mathrm{UF_6}) &= 349.08\,\mathrm{g/mol} \\
M(^{238}\mathrm{UF_6}) &= 352.04\,\mathrm{g/mol}
\end{aligned}$$

that

$$\boxed{u_{\text{rms}}(^{238}\mathrm{UF_6}) < u_{\text{rms}}(^{235}\mathrm{UF_6}) < u_{\text{rms}}(\mathrm{NO_2}) < u_{\text{rms}}(\mathrm{CO_2}) < u_{\text{rms}}(\mathrm{N_2}) < u_{\text{rms}}(\mathrm{O_2}) < u_{\text{rms}}(\mathrm{H_2O})}$$

□

27-7. The speed of sound in an ideal monatomic gas is given by

$$u_{\text{sound}} = \sqrt{\frac{5RT}{3M}}$$

Derive an equation for the ratio $u_{\text{rms}}/u_{\text{sound}}$. Calculate the root-mean-square speed for an argon atom at 20 °C and compare your answer to the speed of sound in argon.

Answer. We have that

$$\begin{aligned}
\frac{u_{\text{rms}}}{u_{\text{sound}}} &= \frac{\sqrt{3RT/M}}{\sqrt{5RT/3M}} \\
\boxed{\frac{u_{\text{rms}}}{u_{\text{sound}}} = \sqrt{9/5}}
\end{aligned}$$

The root mean square speed for an argon atom at 20 °C is given by

$$\begin{aligned}
u_{\text{rms}}(\mathrm{Ar}) &= \sqrt{\frac{3(8.31\,\frac{\mathrm{J}}{\mathrm{mol\,K}})(293\,\mathrm{K})}{0.039\,95\,\frac{\mathrm{kg}}{\mathrm{mol}}}} \\
\boxed{u_{\text{rms}}(\mathrm{Ar}) = 428\,\mathrm{m/s}}
\end{aligned}$$

Similarly, the speed of sound in argon at 20 °C is given by

$$u_{\text{sound}}(\text{Ar}) = \sqrt{\frac{5(8.31\,\frac{\text{J}}{\text{mol K}})(293\,\text{K})}{3(0.039\,95\,\frac{\text{kg}}{\text{mol}})}}$$

$$\boxed{u_{\text{sound}}(\text{Ar}) = 319\,\text{m/s}}$$

and thus that

$$\frac{u_{\text{rms}}(\text{Ar})}{u_{\text{sound}}(\text{Ar})} = \frac{428\,\text{m/s}}{319\,\text{m/s}} = 1.34 \approx \sqrt{9/5}$$

as desired. □

27-12. We can use the equation for $f(u_x)$ to calculate the probability that the x-component of the velocity of a molecule lies within some range. For example, show that the probability that $-u_{x0} \leq u_x \leq u_{x0}$ is given by

$$\begin{aligned}\text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} &= \sqrt{\frac{m}{2\pi k_\text{B}T}} \int_{-u_{x0}}^{u_{x0}} \text{e}^{-mu_x^2/2k_\text{B}T}\,\text{d}u_x \\ &= 2\sqrt{\frac{m}{2\pi k_\text{B}T}} \int_0^{u_{x0}} \text{e}^{-mu_x^2/2k_\text{B}T}\,\text{d}u_x\end{aligned}$$

Now let $mu_x^2/2k_\text{B}T = w^2$ to get the cleaner looking expression

$$\text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} = \frac{2}{\sqrt{\pi}} \int_0^{w_0} \text{e}^{-w^2}\,\text{d}w$$

where $w_0 = u_{x0}\sqrt{m/2k_\text{B}T}$.

It so happens that the above integral cannot be evaluated in terms of any function that we have encountered up to now. It is customary to express the integral in terms of a new function called the **error function**, which is defined by

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \text{e}^{-x^2}\,\text{d}x$$

The error function can be evaluated as a function of z by evaluating its defining integral numerically. Some values of $\text{erf}(z)$ are

z	$\text{erf}(z)$	z	$\text{erf}(z)$
0.20	0.22270	1.20	0.91031
0.40	0.42839	1.40	0.95229
0.60	0.60386	1.60	0.97635
0.80	0.74210	1.80	0.98909
1.00	0.84270	2.00	0.99532

Now show that

$$\text{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} = \text{erf}(w_0)$$

Calculate the probability that $-\sqrt{2k_\text{B}T/m} \leq u_x \leq \sqrt{2k_\text{B}T/m}$.

Answer. The probability distribution $f(u_x)$ of the x-components of the velocity of a system of molecules is given by

$$f(u_x) = \sqrt{\frac{m}{2\pi k_\text{B}T}}\text{e}^{-mu_x^2/2k_\text{B}T}$$

It follows that the probability that the x-component of the velocity of a molecule lies between u_x and $u_x + \mathrm{d}u_x$ is $f(u_x)\,\mathrm{d}u_x$. Thus, to calculate the total probability that the x-component of the velocity of a molecule lies within the range $-u_{x0} \leq u_x \leq u_{x0}$, we can use an integral to sum all of the infinitesimal probabilities $f(u_x)\,\mathrm{d}u_x$ in that range as follows.

$$\begin{aligned}
\operatorname{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} &= \int_{-u_{x0}}^{u_{x0}} f(u_x)\,\mathrm{d}u_x \\
&= \sqrt{\frac{m}{2\pi k_\mathrm{B}T}} \int_{-u_{x0}}^{u_{x0}} \mathrm{e}^{-mu_x^2/2k_\mathrm{B}T}\,\mathrm{d}u_x \\
&= 2\sqrt{\frac{m}{2\pi k_\mathrm{B}T}} \int_{0}^{u_{x0}} \mathrm{e}^{-mu_x^2/2k_\mathrm{B}T}\,\mathrm{d}u_x
\end{aligned}$$

Note that the last equality holds because $f(u_x) = g(u_x^2)$, where u_x^2 is an even function and hence f is even. Now define the function $w(u_x)$ by

$$w^2 = \frac{mu_x^2}{2k_\mathrm{B}T}$$

Since w is monotonically increasing on the range $[0, u_{x0}]$, and

$$w(0) = 0 \qquad w(u_{x0}) = u_{x0}\sqrt{\frac{m}{2k_\mathrm{B}T}} \qquad \begin{aligned}
2w\frac{\mathrm{d}w}{\mathrm{d}u_x} &= \frac{2mu_x}{2k_\mathrm{B}T} \\
\frac{2wk_\mathrm{B}T}{mu_x}\,\mathrm{d}w &= \mathrm{d}u_x \\
\frac{2u_x\sqrt{m/2k_\mathrm{B}T}\,k_\mathrm{B}T}{mu_x}\,\mathrm{d}w &= \mathrm{d}u_x \\
\sqrt{\frac{2k_\mathrm{B}T}{m}}\,\mathrm{d}w &= \mathrm{d}u_x
\end{aligned}$$

we may substitute it into the above integral using the u-substitution method to yield

$$\begin{aligned}
\operatorname{Prob}\{-u_{x0} \leq u_x \leq u_{x0}\} &= 2\sqrt{\frac{m}{2\pi k_\mathrm{B}T}} \cdot \sqrt{\frac{2k_\mathrm{B}T}{m}} \int_{w(0)}^{w(u_{x0})} \mathrm{e}^{-w^2}\,\mathrm{d}w \\
&= \frac{2}{\sqrt{\pi}} \int_0^{w_0} \mathrm{e}^{-w^2}\,\mathrm{d}w
\end{aligned}$$

Naturally, the above equals $\operatorname{erf}(w_0)$ by the definition of the error function.

Lastly, if $u_{x0} = \sqrt{2k_\mathrm{B}T/m}$, then

$$w_0 = u_{x0}\sqrt{m/2k_\mathrm{B}T} = \sqrt{2k_\mathrm{B}T/m} \cdot \sqrt{m/2k_\mathrm{B}T} = 1$$

It follows that

$$\begin{aligned}
\operatorname{Prob}\{-\sqrt{2k_\mathrm{B}T/m} \leq u_x \leq \sqrt{2k_\mathrm{B}T/m}\} &= \operatorname{erf}(w_0) \\
&= \operatorname{erf}(1)
\end{aligned}$$

$$\boxed{\operatorname{Prob}\{-\sqrt{2k_\mathrm{B}T/m} \leq u_x \leq \sqrt{2k_\mathrm{B}T/m}\} = 0.84270}$$

□

27-20. Show that the variance of the equation $I(\nu) \propto \mathrm{e}^{-mc^2(\nu-\nu_0)^2/2\nu_0^2 k_\mathrm{B}T}$ is given by $\sigma^2 = \nu_0^2 k_\mathrm{B}T/mc^2$. Calculate σ for the $3p\ {}^2P_{3/2}$ to $3s\ {}^2S_{1/2}$ transition in atomic sodium vapor (see Figure 8.4 on McQuarrie and Simon (n.d., p. 307)) at 500 K.

Answer. As per MathChapter B of McQuarrie and Simon (n.d.), $I(\nu)$ is a Gaussian distribution, i.e., is of the form $\mathrm{e}^{-(x-\langle x\rangle)^2/2\sigma^2}$ where σ is the standard deviation. It follows by comparing this general form with the given equation for $I(\nu)$ that

$$\sigma^2 = \frac{\nu_0^2 k_\mathrm{B} T}{mc^2}$$

From Figure 8.4, we have that

$$\lambda(3p\ {}^2P_{3/2} \to 3s\ {}^2S_{1/2}) = 5.8899 \times 10^3\ \text{Å}$$

Thus,

$$\nu_0 = \frac{c}{\lambda} = \frac{2.998 \times 10^8\,\mathrm{m\,s^{-1}}}{5.8899 \times 10^{-7}\,\mathrm{m}} = 5.090 \times 10^{14}\,\mathrm{s^{-1}}$$

Therefore, we have that

$$\begin{aligned}
\sigma &= \sqrt{\frac{\nu_0^2 RT}{Mc^2}} \\
&= \sqrt{\frac{(5.090 \times 10^{14}\,\frac{1}{\mathrm{s}})^2 (8.31\,\frac{\mathrm{J}}{\mathrm{mol\,K}})(500\,\mathrm{K})}{(0.022\,99\,\frac{\mathrm{kg}}{\mathrm{mol}})(2.998 \times 10^8\,\frac{\mathrm{m}}{\mathrm{s}})^2}} \\
&\boxed{\sigma = 7.22 \times 10^8\,\mathrm{s^{-1}}}
\end{aligned}$$

□

27-24. Show that the probability that a molecule has a speed less than or equal to u_0 is given by

$$\mathrm{Prob}\{u \leq u_0\} = \frac{4}{\sqrt{\pi}} \int_0^{x_0} x^2 \mathrm{e}^{-x^2}\,\mathrm{d}x$$

where $x_0 = u_0\sqrt{m/2k_\mathrm{B}T}$. This integral cannot be expressed in terms of any known function and must be integrated numerically. Use Simpson's rule or any other integration routine to evaluate $\mathrm{Prob}\{u \leq \sqrt{2k_\mathrm{B}T/m}\}$.

Answer. As in Problem 27-12, we have that

$$\begin{aligned}
\mathrm{Prob}\{u \leq u_0\} &= \int_0^{u_0} F(u)\,\mathrm{d}u \\
&= 4\pi \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \int_0^{u_0} u^2 \mathrm{e}^{-mu^2/2k_\mathrm{B}T}\,\mathrm{d}u \\
&= 4\pi \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \cdot \sqrt{\frac{2k_\mathrm{B}T}{m}} \int_{x(0)}^{x(u_0)} \frac{2k_\mathrm{B}Tx^2}{m} \mathrm{e}^{-x^2}\,\mathrm{d}x \\
&= 4\pi \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \cdot \left(\frac{2k_\mathrm{B}T}{m}\right)^{1/2} \cdot \left(\frac{2k_\mathrm{B}T}{m}\right) \int_0^{x_0} x^2 \mathrm{e}^{-x^2}\,\mathrm{d}x \\
&= \frac{4}{\sqrt{\pi}} \int_0^{x_0} x^2 \mathrm{e}^{-x^2}\,\mathrm{d}x
\end{aligned}$$

We now evaluate

$$\mathrm{Prob}\{u \leq \sqrt{2k_\mathrm{B}T/m}\} = \frac{4}{\sqrt{\pi}} \int_0^1 x^2 \mathrm{e}^{-x^2}\,\mathrm{d}x$$

using Simpson's rule with four subdivisions, each having height $h = 0.25$, as follows.

$$\begin{aligned}
\mathrm{Prob}\{u \leq \sqrt{2k_\mathrm{B}T/m}\} &\approx \frac{0.25}{3}[g(0) + 4g(0.25) + 2g(0.5) + 4g(0.75) + g(1)] \\
&= \frac{1}{12}(0 + 4 \cdot 0.059 + 2 \cdot 0.195 + 4 \cdot 0.321 + 0.367) \\
&\boxed{\mathrm{Prob}\{u \leq \sqrt{2k_\mathrm{B}T/m}\} \approx 0.190}
\end{aligned}$$

□

27-27. Derive an expression for $\sigma_\varepsilon^2 = \langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2$ from the equation for $F(\varepsilon)\,\mathrm{d}\varepsilon$. Now form the ratio $\sigma_\varepsilon / \langle\varepsilon\rangle$. What does this say about the fluctuation in ε?

Answer. We know from class that

$$\langle\varepsilon\rangle = \frac{3}{2}k_\mathrm{B}T$$

Additionally, we can derive that

$$\begin{aligned}\langle\varepsilon^2\rangle &= \int_0^\infty \varepsilon^2 F(\varepsilon)\,\mathrm{d}\varepsilon \\ &= \frac{2\pi}{(\pi k_\mathrm{B}T)^{3/2}}\int_0^\infty \varepsilon^2\cdot\varepsilon^{1/2}\mathrm{e}^{-\varepsilon/k_\mathrm{B}T}\,\mathrm{d}\varepsilon \\ &= \frac{2\pi}{(\pi k_\mathrm{B}T)^{3/2}}\int_0^\infty \varepsilon^{5/2}\mathrm{e}^{-\varepsilon/k_\mathrm{B}T}\,\mathrm{d}\varepsilon \\ &= \frac{2\pi}{(\pi k_\mathrm{B}T)^{3/2}}\cdot\frac{15}{8}\left[\pi(k_\mathrm{B}T)^7\right]^{1/2} \\ &= \frac{15}{4}(k_\mathrm{B}T)^2\end{aligned}$$

Thus, we have that

$$\begin{aligned}\sigma_\varepsilon^2 &= \langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2 \\ &= \frac{15}{4}(k_\mathrm{B}T)^2 - \frac{9}{4}(k_\mathrm{B}T)^2\end{aligned}$$

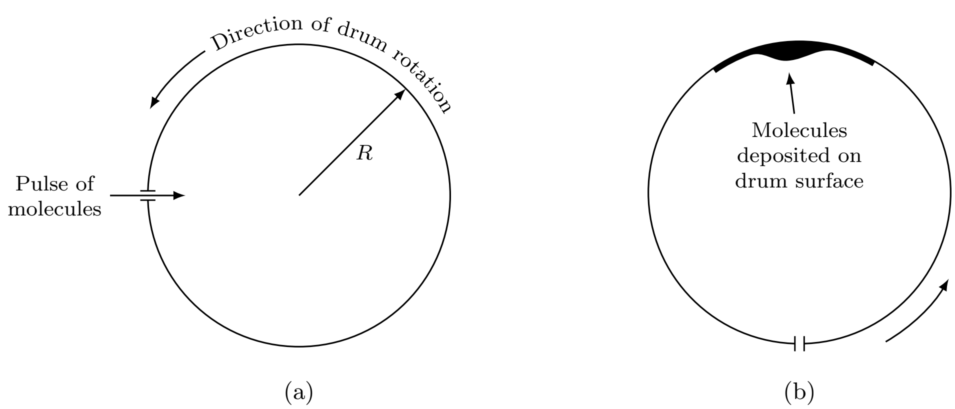
$$\boxed{\sigma_\varepsilon^2 = \frac{2}{3}(k_\mathrm{B}T)^2}$$

Taking

$$\frac{\sigma_\varepsilon}{\langle\varepsilon\rangle} = \frac{\sqrt{2/3}k_\mathrm{B}T}{3k_\mathrm{B}T/2} = \left(\frac{2}{3}\right)^{3/2}$$

reveals that the fluctuation in ε is sizeable with respect to the average energy. □

27-34. The figure below illustrates another method that has been used to determine the distribution of molecular speeds.



A pulse of molecules collimated from a hot oven enters a rotating hollow drum. Let R be the radius of the drum, ν be the rotational frequency, and s be the distance through which the drum rotates during the time it takes for a molecule to travel from the entrance slit to the inner surface of the drum. Show that

$$s = \frac{4\pi R^2\nu}{u}$$

where u is the speed of the molecule.

Use the equation for $\mathrm{d}z_{\text{coll}}$ to show that the distribution of molecular speeds emerging from the over is proportional to $u^3 \mathrm{e}^{-mu^2/2k_\mathrm{B}T}\,\mathrm{d}u$. Now show that the distribution of molecules striking the inner surface of the cylinder is given by

$$I(s)\,\mathrm{d}s = \frac{A}{s^5}\mathrm{e}^{-m(4\pi R^2\nu)^2/2k_\mathrm{B}Ts^2}\,\mathrm{d}s$$

where A is simply a proportionality constant. Plot I versus s for various values of $4\pi R^2\nu/\sqrt{2k_\mathrm{B}T/m}$, say 0.1, 1, and 3. Experimental data are quantitatively described by the above equation.

Answer. Once the molecule enters the drum, it must travel a distance $2R$ before striking the opposite side. It will cover this distance in $2R/u$ seconds. Moreover, we know that the drum rotates once every ν seconds, so the drum will perform $2R\nu/u$ of a rotation in $2R/u$ seconds. Finally, since a point on the inner surface of the drum moves a distance of $2\pi R$ with every rotation, the inner surface of the drum will move a distance

$$s = \frac{4\pi R^2\nu}{u}$$

over the course of the molecule's trip across the interior of the drum. Succinctly,

$$s = \frac{2R \text{ meters}}{1} \times \frac{1 \text{ second}}{u \text{ meters}} \times \frac{\nu \text{ rotations}}{1 \text{ second}} \times \frac{2\pi R \text{ meters}}{1 \text{ rotation}} = \frac{4\pi R^2\nu}{u}$$

The equation for $\mathrm{d}z_{\text{coll}}$ describes the collision frequency of atoms moving in a single direction with a single speed. Since the atoms leave the oven in a single direction, the only variable factor on which $\mathrm{d}z_{\text{coll}}$ depends is $uF(u)\,\mathrm{d}u \propto u^3\mathrm{e}^{-mu^2/2k_\mathrm{B}T}\,\mathrm{d}u$, as desired.

Let $I(u)\,\mathrm{d}u$ be the distribution of molecules that strike the inner surface of the cylinder with speed between u and $u + \mathrm{d}u$. By the above,

$$I(u)\,\mathrm{d}u \propto u^3\mathrm{e}^{-mu^2/2k_\mathrm{B}T}\,\mathrm{d}u$$

Since we have that

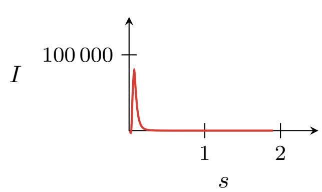
$$u = \frac{4\pi R^2\nu}{s} \qquad\qquad \mathrm{d}u = -\frac{4\pi R^2\nu}{s^2}\,\mathrm{d}s$$

we know that

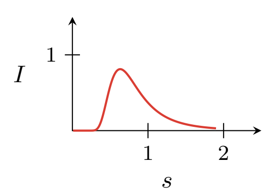
$$I(s)\,\mathrm{d}s \propto \left(\frac{4\pi R^2\nu}{s}\right)^3 \mathrm{e}^{-m(4\pi R^2\nu/s)^2/2k_\mathrm{B}T} \cdot -\frac{4\pi R^2\nu}{s^2}\,\mathrm{d}s = \frac{A}{s^5}\mathrm{e}^{-m(4\pi R^2\nu)^2/2k_\mathrm{B}Ts^2}\,\mathrm{d}s$$

where we have incorporated all external constants into the proportionality constant A.

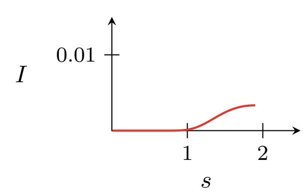
The following are the desired plots □



(a) 0.1



(b) 1



(c) 3

27-36. On the average, what is the time between collisions of a xenon atom at 300 K and...

(a) One torr;

(b) One bar.

27-40. The following table gives the pressure and temperature of the Earth's upper atmosphere as a function of altitude.

Altitude (km)	Pressure (mbar)	Temperature (K)
20.0	56	220
40.0	3.2	260
60.0	0.28	260
80.0	0.013	180

Assuming for simplicity that air consists entirely of nitrogen, calculate the mean free path at each of these conditions.