## PHYS-3301

# Lecture 20

#### Nov. 5, 2024

# **Presentations**

#### 3201-501 (11/19)

Akin, Baker, Birdi, Cole, Delashaw, Ellerbrook, Garcia, Land, Matt, McKinley, O'Donnell, Sory, Torres-Rodriguez, Vasquez, Yoon Group A (5): Birdi, Cole, Ellerbrook, O'Donnell, Yoon Group B (5): Land, McKinley, Sory, Torres-Rodriguez, Vasquez Group C (5): Baker, Delashaw, Garcia, Matt

#### 3201-502 (11/26)

Aravind, Calvert, Campbell, Clapshaw, DeBreau, Higgins, Rucker, Saldivar, Simon Group A (3): Calvert, DeBreau, Saldivar Group B (3): Aravind, Bell, Gist, Simon Group C (3): Clapshaw, Higgins, Rucker

Please send me the title of your presentation (20 min) by 11/14

# Chapter. 9 Statistical Mechanics

#### Outline:

- Historical Overview
- The Boltzmann Distribution
- Maxwell Velocity Distribution
- Equipartition Theorem
- Maxwell Speed Distribution
- Classical and Quantum Statistics
- Fermi-Dirac Statistics
- Bose-Einstein Statistics

# 9.2: Maxwell Velocity Distribution

- There are six parameters—the position (x, y, z) and the velocity  $(v_x, v_y, v_z)$ —per molecule to know the position and instantaneous velocity of an ideal gas.
- The velocity components of the molecules are more important than positions, because the energy of a gas should depend only on the velocities.
   Maxwell: what is the distribution of velocities for an idea gas at a given temperature?

# **Gas: Equation of State**

- It is useful to know how the volume, pressure and temperature of the gas of mass m are related
- The equation that interrelates these quantities is called the equation of state
  - These are generally quite complicated
  - If gas is maintained at a low pressure, the equation becomes much easier
  - This type of a low density gas is commonly referred to as an ideal gas

# The Mole

- The amount of gas in a given volume is expressed in terms of the # of moles
- I-mole of any substance: amount of the substance that contains
   Avogadro's # of constituent particles
  - Avogadro's number,  $N_A = 6.022 \times 10^{23}$
  - The constituent particles can be atoms or molecules
- The number of moles can be determined from the mass of the substance: n = m /M
  - M : the molar mass of the substance
  - *m* : the mass of the sample
  - *n* : the number of moles

# **Gas Laws**

- When a gas is kept at a constant temperature, its pressure is inversely proportional to its volume (Boyle's law)
- When a gas is kept at a constant pressure, its volume is directly proportional to its temperature (Charles and Gay-Lussac's law)

# **Ideal Gas Law**

• The equation of state for an ideal gas combines and summarizes the other gas law

## PV = nRT

- This is known as the ideal gas law
- R is a constant, called the Universal Gas Constant
   R = 8.314 J/mol · K = 0.08214 L · atm/mol · K
- From this, you can determine that I mole of any gas at atmospheric pressure and at 0° C is 22.4 L

# **Ideal Gas Law**

- The **ideal gas law** is often expressed in terms of the total number of molecules, *N*, present in the sample
- $PV = nRT = (N/N_A) RT = Nk_BT$ 
  - $k_{\rm B}$  = Boltzmann's constant [ $k_{\rm B}$  = 1.38 x 10<sup>-23</sup> J/K]
- Common to call P, V, and T the thermodynamic variables of an ideal gas

### 9.2: Maxwell Velocity Distribution

- There are six parameters—the position (x, y, z) and the velocity (v<sub>x</sub>, v<sub>y</sub>, v<sub>z</sub>)—per molecule to know the position and instantaneous velocity of an ideal gas.
- The velocity components of the molecules are more important than positions, because the energy of a gas should depend only on the velocities.
   Maxwell: what is the distribution of velocities for an idea gas at a given temperature?
- Define a velocity distribution function  $f(\vec{v})$  $f(\vec{v}) d^3 \vec{v}$  = the probability of finding a particle with velocity

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where d^3 \vec{v} = dv_x dv_y dv_z
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We can think of f(v) as playing a role analogous to the probability density  $|\Psi|^2$ 

### Maxwell Velocity Distribution

- Maxwell proved that the probability distribution function is proportional to  $\exp\left(-\frac{1}{2}m\sqrt{2}/kT\right)$ Therefore, we may write  $f(\vec{v}) d^3\vec{v} = C \exp\left(-\frac{1}{2}\beta mv^2\right) d^3\vec{v}$ . where *C* is a proportionality factor and  $\beta \equiv (kT)^{-1}$ .
- Because  $v^2 = v_x^2 + v_y^2 + v_z^2$ ,  $f(\vec{v}) d^3 \vec{v} = C \exp(-\frac{1}{2}\beta m v_x^2 - \frac{1}{2}\beta m v_y^2 - \frac{1}{2}\beta m v_z^2) d^3 \vec{v}$
- Rewrite this as the product of three factors.  $g(v_x) dv_x \equiv C' \exp(-\frac{1}{2}\beta m v_x^2) dv_x$   $g(v_y) dv_y \equiv C' \exp(-\frac{1}{2}\beta m v_y^2) dv_y$   $g(v_z) dv_z \equiv C' \exp(-\frac{1}{2}\beta m v_z^2) dv_z$ These eq. give us the distribution of the 3 velocity components  $g(v_z) dv_z \equiv C' \exp(-\frac{1}{2}\beta m v_z^2) dv_z$

#### m: molecular mass, v = molecular speed, k = Boltzmann's constant, T = absolute temperature

#### Maxwell Velocity Distribution

 g(v<sub>x</sub>) dv<sub>x</sub> is the probability that the x component of a gas molecule's velocity lies between v<sub>x</sub> and v<sub>x</sub> + dv<sub>x</sub>.



### Maxwell Velocity Distribution

The mean value of v <sub>x</sub> <sup>2</sup>
$\overline{v_x^2} = C' \int_{-\infty}^{\infty} v_x^2 \exp\left(-\frac{1}{2}\beta m v_x^2\right) dv_x$
$=2C'\int_0^\infty v_x^2 \exp\left(-\frac{1}{2}\beta m v_x^2\right) dv_x$
$\overline{\nu_x^2} = \left(\frac{\beta m}{2\pi}\right)^{1/2} \frac{\sqrt{\pi}}{2} \left(\frac{2}{\beta m}\right)^{3/2} = \frac{1}{\beta m} = \frac{kT}{m}$
$g(0)$ The Maxwell velocity distribution as a function of one velocity dimension $v_x$
$\bigcup_{0.5g(0)} \bigcup_{v_x} = 0$ The velocity component distributes around the peak at $v_x = 0$
$\sqrt{\frac{1}{\beta m}} = \sqrt{\frac{kT}{m}} \qquad \text{at}  v_x = \sqrt{1/\beta m} = \sqrt{kT/m},  g(v_x) = g(0)e^{-1/2}$

### Maxwell Velocity Distribution

- Of course there is nothing special about *x*-direction, so the results for the *x*, *y*, and *z* velocity components are identical.
- The mean translational kinetic energy of a molecule:

$$\overline{K} = \overline{\frac{1}{2}mv^2} = \frac{1}{2}m(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = \frac{1}{2}m\left(\frac{3kT}{m}\right) = \frac{3}{2}kT$$

- We have just confirmed one of the principal results of the kinetic theory!!!
- Purely statistical considerations is good evidence of the validity of this statistical approach to thermodynamics.

# 9.3: Equipartition Theorem

- In a monoatomic gas such as He or Ar, virtually all of the gas's energy is in this form: 3 x (1/2 kT)
- But think of oxygen (O<sub>2</sub>) molecule as two oxygen atom connected by a massless rod, then this can also have rotational KE!
  - How much rotational energy is there, and how is it related to temperature?

#### Equipartition Theorem:

- In equilibrium a mean energy of ½ kT per molecule is associated with each independent quadratic term in the molecule's energy.
- Each independent phase space coordinate:

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→ degree of freedom
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Coordinate, velocity component, angular velocity component, etc.

# **Equipartition Theorem**

e.g. in a monatomic ideal gas (He), each molecule has

$$K = \frac{1}{2}mv^{2} = \frac{1}{2}m(v_{x}^{2} + v_{y}^{2} + v_{z}^{2})$$

- There are 3 independent phase space coordinates (v<sub>x</sub>,v<sub>y</sub>,v<sub>z</sub>); 3 degrees of freedom.
- Mean kinetic energy is  $3(\frac{1}{2}kT) = \frac{3}{2}kT$  per molecule.
- In a gas of *N* helium molecules, the total internal energy is

$$U = N\overline{E} = \frac{3}{2}NkT$$

- The heat capacity at constant volume is  $C_V = \frac{3}{2}Nk$
- For the heat capacity for 1 mole,  $C_V = \frac{3}{2}N_A k = \frac{3}{2}R = 12.5 \text{J/K}$
- The ideal gas constant *R* = 8.31 J/K.

### The Rigid Rotator Model

• For diatomic gases, consider the rigid rotator model.



- The molecule rotates about either the *x* or *y* axis.
   The corresponding rotational energies are <sup>1</sup>/<sub>2</sub> *I*<sub>x</sub> <sup>2</sup>/<sub>x</sub> and <sup>1</sup>/<sub>2</sub> *I*<sub>y</sub> <sup>2</sup>/<sub>y</sub>
- There are five degrees of freedom (three translational and two rotational).

## Molar Heat Capacity

 $C_{V} = \frac{3}{2} N_{A} k = \frac{3}{2} R = 12.5 \text{ J/K}$ 

- The heat capacities of diatomic gases are temperature dependent, indicating that the different degrees of freedom are "turned on" at different temperatures.
- Example of H<sub>2</sub>



#### **Equipartition Theorem**

#### Now, why don't we include rotations about the z-axis?

- In the quantum theory of the rigid rotator the allowed energy levels are  $E = \frac{L^2}{2I} = \frac{\hbar^2 \ell(\ell+1)}{2I}$
- From previous chapter, the mass of an atom is confined to a nucleus that magnitude is smaller than the whole atom.
  - $\longrightarrow$   $I_z$  is smaller than  $I_x$  and  $I_y$ .
  - $\longrightarrow$  Only rotations about x and y are allowed.
- In some circumstances it is better to think of atoms connected to each other by a massless spring.
- The vibrational kinetic energy is  $\frac{1}{2}m(dr/dt)^2$
- There are seven degrees of freedom (three translational, two otational, and two vibrational).