

## The Equipartition of Energy Theorem.

Annotated lecture notes by M. Croft

Note this material is important to this course and is not in the book. This material applies the macroscopic concepts of mechanical energy to microscopic collections of  $\sim 10^{23}$  molecules. In so doing it casts the concepts of temperature and heat transfer in terms of physics you have already learned.

The equipartition (or equal division) of energy theorem involves the concept that, in thermal equilibrium, energy is shared equally among all of its various possible forms (or degree of freedom). Moreover the average amount of energy per degree of freedom is  $kT/2$  per molecule or  $RT/2$  per mole. [Here  $k$  = Boltzmann's constant,  $R = k N_A$  is the ideal gas constant and  $N_A$  is Avogadro's number.] Operationally a degree of freedom is identified with a quadratic term in the total mechanical energy. For this class this means a kinetic energy term involving a velocity component squared. {It is worth noting that it can also be a harmonic oscillator potential energy involving a quadratic displacement from equilibrium but this concept is not required for 203.}


This figure illustrates the application of the equipartition principal to a monatomic ideal gas. Note that there are three degrees of freedom associated with the  $\langle v_x^2 \rangle$ ,  $\langle v_y^2 \rangle$  and  $\langle v_z^2 \rangle$  kinetic energy terms respectively. [Here  $\langle \rangle$  denotes the average taken over all of the molecules of the gas].

By the equal equipartition principal the internal energy of the ideal monatomic gas,  $U$ , is then  $N 3 (kT/2)$ , where  $N$  is the number of molecules (atoms here), 3 comes from 3 degrees of freedom and  $kT/2$  comes from the energy per degree of freedom (from the equipartition principal).

The constant volume specific heat  $C_V = dU/dT|_V$  so that for the ideal monatomic gas  $C_V = N 3k/2$  per molecule or  $C_V = 3R/2$  per mole. {Technically, for the theoretically inclined, the derivative is at constant volume (i.e.  $|_V$ ) and is a partial derivative (all other variables held constant)}

It is worth noting that if the gas were adsorbed onto a surface, where motion in only two directions was possible (2 degrees of freedom), that the  $U$  would be accordingly reduced.

To Generalize see how this comes about.



3 ways energy can be distributed

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

degree of freedom = each term into which energy can be distributed

$$U = N \left( \frac{1}{2} kT \right) + N \left( \frac{1}{2} kT \right) + N \left( \frac{1}{2} kT \right)$$

3 degrees of freedom

$$U = N 3 \left( \frac{1}{2} kT \right) \text{ or } U = n 3 \left( \frac{RT}{2} \right)$$

### Equipartition of Energy Theorem

per particle  $(\frac{1}{2} kT)$  per degree of freedom

OR

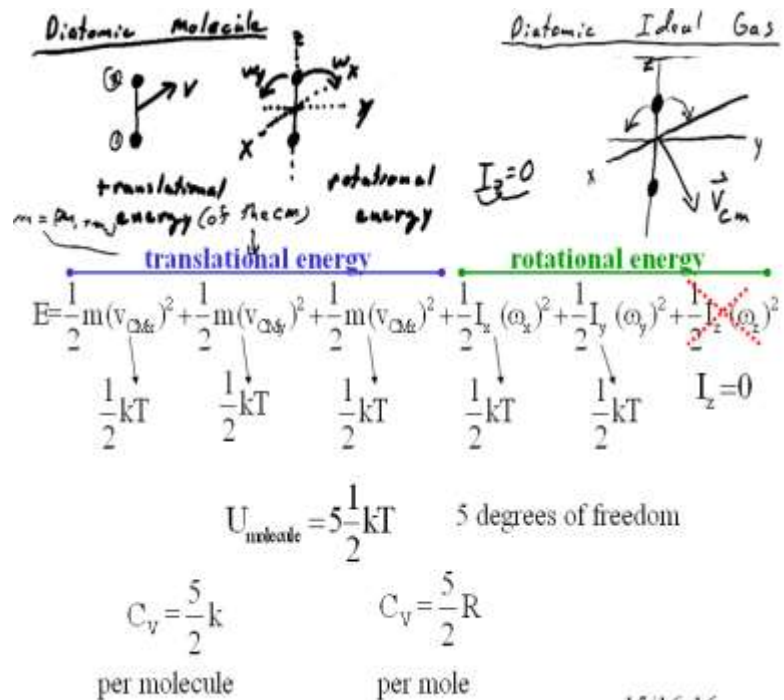
per mole  $(\frac{1}{2} RT)$  per degree of freedom

ave. thermal energy in each degree of freedom

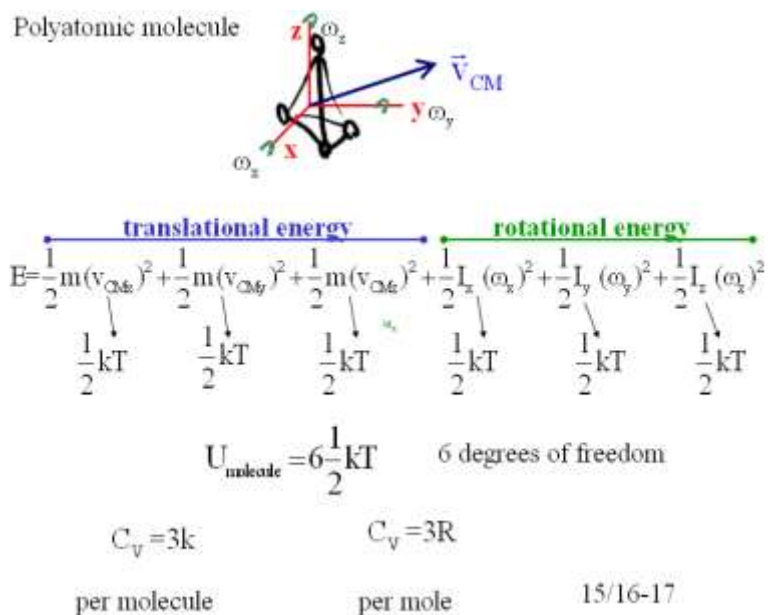
This figure illustrates the application of the equipartition principal to a diatomic ideal gas. Note that there are now: 3 translational degrees of freedom associated with the  $\langle v_x^2 \rangle$ ,  $\langle v_y^2 \rangle$  and  $\langle v_z^2 \rangle$ ; and 2 rotational degrees of freedom associated with the  $\langle \omega_x^2 \rangle$ , and  $\langle \omega_y^2 \rangle$ .

**{Important aside.** Because the atoms are assumed to be point particles located along the z-axis, the moment of inertia for rotations about z is zero and there is no energy (or degree of freedom) associated with it. Although the electron cloud extends a distance from the atoms comparable to their separation, the mass of the atoms is located in the nucleus which is many orders of magnitude smaller so that the point-mass assumption for the mass distribution is an excellent approximation.}

Continuing from before the aside, the equipartition principal dictates the internal energy of the ideal diatomic gas,  $U$ , to be  $N 5 (kT/2)$ . Here the 5 = [3 translational + 2 rotational] degrees of freedom and all else is as defined before. The  $C_V$  is obtained, as before, by taking the derivative of the internal energy and is indicated in the figure.



This figure illustrates the application of the equipartition principal to a polyatomic ideal gas. Note that there are still 3 translational degrees of freedom associated with the  $\langle v_x^2 \rangle$ ,  $\langle v_y^2 \rangle$  and  $\langle v_z^2 \rangle$ . However for the polyatomic molecule there are now the full 3 rotational degrees of freedom associated with the  $\langle \omega_x^2 \rangle$ ,  $\langle \omega_y^2 \rangle$  and  $\langle \omega_z^2 \rangle$ . The equipartition principal therefore dictates the internal energy of the ideal polyatomic gas,  $U$ , to be  $N 6 (kT/2)$ . Here the 6 = [3 translational + 3 rotational] degrees of freedom. The  $C_V$  is obtained, as before, by taking the derivative of the internal energy and is indicated in the figure.



The table at right indicates the specific heats of a number of gases. One can see that the equipartition of energy theorem works exceedingly well in many cases.

CO<sub>2</sub> is in fact a linear molecule and should have a much smaller C<sub>V</sub>, however it has some additional vibrational (bending) degrees of freedom {NOT REQUIRED FOR THIS COURSE}. In fact these low lying vibrations are part of the infrared active modes that make CO<sub>2</sub> a greenhouse gas.

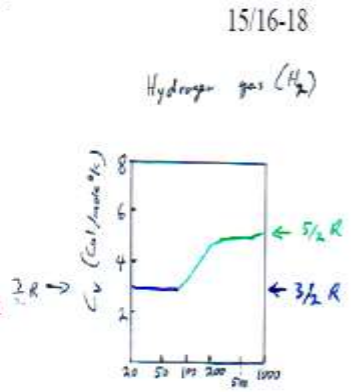
H<sub>2</sub>O similarly has some bending vibrations and is also a greenhouse gas.

Diatomic H<sub>2</sub> gas shows 3 translational degrees of freedom at low temperature because the 2 rotational degrees of freedom “freeze out” due to quantum mechanical effects below about 100K. {This concept is not required for this course but is our first encounter with quantum mechanics. Basically a quantum system has discrete allowed energies and the equipartition principal does not apply. If the average thermal energy, kT, is small compared to the quantum-allowed energy separation then this degree of freedom disappears.}

Let's look at the real world.

gas	C <sub>p</sub>	C <sub>v</sub>	C <sub>p</sub> -C <sub>v</sub>	D <sub>deg</sub> <sup>(100K)</sup>
He	2.3R	1.5R	0.8R	3
Ar	2.5R			
O <sub>2</sub>	3.5R	2.5R	1.0R	5
N <sub>2</sub>	3.5R	2.5R	1.0R	5
H <sub>2</sub>	3.4R			
CO	3.4R			
CO <sub>2</sub>	4.4R	3.4R	1.0R	6.8
H <sub>2</sub> O (100K)	4.4R	3.2R	1.2R	4

metal	C <sub>p</sub>	D <sub>deg</sub>
Al	2.9R	5.95
Cu	3.0R	6.1
Ag	3.0R	6.1
Pb	3.2R	6.4
H <sub>2</sub> O (100K)	4.5R	9.0



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O=C=O !

CO<sub>2</sub> linear !! - should be 5R/2 !!!!

Low energy bending mode vibration

IR active greenhouse gas

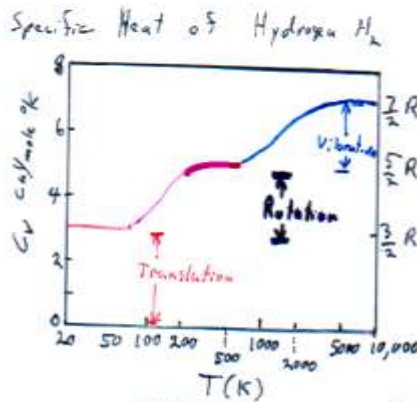
<http://www.lercr.ca/site/projects/ghg.html>

H<sub>2</sub>O similar IR bending - greenhouse gas

<http://www.physics.rutgers.edu/~erulf/H2O-rib.gif>

NOT REQUIRED FOR 203.

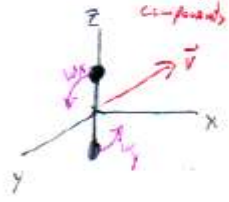
This figure illustrates the temperature dependence of C<sub>V</sub> for diatomic H<sub>2</sub>. The freezing out of the rotational degrees of freedom at low temperature was discussed in the previous slide. However, at very high temperature one should note another step increase in the value of C<sub>V</sub>. This step occurs because two additional degrees of freedom (one kinetic and one potential) associated with the vibration of the H-atoms about the molecular center of mass “freeze out” due to quantum mechanical effects below about 3000K.



← not vibrational part not part of Phys 203

$$E = \frac{1}{2} M (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{1}{2} I (\omega_x^2 + \omega_y^2)$$

for mass of molecule      center of mass velocity components      rotation about CM




$$+ \frac{1}{2} k (s-s_0)^2 + \frac{1}{2} \mu (\dot{s})^2$$

vibration about CM

Note vibrational part is not part of Phys. 203

NOT REQUIRED FOR 203. This figure illustrates the evaluation of  $C_V$  for a monatomic solid. Every atom can be thought of as being bound to a lattice site like a harmonic oscillator. Thus there are three kinetic and three potential degrees of freedom for the vibrations of the atoms about their equilibrium positions. This allows one to calculate the internal energy and specific heat of such a solid and is known as the law of Dulong and Petit.

Simple Solid Ag, Cu, ...



Not required for Physics 203

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \frac{1}{2} k_x x^2 + \frac{1}{2} k_y y^2 + \frac{1}{2} k_z z^2$$

atom  $\bar{E} = 6 \left( \frac{1}{2} kT \right) = 3kT$   $C_V = 3k$

mole  $\bar{E} = 3RT$   $C_V = 3R$

Law of Dulong & Petit

$C_V(\text{Cu}) = 24.6$   
 $C_V(\text{Pb}) = 26.5$

24.9 J/mole

15/16-21