Now if there are N molecules in the box, then

$$\bar{P}V = mv_{1x}^2 + mv_{2x}^2 + mv_{3x}^2 + \dots + mv_{Nx}^2$$
(27)

Or multiplying and dividing the right side by N, we get:

$$\bar{P}V = N \times \frac{1}{N} \sum_{i=1}^{N} m v_{ix}^2 = Nm \times \bar{v_x}^2$$
 (28)

We can drop the bar over the pressure because pressure by definition is an average quantity. Further, the IGL holds that PV = NkT, so we find  $kT = mv_x^2$  or

$$\frac{1}{2}kT = \frac{1}{2}m\bar{v_x^2} \tag{29}$$

Translational symmetry in the gas means that we can drop the x-subscript in  $v_x$  and realize that the above relation holds for each of the three cardinal directions x, y, and z. We then have an expression of the Equipartition Theorem:

The average translational kinetic energy per particle per coordinate direction is  $\frac{1}{2}kT$ .

So, for a gas with only translational degrees of freedom in three dimensions, the average kinetic energy per molecule is (3/2)kT. This is an extremely important result that we will use often.

Note that, at room temperature,

$$kT \approx 4.4 \times 10^{-21} J \approx \frac{1}{40} eV \tag{30}$$

. This is also an important rough number to keep in mind. Its the typical room temperature energy per molecule. How does it compare to binding energies? Well, typical intermolecular binding energies are on the order of 100's of eV's, so there's little chance of much molecular dissociation at room temperature.

The Equipartition Theorem can be used to estimate interesting properties like the average speed of a molecule in the gas. The Equipartition Theorem provides the quantity  $\bar{v}^2$  - the average of the square of the speed which we can tale the square root of to find the root-mean-square or RMS speed:  $\sqrt{\bar{v}^2}$ . Now this is not he same as the average speed  $\bar{v}$ , but it is often more useful and certainly much easier to compute:

$$v_{RMS} = \sqrt{\frac{3kT}{m}} \tag{31}$$

RMS speeds for molecules in this room (at room temperature) are on the order of 100's of m/s.

## 4.1 Getting Started on Problem 1.22

Draw yourself a box full of gas (air). Now draw a small spot on one wall of the box. This spot will eventually be our hole through which gas escapes, but for now just imagine it to be an area in which we want to count particle hits. How many particles strike that area A in a time  $\Delta t$ ? Recall from 1.9 that the pressure exerted by a single particle on an area A is given by

$$P_{\text{single particle}} = \frac{-m\frac{\Delta \bar{v}_x}{\Delta t}}{A} \tag{32}$$

and  $\Delta \bar{v_x} = -2\bar{v_x}$ . So, the pressure exerted by N particles on the area A is

$$P_{\text{N particles}} = N\left(\frac{-m}{A\Delta t}(-2\bar{v_x})\right) = \frac{2Nm\bar{v_x}}{A\Delta t}.$$
(33)

You should be able to take it from here.

## 4.2 Equipartition of Energy: Beyond Translational Freedom

At this point, we understand that each translational degree of freedom contributes  $\frac{1}{2}kT$  to the total kinetic energy of a gas. So, a monatomic gas consisting of N atoms in 3-dimensions has a total kinetic energy of  $\frac{3}{2}NkT$ . We will see in a later section that this equipartition applies to all so-called quadratic degrees of freedom. A quadratic degree of freedom is any energy term that appears quadratically in the total energy. Examples include rotational degrees of freedom characterized by terms like  $\frac{1}{2}I\omega^2$ , or vibrational degrees of freedom that appear quadratically in the potential energy of a molecule (like  $\frac{1}{2}kx^2$ ). The Equipartition Theorem, derived in the context of stat. mech., states that for each of the quadratic degrees of freedom present in a gas, there is a corresponding contribution to the total energy of  $\frac{1}{2}kT$ .

For N particles each with f degrees of freedom, the total thermal energy is

$$U_{thermal} = \frac{1}{2} N f k T \tag{34}$$

Note that  $U_{thermal} \neq U_{total}$  The latter contains terms like rest energy, bond energy, etc. that do not contribute to the thermal energy.

How do we count degrees of freedom?

- Translational Modes: For a monatomic gas, the answer is easy there are three cardinal directions (x,y,z), and only translational modes available, so f = 3.
- Rotational Modes: For a simple molecular gas like  $O_2$  or  $N_2$ , we allow the molecule to rotate around each of the three axes, so you would think that we would add an additional 3 to f. However, the momentum of inertia about the z-axis is small (most of the mass is on the rotation axis, so  $mR^2 \approx 0$ , and this rotational mode is forbidden quantum mechanically, so we add an additional 2 to f. f = 3 (translational) +2 (rotational) = 5 for a diatomic gas with rotational modes expressed.
- Vibrational Modes: When a simple diatom like  $N_2$  or  $O_2$  vibrates, two terms show up in the total thermal energy (1) Kinetic and (2) potential. So, the net addition to f is 2.

In principle, then, a diatomic gas might have a total thermal energy of  $U_{thermal} = \frac{7}{2}NkT$ . However, at most temperatures either vibrational or both vibrational and rotational modes are "frozen out," that is they are inaccessible - there is not enough thermal energy to excite rotational or vibrational modes in the molecules. At room temperature f = 5 - rotational modes are accessible, but vibrational modes are frozen out. The thermal energy of a diatomic gas near room temperature is then

$$U_{\text{diatomic gas}} = \frac{5}{2}NkT.$$
(35)

Equipartition in a Solid In a solid, each atom vibrates in 3 perpendicular directions. There is no translational or rotational modes allowed. Therefore, f = 6 and the total thermal energy of the solid consisting of N atoms is

$$U_{\text{solid}} = 3NkT.$$
(36)

## 5 Energy, Heat, and Work

We want to relate the internal energy change experienced by a substance as a result of the work done on the substance and the heat added to it. Note that both heat and work are forms of energy.

- Work is the transfer of energy into or out of a system. Work is associated with an *agent* it is never spontaneous as can be the transfer of energy via heat.
- heat is teh spontaneous flow of energy from one object to another caused by a difference in temperature between the two objects.

Define the internal thermal energy of a substance to be U. Let Q and W represent the heat added (Q) and the work (W) done on the system. We will follow the slightly unorthodox convention used in the book:

- $Q > 0 \rightarrow$  Heat added to the substance
- $Q < 0 \rightarrow$  Heat removed from substance
- $W > 0 \rightarrow$  Work done on substance
- $W < 0 \rightarrow$  work done by substance on environment

With these conventions, we can write energy conservation in the form:

$$\Delta U = Q + W \tag{37}$$

This is a simple, intuitive statement of conservation of energy - the internal energy of a substance changes in response to the heat added and to the work done on the substance. This is also the FIRST LAW OF THERMODYNAMICS.