The Big Ideas—Chapter 21

(Serway and Beichner, Physics for Scientists and Engineers, 5th Edition)

Section 1

The ideal gas law is the natural result of a very simple model of a gas (in which molecules behave like particles that undergo elastic contact collisions with walls and other molecules) and an interpretation of temperature as a measure of the average energy per molecule.

In this model the pressure arises from the average force of the collisions between the molecules and the walls and is directly associated with the density and the average translational kinetic energy of the molecules. The ideal gas law then reveals temperature as a pure function of the average translational kinetic energy.

$$P_{\text{simple model}} = \frac{2}{3}\left(\frac{N}{V}\right)\left(\tfrac{1}{2}m\overline{v^2}\right)$$

$$T_{\text{ideal gas}} = \frac{2}{3k_{\text{B}}}\left(\tfrac{1}{2}m\overline{v^2}\right)$$

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}k_{\text{B}}T$$

With *far* more generality than is implied by the derivation of this simple model, the “equipartition theorem” says that, for a system in thermal equilibrium, *every possible way* in which a molecule can store energy (each so-called “degree of freedom”) will on average store an energy determined solely by the temperature.

$$\left(\begin{array}{c}\text{Energy per}\\ \text{degreee of}\\ \text{freedom}\end{array}\right) = \tfrac{1}{2}k_{\text{B}}T$$

Section 2

The equipartition theorem allows us easily to determine the internal energy of an ideal gas since the value depends only on how many molecules there are and on how many ways each molecules can translate, rotate and/or vibrate. Knowledge of the relationship between internal energy and temperature allows us to find the “molar specific heat” of the gas.

The “molar specific heat” is defined as the heat (*not* the energy change!) per mole per unit temperature change. Because heat is not a state variable, the molar specific heat will depend on how the process is carried out. We find it useful to define molar specific heats for isovolumetric and isobaric processes.

$$C_V \equiv \frac{1}{n}\frac{dQ}{dT}\bigg|_{\text{constant V}}$$

$$C_P \equiv \frac{1}{n}\frac{dQ}{dT}\bigg|_{\text{constant P}}$$

A constant volume process involves no work so the heat added to the gas which we use to define the “molar specific heat at constant volume” *is* the change in energy. Note well that the second relationship is true even when the process is *not* isovolumetric!

$$dQ_{\text{isovolumetric}} = nC_V dT$$

$$dE_{\text{int}} = nC_V dT \qquad \text{(always!!)}$$

Section 2 (cont'd)	
When heating a gas at constant *pressure*, it simultaneously *loses* energy by doing work. Thus, a greater amount of heat is required to produce the same temperature change. For an ideal gas, the difference between the molar specific heats is *R*.	$dW = PdV = nRdT$ $dQ = dE_{\text{int}} + dW = n(C_V + R)dT$ $C_P = C_V + R$
A *monatomic* gas can store energy only in translational degrees of freedom of which there are three for every molecule. Thus we can find a specific value for the molar specific heat.	$dE_{\text{int}}^{\text{monatomic}} = \frac{3}{2} nRdT$ $C_V^{\text{monatomic}} = \frac{3}{2} R$
Section 3	
In a quasistatic adiabatic expansion, an ideal gas loses energy by doing work. Thus its pressure drops more rapidly than it does for an isothermal process in which the energy is kept constant by simultaneously adding heat.	$PV = \text{constant}$ (isothermal) $PV^{\gamma} = \text{constant}$ (adiabatic) $\gamma \equiv \frac{C_P}{C_V} > 1$
The ratio of specific heats plays the central role in the "slope" of a quasistatic adiabatic process.	
The ideal gas law allows us to express adiabatic relationship in other ways.	$TV^{\gamma - 1} = \text{constant}$
Section 4	
Diatomic and more complex molecules can rotate and vibrate in addition to translating. As a result they have more ways of storing energy and the equipartition theorem predicts that they will have higher molar specific heats. These predictions break down for two reasons that can only be understood via quantum theory.	
First, quantum theory predicts that rotational degrees of freedom are only available at temperatures above a couple hundred K and that vibrational degrees of freedom are only available at temperatures above a couple thousand K.	
Second, quantum theory predicts that rotations that do not produce distinguishable configurations do not exist! Thus, diatomic molecules *cannot* rotate about their axis of symmetry.	

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The result is that, near room temperatures, diatomic gases have five degrees of freedom compared to the three for monatomic gases. More complex gases generally have larger specific heats. We can also use the equipartition theorem to explain the molar specific heat of atomic solids at high temperatures on the basis of the six degrees of freedom per atom.	monatomic 3 degrees of freedom $C_V = \frac{3}{2} R,\ C_P = \frac{5}{2} R,\ \gamma = \frac{5}{3}$ diatomic (~ room temp) 5 degrees of freedom $C_V = \frac{5}{2} R,\ C_P = \frac{7}{2} R,\ \gamma = \frac{7}{5}$ $C_{\text{solid}}^{\text{high T}} \approx 3R$
Sections 5 and 6 **At thermal equilibrium the number of molecules in a particular energy state is proportional to the “Boltzmann factor.”** Among *many* other things, the Boltzmann distribution explains the exponential decrease of density (and pressure) for an isothermal atmosphere. The Boltzmann distribution also explains the Maxwell-Boltzmann velocity distribution for the speeds of gas molecules from which one can derive the rms speed, the average speed, and the most probable speed all three of which are proportional to the square root of the absolute temperature and inversely proportional to the square root of the molecular mass.	$n(E) \quad e^{-E/k_B T}$ $n_V(h) = n_V(0)\, e^{-mgh/k_B T}$ $N_v \quad v^2 e^{-mv^2/2k_B T}$ $v_{\text{rms}} = \sqrt{3k_B T/m}$ $\bar{v} = \sqrt{8k_B T/\pi m}$ $v_{\text{rms}} = \sqrt{2k_B T/m}$
Section 7 **If we refine our ideal gas model by allowing the molecules to become spheres of *nonzero* diameter, we can derive formulas for the mean free path and the collision frequency.**	$l = \frac{1}{\sqrt{2}\pi d^2 n_V}$ $f = \frac{\bar{v}}{l} = \sqrt{2}\pi d^2 \bar{v} n_V$