Theoretical Physics
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Chapter G Notes. The Ideal Gas Law and Thermodynamics

G1. The Ideal Gas Law. The following apply to the ideal gas.

Boyle's Law. Pressure of a gas is inversely related to volume at constant temperature.

$$P \sim \frac{1}{V} \text{ and } P_1 V_1 = P_2 V_2 \text{ as constant temperature.}$$

When temperature is used with the equations in this section, the Kelvin scale is used, i.e., T = Celsius Temperature – 273.

Robert Boyle (1627-1691)

Images from the School of Mathematics and Statistics, Univ. of St. Andrews, Scotland

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Charles's Law. Volume of a gas is proportional to temperature at constant pressure.

$$V \sim T \text{ and } \frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ as constant pressure}$$

and we use the absolute Kelvin temperature scale. Consider this as a definition for the absolute temperature scale: as you cool the gas down at constant pressure, the volume shrinks to zero as temperature goes to zero.

Jacques Charles (1746-1823)

Gay-Lussac's Law. Pressure of a gas is proportional to temperature at constant volume.

$$P \sim T \text{ and } \frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ at constant volume.}$$

Think of this as an alternative definition for temperature on the absolute scale. As you lower the pressure at constant volume, the temperature lowers, both heading towards zero.

Joseph Gay-Lussac (1778-1850)

We can incorporate all these laws in the form:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

The chemists write the ideal gas law as

Temperature

Pressure

Number of Moles

$$PV = nRT$$

Volume

Ideal Gas
Constant

The physicists often like to write

Temperature

Pressure

Number of
Particles

$$PV = NkT$$

Volume

Boltzmann
Constant

The definition of the mole is

$$n = \frac{N}{N_A}$$, where $N_A = 6.022 x 10^{23}$ is called Avogadro's number.

Since $PV = nRT = NkT = nN_A kT$, the physicist's constant is related to the chemist's constant as

$$k = \frac{R}{N_A} .$$

G2. "Derivation" of the Ideal Gas Law

The ideal gas law is an excellent example of a combination of experimental results. We will attempt to "derive" this law since our course is called "Theoretical Physics."

Sir Isaac Newton (1642-1727)

Let's see what we can derive from Newton's Second Law

$$F = ma \,.$$

Bur first, let's summarize what have we accomplished so far in our theoretical analysis of fundamental laws.

We started with the following: Newton's Second Law, Newton's Universal Law of Gravitation, Coulomb's Law, and Special Relativity.

$$F = ma \qquad F_G = \frac{GMm}{r^2} \qquad F_E = \frac{kQq}{r^2} \qquad "x = ct"$$
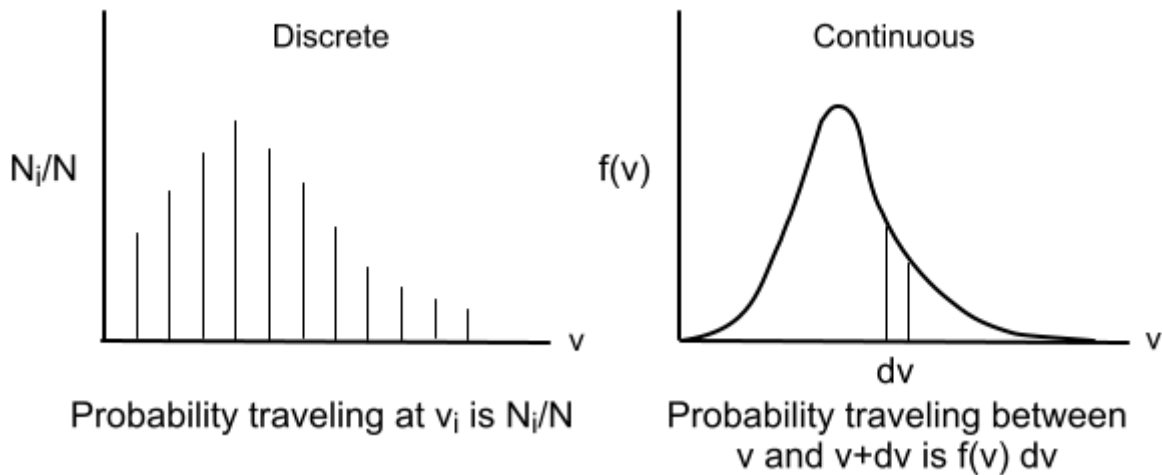
We used the first, third, and fourth to derive the Maxwell equations. From the Maxwell equations we derived the existence of electromagnetic waves, i.e., we obtained optics.

$$\boxed{F = ma \qquad F_E = \frac{kQq}{r^2} \qquad "x = ct"} \quad => \textit{E\&M and Optics}$$

Now we will attempt to arrive at thermodynamics from Newton's Second Law.

$$\boxed{F = ma} \quad => \textit{Thermodynamics}$$

We will consider a box containing a gas. Below is the basic idea of a discrete distribution of velocities and a continuous one.

Discrete

N_i/N

v

Probability traveling at v_i is N_i/N

Continuous

$f(v)$

dv

v

Probability traveling between v and v+dv is f(v) dv

The total probability must be 1 in each case, i.e., the probability that a given gas particle has some velocity is 1. Therefore, for the discrete case,

$$\sum_i \frac{N_i}{N} = 1$$, which is consistent with $N = \sum_i N_i$.

For the continuous case, the total area under the curve must be 1.

$$\int f(v)\, dv = 1$$.

Classically, one integrates from zero to infinity. We are justified in doing this even knowing relativity since our particles no way approach the speed of light. Therefore, our function f(v) will drop to zero before we even get close to the speed of light and it is easier to integrate to infinity when you are dealing with exponential-type functions. We will not get into such details here anyway and at times leave the integration limits off. It is understood that you integrate over all velocities.

We will consider a continuous distribution of velocities for our gas particles. The neat thing about our analysis is that we will never need to worry about the exact form of the function f(v). Watch!
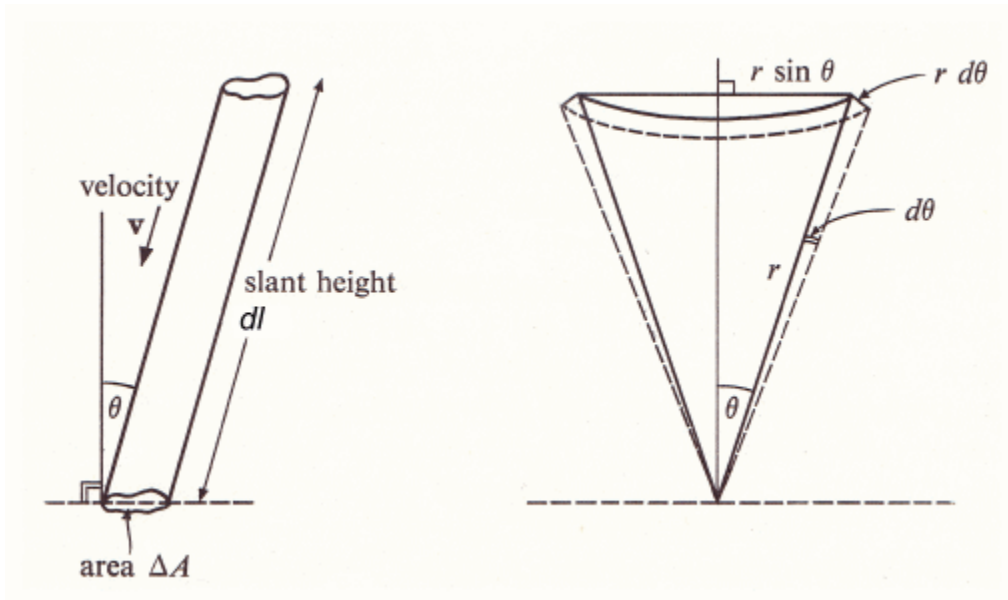
Consider a box with N particles and volume V. The pressure is defined as force per unit area and the force is the change in momentum with respect to time:

$$P = F / A$$ and $$F = dp / dt$$.

A slanted region is shown below where some particles are heading towards the area shown on the floor. From the geometry at the lower right we will determine the probability for a particle to be traveling along the slanted region at velocity v.

The volume element below is $\Delta A \cos \theta \, dl$. We need another piece. The change in momentum when a particle coming in along the slant with velocity V bounces off the bottom floor. The change in momentum is $2mv \cos \theta$.

The following is from Derek L. Livesey, *Atomic and Nuclear Physics* (Waltham, MA, Blaisdell Publishing, 1966). Let the probability distribution for the angle θ be $g(\theta)$.

$$\int_0^{\pi/2} g(\theta) \, d\theta = 1 \qquad g(\theta) \, d\theta = \frac{2\pi r \sin \theta \, r \, d\theta}{2\pi r^2} = \sin \theta \, d\theta .$$

$$dP = \frac{N}{V} \left[\Delta A \cos \theta dl \right] \left[\frac{1}{2} f(v) \, dv \right] \left[\sin \theta d\theta \right] \left[\frac{2mv \cos \theta}{dt} \right] \frac{1}{\Delta A}$$

$$dP = \frac{N}{V} \left[\cos \theta \frac{dl}{dt} \right] \left[\frac{1}{2} f(v) \, dv \right] \left[\sin \theta d\theta \right] \left[2mv \cos \theta \right]$$

$$dP = \frac{Nm}{V}\left[\frac{dl}{dt}\right][vf(v)dv]\left[\cos^2\theta \sin\theta d\theta\right]$$

$$dP = \frac{Nm}{V}\left[v^2 f(v)dv\right]\left[\cos^2\theta \sin\theta d\theta\right]$$

$$P = \frac{Nm}{V}\int_0^\infty v^2 f(v)dv\int_0^{\pi/2}\cos^2\theta \sin\theta d\theta$$

$$P = \frac{Nm}{V}\overline{v^2}\left[-\frac{\cos^3\theta}{3}\right]\Bigg|_0^{\pi/2}$$

$$P = \frac{Nm}{V}\overline{v^2}\left[-0-(-\frac{1}{3})\right]$$

$$P = \frac{N}{V}m\overline{v^2}\frac{1}{3} \quad \text{and} \quad PV = \frac{N}{3}m\overline{v^2}$$

We can define temperature by the total kinetic energy of the gas particles. This total energy is equal to the average kinetic energy the particles times the number of particles,

$$KE = N\frac{m\overline{v^2}}{2}$$

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Since we want the assignment $PV = \frac{N}{3}m\overline{v^2} = NkT$, we find $\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$.

In summary, we have

$$PV = nRT \quad \text{and} \quad PV = NkT \quad \text{with} \quad \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT.$$

G3. The First Law of Thermodynamics and Specific Heats

We will phrase the first law of thermodynamics in terms of our ideal gas. The first law of thermodynamics is the law of conservation of energy: The change in energy of a system is equal to the heat that flows into the gas minus the work that is done by the gas.

$$\Delta U = \Delta Q - \Delta W$$

Expanding Gas Does Work
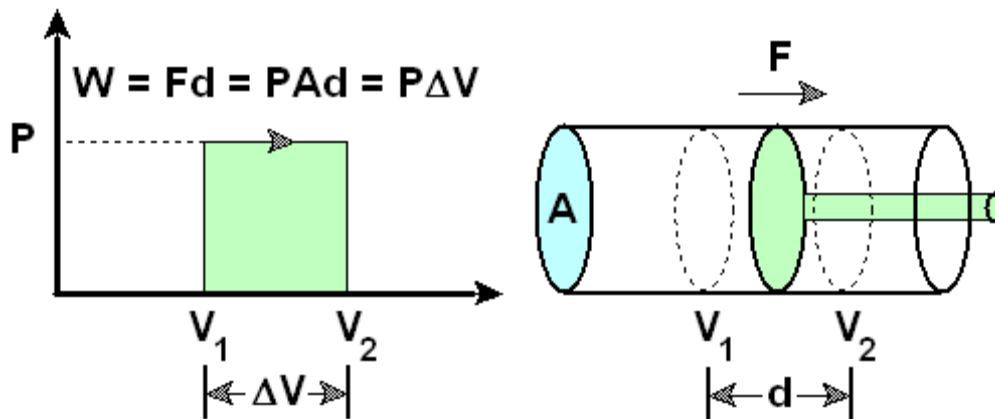
We can therefore also write the first law as

$$\Delta U = \Delta Q - \Delta W$$

Here is an application using the definition of the specific heat at constant volume.

$$c_V \equiv \frac{1}{n}\frac{\Delta Q}{\Delta T}\bigg|_V$$

$$\Delta Q = \Delta U + P\Delta V \quad \text{and} \quad \Delta Q_V = \Delta U$$

$$U = N\frac{1}{2}m\overline{v^2} = \frac{3}{2}NkT = \frac{3}{2}nRT$$

$$c_V \equiv \frac{1}{n}\frac{\Delta Q}{\Delta T}\bigg|_V = \frac{1}{n}\frac{\Delta Q}{\Delta T} = \frac{1}{n}\frac{3}{2}\frac{nR\Delta T}{\Delta T} = \frac{3}{2}R$$

Here is an application using the definition of the specific heat at constant pressure.

$$c_P \equiv \frac{1}{n}\frac{\Delta Q}{\Delta T}\bigg|_P$$

$$\Delta Q = \Delta U + P\Delta V = \frac{3}{2}nR\Delta T + P\Delta V = nc_V\Delta T + P\Delta V$$

Since we want constant pressure, it is better to have a ΔP in the above. We note

$$PV = nRT \quad \text{and} \quad \Delta(PV) = nR\Delta T = P\Delta V + V\Delta P.$$

Then $P\Delta V = nR\Delta T - V\Delta P$ and

$$\Delta Q = nc_V\Delta T + nR\Delta T - V\Delta P = n(c_V + R)\Delta T - V\Delta P.$$

$$c_P \equiv \frac{1}{n}\frac{\Delta Q}{\Delta T}\bigg|_P = c_V + R \quad \text{since} \quad \Delta P = 0.$$

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Summary

$$PV = nRT \quad \text{and} \quad PV = NkT \quad \text{with} \quad \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT.$$

$$U = N\frac{1}{2}m\overline{v^2} = \frac{3}{2}NkT = \frac{3}{2}nRT$$

$$\Delta U = \Delta Q - P\Delta V \quad \text{and} \quad \Delta Q = \Delta U + P\Delta V$$

$$c_V \equiv \frac{1}{n}\frac{\Delta Q}{\Delta T}\bigg|_V , \quad c_P \equiv \frac{1}{n}\frac{\Delta Q}{\Delta T}\bigg|_P , \quad \text{and} \quad c_P = c_V + R$$

For an ideal gas we have $c_V = \frac{3R}{2}$ and $c_P = \frac{5R}{2}$.

G4. Four Thermodynamic Processes

1. Isometric, Isochoric (constant volume): $\Delta V = 0$.

$$W = \int P \, dV = 0$$

2. Isobaric (constant pressure): $\Delta P = 0$.

$$W = \int_{V_1}^{V_2} P \, dV = P \int_{V_1}^{V_2} dV = P(V_2 - V_1)$$

3. Isothermal (constant temperature): $\Delta T = 0$.

$$W = \int_{V_1}^{V_2} P \, dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$W = nRT \ln V \Big|_{V_1}^{V_2} = nRT \ln \frac{V_2}{V_1}$$

4. Adiabatic (no heat flow): $\Delta Q = 0$. Note that we can't say constant heat since heat is not a "regular" variable like P, V, and T. Heat exchange, like work, depends on a path we take in the PV plane. Heat and work are not intrinsic properties of the gas. But energy is. From the earlier section, write

$$\Delta Q = \Delta U + P \Delta V = nc_V \Delta T + P \Delta V \text{ . Remember } U = \frac{3}{2} nRT \text{ .}$$

$$\Delta Q = nc_V \Delta T + nR \Delta T - V \Delta P = n(c_V + R) \Delta T - V \Delta P$$

These equations are

$$\Delta Q = nc_V \Delta T + P \Delta V \quad \text{and} \quad \Delta Q = nc_P \Delta T - V \Delta P \text{ .}$$

For $\Delta Q = 0$ we can write

$$nc_V \Delta T = -P \Delta V \quad \text{and} \quad nc_P \Delta T = V \Delta P \text{ .}$$

$$\frac{nc_P \Delta T}{nc_V \Delta T} = -\frac{V \Delta P}{P \Delta V} \quad \text{leads to} \quad \frac{c_P}{c_V} = -\frac{V}{P}\frac{dP}{dV} \; .$$

We define $\gamma = \dfrac{c_P}{c_V}$. Then, $\gamma = -\dfrac{V}{P}\dfrac{dP}{dV}$

$$\frac{dP}{P} = -\gamma \frac{dV}{V}$$

$$\int_{P_1}^{P_2} \frac{1}{P}\, dP = -\gamma \int_{V_1}^{V_2} \frac{1}{V}\, dV$$

$$\ln P \Big|_{P_1}^{P_2} = -\gamma \ln V \Big|_{V_1}^{V_2}$$

$$\ln \frac{P_2}{P_1} = -\gamma \ln \frac{V_2}{V_1}$$

$$\ln \frac{P_2}{P_1} = \ln \left[\frac{V_2}{V_1}\right]^{-\gamma}$$

$$\frac{P_2}{P_1} = \left[\frac{V_2}{V_1}\right]^{-\gamma} \quad \text{and} \quad \frac{P_2}{P_1} = \left[\frac{V_1}{V_2}\right]^{\gamma}$$

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \text{, i.e., } PV^{\gamma} = const$$

PG1 (Practice Problem). Show that the work done by a gas in an adiabatic expansion from volume V_1 to V_2 is

$$W = const \left[\frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{1-\gamma}\right] = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$$