Exercise 1.1. Many centuries ago, a mariner poured $100 \mathrm{~cm}^{3}$ of water into the ocean. As time passed, the action of currents, tides, and weather mixed the liquid uniformly throughout the earth's oceans, lakes, and rivers. Ignoring salinity, estimate the probability that the next sip (5 $\mathrm{ml})$ of water you drink will contain at least one water molecule that was dumped by the mariner. Assess your chances of ever drinking truly pristine water. (Consider the following facts: $M_{w}$ for water is 18.0 kg per kg-mole, the radius of the earth is 6370 km , the mean depth of the oceans is approximately 3.8 km and they cover $71 \%$ of the surface of the earth.)

Solution 1.1. To get started, first list or determine the volumes involved:

$$
v_{d}=\text { volume of water dumped }=100 \mathrm{~cm}^{3}, v_{c}=\text { volume of a sip }=5 \mathrm{~cm}^{3}, \text { and }
$$

$$
V=\text { volume of water in the oceans }=4 \pi R^{2} D \gamma,
$$

where, $R$ is the radius of the earth, $D$ is the mean depth of the oceans, and $\gamma$ is the oceans' coverage fraction. Here we've ignored the ocean volume occupied by salt and have assumed that the oceans' depth is small compared to the earth's diameter. Putting in the numbers produces:

$$
V=4 \pi\left(6.37 \times 10^{6} \mathrm{~m}\right)^{2}\left(3.8 \times 10^{3} \mathrm{~m}\right)(0.71)=1.376 \times 10^{18} \mathrm{~m}^{3} .
$$

For well-mixed oceans, the probability $P_{o}$ that any water molecule in the ocean came from the dumped water is:

$$
P_{o}=\frac{\left(100 \mathrm{~cm}^{3} \text { of water }\right)}{(\text { oceans' volume })}=\frac{v_{d}}{V}=\frac{1.0 \times 10^{-4} \mathrm{~m}^{3}}{1.376 \times 10^{18} \mathrm{~m}^{3}}=7.27 \times 10^{-23},
$$

Denote the probability that at least one molecule from the dumped water is part of your next sip as $P_{1}$ (this is the answer to the question). Without a lot of combinatorial analysis, $P_{1}$ is not easy to calculate directly. It is easier to proceed by determining the probability $P_{2}$ that all the molecules in your cup are not from the dumped water. With these definitions, $P_{1}$ can be determined from: $P_{1}=1-P_{2}$. Here, we can calculate $P_{2}$ from:
$P_{2}=$ (the probability that a molecule was not in the dumped water) ${ }^{[\text {number of molecules in a sip] }]}$. The number of molecules, $N_{c}$, in one sip of water is (approximately)

$$
N_{c}=5 \mathrm{~cm}^{3} \times \frac{1.00 \mathrm{~g}}{\mathrm{~cm}^{3}} \times \frac{\text { gmole }}{18.0 \mathrm{~g}} \times 6.023 \times 10^{23} \frac{\text { molecules }}{\text { gmole }}=1.673 \times 10^{23} \text { molecules }
$$

Thus, $P_{2}=\left(1-P_{o}\right)^{N_{c}}=\left(1-7.27 \times 10^{-23}\right)^{1.673 \times 10^{23}}$. Unfortunately, electronic calculators and modern computer math programs cannot evaluate this expression, so analytical techniques are required. First, take the natural $\log$ of both sides, i.e.

$$
\ln \left(P_{2}\right)=N_{c} \ln \left(1-P_{o}\right)=1.673 \times 10^{23} \ln \left(1-7.27 \times 10^{-23}\right)
$$

then expand the natural logarithm using $\ln (1-\varepsilon) \approx-\varepsilon$ (the first term of a standard Taylor series for $\varepsilon \rightarrow 0$ )

$$
\ln \left(P_{2}\right) \cong-N_{c} \cdot P_{o}=-1.673 \times 10^{23} \cdot 7.27 \times 10^{-23}=-12.16,
$$

and exponentiate to find:

$$
P_{2} \cong e^{-12.16} \cong 5 \times 10^{-6} \ldots(!)
$$

Therefore, $P_{1}=1-P_{2}$ is very close to unity, so there is a virtual certainty that the next sip of water you drink will have at least one molecule in it from the $100 \mathrm{~cm}^{3}$ of water dumped many years ago. So, if one considers the rate at which they themselves and everyone else on the planet uses water it is essentially impossible to enjoy a truly fresh sip.

Exercise 1.2. An adult human expels approximately 500 ml of air with each breath during ordinary breathing. Imagining that two people exchanged greetings (one breath each) many centuries ago, and that their breath subsequently has been mixed uniformly throughout the atmosphere, estimate the probability that the next breath you take will contain at least one air molecule from that age-old verbal exchange. Assess your chances of ever getting a truly fresh breath of air. For this problem, assume that air is composed of identical molecules having $M_{w}=$ 29.0 kg per kg -mole and that the average atmospheric pressure on the surface of the earth is 100 kPa . Use 6370 km for the radius of the earth and $1.20 \mathrm{~kg} / \mathrm{m}^{3}$ for the density of air at room temperature and pressure.

Solution 1.2. To get started, first determine the masses involved.
$m=$ mass of air in one breath $=$ density $\mathbf{x}$ volume $=\left(1.20 \mathrm{~kg} / \mathrm{m}^{3}\right)\left(0.5 \times 10^{-3} \mathrm{~m}^{3}\right)=0.60 \times 10^{-3} \mathrm{~kg}$
$M=$ mass of air in the atmosphere $=4 \pi R^{2} \int_{z=0}^{\infty} \rho(z) d z$
Here, $R$ is the radius of the earth, $z$ is the elevation above the surface of the earth, and $\rho(z)$ is the air density as function of elevation. From the law for static pressure in a gravitational field, $d P / d z=-\rho g$, the surface pressure, $P_{s}$, on the earth is determined from $P_{s}-P_{\infty}=\int_{z=0}^{z=+\infty} \rho(z) g d z$ so
that:

$$
M=4 \pi R^{2} \frac{P_{s}-P_{\infty}}{g}=4 \pi\left(6.37 \times 10^{6} \mathrm{~m}\right)^{2} \frac{\left(10^{5} \mathrm{~Pa}\right)}{9.81 \mathrm{~ms}^{-2}}=5.2 \times 10^{18} \mathrm{~kg}
$$

where the pressure (vacuum) in outer space $=P_{\infty}=0$, and $g$ is assumed constant throughout the atmosphere. For a well-mixed atmosphere, the probability $P_{o}$ that any molecule in the atmosphere came from the age-old verbal exchange is

$$
P_{o}=\frac{2 \times(\text { mass of one breath })}{(\text { mass of the whole atmosphere })}=\frac{2 \mathrm{~m}}{M}=\frac{1.2 \times 10^{-3} \mathrm{~kg}}{5.2 \times 10^{18} \mathrm{~kg}}=2.31 \times 10^{-22},
$$

where the factor of two comes from one breath for each person. Denote the probability that at least one molecule from the age-old verbal exchange is part of your next breath as $P_{1}$ (this is the answer to the question). Without a lot of combinatorial analysis, $P_{1}$ is not easy to calculate directly. It is easier to proceed by determining the probability $P_{2}$ that all the molecules in your next breath are not from the age-old verbal exchange. With these definitions, $P_{1}$ can be determined from: $P_{1}=1-P_{2}$. Here, we can calculate $P_{2}$ from:
$P_{2}=$ (the probability that a molecule was not in the verbal exchange) ${ }^{[\text {number of molecules in one breath] }}$. The number of molecules, $N_{b}$, involved in one breath is

$$
N_{b}=\frac{0.6 \times 10^{-3} \mathrm{~kg}}{29.0 \mathrm{~g} / \text { gmole }} \times \frac{10^{3} \mathrm{~g}}{\mathrm{~kg}} \times 6.023 \times 10^{23} \frac{\text { molecules }}{\text { gmole }}=1.25 \times 10^{22} \text { molecules }
$$

Thus, $P_{2}=\left(1-P_{o}\right)^{N_{b}}=\left(1-2.31 \times 10^{-22}\right)^{1.25 \times 10^{22}}$. Unfortunately, electronic calculators and modern computer math programs cannot evaluate this expression, so analytical techniques are required. First, take the natural $\log$ of both sides, i.e.

$$
\ln \left(P_{2}\right)=N_{b} \ln \left(1-P_{o}\right)=1.25 \times 10^{22} \ln \left(1-2.31 \times 10^{-22}\right)
$$

then expand the natural logarithm using $\ln (1-\varepsilon) \approx-\varepsilon$ (the first term of a standard Taylor series for $\varepsilon \rightarrow 0$ )

$$
\ln \left(P_{2}\right) \cong-N_{b} \cdot P_{o}=-1.25 \times 10^{22} \cdot 2.31 \times 10^{-22}=-2.89,
$$

and exponentiate to find:

$$
P_{2} \cong e^{-2.89}=0.056 .
$$

Therefore, $P_{1}=1-P_{2}=0.944$ so there is a better than $94 \%$ chance that the next breath you take will have at least one molecule in it from the age-old verbal exchange. So, if one considers how often they themselves and everyone else breathes, it is essentially impossible to get a breath of truly fresh air.

Exercise 1.3. The Maxwell probability distribution, $f(\mathbf{v})=f\left(v_{1}, v_{2}, v_{3}\right)$, of molecular velocities in a gas flow at a point in space with average velocity $\mathbf{u}$ is given by (1.1).
a) Verify that $\mathbf{u}$ is the average molecular velocity, and determine the standard deviations ( $\sigma_{1}$, $\sigma_{2}, \sigma_{3}$ ) of each component of $\mathbf{u}$ using $\sigma_{i}=\left[\frac{1}{n} \iiint_{\text {allv}}\left(v_{i}-u_{i}\right)^{2} f(\mathbf{v}) d^{3} v\right]^{1 / 2}$ for $i=1,2$, and 3 .
b) Using (1.27) or (1.28), determine $n=N / V$ at room temperature $T=295 \mathrm{~K}$ and atmospheric pressure $p=101.3 \mathrm{kPa}$.
c) Determine $N=n V=$ number of molecules in volumes $V=(10 \mu \mathrm{~m})^{3}, 1 \mu \mathrm{~m}^{3}$, and $(0.1 \mu \mathrm{~m})^{3}$.
d) For the $i^{\text {th }}$ velocity component, the standard deviation of the average, $\sigma_{a, i}$, over $N$ molecules is $\sigma_{a, i}=\sigma_{i} / \sqrt{N}$ when $N \gg 1$. For an airflow at $\mathbf{u}=\left(1.0 \mathrm{~ms}^{-1}, 0,0\right)$, compute the relative uncertainty, $2 \sigma_{a, 1} / u_{1}$, at the $95 \%$ confidence level for the average velocity for the three volumes listed in part c).
e) For the conditions specified in parts b) and d), what is the smallest volume of gas that ensures a relative uncertainty in $U$ of one percent or less?

Solution 1.3. a) Use the given distribution, and the definition of an average:

$$
(\mathbf{v})_{\text {ave }}=\frac{1}{n} \iiint_{a l \mathbf{u}} \mathbf{v} f(\mathbf{v}) d^{3} v=\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathbf{v} \exp \left\{-\frac{m}{2 k_{B} T}|\mathbf{v}-\mathbf{u}|^{2}\right\} d^{3} v .
$$

Consider the first component of $\mathbf{v}$, and separate out the integrations in the " 2 " and " 3 " directions.

$$
\begin{aligned}
\left(v_{1}\right)_{\text {ave }} & =\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_{1} \exp \left\{-\frac{m}{2 k_{B} T}\left[\left(v_{1}-u_{1}\right)^{2}+\left(v_{2}-u_{2}\right)^{2}+\left(v_{3}-u_{3}\right)^{2}\right]\right\} d v_{1} d v_{2} d v_{3} \\
& =\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} v_{1} \exp \left\{-\frac{m\left(v_{1}-u_{1}\right)^{2}}{2 k_{B} T}\right\} d v_{1} \int_{-\infty}^{+\infty} \exp \left\{-\frac{m\left(v_{2}-u_{2}\right)^{2}}{2 k_{B} T}\right\} d v_{2} \int_{-\infty}^{+\infty} \exp \left\{-\frac{m\left(v_{3}-u_{3}\right)^{2}}{2 k_{B} T}\right\} d v_{3}
\end{aligned}
$$

The integrations in the " 2 " and " 3 " directions are equal to: $\left(2 \pi k_{B} T / m\right)^{1 / 2}$, so

$$
\left(v_{1}\right)_{\text {ave }}=\left(\frac{m}{2 \pi k_{B} T}\right)^{1 / 2} \int_{-\infty}^{+\infty} v_{1} \exp \left\{-\frac{m\left(v_{1}-u_{1}\right)^{2}}{2 k_{B} T}\right\} d v_{1}
$$

The change of integration variable to $\beta=\left(v_{1}-u_{1}\right)\left(m / 2 k_{B} T\right)^{1 / 2}$ changes this integral to:

$$
\left(v_{1}\right)_{\text {ave }}=\frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty}\left(\beta\left(\frac{2 k_{B} T}{m}\right)^{1 / 2}+u_{1}\right) \exp \left\{-\beta^{2}\right\} d \beta=0+\frac{1}{\sqrt{\pi}} u_{1} \sqrt{\pi}=u_{1},
$$

where the first term of the integrand is an odd function integrated on an even interval so its contribution is zero. This procedure is readily repeated for the other directions to find $\left(v_{2}\right)_{\text {ave }}=u_{2}$, and $\left(v_{3}\right)_{\text {ave }}=u_{3}$. Thus, $\mathbf{u}=\left(u_{1}, u_{2}, u_{3}\right)$ is the average molecular velocity.

Using the same simplifications and change of integration variables produces:

$$
\begin{aligned}
\sigma_{1}^{2} & =\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty}\left(v_{1}-u_{1}\right)^{2} \exp \left\{-\frac{m}{2 k_{B} T}\left[\left(v_{1}-u_{1}\right)^{2}+\left(v_{2}-u_{2}\right)^{2}+\left(v_{3}-u_{3}\right)^{2}\right]\right\} d v_{1} d v_{2} d v_{3} \\
& =\left(\frac{m}{2 \pi k_{B} T}\right)^{1 / 2} \int_{ \pm \infty}^{+\infty}\left(v_{1}-u_{1}\right)^{2} \exp \left\{-\frac{m\left(v_{1}-u_{1}\right)^{2}}{2 k_{B} T}\right\} d v_{1}=\frac{1}{\sqrt{\pi}}\left(\frac{2 k_{B} T}{m}\right)_{ \pm \infty}^{+\infty} \int_{ \pm}^{2} \exp \left\{-\beta^{2}\right\} d \beta .
\end{aligned}
$$

The final integral over $\beta$ is: $\sqrt{\pi} / 2$, so the standard deviations of molecular speed are

$$
\sigma_{1}=\left(k_{B} T / m\right)^{1 / 2}=\sigma_{2}=\sigma_{3},
$$

where the second two equalities follow from repeating this calculation for the second and third directions.
b) From (1.27), $n / V=p / k_{B} T=(101.3 \mathrm{kPa}) /\left[1.381 \times 10^{-23} \mathrm{~J} / \mathrm{K} \cdot 295 \mathrm{~K}\right]=2.487 \times 10^{25} \mathrm{~m}^{-3}$
c) From $n / V$ from part b): $\quad n=2.487 \times 10^{10}$ for $V=10^{3} \mu m^{3}=10^{-15} \mathrm{~m}^{3}$

$$
\begin{aligned}
& n=2.487 \times 10^{7} \text { for } V=1.0 \mu m^{3}=10^{-18} m^{3} \\
& n=2.487 \times 10^{4} \text { for } V=0.001 \mu^{3}=10^{-21} \mathrm{~m}^{3}
\end{aligned}
$$

d) From (1.29), the gas constant is $R=\left(k_{B} / m\right)$, and $R=287 \mathrm{~m}^{2} / \mathrm{s}^{2} K$ for air. Compute:
$2 \sigma_{a, 1} / u_{1}=2\left(k_{B} T / m n\right)^{1 / 2} /[1 m / s]=2(R T / n)^{1 / 2} / 1 m / s=2(287 \cdot 295 / n)^{1 / 2}=582 / \sqrt{n}$. Thus,
for $\quad V=10^{-15} \mathrm{~m}^{3}: 2 \sigma_{a, 1} / u_{1}=0.00369$,
$V=10^{-18} \mathrm{~m}^{3}: 2 \sigma_{a, 1} / u_{1}=0.117$, and
$V=10^{-21} \mathrm{~m}^{3}: 2 \sigma_{a, 1} / u_{1}=3.69$.
e) To achieve a relative uncertainty of $1 \%$ we need $n \approx(582 / 0.01)^{2}=3.39 \times 10^{9}$, and this corresponds to a volume of $1.36 \times 10^{-16} \mathrm{~m}^{3}$ which is a cube with side dimension $\approx 5 \mu \mathrm{~m}$.

Exercise 1.4. Using the Maxwell molecular speed distribution given by (1.4),
a) determine the most probable molecular speed,
b) show that the average molecular speed is as given in (1.5),
c) determine the root-mean square molecular speed $=v_{r m s}=\left[\frac{1}{n} \int_{0}^{\infty} v^{2} f(v) d v\right]^{1 / 2}$,
d) and compare the results from parts a$), \mathrm{b}$ ) and c ) with $c=$ speed of sound in a perfect gas under the same conditions.

Solution 1.4. a) The most probable speed, $v_{m p}$, occurs where $f(v)$ is maximum. Thus, differentiate (1.4) with respect $v$, set this derivative equal to zero, and solve for $v_{m p}$. Start from:

$$
\begin{gathered}
f(v)=4 \pi n\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} v^{2} \exp \left\{-\frac{m v^{2}}{2 k_{B} T}\right\}, \text { and differentiate } \\
\frac{d f}{d v}=4 \pi n\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2}\left[2 v_{m p} \exp \left\{-\frac{m v_{m p}^{2}}{2 k_{B} T}\right\}-\frac{m v_{m p}^{3}}{k_{B} T} \exp \left\{-\frac{m v_{m p}^{2}}{2 k_{B} T}\right\}\right]=0
\end{gathered}
$$

Divide out common factors to find:

$$
2-\frac{m v_{m p}^{2}}{k_{B} T}=0 \quad \text { or } v_{m p}=\sqrt{\frac{2 k_{B} T}{m}} .
$$

b) From (1.5), the average molecular speed $\bar{v}$ is given by:

$$
\bar{v}=\frac{1}{n} \int_{0}^{\infty} v f(v) d v=4 \pi\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{0}^{\infty} v^{3} \exp \left\{-\frac{m v^{2}}{2 k_{B} T}\right\} d v .
$$

Change the integration variable to $\beta=m v^{2} / 2 k_{B} T$ to simplify the integral:

$$
\bar{v}=4\left(\frac{m}{2 \pi k_{B} T}\right)^{1 / 2} \frac{k_{B} T}{m} \int_{0}^{\infty} \beta \exp \{-\beta\} d \beta=\left(\frac{8 k_{B} T}{\pi m}\right)^{1 / 2}\left(-\beta e^{-\beta}-e^{-\beta}\right)_{0}^{\infty}=\left(\frac{8 k_{B} T}{\pi m}\right)^{1 / 2},
$$

and this matches the result provided in (1.5).
c) The root-mean-square molecular speed $v_{r m s}$ is given by:

$$
v_{r m s}^{2}=\frac{1}{n} \int_{0}^{\infty} v^{2} f(v) d v=4 \pi\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{0}^{\infty} v^{4} \exp \left\{-\frac{m v^{2}}{2 k_{B} T}\right\} d v .
$$

Change the integration variable to $\beta=v\left(m / 2 k_{B} T\right)^{1 / 2}$ to simplify the integral:

$$
v_{r m s}^{2}=\frac{4}{\sqrt{\pi}}\left(\frac{2 k_{B} T}{m}\right)^{1 / 2} \int_{0}^{\infty} \beta^{4} \exp \left\{-\beta^{2}\right\} d \beta=\frac{4}{\sqrt{\pi}}\left(\frac{2 k_{B} T}{m}\right) \frac{3 \sqrt{\pi}}{8}=\frac{3 k_{B} T}{m} .
$$

Thus, $v_{r m s}=\left(3 k_{B} T / m\right)^{1 / 2}$.
d) From (1.28), $R=\left(k_{B} / m\right)$ so $v_{m p}=\sqrt{2 R T}, \bar{v}=\sqrt{(8 / \pi) R T}$, and $v_{r m s}=\sqrt{3 R T}$. All three speeds have the same temperature dependence the speed of sound in a perfect gas: $c=\sqrt{\gamma R T}$, but are factors of $\sqrt{2 / \gamma}, \sqrt{8 / \pi \gamma}$ and $\sqrt{3 / \gamma}$, respectively, larger than $c$.

Exercise 1.5. By considering the volume swept out by a moving molecule, estimate how the mean-free path, $l$, depends on the average molecular cross section dimension $\bar{d}$ and the molecular number density $n$ for nominally spherical molecules. Find a formula for $l n^{1 / 3}$ (the ratio of the mean-free path to the mean intermolecular spacing) in terms of the nominal molecular volume $\left(\bar{d}^{3}\right)$ and the available volume per molecule ( $1 / n$ ). Is this ratio typically bigger or smaller than one?

Solution 1.5. The combined collision cross section for two spherical molecules having diameter $\bar{d}$ is $\pi \bar{d}^{2}$. The mean free path $l$ is the average distance traveled by a molecule between collisions. Thus, the average molecule should experience one collision when sweeping a volume equal to $\pi \bar{d}^{2} l$. If the molecular number density is $n$, then the volume per molecule is $n^{-1}$, and the mean intermolecular spacing is $n^{-1 / 3}$. Assuming that the swept volume necessary to produce one collision is proportional to the volume per molecule produces:


$$
\pi \bar{d}^{2} l=C / n \quad \text { or } l=C /\left(n \pi \bar{d}^{2}\right),
$$

where $C$ is a dimensionless constant presumed to be of order unity. The dimensionless version of this equation is:

$$
\begin{aligned}
\frac{\text { mean free path }}{\text { mean intermolecular spacing }} & =\frac{l}{n^{-1 / 3}}=\ln ^{1 / 3} \\
& =\frac{C}{n^{2 / 3} \pi \bar{d}^{2}}=\frac{C}{\left(n \bar{d}^{3}\right)^{2 / 3}}=C\left(\frac{n^{-1}}{\bar{d}^{3}}\right)^{2 / 3}=C\left(\frac{\text { volume per molecule }}{\text { molecular volume }}\right)^{2 / 3},
\end{aligned}
$$

where all numerical constants like $\pi$ have been combined into $C$. Under ordinary conditions in gases, the molecules are not tightly packed so $l \gg n^{-1 / 3}$. In liquids, the molecules are tightly packed so $l \sim n^{-1 / 3}$.

Exercise 1.6. Compute the average relative speed, $\bar{v}_{r}$, between molecules in a gas using the Maxwell speed distribution $f$ given by (1.4) via the following steps.
a) If $\mathbf{u}$ and $\mathbf{v}$ are the velocities of two molecules then their relative velocity is: $\mathbf{v}_{\mathbf{r}}=\mathbf{u}-\mathbf{v}$. If the angle between $\mathbf{u}$ and $\mathbf{v}$ is $\theta$, show that the relative speed is: $v_{r}=\left|\mathbf{v}_{\mathrm{r}}\right|=\sqrt{u^{2}+v^{2}-2 u v \cos \theta}$ where $u=|\mathbf{u}|$, and $v=|\mathbf{v}|$.
b) The averaging of $v_{r}$ necessary to determine $\bar{v}_{r}$ must include all possible values of the two speeds ( $u$ and $v$ ) and all possible angles $\theta$. Therefore, start from:

$$
\bar{v}_{r}=\frac{1}{2 n^{2}} \int_{\text {all }} \int_{v, v} v_{r} f(u) f(v) \sin \theta d \theta d v d u,
$$

and note that $\bar{v}_{r}$ is unchanged by exchange of $u$ and $v$, to reach:

$$
\bar{v}_{r}=\frac{1}{n^{2}} \int_{u=0}^{\infty} \int_{v=u}^{\infty} \int_{\theta=0}^{\pi} \sqrt{u^{2}+v^{2}-2 u v \cos \theta} \sin \theta f(u) f(v) d \theta d v d u
$$

c) Note that $v_{r}$ must always be positive and perform the integrations, starting with the angular one, to find:

$$
\bar{v}_{r}=\frac{1}{3 n^{2}} \int_{u=0}^{\infty} \int_{v=u}^{\infty} \frac{2 u^{3}+6 u v^{2}}{u v} f(u) f(v) d v d u=\left(\frac{16 k_{B} T}{\pi}\right)^{1 / 2}=\sqrt{2} \bar{v} .
$$

Solution 1.6. a) Compute the dot produce of $\mathbf{v}_{\mathrm{r}}$ with itself:

$$
\left|\mathbf{v}_{\mathrm{r}}\right|^{2}=\mathbf{v}_{\mathrm{r}} \cdot \mathbf{v}_{\mathrm{r}}=(\mathbf{u}-\mathbf{v}) \cdot(\mathbf{u}-\mathbf{v})=\mathbf{u} \cdot \mathbf{u}-2 \mathbf{u} \cdot \mathbf{v}+\mathbf{v} \cdot \mathbf{v}=u^{2}-2 u v \cos \theta+v^{2} .
$$

Take the square root to find: $\left|\mathbf{v}_{\mathrm{r}}\right|=\sqrt{u^{2}+v^{2}-2 u v \cos \theta}$.
b) The average relative speed must account for all possible molecular speeds and all possible angles between the two molecules. [The coefficient $1 / 2$ appears in the first equality below because the probability density function of for the angle $\theta$ in the interval $0 \leq \theta \leq \pi$ is $(1 / 2) \sin \theta$.]

$$
\begin{aligned}
\bar{v}_{r} & =\frac{1}{2 n^{2}} \int_{\text {all }} v_{u, v, \theta} f(u) f(v) \sin \theta d \theta d v d u \\
& =\frac{1}{2 n^{2}} \int_{\text {all } u, v, \theta} \sqrt{u^{2}+v^{2}-2 u v \cos \theta} f(u) f(v) \sin \theta d \theta d v d u \\
& =\frac{1}{2 n^{2}} \int_{u=0}^{\infty} \int_{v=0}^{\infty} \int_{\theta=0}^{\pi} \sqrt{u^{2}+v^{2}-2 u v \cos \theta} \sin \theta f(u) f(v) d \theta d v d u .
\end{aligned}
$$

In $u-v$ coordinates, the integration domain covers the first quadrant, and the integrand is unchanged when $u$ and $v$ are swapped. Thus, the $u-v$ integration can be completed above the line $u=v$ if the final result is doubled. Thus,

$$
\bar{v}_{r}=\frac{1}{n^{2}} \int_{u=0}^{\infty} \int_{v=u}^{\infty} \int_{\theta=0}^{\pi} \sqrt{u^{2}+v^{2}-2 u v \cos \theta} \sin \theta f(u) f(v) d \theta d v d u .
$$

Now tackle the angular integration, by setting $\beta=u^{2}+v^{2}-2 u v \cos \theta$ so that $d \beta=+2 u v \sin \theta d \theta$. This leads to

$$
\bar{v}_{r}=\frac{1}{n^{2}} \int_{u=0}^{\infty} \int_{v=u}^{\infty} \int_{\beta=(v-u)^{2}}^{(v+u)^{2}} \beta^{1 / 2} \frac{d \beta}{2 u v} f(u) f(v) d v d u,
$$


and the $\beta$-integration can be performed:

$$
\bar{v}_{r}=\frac{1}{2 n^{2}} \int_{u=0}^{\infty} \int_{v=u}^{\infty} \frac{2}{3}\left(\beta^{3 / 2}\right)_{(v-u)^{(v+u)^{2}}}^{\left(\frac{2}{2}(u)\right.} \frac{f(v)}{v} d v d u=\frac{1}{3 n^{2}} \int_{u=0}^{\infty} \int_{v=u}^{\infty}\left((v+u)^{3}-(v-u)^{3}\right) \frac{f(u)}{u} \frac{f(v)}{v} d v d u .
$$

Expand the cubic terms, simplify the integrand, and prepare to evaluate the $v$-integration:

$$
\begin{aligned}
\bar{v}_{r} & =\frac{1}{3 n^{2}} \int_{u=0}^{\infty} \int_{v=u}^{\infty}\left(2 u^{3}+6 u v^{2}\right) \frac{f(v)}{v} d v \frac{f(u)}{u} d u \\
& =\frac{1}{3 n} \int_{u=0}^{\infty} \int_{v=u}^{\infty}\left(2 u^{3}+6 u v^{2}\right) \frac{4 \pi}{v}\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} v^{2} \exp \left\{-\frac{m v^{2}}{2 k_{B} T}\right\} d v \frac{f(u)}{u} d u .
\end{aligned}
$$

Use the variable substitution: $\alpha=m v^{2} / 2 k_{B} T$ so that $d \alpha=m v d v / k_{B} T$, which reduces the $v$ integration to:

$$
\begin{aligned}
\bar{v}_{r} & =\frac{1}{3 n} \int_{u=0}^{\infty} \int_{m u^{2} / k_{B} T}^{\infty}\left(2 u^{3}+6 u \frac{k_{B} T}{m} \alpha\right) 4 \pi\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \exp \{-\alpha\} \frac{k_{B} T}{m} d \alpha \frac{f(u)}{u} d u \\
& =\frac{2}{3 n}\left(\frac{m}{2 \pi k_{B} T}\right)^{1 / 2} \int_{u=0}^{\infty} \int_{m u^{2} / k_{B} T}^{\infty}\left(2 u^{3}+6 u \frac{k_{B} T}{m} \alpha\right) e^{-\alpha} d \alpha \frac{f(u)}{u} d u \\
& =\frac{2}{3 n}\left(\frac{m}{2 \pi k_{B} T}\right)^{1 / 2} \int_{u=0}^{\infty}\left(-2 u^{3} e^{-\alpha}+6 u \frac{k_{B} T}{m}\left(-\alpha e^{-\alpha}-e^{-\alpha}\right)\right)_{m u^{2} / k_{B} T}^{\infty} \frac{f(u)}{u} d u \\
& =\frac{2}{3 n}\left(\frac{m}{2 \pi k_{B} T}\right)^{1 / 2} \int_{u=0}^{\infty}\left(8 u^{3}+12 u \frac{k_{B} T}{m}\right) \exp \left(-\frac{m u^{2}}{2 k_{B} T}\right) \frac{f(u)}{u} d u .
\end{aligned}
$$

The final $u$-integration may be completed by substituting in for $f(u)$ and using the variable substitution $\gamma=u\left(m / k_{B} T\right)^{1 / 2}$.

$$
\begin{aligned}
\bar{v}_{r} & =\frac{1}{3}\left(\frac{2 m}{\pi k_{B} T}\right)^{1 / 2} \int_{0}^{\infty}\left(8\left(\frac{k_{B} T}{m}\right)^{3 / 2} \gamma^{3}+12\left(\frac{k_{B} T}{m}\right)^{3 / 2} \gamma\right) 4 \pi\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2}\left(\frac{k_{B} T}{m}\right) \gamma \exp \left(-\gamma^{2}\right) d \gamma \\
& =\frac{2}{3 \pi}\left(\frac{k_{B} T}{m}\right)^{1 / 2} \int_{0}^{\infty}\left(8 \gamma^{4}+12 \gamma^{2}\right) \exp \left(-\gamma^{2}\right) d \gamma=\frac{2}{3 \pi}\left(\frac{k_{B} T}{m}\right)^{1 / 2}\left(8 \frac{3}{8} \sqrt{\pi}+12 \frac{1}{4} \sqrt{\pi}\right) \\
& =\frac{4}{\sqrt{\pi}}\left(\frac{k_{B} T}{m}\right)^{1 / 2}=\left(\frac{16 k_{B} T}{\pi m}\right)^{1 / 2}=\sqrt{2} \bar{v}
\end{aligned}
$$

Here, $\bar{v}$ is the mean molecular speed from (1.5).

Exercise 1.7. In a gas, the molecular momentum flux $\left(M F_{i j}\right)$ in the $j$-coordinate direction that crosses a flat surface of unit area with coordinate normal direction $i$ is:
$M F_{i j}=\frac{1}{V} \iiint_{a l l} m v_{i} v_{j} f(\mathbf{v}) d^{3} v$ where $f(\mathbf{v})$ is the Maxwell velocity distribution (1.1). For a perfect gas that is not moving on average (i.e., $\mathbf{u}=0$ ), show that $M F_{i j}=p$ (the pressure), when $i=j$, and that $M F_{i j}=0$, when $i \neq j$.

Solution 1.7. Start from the given equation using the Maxwell distribution:

$$
M F_{i j}=\frac{1}{V} \iiint_{\text {all } \mathbf{u}} m v_{i} v_{j} f(\mathbf{v}) d^{3} v=\frac{n m}{V}\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_{i} v_{j} \exp \left\{-\frac{m}{2 k_{B} T}\left(v_{1}^{2}+v_{2}^{2}+v_{3}^{2}\right)\right\} d v_{1} d v_{2} d v_{3}
$$

and first consider $i=j=1$, and recognize $\rho=n m / V$ as the gas density, as in (1.28).

$$
\begin{aligned}
M F_{11} & =\rho\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_{1}^{2} \exp \left\{-\frac{m}{2 k_{B} T}\left(v_{1}^{2}+v_{2}^{2}+v_{3}^{2}\right)\right\} d v_{1} d v_{2} d v_{3} \\
& =\rho\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} v_{1}^{2} \exp \left\{-\frac{m v_{1}^{2}}{2 k_{B} T}\right\} d v_{1} \int_{-\infty}^{+\infty} \exp \left\{-\frac{m v_{2}^{2}}{2 k_{B} T}\right\} d v_{2} \int_{-\infty}^{+\infty} \exp \left\{-\frac{m v_{3}^{2}}{2 k_{B} T}\right\} d v_{3}
\end{aligned}
$$

The first integral is equal to $\left(2 k_{B} T / m\right)^{3 / 2}(\sqrt{\pi} / 2)$ while the second two integrals are each equal to $\left(2 \pi k_{B} T / m\right)^{1 / 2}$. Thus:

$$
M F_{11}=\rho\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2}\left(\frac{2 k_{B} T}{m}\right)^{3 / 2} \frac{\sqrt{\pi}}{2}\left(\frac{2 \pi k_{B} T}{m}\right)^{1 / 2}\left(\frac{2 \pi k_{B} T}{m}\right)^{1 / 2}=\rho \frac{k_{B} T}{m}=\rho R T=p
$$

where $k_{B} / m=R$ from (1.28). This analysis may be repeated with $i=j=2$, and $i=j=3$ to find: $M F_{22}=M F_{33}=p$, as well.

Now consider the case $i \neq j$. First note that $M F_{i j}=M F_{j i}$ because the velocity product under the triple integral may be written in either order $v_{i} v_{j}=v_{j} v_{i}$, so there are only three cases of interest. Start with $i=1$, and $j=2$ to find:

$$
\begin{aligned}
M F_{12} & =\rho\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} v_{1} v_{2} \exp \left\{-\frac{m}{2 k_{B} T}\left(v_{1}^{2}+v_{2}^{2}+v_{3}^{2}\right)\right\} d v_{1} d v_{2} d v_{3} \\
& =\rho\left(\frac{m}{2 \pi k_{B} T}\right)^{3 / 2} \int_{-\infty}^{+\infty} v_{1} \exp \left\{-\frac{m v_{1}^{2}}{2 k_{B} T}\right\} d v_{1} \int_{-\infty}^{+\infty} v_{2} \exp \left\{-\frac{m v_{2}^{2}}{2 k_{B} T}\right\} d v_{2} \int_{-\infty}^{+\infty} \exp \left\{-\frac{m v_{3}^{2}}{2 k_{B} T}\right\} d v_{3}
\end{aligned}
$$

Here we need only consider the first integral. The integrand of this integral is an odd function because it is product of an odd function, $v_{1}$, and an even function, $\exp \left\{-m v_{1}^{2} / 2 k_{B} T\right\}$. The integral of an odd function on an even interval $[-\infty,+\infty]$ is zero, so $M F_{12}=0$. And, this analysis may be repeated for $i=1$ and $j=3$, and $i=2$ and $j=3$ to find $M F_{13}=M F_{23}=0$.

Exercise 1.8. Consider the viscous flow in a channel of width $2 b$. The channel is aligned in the $x$-direction, and the velocity $u$ in the $x$-direction at a distance $y$ from the channel centerline is given by the parabolic distribution $u(y)=U_{0}\left[1-(y / b)^{2}\right]$. Calculate the shear stress $\tau$ as a function $y, \mu, b$, and $U_{0}$. What is the shear stress at $y=0$ ?

Solution 1.8. Start from (1.3): $\tau=\mu \frac{d u}{d y}=\mu \frac{d}{d y} U_{o}\left[1-\left(\frac{y}{b}\right)^{2}\right]=-2 \mu U_{o} \frac{y}{b^{2}}$. At $y=0$ (the location of maximum velocity) $\tau=0$. At At $y= \pm b$ (the locations of zero velocity), $\tau=\mp 2 \mu U_{o} / b$.

Exercise 1.9. Hydroplaning occurs on wet roadways when sudden braking causes a moving vehicle's tires to stop turning when the tires are separated from the road surface by a thin film of water. When hydroplaning occurs the vehicle may slide a significant distance before the film breaks down and the tires again contact the road. For simplicity, consider a hypothetical version of this scenario where the water film is somehow maintained until the vehicle comes to rest.
a) Develop a formula for the friction force delivered to a vehicle of mass $M$ and tire-contact area $A$ that is moving at speed $u$ on a water film with constant thickness $h$ and viscosity $\mu$.
b) Using Newton's second law, derive a formula for the hypothetical sliding distance $D$ traveled by a vehicle that started hydroplaning at speed $U_{o}$
c) Evaluate this hypothetical distance for $M=1200 \mathrm{~kg}, A=0.1 \mathrm{~m}^{2}, U_{o}=20 \mathrm{~m} / \mathrm{s}, h=0.1 \mathrm{~mm}$, and $\mu=0.001 \mathrm{kgm}^{-1} \mathrm{~s}^{-1}$. Compare this to the dry-pavement stopping distance assuming a tire-road coefficient of kinetic friction of 0.8 .

Solution 1.9. a) Assume that viscous friction from the water layer transmitted to the tires is the only force on the sliding vehicle. Here viscous shear stress at any time will be $\mu u(t) / h$, where $u(t)$ is the vehicle's speed. Thus, the friction force will be $A \mu u(t) / h$.
b) The friction force will oppose the motion so Newton's second law implies: $M \frac{d u}{d t}=-A \mu \frac{u}{h}$.

This equation is readily integrated to find an exponential solution: $u(t)=U_{o} \exp (-A \mu t / M h)$, where the initial condition, $u(0)=U_{o}$, has been used to evaluate the constant of integration. The distance traveled at time $t$ can be found from integrating the velocity:

$$
x(t)=\int_{o}^{t} u\left(t^{\prime}\right) d t^{\prime}=U_{o} \int_{o}^{t} \exp \left(-A \mu t^{\prime} / M h\right) d t^{\prime}=\left(U_{o} M h / A \mu\right)[1-\exp (-A \mu t / M h)] .
$$

The total sliding distance occurs for large times where the exponential term will be negligible so:

$$
D=U_{o} M h / A \mu
$$

c) For $M=1200 \mathrm{~kg}, A=0.1 \mathrm{~m}^{2}, U_{o}=20 \mathrm{~m} / \mathrm{s}, h=0.1 \mathrm{~mm}$, and $\mu=0.001 \mathrm{kgm}^{-1} \mathrm{~s}^{-1}$, the stopping distance is: $D=(20)(1200)\left(10^{-4}\right) /(0.1)(0.001)=24 \mathrm{~km}$ ! This is an impressively long distance and highlights the dangers of driving quickly on water covered roads.

For comparison, the friction force on dry pavement will be $-0.8 M g$, which leads to a vehicle velocity of: $u(t)=U_{o}-0.8 g t$, and a distance traveled of $x(t)=U_{o} t-0.4 g t^{2}$. The vehicle stops when $u=0$, and this occurs at $t=U_{o} /(0.8 g)$, so the stopping distance is

$$
D=U_{o}\left(\frac{U_{o}}{0.8 g}\right)-0.4 g\left(\frac{U_{o}}{0.8 g}\right)^{2}=\frac{U_{o}^{2}}{1.6 g},
$$

which is equal to 25.5 m for the conditions given. (This is nearly three orders of magnitude less than the estimated stopping distance for hydroplaning.)

Exercise 1.10. Estimate the height to which water at $20^{\circ} \mathrm{C}$ will rise in a capillary glass tube 3 mm in diameter that is exposed to the atmosphere. For water in contact with glass the contact angle is nearly $0^{\circ}$. At $20^{\circ} \mathrm{C}$, the surface tension of a water-air interface is $\sigma=0.073 \mathrm{~N} / \mathrm{m}$.

Solution 1.10. Start from the result of Example 1.4.

$$
h=\frac{2 \sigma \cos \alpha}{\rho g R}=\frac{2(0.073 \mathrm{~N} / \mathrm{m}) \cos \left(0^{\circ}\right)}{\left(10^{3} \mathrm{~kg} / \mathrm{m}^{3}\right)\left(9.81 \mathrm{~m} / \mathrm{s}^{2}\right)\left(1.5 \times 10^{-3} \mathrm{~m}\right)}=9.92 \mathrm{~mm}
$$

Exercise 1.11. A manometer is a U-shaped tube containing mercury of density $\rho_{\mathrm{m}}$. Manometers are used as pressure-measuring devices. If the fluid in tank A has a pressure $p$ and density $\rho$, then show that the gauge pressure in the tank is: $p-p_{\text {atm }}=\rho_{\mathrm{m}} g h-\rho g a$. Note that the last term on the right side is negligible if $\rho<\rho_{\mathrm{m}}$. (Hint: Equate the pressures at $X$ and $Y$.)


Solution 1.9. Start by equating the pressures at $X$ and $Y$.

$$
p_{X}=p+\rho g a=p_{a t m}+\rho_{m} g h=p_{Y} .
$$

Rearrange to find:

$$
p-p_{a t m}=\rho_{m} g h-\rho g a .
$$

Exercise 1.12. Prove that if $e(T, v)=e(T)$ only and if $h(T, p)=h(T)$ only, then the (thermal) equation of state is (1.28) or $p v=k T$, where $k$ is constant.

Solution 1.12. Start with the first equation of (1.24): $d e=T d s-p d v$, and rearrange it:

$$
d s=\frac{1}{T} d e+\frac{p}{T} d v=\left(\frac{\partial s}{\partial e}\right)_{v} d e+\left(\frac{\partial s}{\partial v}\right)_{e} d v
$$

where the second equality holds assuming the entropy depends on $e$ and $v$. Here we see that:

$$
\frac{1}{T}=\left(\frac{\partial s}{\partial e}\right)_{v}, \text { and } \frac{p}{T}=\left(\frac{\partial s}{\partial v}\right)_{e} .
$$

Equality of the crossed second derivatives of $s,\left(\frac{\partial}{\partial v}\left(\frac{\partial s}{\partial e}\right)_{v}\right)_{e}=\left(\frac{\partial}{\partial e}\left(\frac{\partial s}{\partial v}\right)_{e}\right)_{v}$, implies:

$$
\left(\frac{\partial(1 / T)}{\partial v}\right)_{e}=\left(\frac{\partial(p / T)}{\partial e}\right)_{v}
$$

However, if $e$ depends only on $T$, then $(\partial / \partial v)_{e}=(\partial / \partial v)_{T}$, thus $\left(\frac{\partial(1 / T)}{\partial v}\right)_{e}=\left(\frac{\partial(1 / T)}{\partial v}\right)_{T}=0$, so $\left(\frac{\partial(p / T)}{\partial e}\right)_{v}=0$, which can be integrated to find: $p / T=f_{1}(v)$, where $f_{1}$ is an undetermined function.

Now repeat this procedure using the second equation of (1.24), $d h=T d s+v d p$.

$$
d s=\frac{1}{T} d h-\frac{v}{T} d p=\left(\frac{\partial s}{\partial h}\right)_{p} d h+\left(\frac{\partial s}{\partial p}\right)_{h} d p
$$

Here equality of the coefficients of the differentials implies: $\frac{1}{T}=\left(\frac{\partial s}{\partial h}\right)_{p}$, and $-\frac{v}{T}=\left(\frac{\partial s}{\partial p}\right)_{h}$.
So, equality of the crossed second derivatives implies: $\left(\frac{\partial(1 / T)}{\partial p}\right)_{h}=-\left(\frac{\partial(v / T)}{\partial h}\right)_{p}$. Yet, if $h$ depends only on $T$, then $(\partial / \partial p)_{h}=(\partial / \partial p)_{T}$, thus $\left(\frac{\partial(1 / T)}{\partial p}\right)_{h}=\left(\frac{\partial(1 / T)}{\partial p}\right)_{T}=0$, so $-\left(\frac{\partial(v / T)}{\partial h}\right)_{p}=0$, which can be integrated to find: $v / T=f_{2}(p)$, where $f_{2}$ is an undetermined function.

Collecting the two results involving $f_{1}$ and $f_{2}$, and solving for $T$ produces:

$$
\frac{p}{f_{1}(v)}=T=\frac{v}{f_{2}(p)} \quad \text { or } \quad p f_{2}(p)=v f_{1}(v)=k,
$$

where $k$ must be is a constant since $p$ and $v$ are independent thermodynamic variables. Eliminating $f_{1}$ or $f_{2}$ from either equation on the left, produces $p v=k T$.

And finally, using both versions of (1.24) we can write: $d h-d e=v d p+p d v=d(p v)$. When $e$ and $h$ only depend on $T$, then $d h=c_{\mathrm{p}} d T$ and $d e=c_{\mathrm{v}} d T$, so

$$
d h-d e=\left(c_{\mathrm{p}}-c_{\mathrm{v}}\right) d T=d(p v)=k d T, \text { thus } k=c_{\mathrm{p}}-c_{\mathrm{v}}=R,
$$

where $R$ is the gas constant. Thus, the final result is the perfect gas law: $p=k T / v=\rho R T$.

Exercise 1.13. Starting from the property relationships (1.24) prove (1.31) and (1.32) for a reversible adiabatic process involving a perfect gas when the specific heats $c_{\mathrm{p}}$ and $c_{\mathrm{v}}$ are constant.

Solution 1.13. For an isentropic process: $d e=T d s-p d v=-p d v$, and $d h=T d s+v d p=+v d p$. Equations (1.31) and (1.32) apply to a perfect gas so the definition of the specific heat capacities (1.20), and (1.21) for a perfect gas, $d h=c_{\mathrm{p}} d T$, and $d e=c_{\mathrm{v}} d T$, can be used to form the ratio $d h / d e$ :

$$
\frac{d h}{d e}=\frac{c_{\mathrm{p}} d T}{c_{\mathrm{v}} d T}=\frac{c_{\mathrm{p}}}{c_{\mathrm{v}}}=\gamma=-\frac{v d p}{p d v} \quad \text { or }-\gamma \frac{d v}{v}=\gamma \frac{d \rho}{\rho}=\frac{d p}{p} .
$$

The final equality integrates to: $\ln (p)=\gamma \ln (\rho)+$ const which can be exponentiated to find:

$$
p=\text { const } . \rho^{\gamma},
$$

which is (1.31). The constant may be evaluated at a reference condition $p_{o}$ and $\rho_{o}$ to find: $p / p_{o}=\left(\rho / \rho_{o}\right)^{\gamma}$ and this may be inverted to put the density ratio on the left

$$
\rho / \rho_{o}=\left(p / p_{o}\right)^{1 / v},
$$

which is the second equation of (1.32). The remaining relationship involving the temperature is found by using the perfect gas law, $p=\rho R T$, to eliminate $\rho=p / R T$ :

$$
\frac{\rho}{\rho_{o}}=\frac{p / R T}{p_{o} / R T_{o}}=\frac{p T_{o}}{p_{o} T}=\left(\frac{p}{p_{o}}\right)^{1 / \gamma} \text { or } \frac{T}{T_{o}}=\frac{p}{p_{o}}\left(\frac{p}{p_{o}}\right)^{-1 / \gamma}=\left(\frac{p}{p_{o}}\right)^{(\gamma-1) / \gamma},
$$

which is the first equation of (1.32).

Exercise 1.14. A cylinder contains 2 kg of air at $50^{\circ} \mathrm{C}$ and a pressure of 3 bars. The air is compressed until its pressure rises to 8 bars. What is the initial volume? Find the final volume for both isothermal compression and isentropic compression.

Solution 1.14. Use the perfect gas law but explicitly separate the mass $M$ of the air and the volume $V$ it occupies via the substitution $\rho=M / V$ :

$$
p=\rho R T=(M / V) R T .
$$

Solve for $V$ at the initial time:

$$
V_{i}=\text { initial volume }=M R T / p_{i}=(2 \mathrm{~kg})\left(287 \mathrm{~m}^{2} / \mathrm{s}^{2} \mathrm{~K}\right)\left(273+50^{\circ}\right) /(300 \mathrm{kPa})=0.618 \mathrm{~m}^{3} .
$$

For an isothermal process:

$$
V_{f}=\text { final volume }=M R T / p_{f}=(2 \mathrm{~kg})\left(287 \mathrm{~m}^{2} / \mathrm{s}^{2} \mathrm{~K}\right)\left(273+50^{\circ}\right) /(800 \mathrm{kPa})=0.232 \mathrm{~m}^{3} .
$$

For an isentropic process:

$$
V_{f}=V_{i}\left(p_{i} / p_{f}\right)^{1 / \gamma}=0.618 m^{3}(300 \mathrm{kPa} / 800 \mathrm{kPa})^{1 / 1.4}=0.307 \mathrm{~m}^{3} .
$$

Exercise 1.15. Derive (1.35) starting from Figure 1.9 and the discussion at the beginning of Section 1.10.

Solution 1.15. Take the $z$ axis vertical, and consider a small fluid element $\delta m$ of fluid having volume $\delta V$ that starts at height $z_{0}$ in a stratified fluid medium having a vertical density profile $=$ $\rho(z)$, and a vertical pressure profile $p(z)$. Without any vertical displacement, the small mass and its volume are related by $\delta m=\rho\left(z_{0}\right) \delta V$. If the small mass is displaced vertically a small distance $\zeta$ via an isentropic process, its density will change isentropically according to:

$$
\rho_{a}\left(z_{0}+\zeta\right)=\rho\left(z_{0}\right)+\left(d \rho_{a} / d z\right) \zeta+\ldots
$$

where $d \rho_{a} / d z$ is the isentropic density gradient at $z_{0}$. For a constant $\delta m$, the volume of the fluid element will be:

$$
\delta V=\frac{\delta m}{\rho_{a}}=\frac{\delta m}{\rho\left(z_{0}\right)+\left(d \rho_{a} / d z\right) \zeta+\ldots}=\frac{\delta m}{\rho\left(z_{0}\right)}\left(1-\frac{1}{\rho\left(z_{0}\right)} \frac{d \rho_{a}}{d z} \zeta+\ldots\right)
$$

The background density at $z_{0}+\xi$ is:

$$
\rho\left(z_{0}+\xi\right)=\rho\left(z_{0}\right)+(d \rho / d z) \zeta+\ldots
$$

If $g$ is the acceleration of gravity, the (upward) buoyant force on the element at the vertically displaced location will be $g \rho\left(z_{0}+\zeta\right) \delta V$, while the (downward) weight of the fluid element at any vertical location is $g \delta m$. Thus, a vertical application Newton's second law implies:

$$
\delta m \frac{d^{2} \zeta}{d t^{2}}=+g \rho\left(z_{0}+\zeta\right) \delta V-g \delta m=g\left(\rho\left(z_{0}\right)+(d \rho / d z) \zeta+\ldots\right) \frac{\delta m}{\rho\left(z_{0}\right)}\left(1-\frac{1}{\rho\left(z_{0}\right)} \frac{d \rho_{a}}{d z} \zeta+\ldots\right)-g \delta m
$$

where the second equality follows from substituting for $\rho\left(z_{0}+\zeta\right)$ and $\delta V$ from the above equations. Multiplying out the terms in (,)-parentheses and dropping second order terms produces:

$$
\delta m \frac{d^{2} \zeta}{d t^{2}}=g \delta m+\frac{g \delta m}{\rho\left(z_{0}\right)} \frac{d \rho}{d z} \zeta-\frac{g \delta m}{\rho\left(z_{0}\right)} \frac{d \rho_{a}}{d z} \zeta+\ldots-g \delta m \cong \frac{g \delta m}{\rho\left(z_{0}\right)}\left(\frac{d \rho}{d z}-\frac{d \rho_{a}}{d z}\right) \zeta
$$

Dividing by $\delta m$ and moving all the terms to the right side of the equation produces:

$$
\frac{d^{2} \zeta}{d t^{2}}-\frac{g}{\rho\left(z_{0}\right)}\left(\frac{d \rho}{d z}-\frac{d \rho_{a}}{d z}\right) \zeta=0
$$

Thus, for oscillatory motion at frequency $N$, we must have

$$
N^{2}=-\frac{g}{\rho\left(z_{0}\right)}\left(\frac{d \rho}{d z}-\frac{d \rho_{a}}{d z}\right),
$$

which is (1.35).

Exercise 1.16. Starting with the hydrostatic pressure law (1.14), prove (1.36) without using perfect gas relationships.

Solution 1.16. The adiabatic temperature gradient $d T_{a} / d z$, can be written terms of the pressure gradient:

$$
\frac{d T_{a}}{d z}=\left(\frac{\partial T}{\partial p}\right)_{s} \frac{d p}{d z}=-g \rho\left(\frac{\partial T}{\partial p}\right)_{s}
$$

where the hydrostatic law $d p / d z=-\rho g$ has been used to reach the second equality. Here, the final partial derivative can be exchanged for one involving $v=1 / \rho$ and $s$, by considering:

$$
d h=\left(\frac{\partial h}{\partial s}\right)_{p} d s+\left(\frac{\partial h}{\partial p}\right)_{s} d p=T d s+v d p
$$

Equality of the crossed second derivatives of $h,\left(\frac{\partial}{\partial p}\left(\frac{\partial h}{\partial s}\right)_{p}\right)_{s}=\left(\frac{\partial}{\partial s}\left(\frac{\partial h}{\partial p}\right)_{s}\right)_{p}$, implies:

$$
\left(\frac{\partial T}{\partial p}\right)_{s}=\left(\frac{\partial v}{\partial s}\right)_{p}=\left(\frac{\partial v}{\partial T}\right)_{p}\left(\frac{\partial T}{\partial s}\right)_{p}=\left(\frac{\partial v}{\partial T}\right)_{p} /\left(\frac{\partial s}{\partial T}\right)_{p}
$$

where the second two equalities are mathematical manipulations that allow the introduction of

$$
\alpha=-\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{p}=\rho\left(\frac{\partial v}{\partial T}\right)_{p}, \text { and } c_{\mathrm{p}}=\left(\frac{\partial h}{\partial T}\right)_{p}=T\left(\frac{\partial s}{\partial T}\right)_{p} .
$$

Thus,

$$
\frac{d T_{a}}{d z}=-g \rho\left(\frac{\partial T}{\partial p}\right)_{s}=-g \rho\left(\frac{\partial v}{\partial T}\right)_{p} /\left(\frac{\partial s}{\partial T}\right)_{p}=-g \alpha /\left(\frac{c_{\mathrm{p}}}{T}\right)=-\frac{g \alpha T}{c_{\mathrm{p}}} .
$$

Exercise 1.17. Assume that the temperature of the atmosphere varies with height $z$ as $T=T_{0}+$ $K z$ where $K$ is a constant. Show that the pressure varies with height as $p=p_{0}\left(\frac{T_{0}}{T_{0}+K z}\right)^{g / K R}$ where $g$ is the acceleration of gravity and $R$ is the gas constant for the atmospheric gas.

Solution 1.17. Start with the hydrostatic and perfect gas laws, $d p / d z=-\rho g$, and $p=\rho R T$, eliminate the density, and substitute in the given temperature profile to find:

$$
\frac{d p}{d z}=-\rho g=-\frac{p}{R T} g=-\frac{p}{R\left(T_{0}+K z\right)} g \text { or } \frac{d p}{p}=-\frac{g}{R} \frac{d z}{\left(T_{0}+K z\right)} .
$$

The final form may be integrated to find:

$$
\ln p=-\frac{g}{R K} \ln \left(T_{0}+K z\right)+\text { const } .
$$

At $z=0$, the pressure must be $p_{0}$, therefore:

$$
\ln p_{0}=-\frac{g}{R K} \ln \left(T_{0}\right)+\text { const } .
$$

Subtracting this from the equation above and invoking the properties of logarithms produces:

$$
\ln \left(\frac{p}{p_{0}}\right)=-\frac{g}{R K} \ln \left(\frac{T_{0}+K z}{T_{0}}\right)
$$

Exponentiating produces:

$$
\frac{p}{p_{0}}=\left[\frac{T_{0}+K z}{T_{0}}\right]^{-8 / K R} \text {, which is the same as: } p=p_{0}\left[\frac{T_{0}}{T_{0}+K z}\right]^{8 / K R} .
$$

