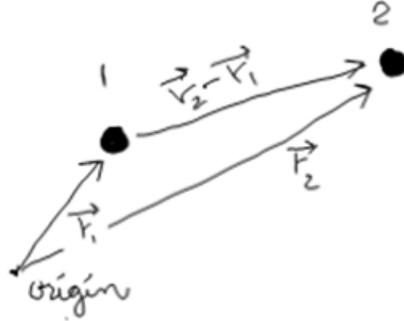


1 Introduction

While studying Newton's laws of motion last semester, we came to the realization that physical science is all about the power of prediction. Given the state of a system in the present, we wish to find the state of a system in the future, or vice versa. The link between past, present, and future, is provided by Newton's laws of motion. For example, for a single particle with mass m , if you know the *initial* position and velocity, \vec{r}_i and \vec{v}_i , Newton's second law $\vec{F} = m\vec{a}$ allows you to integrate forward in time to find *final* position and velocity, \vec{r}_f and \vec{v}_f , at some time in the future (or even at some time in the past). Knowing the *state* of a single particle is tantamount to knowing \vec{r} and \vec{v} .

Consider a bigger system - suppose that the system consists of not one, but two particles! Then the state of the system is specified if one knows \vec{r} and \vec{v} for both of them. The force $\vec{F}_{1,2}$ of particle 1 on particle 2 is also known if one knows the coordinates of the particles, since this typically depends on the relative displacement $\vec{r}_1 - \vec{r}_2$, as for example in the case of gravitational forces, or electrical attraction/repulsion. This is everything one needs to be able to integrate Newton's equations of motion forward in time to predict the two-particle state some time in the future.



These same ideas for two particles apply to the macroscopic systems we deal with in our everyday life, consisting of enormous numbers of atoms or molecules, on the order of one mole, i.e. 6.02×10^{23} particles, or even many hundreds of thousands of moles. When we attempt to extrapolate these ideas to large systems, there is good news and there is bad news, however. The bad news is that it becomes impossible to integrate Newton's equations of motion because we can't keep even begin to enumerate the positions and velocities of a mole of particles, let alone solve for their positions and velocities in the future. Thus the precise *microscopic state* of a large system is impossible to write down. The good news is that, for large systems in equilibrium, we tend to focus our attention on *macroscopic* properties that are insensitive to the individual positions and velocities. We don't need precise knowledge of all 6.02×10^{23} individual positions and velocities to describe the macroscopic properties of a system. Properties

of interest that specify the *macroscopic state* of a system in equilibrium, such as pressure, volume, and temperature, are called *thermodynamic variables*. The science that establishes the relationships between thermodynamic variables was developed in the 1800's, and is called *thermodynamics*. This will be the focus of our attention for the first month in Physics 1320.

2 The Ideal Gas

Let us begin our study of thermodynamics by considering fluids. It is a *fact of our experience* that the (macroscopic) state of a fluid, in equilibrium, is completely described by two variables, pressure P and volume V . It can also be described by P and the temperature T . It can also be described by V and T . You don't need all three, because if you know any two, you can always find the third. The relation between P , V , and T is called the *equation of state*.

A relatively simple equation of state is the relation for a noninteracting gas (also called ideal gas, and also called perfect gas) that you are familiar with from your high school chemistry class,

$$PV = nRT. \tag{1}$$

Here n is the number of moles, $R \simeq 8.314 \text{ J}/(\text{mole} \cdot \text{K})$ is the universal gas constant. (It is often convenient to use $R \simeq 0.08206 \text{ liter-atm}/(\text{mole} \cdot \text{K})$). The temperature T must be taken in Kelvin (the absolute temperature scale). The modern (>1967) Kelvin scale is defined by two reference points. First, absolute zero is assigned $T = 0 \text{ K}$. Second, the single temperature at which all three phases of water (vapor, liquid, solid) coexist in equilibrium is assigned the value $T = 273.16 \text{ K}$. In the modern definition of Celsius, the triple point is assigned to be 0.01°C , so that the conversion between Kelvin and Celsius is exactly

$$273.15 \text{ K} = 0^\circ\text{C}.$$

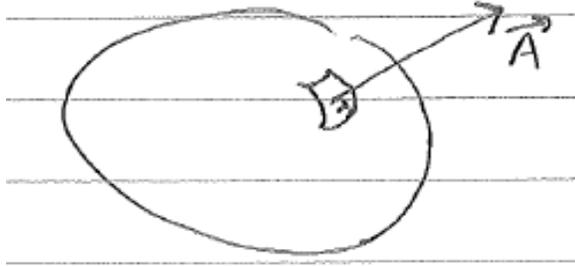
We will often round this to 273 K in our discussions.

The pressure P is often expressed in terms of Pascals ($1 \text{ Pa} = 1 \text{ N}/\text{m}^2$), but also in atmospheres ($1 \text{ atm} \simeq 1.01 \times 10^5 \text{ Pa}$). You will probably encounter many other units of pressure such as the Bar, the Torr, or psi ($1 \text{ atm} = 14.7 \text{ lbs}/\text{in}^2$). The volume is usually expressed in cubic meters, but you may also encounter cubic centimeters, liters, and cubic decimeters. (1 liter = 1 cubic decimeter). The outward force \vec{F} that a gas exerts on a small patch of the surface of a container is the product of the pressure and the surface area,

$$\vec{F} = P \vec{A} \tag{2}$$

The the force is perpendicular to the surface, and points outward from the surface (as though the gas were trying to escape). To account for the directionality of the force, it is customary to write the surface area \vec{A} as though it were a vector. The magnitude of \vec{A} is just the area in square meters, but the direction

is assigned so that the vector points perpendicularly out of the container, so that $P \vec{A}$ properly gives the direction of the force at that point.



Example: If gas is confined to a cubic container with sides of length 1 meter, at a pressure of 1 atm, what is the force on each side of the container?

Answer: The area of any one of the six faces of the cube is $A = 1 \text{ m}^2$. Converting 1 atm into 14.7 lbs/in^2 , we find that

$$F = 1\text{m}^2 \times \left(\frac{100\text{cm}}{1\text{m}}\right)^2 \times \left(\frac{1\text{in}}{2.54\text{cm}}\right)^2 \times 14.7\frac{\text{lbs}}{\text{in}^2} = 22,800 \text{ lbs}$$

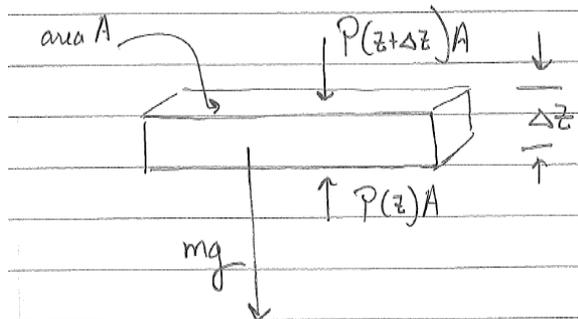
As you can see, this is half the weight of a Greyhound bus. As long as the air outside the container pushes back with the same pressure, the container will stay intact. Problems arise when there is an imbalance between the pressure on the inside and the pressure on the outside, for then the container could implode, or explode.

3 Laplace's Law of Atmospheres.

As we have seen from the example above, the atmosphere can exert an enormous force. At sea level, the pressure is 14.7 lbs per square inch. The pressure is a result of the weight of all of the air on top of you, held down by gravity. The higher you go in elevation, the less air there is above you, and the lower will be the pressure; indeed, the air pressure falls to zero when you reach outer space. It is instructive to figure out how the pressure decreases with elevation. In fact, let us calculate how much lower the air pressure is in Albuquerque as compared to its value at sea level.

Consider a thin parcel of air, with some thickness Δz in the vertical direction, and some cross sectional area A . Air is 80% nitrogen and 20% oxygen, but for simplicity let us assume that it is all nitrogen, having a molecular weight $\bar{M} = 28$ grams per mole (nitrogen is a diatomic gas, so you have to take twice 14 g/mole). The parcel of air is supported by the upward force from the parcel of gas beneath it, $P(z)A$. It is forced down by the gravitational force mg on the mass in the

parcel, as well as the force from the parcel of gas above it, $P(z + \Delta z)A$. The sum of the forces in the vertical direction must be zero in equilibrium.



This force balance is written as

$$P(z + \Delta z)A + mg = P(z)A \quad (3)$$

The mass m contained in the volume $A\Delta z$ is given by,

$$m = \rho A \Delta z, \quad (4)$$

where ρ is the mass density. Using (4), we can rewrite (3) as

$$P(z + \Delta z)A + \rho g A \Delta z = P(z)A \quad (5)$$

Notice that now the area A cancels out on both sides of (5). Bringing $\rho\Delta z$ to the right, and $P(z)$ to the left, and dividing by Δz , we have

$$\frac{P(z + \Delta z) - P(z)}{\Delta z} = -\rho g \quad (6)$$

The left hand side is a first derivative in the limit $\Delta z \rightarrow 0$, so we come up with an equation involving the first derivative of the pressure with elevation,

$$\frac{dP}{dz} = -\rho g. \quad (7)$$

This would be a simple equation to solve if the density ρ were constant. We have to remember that air is compressible, however, and so the density $\rho = \rho(z)$ will be a function of the height. Unless we know exactly how ρ depends on z , we are stuck.

This is where the equation of state comes in. If we approximate the behavior of the atmosphere under normal conditions as that of an ideal gas, we can find the density from (1). Rearranging (1), we see that the number of moles per unit volume,

$$\frac{n}{V} = \frac{P}{RT} \quad (8)$$

can be written in terms of the pressure and the temperature. The mass density is found by multiplying the number of moles per unit volume by the number of grams per mole,

$$\rho = \frac{\text{grams}}{\text{m}^3} = \left(\frac{\text{grams}}{\text{mole}}\right)\left(\frac{\text{moles}}{\text{m}^3}\right) = \bar{M} \frac{n}{V} = \bar{M} \frac{P}{RT} \quad (9)$$

Inserting (9) into (7), we have

$$\frac{dP}{dz} = -\bar{M} \frac{P}{RT} g \quad (10)$$

We can now slide the P from the upper right to the lower left side of the equation, and slide the dz from the lower left to the upper right side of the equation, writing

$$\frac{dP}{P} = -\frac{\bar{M} g}{RT} dz \quad (11)$$

If we formally integrate both sides, we have

$$\int_{\text{initial}}^{\text{final}} \frac{dP}{P} = -\int_{\text{initial}}^{\text{final}} \frac{\bar{M} g}{RT} dz. \quad (12)$$

Let us now assume that the temperature does not change much as a function of elevation, so that we can pull it out of the integral over z on the right hand side, along with the other constants \bar{M} , g , and R .

$$\int_{\text{initial}}^{\text{final}} \frac{dP}{P} \simeq -\frac{\bar{M} g}{RT} \int_{\text{initial}}^{\text{final}} dz.$$

The left hand integral results in a natural log, and the right hand integral is just a difference between the initial and final elevations,

$$\ln P|_{\text{initial}}^{\text{final}} = \ln \left(\frac{P_{\text{final}}}{P_{\text{initial}}} \right) = -\frac{\bar{M} g}{RT} (z_{\text{final}} - z_{\text{initial}}). \quad (13)$$

Exponentiating both sides, we can get rid of the logarithm, and obtain a famous result called Laplace's Law of Atmospheres,

$$P_{\text{final}} = P_{\text{initial}} \exp \left(-\frac{\bar{M} g}{RT} h \right). \quad (14)$$

Here we have set $h = (z_{\text{final}} - z_{\text{initial}})$. Before putting any numbers into the expression, let us pause to savor the qualitative predictions of the formula.

4 Savoring the Isothermal Atmosphere Formula

Let us study the final answer, as expressed by (14). First, notice that the air pressure decreases exponentially with the elevation h above sea level. This implies that the atmosphere doesn't simply come to an abrupt end at the "edge" of

space, but trails on forever, always diminishing in concentration. This assumes, of course, that the temperature remains constant, which may well be nonsense when you get beyond the elevation of, say, 10,000'. (There is an adiabatic version of this formula that is more accurate over large temperature changes.) Please notice the manner with which the rate of decay of the exponential depends on temperature. Notice that temperature is in the denominator of the exponent. The lower the temperature, the faster the exponential decay. This implies that the ratio $P_{\text{final}}/P_{\text{initial}}$ will be smaller in the winter than in the summer. For the same elevation change, the pressure will decrease more in Minnesota than it does in Florida. Notice also that the rate of fall-off is proportional to the molecular weight (The mass is multiplied by the gravitational constant, so it really is the weight of the gas molecules that comes in, and not just their mass). This means that the partial pressure of heavier gasses will decrease more quickly with elevation. Notice that the atmospheric composition at extremely high elevations will be dominated by lighter elements, such as hydrogen.

Now let's put some numbers into the expression. Consider the change in pressure in going from sea level to Albuquerque, which is about 1 mile, or 1.6 km high. Using a molecular weight of 28 grams per mole for nitrogen (it is a diatomic gas!), and taking $T = 273 \text{ K}$, we have

$$\begin{aligned}
 P_{\text{Alb}} &= P_{\text{sea level}} \exp\left(-\frac{28 \frac{\text{g}}{\text{mole}} \times \frac{1 \text{kg}}{1000 \text{g}} 9.8 \frac{\text{m}}{\text{s}^2}}{8.314 \frac{\text{J}}{\text{mole}\cdot\text{K}}} 1.6 \times 10^3 \text{m}\right) \\
 &= 1 \text{atm} \cdot \exp(-0.193) \\
 &\simeq 1 \text{atm} \cdot (1 - 0.193) = 0.81 \text{ atm}
 \end{aligned} \tag{15}$$

The air pressure is lower in Albuquerque than at sea level, by about 20%.

Notice how the exponent is a competition between two energies. The numerator is $\bar{M}gh$, and has units of Joules per mole. The denominator is RT , and has units of Joules per mole. When this ratio is large, there is a big reduction in pressure. We recognize the energy $\bar{M}gh$ as the work to carry a mole of molecules to a height h . Why do you suppose that this is paired off with the energy RT ? Should we call the product RT a "thermal energy"? What would be different if this were the moon? What if this were ozone gas? What is the air pressure in the Andes, at 22,000'? Do you like to write the exponential function as e^{-x} , or as $\exp(-x)$? Can you sketch a graph of the exponential decay of pressure with elevation? What would the graph of pressure versus elevation look like on semi-log graph paper? Are you getting tired of all these questions?

This is a typical illustration of what will come up repeatedly in this class. You will spend time learning how to derive a formula, but that's not enough. You must also spend time applying the formula, or at least talking about the formula. At the end of the day, you need to know how to derive things (quickly, without peeking at the notes). But you also should have many important formulae memorized, so that you can actually use them efficiently, in every-day discussions (and exams). For example, if you're standing in the cafeteria line some evening, and someone nearby casually happens to mention that ex-governor Gary Johnson climbed Mt. Everest without oxygen tanks, you should be able to quickly

estimate the partial pressure of oxygen on top of Mt. Everest, and jump right into the conversation, blurting out "You know, the partial pressure of oxygen on top of Mt. Everest is only 30% of what it is at sea level." (Quite frankly, if you are reasonably curious, I would be surprised if you had not already worked out the case of Mt. Everest before going to dinner.) If your new friends want to know how you figured this out so fast, invite them all to sit at your table, and go through the derivation on a napkin. Derivations like this at the dinner table can be great social ice breakers.

One of the best ways to memorize a formula is to think about the placement of every term. Think about how the result would change if that term were large, or if that term were small. Why must the term be in its location for dimensional reasons? Come up with physical justifications whenever possible. Look for patterns.

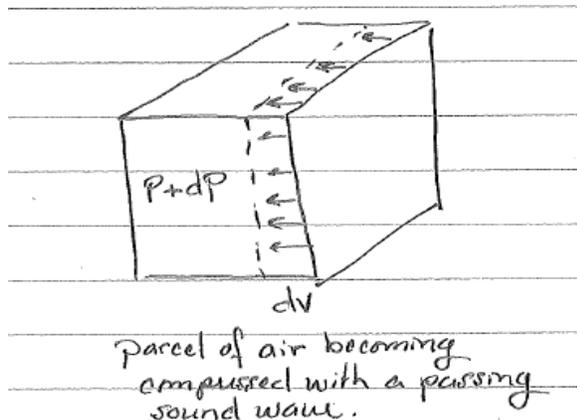
5 Bulk Modulus

Another topic of interest is the "springiness" of air. You may recall our discussion of sound waves from last semester; when a sound wave passes through air, the air is compressed, and then re-expands, like the coil of a slinky. Just as the stiffness of a slinky determines the speed of the wave passing through, the stiffness of the air determines the speed of sound. The measurement of the stiffness of a fluid is called the bulk modulus, and is denoted as

$$B = -V \frac{dP}{dV} \quad (16)$$

The pressure of a gas decreases if the volume increases. The ratio of the change in pressure to the change in volume will be negative, but becomes positive when you multiply with a negative sign. For a given change dV in volume, the change dP in pressure is very small if the volume is large, so in the limit of an enormous volume this ratio goes to zero. Multiplying the ratio by V compensates for this, rendering a finite value for B in the limit in which the volume tends to infinity. In effect, the bulk modulus is a measure of the change in pressure as compared to the *relative* change in volume, dV/V .

If the compression takes place quickly, so that the air heats up, wave propagation is governed by the adiabatic bulk modulus. If the compression takes place slowly, so that there is time for heat to dissipate, wave propagation is determined by the isothermal bulk modulus. The difference in these two depends on what is held constant when evaluating the derivative dP/dV in (16). For audible frequencies, it is the adiabatic bulk modulus that comes into play. We will look at this later. For the present, let us consider the isothermal bulk modulus.



To denote the isothermal bulk modulus, let us write

$$B_T = -V \left(\frac{dP}{dV} \right)_T \quad (17)$$

with the parentheses around dP/dV and the subscript T indicating that T is to be held constant. Some people would rather write this as

$$B_T = -V \left(\frac{\partial P}{\partial V} \right) \quad (18)$$

where the *partial derivative* $\partial P/\partial V$ is to be used as an alternate notation reminding them that T is to be held constant. In thermodynamics it is customary to combine both notations, writing the redundant form,

$$B_T = -V \left(\frac{\partial P}{\partial V} \right)_T \quad (19)$$

As an illustration, let us calculate the isothermal bulk modulus of an ideal gas at STP (standard temperature and pressure) of 273 K and 1 atm. Starting with the ideal gas equation of state, divide by V to isolate the pressure;

$$P = \frac{nRT}{V} \quad (20)$$

Now take the derivative of P with respect to V , and in doing so, treat the factor nRT in the numerator as though it were a constant. As you know from the power-law-rule, the derivative of V^{-1} is $-V^{-2}$, so it follows that

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{nRT}{V^2} \quad (21)$$

Next, multiply by $-V$ to get the bulk modulus. The negative signs cancel, giving a positive result,

$$B_T = -V \left(-\frac{nRT}{V^2} \right) = \frac{nRT}{V} = P = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa.} \quad (22)$$

The isothermal bulk modulus of an ideal gas is the same as its pressure! This is equal to 10^5 Pa at STP. For comparison, water is much stiffer, with $B \simeq 2 \times 10^9$ Pa, and steel is even stiffer, with $B \simeq 190 \times 10^9$ Pa. (I am not sure if these values for water and steel are isothermal or adiabatic bulk moduli.)

6 Compressibility

The isothermal compressibility k_T is just the reciprocal of the isothermal bulk modulus.

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (23)$$

Here we are looking at the ratio of the relative change in volume dV/V , to a small increase in pressure dP , holding the temperature constant. If you are more excited by the "squishiness" of substances than you are by the "stiffness" of substances, you will probably talk in terms of k_T in preference to B_T , even though they are just reciprocals of each other.

7 PV Diagrams and the Ideal Gas Equation of State

We should spend some time examining the ideal gas equation of state, even if only to help with remembering the form. It is common to visualize the relation by making a plot of P versus V . Start with the equation of state $PV = nRT$, and divide both sides by V , writing

$$P = \frac{n}{V} RT \quad (24)$$

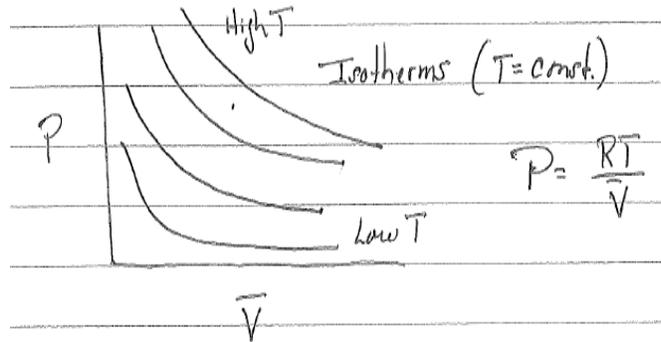
For a constant T , you can see that P decreases as V increases, as $1/V$. To show this behavior on a graph, one usually draws a set of curves of P as a function of V for different values of T , a family of *isotherms*. What shall we choose for the number of moles n ? We can actually avoid this discussion by plotting on the x-axis of the graph the specific volume, the volume per mole,

$$\bar{V} = \frac{V}{n}.$$

On an xy graph, the isotherms have a shape described by

$$y = \frac{\text{const.}}{x},$$

where $y = P$, $x = \bar{V}$, and the constant, RT , is large for high temperatures, and small for low temperatures.



Other curves of interest are *isochors*, and *isobars*. An isochor is a line of constant volume. An isobar is a line of constant pressure.

8 Van der Waals Equation of State

At high densities, interactions between molecules become important, and the gas can no longer be considered an ideal gas. There is still a relation between P , V , and T , but it is no longer as simple. An equation proposed by Van der Waals in 1873 to describe non-ideal gases has the form,

$$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT \quad (25)$$

where a and b are called the Van der Waals constants, and depend on temperature.

To gain some familiarity with the Van der Waals (VDW) equation of state, one *activity* is to check to make sure that it reduces to the ideal gas equation when the density is low. Notice first off that when \bar{V} is very large (dilute gas), you can ignore the b in the factor $(\bar{V} - b)$, and you can ignore a/\bar{V}^2 as compared to P in the factor $(P + \frac{a}{\bar{V}^2})$, and the VDW equation of state reduces to the ideal gas equation of state,

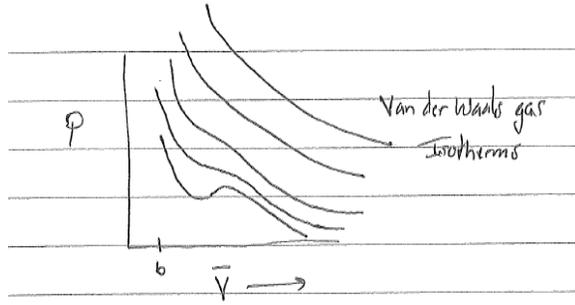
$$P \bar{V} = RT \quad (26)$$

as you would expect.

The meaning of the factor $(\bar{V} - b)$ is that the volume is reduced from what you would have in an ideal gas. The coefficient b accounts for the fact that the molecules in the gas are not point particles, and each molecule has less room to maneuver due to the presence of the others. The term a/\bar{V}^2 accounts for a reduction in pressure that arises due to the attractive interaction between pairs of gas molecules. The factor \bar{V}^{-2} is proportional to the probability that any two molecules find themselves close enough to interact.

The presence of b in the equation of state causes the pressure to diverge to ∞ , not at $\bar{V} = 0$, but at $\bar{V} = b$. The presence of a in the equation of state causes an inflection in the pressure as the temperature is lowered. At sufficiently low

temperatures, the equation of state becomes multivalued (three values of \bar{V} for one value of P); this is indicative of a phase transition from gas to liquid.



A table of Van der Waals constants for different gases can be found here:
http://en.wikipedia.org/wiki/Van_der_Waals_constants_%28data_page%29