PHY 121 Mechanics *S.G. Rajeev*

Lecture 25

Kinetic Theory

• Thermodynamics was originally conceived as an independent branch of physics, with its own laws. But about a hundred years ago, it was seen that the laws of thermodynamics can be derived from those of mechanics.

• The link between the two is *Statistical Mechanics*, the study of random motion.

• The simplest phase of matter to study is a gas: the molecules are far apart so they can be treated as free particles. This is the *kinetic theory* of gases.

The Ideal Gas

• The thermodynamic state of a quantity of gas is determined by its *pressure* p, *volume* V and *temperature* T. But these are not independent of each other.

• *At constant temperature, pressure is inversely proportional to volume.*

• *At constant volume, pressure is proprtional to temperature.*

• *At fixed volume and temperature, the pressure is proportional to the amount of gas.*

• There are small deviations from these laws. If we ignore them we get a theoretical construct, the *Ideal gas*.

The Law of Ideal Gases

• The phrase 'amount of gas' above does not mean the mass of the gas: it is rather the *number of molecules*. Chemists had a unit of the number of molecules: the *mole*.

• The modern definition is: *one mole is the number of molecules in* $12\,g$ *of* $C-12$.

• The law of ideal gases is

$$pV = nRT$$

where n is the number of moles of the gas and R is a constant.

• R is called the *gas constant*; it is the same for all gases, $R = 8.31 J/(mol\ K)$.

Avogadro's Number

• The number of molecules present in one mole is *Avogadro's number*. Now we know that it is

$$N_A = 6.02 \times 10^{23}$$

A big number.

• A digression: how do you 'count' such a large number of molecules?

• The key was to understand a phenomenon called Brownian motion. It was seen that particles in suspension in a liquid moved about randomly: they behaved like a gas. They were made of a huge number of molecules so they were visible to optical microscopes.

• You could measure their average velocity by painstaking measurements. Their mass can be determined by chemical methods. The temperature is known. Using the relation between temperature and average kinetic energy (see below) we can determine Boltzmann's constant. Then knowing the gas constant we can find N_A .

The Meaning of Temperature

• We will now see that *the average energy of a molecule is proportional to temperature.*

• This is the mechanical meaning of temperature: it is just a measure of the average energy of the random motion of molecules.

• Think of a gas enclosed in a cubical container of side L . Kinetic theory supposes that the molecules of the gas are moving in all possible directions.

• Also, all collisions of the molecules with each other and with the wall are assumed to be elastic.

Molecular Origin of Pressure

• When a molecule hits the wall (say the wall in the x -direction) with a velocity $\mathbf{v}$, it bounces back with v_x reversed in sign. The amount of momentum that the wall imparted to the molecules is thus $2mv_x$ where m is the mass of the molecule.

• The pressure of the gas is just the force per unit area that the walls exert to keep the gas confined. If we know the number of collisions per unit area per unit time we can find the pressure.

• Assume that there are no collisions between molecules at first. The time between collisions Δt at

a given wall is $\frac{2L}{v_x}$: the time it takes to go to the opposite wall and bounce back. Thus the change of momentum per unit time (i.e., force exerted by the wall) of this molecule is

$$\frac{2mv_x}{\frac{2L}{v_x}} = \frac{mv_x^2}{L}.$$

• We now multiply by the number of molecules nN_A and divide by the area to get the pressure. Also, over many collisions we can replace v_x^2 by its average value $\bar{v^2}_x$:

$$p = \frac{nN_A m}{L^3}\bar{v^2}_x$$

• Now the averages in the different directions are all equal: $\bar{v^2}_x =$

$\bar{v^2}^2_y = \bar{v^2}_z$. Thus

$$\bar{v}_x^2 = \frac{1}{3}\bar{\mathbf{v^2}}, \quad pV = nN_A\frac{1}{3}m\bar{\mathbf{v^2}}$$

•Comparing with the law of ideal gases we get

$$RT = N_A\frac{1}{3}m\bar{\mathbf{v^2}}$$

•The ratio $\frac{R}{N_A} = k_B$ is a constant now known as *Boltzmann's constant*.

•We see that temperature is proportional to average energy:

$$k_BT = \frac{2}{3}\left(\frac{1}{2}m\bar{\mathbf{v}^2}\right).$$