

Exercise 1.1. Many centuries ago, a mariner poured 100 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 cup 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. [Some possibly useful 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. One cup is $\sim 240 \text{ ml}$.]

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

$$v_d = \text{volume of water dumped} = 100 \text{ cm}^3, v_c = \text{volume of a cup} \approx 240 \text{ cm}^3, \text{ and}$$

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

where, R is the radius of the earth, D is the mean depth of the oceans, and γ 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:

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

For well-mixed oceans, the probability P_o that any water molecule in the ocean came from the dumped water is:

$$P_o = \frac{(100 \text{ cm}^3 \text{ of water})}{(\text{oceans' volume})} = \frac{v_d}{V} = \frac{1.0 \times 10^{-4} \text{ m}^3}{1.376 \times 10^{18} \text{ m}^3} = 7.27 \times 10^{-23},$$

Denote the probability that at least one molecule from the dumped water is part of your next cup 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:

$$P_2 = (\text{the probability that a molecule was not in the dumped water})^{[\text{number of molecules in a cup}]}$$

The number of molecules, N_c , in one cup of water is

$$N_c = 240 \text{ cm}^3 \times \frac{1.00 \text{ g}}{\text{cm}^3} \times \frac{\text{gmole}}{18.0 \text{ g}} \times 6.023 \times 10^{23} \frac{\text{molecules}}{\text{gmole}} = 8.03 \times 10^{24} \text{ molecules}$$

Thus, $P_2 = (1 - P_o)^{N_c} = (1 - 7.27 \times 10^{-23})^{8.03 \times 10^{24}}$. 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.

$$\ln(P_2) = N_c \ln(1 - P_o) = 8.03 \times 10^{24} \ln(1 - 7.27 \times 10^{-23})$$

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

$$\ln(P_2) \cong -N_c \cdot P_o = -8.03 \times 10^{24} \cdot 7.27 \times 10^{-23} = -584,$$

and exponentiate to find:

$$P_2 \cong e^{-584} \cong 10^{-254} \dots (!)$$

Therefore, $P_1 = 1 - P_2$ is very-very close to unity, so there is a virtual certainty that the next cup of water you drink will have at least one molecule in it from the 100 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 get a truly fresh cup to drink.

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 $M_w = 29.0 \text{ kg per kg-mole}$ 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 kg/m^3 for the density of air at room temperature and pressure.

Solution 1.2. To get started, first determine the masses involved.

$$m = \text{mass of air in one breath} = \text{density} \times \text{volume} = (1.20 \text{ kg/m}^3)(0.5 \times 10^{-3} \text{ m}^3) = 0.60 \times 10^{-3} \text{ kg}$$

$$M = \text{mass of air in the atmosphere} = 4\pi R^2 \int_{z=0}^{\infty} \rho(z) dz$$

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,

$$dP/dz = -\rho g, \text{ the surface pressure, } P_s, \text{ on the earth is determined from } P_s - P_\infty = \int_{z=0}^{z=\infty} \rho(z) g dz \text{ so}$$

$$\text{that: } M = 4\pi R^2 \frac{P_s - P_\infty}{g} = 4\pi (6.37 \times 10^6 \text{ m})^2 (10^5 \text{ Pa}) = 5.2 \times 10^{18} \text{ kg}.$$

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

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

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:

$P_2 = (\text{the probability that a molecule was not in the verbal exchange})^{\text{[number of molecules in a breath]}}$.
The number of molecules, N_b , involved in one breath is

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

Thus, $P_2 = (1 - P_o)^{N_b} = (1 - 2.31 \times 10^{-22})^{1.25 \times 10^{22}}$. 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.

$$\ln(P_2) = N_b \ln(1 - P_o) = 1.25 \times 10^{22} \ln(1 - 2.31 \times 10^{-22})$$

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

$$\ln(P_2) \cong -N_b \cdot P_o = -1.25 \times 10^{22} \cdot 2.31 \times 10^{-22} = -2.89,$$

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. In Cartesian coordinates, the Maxwell probability distribution, $f(\mathbf{u}) = f(u_1, u_2, u_3)$, of molecular velocities in a gas flow with average velocity $\mathbf{U} = (U_1, U_2, U_3)$ is

$$f(\mathbf{u}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left\{ -\frac{m}{2k_B T} |\mathbf{u} - \mathbf{U}|^2 \right\}$$

where n is the number of gas molecules in volume V , m is the molecular mass, k_B is Boltzmann's constant and T is the absolute temperature.

a) Verify that \mathbf{U} is the average molecular velocity, and determine the standard deviations (σ_1 , σ_2 , σ_3) of each component of \mathbf{U} using $\sigma_i = \left[\iiint_{all \mathbf{u}} (u_i - U_i)^2 f(\mathbf{u}) d^3 u \right]^{1/2}$ for $i = 1, 2$, and 3.

b) Using the molecular version of perfect gas law (1.21), determine n/V at room temperature $T = 295$ K and atmospheric pressure $p = 101.3$ kPa.

c) Determine n for volumes $V = (10 \mu m)^3$, $1 \mu m^3$, and $(0.1 \mu m)^3$.

d) For the i^{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 $\mathbf{U} = (1.0 \text{ ms}^{-1}, 0, 0)$, 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 less than one percent?

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

$$\mathbf{u}_{ave} = \iiint_{all \mathbf{u}} \mathbf{u} f(\mathbf{u}) d^3 u = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathbf{u} \exp \left\{ -\frac{m}{2k_B T} |\mathbf{u} - \mathbf{U}|^2 \right\} d^3 u.$$

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

$$\begin{aligned} (u_1)_{ave} &= \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_1 \exp \left\{ -\frac{m}{2k_B T} [(u_1 - U_1)^2 + (u_2 - U_2)^2 + (u_3 - U_3)^2] \right\} du_1 du_2 du_3 \\ &= \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} u_1 \exp \left\{ -\frac{m(u_1 - U_1)^2}{2k_B T} \right\} du_1 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{m(u_2 - U_2)^2}{2k_B T} \right\} du_2 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{m(u_3 - U_3)^2}{2k_B T} \right\} du_3 \end{aligned}$$

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

$$(u_1)_{ave} = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{+\infty} u_1 \exp \left\{ -\frac{m(u_1 - U_1)^2}{2k_B T} \right\} du_1$$

The change of integration variable to $\beta = (u_1 - U_1)(m/2k_B T)^{1/2}$ changes this integral to:

$$(u_1)_{ave} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \left(\beta \left(\frac{2k_B T}{m} \right)^{1/2} + U_1 \right) \exp \{-\beta^2\} d\beta = 0 + \frac{1}{\sqrt{\pi}} U_1 \sqrt{\pi} = U_1,$$

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 $(u_2)_{ave} = U_2$, and $(u_3)_{ave} = U_3$. Using the same simplifications and change of integration variables produces:

$$\sigma_1^2 = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (u_1 - U_1)^2 \exp \left\{ -\frac{m}{2k_B T} [(u_1 - U_1)^2 + (u_2 - U_2)^2 + (u_3 - U_3)^2] \right\} du_1 du_2 du_3$$

$$= \left(\frac{m}{2\pi k_B T} \right)^{1/2} \int_{-\infty}^{+\infty} (u_1 - U_1)^2 \exp \left\{ -\frac{m(u_1 - U_1)^2}{2k_B T} \right\} du_1 = \frac{1}{\sqrt{\pi}} \left(\frac{2k_B T}{m} \right) \int_{-\infty}^{+\infty} \beta^2 \exp \{-\beta^2\} d\beta.$$

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

$$\sigma_1 = (k_B T/m)^{1/2} = \sigma_2 = \sigma_3,$$

where the second two equalities follow from repeating this calculation for the second and third directions.

b) From (1.21), $n/V = p/k_B T = (101.2 \text{ kPa}) / [1.381 \times 10^{-23} \text{ J/K} \cdot 295 \text{ K}] = 2.487 \times 10^{25} \text{ m}^{-3}$

c) From n/V from part b):
 $n = 2.487 \times 10^{10}$ for $V = 10^3 \mu\text{m}^3 = 10^{-15} \text{ m}^3$
 $n = 2.487 \times 10^7$ for $V = 1.0 \mu\text{m}^3 = 10^{-18} \text{ m}^3$
 $n = 2.487 \times 10^4$ for $V = 0.001 \mu\text{m}^3 = 10^{-21} \text{ m}^3$

d) From (1.22), the gas constant is $R = (k_B/m)$, and $R = 287 \text{ m}^2/\text{s}^2\text{K}$ for air. Compute:

$2\sigma_{a,1}/U_1 = 2(k_B T/mn)^{1/2} / [1 \text{ m/s}] = 2(RT/n)^{1/2} / 1 \text{ m/s} = 2(287 \cdot 295/n)^{1/2} = 582/\sqrt{n}$. Thus,

for $V = 10^{-15} \text{ m}^3$: $2\sigma_{a,1}/U_1 = 0.00369$,

$V = 10^{-18} \text{ m}^3$: $2\sigma_{a,1}/U_1 = 0.117$, and

$V = 10^{-21} \text{ m}^3$: $2\sigma_{a,1}/U_1 = 3.69$.

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 $1.36 \times 10^{-16} \text{ m}^3$ which is a cube with side dimension $\approx 5 \mu\text{m}$.

Exercise 1.4. Using the Maxwell molecular velocity distribution given in Exercise 1.3 with $\mathbf{U} = 0$, determine the average molecular speed $= \bar{v} = \left[\iiint_{all \mathbf{u}} |\mathbf{u}|^2 f(\mathbf{u}) d^3 u \right]^{1/2}$ and compare it with $c =$ speed of sound in a perfect gas under the same conditions.

Solution 1.4. Use the specified form for \bar{v} and the Maxwell distribution

$$\bar{v}^2 = \iiint_{all \mathbf{u}} |\mathbf{u}|^2 f(\mathbf{u}) d^3 u = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (u_1^2 + u_2^2 + u_3^2) \exp \left\{ -\frac{m}{2k_B T} (u_1^2 + u_2^2 + u_3^2) \right\} du_1 du_2 du_3.$$

This can be re-arranged and expanded into a total of nine one-variable integrations:

$$\begin{aligned} \bar{v}^2 &= \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} u_1^2 \exp \left\{ -\frac{m u_1^2}{2k_B T} \right\} du_1 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{m u_2^2}{2k_B T} \right\} du_2 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{m u_3^2}{2k_B T} \right\} du_3 \\ &+ \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \exp \left\{ -\frac{m u_1^2}{2k_B T} \right\} du_1 \int_{-\infty}^{+\infty} u_2^2 \exp \left\{ -\frac{m u_2^2}{2k_B T} \right\} du_2 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{m u_3^2}{2k_B T} \right\} du_3 \\ &+ \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \exp \left\{ -\frac{m u_1^2}{2k_B T} \right\} du_1 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{m u_2^2}{2k_B T} \right\} du_2 \int_{-\infty}^{+\infty} u_3^2 \exp \left\{ -\frac{m u_3^2}{2k_B T} \right\} du_3. \end{aligned}$$

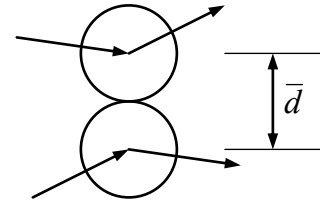
In this arrangement, the six off-diagonal integrals are equal to $(2\pi k_B T/m)^{1/2}$ and the three on-diagonal integrals are equal to $(2k_B T/m)^{3/2} (\sqrt{\pi}/2)$. Thus,

$$\bar{v}^2 = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \left(\frac{2\pi k_B T}{m} \right) \left[\left(\frac{2k_B T}{m} \right)^{3/2} + \left(\frac{2k_B T}{m} \right)^{3/2} + \left(\frac{2k_B T}{m} \right)^{3/2} \right] \frac{\sqrt{\pi}}{2}, \text{ or } \bar{v}^2 = \frac{3k_B T}{m}.$$

From (1.22), $R = (k_B/m)$ so $\bar{v} = \sqrt{3RT}$ and this speed has the same temperature dependence but is a factor of $\sqrt{3/\gamma}$ larger than the speed of sound in a perfect gas: $c = \sqrt{\gamma RT}$.

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 \tilde{n} for nominally spherical molecules. Find a formula for $l\tilde{n}^{1/3}$ (= the ratio of the mean-free path to the mean intermolecular spacing) in terms of the *molecular volume* (\bar{d}^3) and the available *volume per molecule* ($1/\tilde{n}$). 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 $\pi\bar{d}^2l$. If the molecular number density is \tilde{n} , then the volume per molecule is \tilde{n}^{-1} , and the mean intermolecular spacing is $\tilde{n}^{-1/3}$. Assuming that the swept volume necessary to produce one collision is proportional to the volume per molecule produces:



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

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

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

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

Exercise 1.6. In a gas, the molecular momentum flux (MF_{ij}) in the j -coordinate direction that crosses a flat surface of unit area with coordinate normal direction i is:

$MF_{ij} = \frac{n}{V} \iiint_{all \mathbf{u}} mu_i u_j f(\mathbf{u}) d^3 u$ where $f(\mathbf{u})$ is the Maxwell distribution given in Exercise 1.3. For a perfect gas that is not moving on average (i.e. $\mathbf{U} = 0$), show that $MF_{ij} = p$, the pressure, when $i = j$, and that $MF_{ij} = 0$, when $i \neq j$.

Solution 1.6. Start from the given equation using the Maxwell distribution:

$$MF_{ij} = \frac{n}{V} \iiint_{all \mathbf{u}} mu_i u_j f(\mathbf{u}) d^3 u = \frac{nm}{V} \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_i u_j \exp \left\{ -\frac{m}{2k_B T} (u_1^2 + u_2^2 + u_3^2) \right\} du_1 du_2 du_3$$

and first consider $i = j = 1$, and recognize $\rho = nm/V$ as the gas density (see (1.22)).

$$\begin{aligned} MF_{11} &= \rho \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_1^2 \exp \left\{ -\frac{m}{2k_B T} (u_1^2 + u_2^2 + u_3^2) \right\} du_1 du_2 du_3 \\ &= \rho \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} u_1^2 \exp \left\{ -\frac{mu_1^2}{2k_B T} \right\} du_1 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{mu_2^2}{2k_B T} \right\} du_2 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{mu_3^2}{2k_B T} \right\} du_3 \end{aligned}$$

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

$$MF_{11} = \rho \left(\frac{m}{2\pi k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right)^{3/2} \frac{\sqrt{\pi}}{2} \left(\frac{2\pi k_B T}{m} \right)^{1/2} \left(\frac{2\pi k_B T}{m} \right)^{1/2} = \rho \frac{k_B T}{m} = \rho RT = p$$

where $k_B/m = R$ from (1.22). This analysis may be repeated with $i = j = 2$, and $i = j = 3$ to find: $MF_{22} = MF_{33} = p$, as well.

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

$$\begin{aligned} MF_{12} &= \rho \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} u_1 u_2 \exp \left\{ -\frac{m}{2k_B T} (u_1^2 + u_2^2 + u_3^2) \right\} du_1 du_2 du_3 \\ &= \rho \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_{-\infty}^{+\infty} u_1 \exp \left\{ -\frac{mu_1^2}{2k_B T} \right\} du_1 \int_{-\infty}^{+\infty} u_2 \exp \left\{ -\frac{mu_2^2}{2k_B T} \right\} du_2 \int_{-\infty}^{+\infty} \exp \left\{ -\frac{mu_3^2}{2k_B T} \right\} du_3 \end{aligned}$$

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, u_1 , and an even function, $\exp \left\{ -mu_1^2/2k_B T \right\}$. The integral of an odd function on an even interval $[-\infty, +\infty]$ is zero, so $MF_{12} = 0$. And, this analysis may be repeated for $i = 1$ and $j = 3$, and $i = 2$ and $j = 3$ to find $MF_{13} = MF_{23} = 0$.

Exercise 1.7. Consider the viscous flow in a channel of width $2b$. 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 τ as a function of y , μ , b , and U_0 . What is the shear stress at $y = 0$?

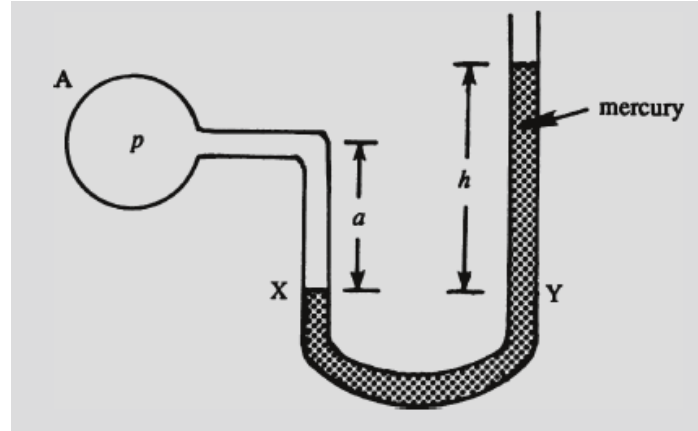
Solution 1.7. Start from (1.3): $\tau = \mu \frac{du}{dy} = \mu \frac{d}{dy} U_0 \left[1 - \left(\frac{y}{b} \right)^2 \right] = -2\mu U_0 \frac{y}{b^2}$. At $y = 0$ (the location of maximum velocity) $\tau = 0$. At $y = \pm b$ (the locations of zero velocity), $\tau = \mp 2\mu U_0 / b$.

Exercise 1.8. Estimate the height to which water at 20 °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 wetting angle is nearly 90°. At 20 °C, the surface tension of an water-air interface is $\sigma = 0.073$ N/m. (*Answer: $h = 0.99$ cm.*)

Solution 1.8. Start from the result of Example 1.1.

$$h = \frac{2\sigma \sin \alpha}{\rho g R} = \frac{2(0.073 \text{ N/m}) \sin(90^\circ)}{(10^3 \text{ kg/m}^3)(9.81 \text{ m/s}^2)(1.5 \times 10^{-3} \text{ m})} = 9.92 \text{ mm}$$

Exercise 1.9. A *manometer* is a U-shaped tube containing mercury of density ρ_m . Manometers are used as pressure measuring devices. If the fluid in the tank A has a pressure p and density ρ , then show that the gauge pressure in the tank is: $p - p_{atm} = \rho_m g h - \rho g a$. Note that the last term on the right side is negligible if $\rho \ll \rho_m$. (*Hint*: Equate the pressures at X and Y.)



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

$$p_X = p + \rho g a = p_{atm} + \rho_m g h = p_Y.$$

Rearrange to find:

$$p - p_{atm} = \rho_m g h - \rho g a.$$

Exercise 1.10. Prove that if $e(T, \nu) = e(T)$ only and if $h(T, p) = h(T)$ only, then the (thermal) equation of state is (1.22) or $p\nu = kT$.

Solution 1.10. Start with the first member of (1.18): $de = Tds - pd\nu$, and rearrange it:

$$ds = \frac{1}{T} de + \frac{p}{T} d\nu = \left(\frac{\partial s}{\partial e} \right)_{\nu} de + \left(\frac{\partial s}{\partial \nu} \right)_{e} d\nu,$$

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

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

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

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

However, if e depends only on T , then $(\partial/\partial \nu)_e = (\partial/\partial \nu)_T$, thus $\left(\frac{\partial(1/T)}{\partial \nu} \right)_{e} = \left(\frac{\partial(1/T)}{\partial \nu} \right)_{T} = 0$, so $\left(\frac{\partial(p/T)}{\partial e} \right)_{\nu} = 0$, and this can be integrated once to find: $p/T = f_1(\nu)$, where f_1 is an undetermined function.

Now repeat this procedure using the second member of (1.18), $dh = Tds + \nu dp$.

$$ds = \frac{1}{T} dh - \frac{\nu}{T} dp = \left(\frac{\partial s}{\partial h} \right)_{p} dh + \left(\frac{\partial s}{\partial p} \right)_{h} dp.$$

Here equality of the coefficients of the differentials implies: $\frac{1}{T} = \left(\frac{\partial s}{\partial h} \right)_{p}$, and $-\frac{\nu}{T} = \left(\frac{\partial s}{\partial p} \right)_{h}$.

So, equality of the crossed second derivatives implies: $\left(\frac{\partial(1/T)}{\partial p} \right)_{h} = - \left(\frac{\partial(\nu/T)}{\partial h} \right)_{p}$.

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 $- \left(\frac{\partial(\nu/T)}{\partial h} \right)_{p} = 0$, and this can be integrated once to find: $\nu/T = f_2(p)$, where f_2 is an undetermined function.

Collecting the two results involving f_1 and f_2 , and solving for T produces:

$$\frac{p}{f_1(\nu)} = T = \frac{\nu}{f_2(p)} \quad \text{or} \quad pf_2(p) = \nu f_1(\nu) = k,$$

where k must be a constant since p and ν are independent thermodynamic variables. Eliminating f_1 or f_2 from either equation of the left, produces $p\nu = kT$.

And finally, using both versions of (1.18) we can write: $dh - de = \nu dp + pd\nu = d(p\nu)$. When e and h only depend on T , then $dh = C_p dT$ and $de = C_v dT$, so

$$dh - de = (C_p - C_v) dT = d(p\nu) = kdT, \text{ thus } k = C_p - C_v = R,$$

where R is the gas constant. Thus, the final result is the perfect gas law: $p = kT/\nu = \rho RT$.

Exercise 1.11. Starting from the property relationships (1.18) prove (1.25) and (1.26) for a reversible adiabatic process when the specific heats C_p and C_v are constant.

Solution 1.11. For an isentropic process: $de = Tds - pdv = -pdv$, and $dh = Tds + vdp = +vdp$. Equations (1.25) and (1.26) apply to a perfect gas so the definition of the specific heat capacities (1.14), and (1.15) for a perfect gas, $dh = C_p dT$, and $de = C_v dT$, can be used to form the ratio dh/de :

$$\frac{dh}{de} = \frac{C_p dT}{C_v dT} = \frac{C_p}{C_v} = \gamma = -\frac{v dp}{p dv} \quad \text{or} \quad -\gamma \frac{dv}{v} = \gamma \frac{d\rho}{\rho} = \frac{dp}{p}.$$

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

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

which is (1.25). The constant may be evaluated at a reference condition p_o and ρ_o to find:

$p/p_o = (\rho/\rho_o)^\gamma$ and this may be inverted to put the density ratio on the left

$$\rho/\rho_o = (p/p_o)^{1/\gamma},$$

which is the second member of (1.26). The remaining relationship involving the temperature is found by using the perfect gas law, $p = \rho RT$, to eliminate $\rho = p/RT$:

$$\frac{\rho}{\rho_o} = \frac{p/RT}{p_o/RT_o} = \frac{p T_o}{p_o T} = \left(\frac{p}{p_o}\right)^{1/\gamma} \quad \text{or} \quad \frac{T}{T_o} = \frac{p}{p_o} \left(\frac{p}{p_o}\right)^{-1/\gamma} = \left(\frac{p}{p_o}\right)^{(\gamma-1)/\gamma},$$

which is the first member of (1.26).

Exercise 1.12. A cylinder contains 2 kg of air at 50 °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 1.12. Use the perfect gas law but explicitly separate the mass M of the air and the volume V it occupies via the substitution $\rho = M/V$:

$$p = \rho RT = (M/V)RT.$$

Solve for V at the initial time:

$$V_i = \text{initial volume} = MRT/p_i = (2 \text{ kg})(287 \text{ m}^2/\text{s}^2\text{K})(273 + 50^\circ)/(300 \text{ kPa}) = 0.618 \text{ m}^3.$$

For an isothermal process:

$$V_f = \text{final volume} = MRT/p_f = (2 \text{ kg})(287 \text{ m}^2/\text{s}^2\text{K})(273 + 50^\circ)/(800 \text{ kPa}) = 0.232 \text{ m}^3.$$

For an isentropic process:

$$V_f = V_i (p_i/p_f)^{1/\gamma} = 0.618 \text{ m}^3 (300 \text{ kPa}/800 \text{ kPa})^{1/1.4} = 0.307 \text{ m}^3.$$

Exercise 1.13. Derive (1.29) starting from the arguments provided at the beginning of Section 1.10 and Figure 1.8.

Solution 1.13. Take the z axis vertical, and consider a small fluid element δm of fluid having volume δV 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 $\delta m = \rho(z_0)\delta V$. If the small mass is displaced vertically a small distance ζ via an isentropic process, its density will change isentropically according to:

$$\rho_a(z_0 + \zeta) = \rho(z_0) + (d\rho_a/dz)\zeta + \dots$$

where $d\rho_a/dz$ is the isentropic density at z_0 . For a constant δm , the volume of the fluid element will be:

$$\delta V = \frac{\delta m}{\rho_a} = \frac{\delta m}{\rho(z_0) + (d\rho_a/dz)\zeta + \dots} = \frac{\delta m}{\rho(z_0)} \left(1 - \frac{1}{\rho(z_0)} \frac{d\rho_a}{dz} \zeta + \dots \right)$$

The background density at $z_0 + \zeta$ is:

$$\rho(z_0 + \zeta) = \rho(z_0) + (d\rho/dz)\zeta + \dots$$

If g is the acceleration of gravity, the (upward) buoyant force on the element at the vertically displaced location will be $g\rho(z_0 + \zeta)\delta V$, 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:

$$\delta m \frac{d^2\zeta}{dt^2} = +g\rho(z_0 + \zeta)\delta V - g\delta m = g(\rho(z_0) + (d\rho/dz)\zeta + \dots) \frac{\delta m}{\rho(z_0)} \left(1 - \frac{1}{\rho(z_0)} \frac{d\rho_a}{dz} \zeta + \dots \right) - g\delta m,$$

where the second equality follows from substituting for $\rho(z_0 + \zeta)$ and δV from the above equations. Multiplying out the terms in (,)-parentheses and dropping second order terms produces:

$$\delta m \frac{d^2\zeta}{dt^2} = g\delta m + \frac{g\delta m}{\rho(z_0)} \frac{d\rho}{dz} \zeta - \frac{g\delta m}{\rho(z_0)} \frac{d\rho_a}{dz} \zeta + \dots - g\delta m \cong \frac{g\delta m}{\rho(z_0)} \left(\frac{d\rho}{dz} - \frac{d\rho_a}{dz} \right) \zeta$$

Dividing by δm and moving all the terms to the right side of the equation produces:

$$\frac{d^2\zeta}{dt^2} - \frac{g}{\rho(z_0)} \left(\frac{d\rho}{dz} - \frac{d\rho_a}{dz} \right) \zeta = 0$$

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

$$N^2 = -\frac{g}{\rho(z_0)} \left(\frac{d\rho}{dz} - \frac{d\rho_a}{dz} \right),$$

which is (1.29).

Exercise 1.14. Starting with the hydrostatic pressure law (1.8), prove (1.30) without using perfect gas relationships.

Solution 1.14. The adiabatic temperature gradient dT_a/dz , can be written terms of the pressure gradient:

$$\frac{dT_a}{dz} = \left(\frac{\partial T}{\partial p} \right)_s \frac{dp}{dz} = -g\rho \left(\frac{\partial T}{\partial p} \right)_s$$

where the hydrostatic law $dp/dz = -\rho g$ 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:

$$dh = \left(\frac{\partial h}{\partial s} \right)_p ds + \left(\frac{\partial h}{\partial p} \right)_s dp = Tds + vdp.$$

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

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p = \rho \left(\frac{\partial v}{\partial T} \right)_p, \text{ and } C_p = \left(\frac{\partial h}{\partial T} \right)_p = T \left(\frac{\partial s}{\partial T} \right)_p.$$

Thus,

$$\frac{dT_a}{dz} = -g\rho \left(\frac{\partial T}{\partial p} \right)_s = -g\rho \left(\frac{\partial v}{\partial T} \right)_p / \left(\frac{\partial s}{\partial T} \right)_p = -g\alpha / \left(\frac{C_p}{T} \right) = -\frac{g\alpha T}{C_p}.$$

Exercise 1.15. Assume that the temperature of the atmosphere varies with height z as $T = T_0 + Kz$ where K is a constant. Show that the pressure varies with height as $p = p_0 \left[\frac{T_0}{T_0 + Kz} \right]^{g/KR}$, where g is the acceleration of gravity and R is the gas constant for the atmospheric gas.

Solution 1.15. Start with the hydrostatic and perfect gas laws, $dp/dz = -\rho g$, and $p = \rho RT$, eliminate the density, and substitute in the given temperature profile to find:

$$\frac{dp}{dz} = -\rho g = -\frac{p}{RT} g = -\frac{p}{R(T_0 + Kz)} g \quad \text{or} \quad \frac{dp}{p} = -\frac{g}{R} \frac{dz}{(T_0 + Kz)}.$$

The final form may be integrated to find:

$$\ln p = -\frac{g}{RK} \ln(T_0 + Kz) + \text{const.}$$

At $z = 0$, the pressure must be p_0 , therefore:

$$\ln p_0 = -\frac{g}{RK} \ln(T_0) + \text{const.}$$

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

$$\ln\left(\frac{p}{p_0}\right) = -\frac{g}{RK} \ln\left(\frac{T_0 + Kz}{T_0}\right)$$

Exponentiating produces:

$$\frac{p}{p_0} = \left[\frac{T_0 + Kz}{T_0} \right]^{-g/KR}, \quad \text{which is the same as: } p = p_0 \left[\frac{T_0}{T_0 + Kz} \right]^{g/KR}.$$

Exercise 1.16. Suppose the atmospheric temperature varies according to: $T = 15 - 0.001z$, where T is in degrees Celsius and height z is in meters. Is this atmosphere stable?

Solution 1.16. Compute the temperature gradient:

$$\frac{dT}{dz} = \frac{d}{dz}(15 - 0.001z) = -0.001 \frac{^{\circ}\text{C}}{\text{m}} = -1.0 \frac{^{\circ}\text{C}}{\text{km}}.$$

For air in the earth's gravitational field, the adiabatic temperature gradient is:

$$\frac{dT_a}{dz} = -\frac{g\alpha T}{C_p} = \frac{(9.81\text{m/s}^2)(1/T)T}{1004\text{m}^2/\text{s}^2\text{^{\circ}\text{C}}} = -9.8 \frac{^{\circ}\text{C}}{\text{km}}.$$

Thus, the given temperature profile is *stable* because the magnitude of its gradient is less than the magnitude of the adiabatic temperature gradient.

Exercise 1.17. Consider the case of a pure gas planet where the hydrostatic law is: $dp/dz = -\rho(z)Gm(z)/z^2$. Here G is the gravitational constant, and $m(z) = 4\pi \int_0^z \rho(\zeta)\zeta^2 d\zeta$ is the planetary mass up to distance z from the center of the planet. If the planetary gas is perfect with gas constant R , determine $\rho(z)$ and $p(z)$ if this atmosphere is isothermal at temperature T . Are these vertical profiles of ρ and p valid as z increases without bound?

Solution 1.17. Start with the given relationship for $m(z)$, differentiate it with respect to z , and use the perfect gas law, $p = \rho RT$ to replace the ρ with p .

$$\frac{dm}{dz} = \frac{d}{dz} \left(4\pi \int_0^z \rho(\zeta)\zeta^2 d\zeta \right) = 4\pi z^2 \rho(z) = 4\pi z^2 \frac{p(z)}{RT}.$$

Now use this and the hydrostatic law to obtain a differential equation for $m(z)$,

$$\frac{dp}{dz} = -\rho(z) \frac{Gm(z)}{z^2} \rightarrow \frac{d}{dz} \left(\frac{RT}{4\pi z^2} \frac{dm}{dz} \right) = - \left(\frac{1}{4\pi z^2} \frac{dm}{dz} \right) \frac{Gm(z)}{z^2}.$$

After recognizing T as a constant, the nonlinear second-order differential equation for $m(z)$ simplifies to:

$$\frac{RT}{G} \frac{d}{dz} \left(\frac{1}{z^2} \frac{dm}{dz} \right) = - \frac{1}{z^4} m \frac{dm}{dz}.$$

This equation can be solved by assuming a power law: $m(z) = Az^n$. When substituted in, this trial solution produces:

$$\frac{RT}{G} \frac{d}{dz} (z^{-2} Anz^{n-1}) = \frac{RT}{G} (n-3) Anz^{n-4} = -z^{-4} A^2 n z^{2n-1}.$$

Matching exponents of z across the last equality produces: $n-4 = 2n-5$, and this requires $n = 1$. For this value of n , the remainder of the equation is:

$$\frac{RT}{G} (-2) Az^{-3} = -z^{-4} A^2 z^1, \text{ which reduces to: } A = 2 \frac{RT}{G}.$$

Thus, we have $m(z) = 2RTz/G$, and this leads to:

$$\rho(z) = \frac{2RT}{G} \frac{1}{4\pi z^2}, \text{ and } p(z) = \frac{2R^2 T^2}{G} \frac{1}{4\pi z^2}.$$

Unfortunately, these profiles are *not* valid as z increases without bound, because this leads to an unbounded planetary mass.

Exercise 1.18. Consider a heat-insulated enclosure that is separated into two compartments of volumes V_1 and V_2 , containing perfect gases with pressures and temperatures of p_1, p_2 , and T_1, T_2 , respectively. The compartments are separated by an impermeable membrane that conducts heat (but not mass). Calculate the final steady-state temperature assuming each gas has constant specific heats.

Solution 1.18. Since no work is done and no heat is transferred out of the enclosure, the final energy E_f is the sum of the energies, E_1 and E_2 , in the two compartments.

$$E_1 + E_2 = E_f \text{ implies } \rho_1 V_1 C_{v1} T_1 + \rho_2 V_2 C_{v2} T_2 = (\rho_1 V_1 C_{v1} + \rho_2 V_2 C_{v2}) T_f,$$

where the C_v 's are the specific heats at constant volume for the two gases. The perfect gas law can be used to find the densities: $\rho_1 = p_1/R_1 T_1$ and $\rho_2 = p_2/R_2 T_2$, so

$$p_1 V_1 C_{v1}/R_1 + p_2 V_2 C_{v2}/R_2 = (p_1 V_1 C_{v1}/R_1 T_1 + p_2 V_2 C_{v2}/R_2 T_2) T_f.$$

A little more simplification is possible, $C_{v1}/R_1 = 1/(\gamma_1 - 1)$ and $C_{v2}/R_2 = 1/(\gamma_2 - 1)$. Thus, the final temperature is:

$$T_f = \frac{p_1 V_1 / (\gamma_1 - 1) + p_2 V_2 / (\gamma_2 - 1)}{p_1 V_1 / [(\gamma_1 - 1) T_1] + p_2 V_2 / [(\gamma_2 - 1) T_2]}.$$