

## Particles in a Box

Uri Lachish, Rehovoth  
urila@zahav.net.il

### Particle in a box

#### Elastic Collisions Between Gas Particles and a Wall

Consider the elastic collision between two bodies of masses  $m$  and  $M$  moving along a straight line <sup>1,2</sup>. The velocities of these bodies before the collision are  $v_m$  and  $v_M$  respectively, and after the collision they are  $v_{m'}$  and  $v_{M'}$ . The law of conservation of linear momentum states that:

$$mv_m + Mv_M = mv_{m'} + Mv_{M'} \quad (1)$$

and the law of conservation of energy states that:

$$mv_m^2 + Mv_M^2 = mv_{m'}^2 + Mv_{M'}^2 \quad (2)$$

From these two laws it is found that:

$$v_m - v_M = v_{M'} - v_{m'} \quad (3)$$

Namely, the magnitude of the relative velocity is conserved during the collision, while the direction is reversed. It is also found from eqns. (1) and (2) that:

$$(1 + m/M) v_{M'} - (1 - m/M) v_M = (m/M) 2v_m \quad (4)$$

$$(1 + m/M) v_{m'} - (1 - m/M) v_m = (m/M) 2v_M \quad (5)$$

Now, assume that  $m$  is a microscopic body while  $M$  is macroscopic. Thus, in the limit  $m/M = 0$ , it is found that:

$$v_{M'} = v_M \quad (6)$$

$$v_{m'} = -(v_m - 2v_M) \quad (7)$$

As should be expected, the velocity of the macroscopic body is not affected by the collision, while the magnitude of the velocity of the microscopic body is changed by the amount  $2v_M$  and its direction is

reversed. If the velocity of the macroscopic body is much slower than that of the microscopic one,  $v_M \ll v_m$ , then the amount of kinetic energy ( $\Delta Ek$ ) which is transferred upon a collision will be:

$$\Delta Ek = 2mv_m v_M \quad (8)$$

This amount is proportional to the velocity of the macroscopic body and is independent of its mass. Energy is transferred from the microscopic body to the macroscopic one when they are moving in the same direction, and it is transferred in the reverse direction when they are moving towards each other.

These results will now be applied to analyzing the properties of a gas confined in a box. For simplicity, it is assumed that the gas is monoatomic (thus it has no internal degrees of freedom) and that its particles do not interact with each other.

### **The gas pressure**

The calculation of the pressure of the gas on the walls is well known and will be repeated briefly.

The atoms which may collide with a wall surface of area  $A$  in a time interval  $\Delta t$ , are contained in the volume specified by base area  $A$  and height  $v\Delta t$ , where  $v$  is their average velocity. Since they are free to move in all directions, only 1/6 of them will actually strike the wall. Therefore, the average number of collisions with the wall during the interval  $\Delta t$  is:

$$(1/6)(N/V)Av\Delta t \quad (9)$$

$N$  is the number of atoms in the box and  $V$  is its volume. For each collision a momentum  $2mv$  is given to the wall and, therefore, the overall momentum transferred to the wall during  $\Delta t$  is:

$$F\Delta t = (1/3) (N/V) Av^2\Delta t \quad (10)$$

So, it is found that the pressure of the gas on the wall is:

$$p = F/A = (1/3) (N/V) v^2 \quad (11)$$

The state equation of an ideal gas  $pV = NkT$ , may be derived from eqn. (11) by using the thermodynamic relationship  $\varepsilon_k = (1/2)kT$ , where  $\varepsilon_k$  is the average kinetic energy per degree of freedom of the gas particle. An exact calculation which takes the real distribution of the velocities into account, yields the same results.

If the wall  $A$  is moving with velocity  $v_M$ , then every atom that collides with its surface, will transfer to it the kinetic energy  $2mvv_M$  (eqn. (8)). The overall energy which is transferred to the wall during  $\Delta t$  is (by eqn. (9) and eqn. (11)):

$$(1/3) (N/V) mv^2 Av_M \Delta t = pdV \quad (12)$$

where  $dV = Av_M \Delta t$  is the change in the volume of the box. (A similar calculation in three dimensions is found in ref. (1).)

It is seen by this calculation that the process of elastic collisions, between the atoms of the gas and the moving wall, is the mechanism by which the thermal kinetic energy of the atoms is transformed into macroscopic mechanical work. The cumulative effect of many collisions causes the pushing of the wall, but during each single collision the transfer of energy is determined only by the wall instantaneous movement. These conclusions are results of the laws of conservation of momentum and energy.

### **Adiabatic Expansion of a Gas**

When a gas is heated (or cooled) through a wall, atoms which strike its surface will leave it with a higher (or lower) average velocity. In this case the velocity of the atom after the collision does not depend wholly on its velocity before the collision, in contrast to the process of elastic collisions, where the relationship between these velocities is unique (eqn. (7)). Therefore, elastic collisions cannot transfer heat between the gas and the walls, and if a process consists of only such collisions, it will be adiabatic.

The equations that describe adiabatic expansion of a gas are derived as follows:

It is seen from eqn. (9) that the probability that a single atom will collide with the wall during the time interval  $\Delta t$  is  $(1/6)(1/V)Av\Delta t$ . For each such a collision the atom loses (or gains) the velocity  $2v_M$  (eqn. (1)), so the change of velocity,  $dv$ , during  $\Delta t$  is:

$$dv = -(v/3)(v_M A \Delta t / V) = -(v/3)(dV/V) \quad (13)$$

By integrating this equation, it is found that:

$$v/v_0 = (V_0/V)^{1/3} \quad (14)$$

or by the use of eqn. (11):

$$p/p_0 = (V_0/V)^{5/3} \quad (15)$$

This is the equation of adiabatic expansion of a monoatomic gas. By use of the ideal gas equation,  $pV = NkT$ , it can be written also in the form:  $T/T_0 = (V_0/V)^{2/3}$ , or,  $p/p_0 = (T/T_0)^{5/2}$ . The calculation can be extended to molecular gases by taking into account transfer of energy between the translational and internal degrees of freedom of the molecules.

### Quantum expansion

The quantum mechanical calculation of adiabatic expansion of a quantum gas is direct <sup>3</sup>, and is based on the "adiabatic theorem" <sup>4</sup>, which states that under certain conditions a slow and continuous change in the parameters of a system causes a similar continuous change in the wave functions and energy levels, and it does not induce transitions between different states.

In order to demonstrate the similarity between the classical and quantum mechanical cases, the adiabatic theorem will be verified for a one dimensional infinite square well potential <sup>5</sup>.

The ground state of a particle in an infinite square potential, which extends from  $x = 0$  to  $x = L$ , can be written as combination of two travelling waves in opposite directions:

$$\psi(x, t) = (i/(2L)^{1/2})(e^{-i(kx + wt)} - e^{i(kx - wt)}) \quad (16)$$

where  $k = \pi/L$  and  $w = \hbar p^2/2mL^2$ . Now, if the boundary at  $x = L$  is moving slowly with velocity  $v_M$ , then when the waves are reflected from it, their wave number (and frequency) will be shifted according to the Doppler effect:

$$k' = k (1 - 2v_M/c) \quad (17)$$

where  $c = w/k$  is the velocity of the waves.

During the time interval  $\Delta t$  each wave is reflected  $c\Delta t/2L$  times by the moving boundary, so the overall shift of the wave number will be:

$$\Delta k = -(kv_M\Delta t/L) = -\pi\Delta L/L^2 \quad (18)$$

If the square well expands from  $L_1$  to  $L_2$ , then by eqn. (18) the wave number will be shifted from  $\pi/L_1$  to  $\pi/L_2$ . Therefore, the ground state function at  $L_1$ , will be transformed into the ground state function at  $L_2$ . (By similar calculation, this result is valid also for the higher states.) In this case the condition for adiabatic process is that in a single reflection the

Doppler shift of the wavenumber (or frequency) will be small compared to the difference between successive states.

## References

1. Sears. F. W., and Salinger, G. L., "Thermodynamics. Kinetic Theory and Statistical Thermodynamics", 3rd Ed., Addison-Wesley, Reading, Massachusetts, 1975, p. 262.
2. Lachish. U., "Derivation of Some Basic Properties of Ideal Gases and Solutions from Processes of Elastic Collisions", J. Chem. Ed., vol. 55 (6), p. 369-371 (1978)
3. Tolman. R. C., "The Principles of Statistical Mechanics", Oxford University Press, New York. 1938, p. 386.
4. Shiff, L. I., "Quantum Mechanic", 3rd Ed., McGraw-Hill, New York, 1968, p. 289.
5. Born, M., "Atomic Physics", 7th Ed., Blackie. London. 1965, pp. 12-24.

On the net: January 2021

[Particles in a box](#)

DOI: 10.13140/RG.2.2.18559.12960

[The Sun and the Moon a Riddle in the Sky](#)

[Blue Marble the Uniform Earth Image](#)

*Think that this page is correct? Please pass it on to others.*