U.P.B. Sci. Bull., Series D, Vol. 76, Iss. 4, 2014 ISSN 1454-2358

SOME KINETIC-MOLECULAR CONSIDERATIONS ON GAS-PISTON INTERACTION AND THEIR IMPLICATIONS AT MACROSCOPIC SCALE

Arpad TÖRÖK[1], Stoian PETRESCU[2], Gheorghe POPESCU[3], Michel FEIDT[4]

The present study aims to offer a microscopic description of the behavioral pattern of a gas system interacting with a mobile wall based on Clausius model and on its ensuing models. Starting from this analysis, the first part of this study comes to validate the equations published in the early works in Finite Speed Thermodynamics, while the second part deals with the interaction between the gas system and a mobile wall set off at a certain angle to its moving trajectory. The study conclusions are applies to the analysis of the interaction between gas or vapor systems and the mobile units of rotating devices.

Keywords: Clausius model, gas-piston interaction, bent piston

1. Introduction

Referring to the kinetic-molecular theory or to quantum mechanics has always been a way to provide convincing arguments in the hypothesis validation for macroscopic behavior of systems or in the interpretation of experimental results. A similar approach has been undertaken since the early stage of formulating the principles of Thermodynamics by Clausius who drew up the first coherent, well structured, kinetic-molecular model for the gas systems in thermodynamic equilibrium.

The elementary displacement (or deformation) of the mobile frontier of the gas system's causes an elementary variation dV of the volume of the system, reflected in the value of the elementary mechanical work $\delta L = p \cdot dV$ carried out by the system upon the environment, or the other way round. For gases, this transfer of mechanical energy is always accompanied by thermal interactions (system temperature variation and/or heat exchange with its environment) according to the first principle of thermodynamics. For reversible evolutions:

$$dU_{rev} = \delta Q_{rev} - \delta L_{rev} = \delta Q_{rev} - p \cdot dV \tag{1}$$

---

[1] PhD Student, University POLITEHNICA of Bucharest, Department of Engineering Thermodynamics, 313 Splaiul Independentei, 060042 Bucharest, Romania, e-mail arpi_torok@yahoo.com

[2] Prof., University POLITEHNICA of Bucharest, Department of Engineering Thermodynamics, Romania

[3] Prof., University POLITEHNICA of Bucharest, Department of Engineering Thermodynamics, Romania

[4] Prof., L.E.M.T.A., U.R.A. C.N.R.S. 7563, Universite de Lorainne Nancy, 12 avenue de la Foret de Haye, 54516 Vandeuvre-les-Nancy, France

where $\delta L_{rev}= p\cdot dV$ stands for the work carried out/ consumed in a reversible conversion.

But, since real processes are irreversible, this equation, as well as the whole Classical Thermodynamics, is applicable within a limited framework of action for thermodynamic processes. As it studies processes with a development speed close to zero, Reversible Thermodynamics does not make any references to the transport speed for mass, energy, and entropy, very important aspects for thermo-technicians. There are two approaches that can be used to obtain this type of data ([3], [4]):

- by studying of the microscopic behavior of particles and applying methods of statistical mediation
- by studying the macroscopic behavior of the system while taking into consideration the pairs of forces and thermodynamic flows as requested by the Irreversible Phenomenological Thermodynamics.

For the study of the gas-piston interaction in thermodynamic processes with w as the finite speed of the system, Stoicescu and Petrescu proposed 4 models ([1], [2], [3], [4]), two of which are of kinetic nature, while the other two are of a phenomenological type, and obtained the following for the work carried out/ consumed in an irreversible conversion:

a) in the elementary kinetic-molecular model suggested by Sommerfeld [7] and Macke[8], L. Stoicescu and S. Petrescu [1, 2] found, in 1964, **the first expression for the Irreversible Mechanical Work with finite speed**:

$$\delta L_{ir} = p_{m,i} \cdot \left[1 \pm \frac{aw}{c} + \frac{bw^2}{c^2} \pm \ldots \right] \cdot dV \,, \tag{2}$$

where $p_{m,i}$ labels the instantaneous average pressure inside the system, a=2, b=5

b) in the advanced kinetic-molecular model, built on Maxwell-Boltzmann's distribution and on accepting the finite relaxation time, in 1971, S. Petrescu [9] found, **the second expression for the Irreversible Mechanical Work with finite speed** :

$$\delta L_{ir} = p_{m,i} \cdot \left[1 \pm \frac{aw}{c} + \frac{bw^2}{c^2} \pm \frac{dw^3}{c^3} \pm \ldots \right] \cdot dV \tag{3}$$

where a = 2,764; b = 3; d = 1,283

c) in the phenomenological model founded on the transmission of the pressure waves at the speed of sound, L. Stoicescu and S. Petrescu demonstrated in 1964, the expression [1,2] :

$$\delta L_{ir} = p_{m,i} \cdot \left[1 \pm \frac{aw}{c} \right] \cdot dV = p_{m,i} \cdot \left[1 \pm k \cdot M \right] \cdot dV \tag{4}$$

where $a = \sqrt{3k}$, k =C_p/C_v is the adiabatic exponent, $c = \sqrt{3RT_{m,i}}$ is the average molecular speed, $T_{m,i}$ is the average instantaneous temperature, and M is the Mach number corresponding to the flow thrmodynamic conditions. This expression is very important because it correlates for the first time, the *a* parameter with the adiabatic exponent *k*, making possible to calculate it not only for monatomic gas (where $k = 1.66$), but for the diatomic ($k = 1.4$) and polyatomic ($k = 1.3$) gas also.

d) in the model based on the **Irreversible Linear Phenomenological Thermodynamics** [10, 11], [12] found in 1969, the fourth expression for **the Irreversible Mechanical Work with finite speed** :

$$\delta L_{ir} = p_{m,i} \cdot (1 \pm K_1 \cdot w) \cdot dV \tag{5}$$

where $K_1 = \frac{a}{c_m} = \frac{a}{\sqrt{3RT_{m.i}}}$ is a constant influenced by the properties and the average temperature of the gas, but which can only be calculated based on experiments or based by a structural theory [that is, the equation (2), (3) or (4)].

In the present study we are going to analyze the gas-piston interaction in thermodynamic processes with the finite speed *w* of the piston relying on the Clausius' kinetic-molecular model. This model was used by Clausius to determine the analytical expressions of temperature, internal energy, and pressure for a system of prefect gases in equilibrium, depending on the total number and the speed of the inside molecules. Thus, our approach is using the same type of systems but, because of the piston's finite speed, the thermodynamic processes taking place during this interaction are not in equilibrium. Therefore, we will take into consideration the finite speed of the piston and the finite time to be sent the changes of intensive parameters: the state variables we are going to operate with are no longer global (defined for the system as a whole), but local, defined for limited areas within the system and for which the maximal differences in values taken from different spots of the area are much lower than the variables' value itself. The systems in non-equilibrium can be characterized by a certain distribution of all the state parameters, at a certain moment (a currently field for that parameter). In each micro-area of this kind, at a certain moment in time, local parameters are uniformly distributed and, in these circumstances, the equations of Reversible Thermodynamics can be applied to the variables. The entire system can be described by outlining a system of averages for the momentary (instantaneous) state parameters, calculated from the system as a whole, at a certain point in time, on the particular local parameters. The instantaneous state parameters are not arbitrary calculating quantities since they have a precise physical relevance: if in the instant when these average values are measured there is a sudden break in the thermodynamic force causing the loss of equilibrium, then, after a period of relaxation, a state of thermodynamic equilibrium, defined by the very same instantaneous average parameters, will be restored in the system ([3], [4], [5]).

2. The gas-piston interaction in Clausius' kinetic-molecular model

This kinetic-molecular model [3] applies to perfect gases. For real gases, the conclusions drawn based on these abstract considerations are closer to experimental results when the gas state's deviation from the curve of saturated vapors (warm, rarefied gases) is more pronounced. The remarks below are valid for monatomic gases and for the translation movement of polyatomic molecules.

We will consider a cylinder with volume V where there is a total number N of monatomic molecules of a perfect gas, with various speed values from a minimum speed threshold C_1 and a maximum one C_N. We assume that all molecules can have, on a continuous scale, any speed value within this range. From the set of real numbers, we will select a range from a minimum value smaller than C_1 and a maximum value larger than C_N where we can separate a number n of equal intervals with an individual width dC. We will label C_i, (i=1, 2, …, n) the average value of speed inside the interval $[(i-1)\cdot dC, i\cdot dC)$ and N_i the sum of molecules with a speed value inside the above mentioned interval. As a direct consequence of the elementary disorder principle, the extreme values of the speed vectors C_i have a uniform distribution on a sphere with the radius C_i (Fig. 1) in a three-dimensional orthogonal space. The total number $N_{i,\theta}$ of molecules with the speed C_i and set at the angle θ from axis X-X' of the piston (in any plane containing the axis, as θ can endorse values between 0 and π) was calculated by Clausius as:

$$dN_{i,\theta} = \frac{N_i}{2} \sin\theta \cdot d\theta \qquad (6)$$

Because of the elementary chaos, the molecules inside the cylinder had a homogenous density defined by the following equation:

$$\rho_\theta = dN_{i,\theta} / V = \frac{N_i}{2V} \sin\theta \cdot d\theta \qquad (7)$$

If after collision a certain number of molecules changes its trajectory and leaves the cluster, they are immediately replaced by an equal number of molecules migrated from other clusters.

Fig. 2. is a representation of a distribution on θ directions of the molecules at speed C_i, both for expansion and compression. If in a time unit the piston covers the distance w, and the molecules, a distance C_i, the distance between the piston and each molecule, measured on X-X' axis, will vary in the same time unit with $C_i \cdot \cos\theta \pm w$.

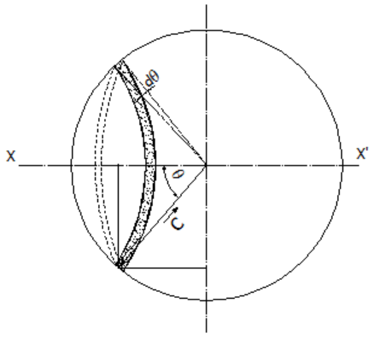
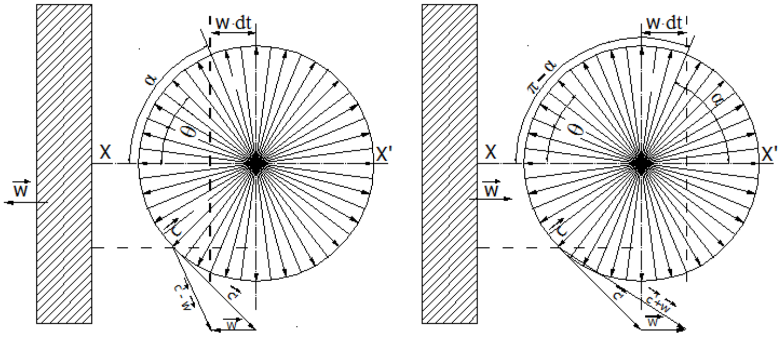


Fig. 1. The sphere with the extreme values of the speed vectors



(A) (B)

Fig. 2. The kinetic-molecular model of expansion (A) and compression (B) for the processes where the piston has a finite speed

The + sign pertains to a piston movement in the direction of the compression, while the – sign will indicate a movement in the direction of the expansion. In Clausius' model, the gas pressure is caused by the impulse fluctuation of the molecules colliding against an area unit in a restrained timeframe. For a unique molecule, he calculated that the impulse fluctuation is equal to $2m \cdot C_i \cdot \cos\theta$, where m is the mass of the molecule. If the surface against which the molecules collide is moving at a speed w, as it happens with the piston, the impulse fluctuation of one molecule will equal $2m(C_i \cdot \cos\theta + w)$ if compression happens, and $2m(C_i \cdot \cos\theta - w)$ if expansion takes place.

From an energetic point of view, the perfectly elastic collision with a fixed surface at a temperature equal to the one of the gas does not result in a change of the molecular speed module (of their kinetic energy). Therefore, there is no influence on the temperature of the neighboring areas. For perfectly elastic collisions with a mobile piston, the impulse variation determines, for compression, an increase in the molecules' speed module, and for expansion, a decrease in this module. This triggers, in the first instance, a temperature increase in the area immediately neighboring the piston, and a corresponding decrease in the latter case. . For very slow movements of the piston (the case of Reversible Thermodynamics), the changes in the molecular speed module (and, consequently, in the local temperature of the gas) are of low amplitude, and the difference will significantly decrease after a small number of intermolecular collisions, while the corresponding kinetic energy will regularly diffuse through the entire mass of the system, leading to a uniform change in temperature and pressure for the system as a whole. In the case of finite speed of the piston, the variation of the molecular velocity due to the interaction of molecules with the piston (ie local temperature changes in the neighboring areas) has a higher magnitude as the piston speed is higher. The leveling process of a system's temperatures and pressures until the establishment of global values as a result of molecular agitation is also taking place at a finite speed which leads to the formation, inside the system, of fields of temperatures and pressures. For reciprocating compressors and expanders, due to their symmetrical structure, the temperature and pressure fields will organize in a monotonous decreasingly array, in parallel planes to the surface of the piston.

The pressure exerted on the piston is the result of the energy transmitted to the molecules through the collisions between them and the piston and it will be determined by their impulse variation in a time unit on one unit of the piston's surface. For the **expansion** case, all molecules in cluster $dN_{i,\theta}$ interacting with the piston in a time unit are located in a straight cylinder with one base supported by the piston, while the other base is situated at a distance of $C_i \cdot \cos\theta - w$. The volume of this cylinder is of $S \cdot (C_i \cdot \cos\theta - w)$, where S is the area of the piston. Inside this volume, many molecules will collide with the piston after one, or several collisions with the walls of the enclosure. But these collisions are perfectly elastic and symmetrical to the perpendicular on the wall (Figure 3.). Therefore, the molecules do not alter their speed module. The change in the angle formed by the movement direction with the wall of the cylinder, from θ to $-\theta$, does not lead to a change in the angle formed with the X-X' axis, and neither to the leave of $N_{i,\theta}$ cluster. Thus, the pressure $P_{i,\theta}$ exerted on the piston by the molecules of this cluster, in a time unit, is defined as the product of the impulse variation of one molecule $\Delta P_{i,\theta}$, the volume of the cylinder where the molecules getting to the piston are located, and the density ρ_θ of the inside molecules hitting the piston in this time unit, product which is then divided by the area of the piston:

$$P_{i,\theta} = \frac{1}{S} 2m\left(C_i \cos\theta - w\right) S \left(C_i \cos\theta - w\right) \frac{N_i}{2V} \sin\theta \cdot d\theta = \frac{N_i \cdot m}{V} (C_i \cos\theta - w)^2 \sin\theta \cdot d\theta \qquad (8)$$

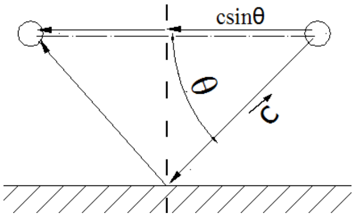


Fig. 3. Perfectly elastic collision between a molecule and the wall

As shown in Fig. 2., the molecules with the axial component of their speed smaller that the speed w of the piston ($\theta < \alpha$, where $\cos\alpha = w/C_i$) will not get to hit the piston. Therefore, in order to determine the pressure exerted by all the molecules with speed C_i, regardless of their trajectories, we will integrate the equation (8) for θ within the range 0 and α.:

$$P_i = \frac{N_i \cdot m \cdot C_i^2}{V} \int_0^{\alpha} \left(\cos\theta - \frac{w}{C_i} \right)^2 \sin\theta \cdot d\theta = \frac{N_i \cdot m \cdot C_i^2}{3V} \cdot \left(1 - \frac{w}{C_i} \right)^3$$

The value of the pressure exerted by the gas on the piston is calculated as the sum of the pressures exerted by all the molecules, regardless of their speed:

$$P_p = \sum P_i = \sum_i \frac{N_i \cdot m \cdot C_i^2}{3V} \cdot \left(1 - \frac{w}{C_i} \right)^3 \tag{9}$$

In Clausius' model, the pressure exerted by the gas on the fixed piston is calculated as:

$$P_g = \sum_i \frac{N_i \cdot m \cdot C_i^2}{3V} = \frac{m}{3V} \left(N_1 C_1^2 + N2 C_2^2 + \ldots + N_i C_i^2 + \ldots \right) \tag{10}$$

In a first approximation, if we consider that all molecules have the same speed C, equal to the root-mean-square speed, then:

$$C = \sqrt{\frac{\left(N_1 C_1^2 + N_2 C_2^2 + \ldots + N_i C_i^2 + \ldots \right)}{N_1 + N_2 + \ldots + N_i + \ldots}} = \sqrt{\frac{\sum N_i C_i^2}{\sum N_i}} = \sqrt{\frac{\sum N_i C_i^2}{N}} \tag{11}$$

Equation (9) becomes:

$$P_p = \sum P_i = \underbrace{\left(1 - \frac{w}{C} \right)^3}_{\beta_{md}} \frac{m}{3V} \cdot C^2 \cdot N = \beta_{md} \cdot P_g \tag{12}$$

The pressure P_g is the gas pressure inside the cylinder. In Finite Speed Thermodynamics, it is the average instantaneous pressure $p_{m,i}$, computed as the mean of all local pressures at a certain moment in time, and it carries the value of the pressure that would appear in the system if at that specific moment the piston stopped moving.

For the **compression** case, the molecules interacting with the piston in a time unit are located inside a straight cylinder with the base coinciding with the surface of the piston and the height defined by $C_i \cdot cos\theta - w$. The volume of this cylinder is equal to $S(C_i \cdot cos\theta + w)$, where S is the area of the piston. The pressure $P_{i,\theta}$ exerted by these molecules on the piston in a time unit is defined as the product of the impulse variation of one molecule $\Delta P_{i,\theta}$, the volume of the cylinder where the molecules interacting with the piston are located, and the density ρ_θ of the molecules from this group, divided by the area of the piston. But, as shown in Figure 2., inside this cylinder there are two categories of molecules with a dissimilar behavior from the point of view of impulse variation: the ones heading towards the piston (where $0<\theta<\pi/2$), where $\Delta P_{i,\theta} = 2m(C_i \cos\theta + w)$ and the ones pulling back from the piston with an axial component of speed smaller than the speed of the piston, which means that they will be reached by the piston (where $\pi/2<\theta<\pi-\alpha$, with the $cos\alpha = w/C_i$) . For the latter molecular group, where $\theta>\pi/2$, the speed projection on axis X-X' gets a negative value. Therefore, the equation $\Delta P_{i,\theta} =$ accurately defines the impulse variation also in this situation. Thus, for $0<\theta<\pi/2+\alpha$ we have:

$$P_{i,\theta} = \frac{1}{S} 2m(C_i \cos\theta + w) S (C_i \cos\theta + w) \cdot \frac{N_i}{2V} \sin\theta \cdot d\theta = \frac{N_i \cdot m}{V} (C_i \cos\theta + w)^2 \sin\theta \cdot d\theta$$

$$P_i = \frac{N_i \cdot m \cdot C_i^2}{V} \int_0^{\pi-\alpha} \left(\cos\theta + \frac{w}{C_i} \right)^2 \sin\theta \cdot d\theta = \frac{N_i \cdot m \cdot C_i^2}{3V} \cdot \left(1 + \frac{w}{C_i} \right)^3 \qquad (13)$$

Under the circumstances of the previous assumption (all molecules have the same speed), the pressure exerted by the piston is calculated by summing up the pressures exerted by all the molecules:

$$P_p = \sum P_i = \sum \frac{N_i \cdot m \cdot C_i^2}{3V} \left(1 + 3\frac{w}{C_i} + 3\frac{w^2}{C_i^2} + \frac{w^3}{C_i^3} \right) = \left(1 + \frac{w}{C} \right)^3 \cdot P_g = \beta_{mc} \cdot P_{m,i} \qquad (14)$$

The result allows us to introduce a new formula for calculating the mechanical work occurring during the finite speed gas-piston interaction:

$$\delta L_{ir} = p_{m,i} \cdot \left[1 \pm \frac{w}{c} \right]^3 \cdot dV \qquad (15)$$

The formula we found has a simple format and the coefficients in the equation are close to the ones in equation (3), derived from the Maxwell-Boltzmann distribution model.

If we divide the sums from equations (9) and (14) by N, we get the following mathematical expression:

$P_p = \sum_{i=1}^{n} P_i = N \sum_{i=1}^{n} \frac{N_i}{N} \cdot \frac{m \cdot C_i^2}{3V} \cdot \left(1 \pm \frac{w}{C_i} \right)^3$, where the + sign is applicable to compression, while the – sign pertains to expansion.

In this equation, $\frac{N_i}{N}$ represents just the probability for the molecular speed to be included in the interval [*(i-1)·dC, i·dC*]. Statistical Thermodynamics and Quantum Physics propose several distribution equations for calculating this probability depending on the state of the system (e.g. for low temperatures, the distribution Bose-Einstein is applied to bosons and the Fermi-Dirac one, to fermions). In Clausius' model, the distribution of energetic states is defined by the Boltzmann's distribution equation used by Maxwell to derive the speed distribution equation: the probability for the speed of a molecule to reach the value C_i in a system in equilibrium is:

$$P(c = C_i) = \left(\frac{m}{2\pi \cdot k_B \cdot T}\right)^{\frac{3}{2}} \cdot 4\pi \cdot C_i^{\,2} \cdot e^{-\frac{mC_i^2}{2k_B \cdot T}}$$, where k_B is Boltzmann's constant. (16)

The relationship defined by Maxwell is valid only for systems in equilibrium. We will consider that the piston moves in small strokes, each of them being followed by a short period of relaxation needed before the equilibrium can be reinstalled [2]. Thus, we can apply this formula for the case under our analysis. In the next paragraph we will prove that this hypothesis is not mandatory.

$$P_p = \sum_{i=1}^{n} P_i = N \sum_{i=1}^{n} \left(\frac{m}{2\pi \cdot k_B \cdot T}\right)^{\frac{3}{2}} \cdot 4\pi \cdot C_i^{\,2} \cdot e^{-\frac{mC_i^2}{2k_B \cdot T}} \cdot \frac{m \cdot C_i^2}{3V} \cdot \left(1 \pm \frac{w}{C_i}\right)^3 =$$

$$= 4\pi \cdot \frac{m \cdot N}{3V} \left(\frac{m}{2\pi \cdot k_B \cdot T}\right)^{\frac{3}{2}} \sum_{i=1}^{n} C_i^{\,4} \cdot \left(1 \pm \frac{w}{C_i}\right)^3 \cdot e^{-\frac{mC_i^2}{2k_B \cdot T}} \qquad (17)$$

where, $v_p = \sqrt{\frac{2 \cdot k_B \cdot T}{m}}$ (18) is the speed with the highest probability of happening.

For pressure calculation, it is also important to have the square-mean speed value:

$$C = \sqrt{\frac{\sum N_i C_i^2}{\sum N_i}} = \sqrt{\frac{3 \cdot k_B \cdot T}{m}} = v_p \sqrt{\frac{3}{2}} \qquad (19)$$

If the total number *n* of speed intervals is very high, the sum in equation (17) becomes an integral and C_i becomes the continuous variable *c*:

$$P_p = \frac{m \cdot N}{3V} \int_0^\infty P(c) \cdot c^2 \cdot \left(1 \pm \frac{w}{c}\right)^3 \cdot dc$$ By developing (20)

$$P_p = 4\pi \cdot \frac{m \cdot N}{3V} \left(\frac{m}{2\pi \cdot k_B \cdot T}\right)^{\frac{3}{2}} \int_0^\infty c^4 \cdot \left(1 \pm \frac{w}{c}\right)^3 \cdot e^{-\frac{mc^2}{2k_B \cdot T}} \cdot dc =$$

$$= \frac{m \cdot N}{3V} \cdot \frac{4}{\sqrt{\pi}} \cdot v_p^{-3} \cdot \left(\int_0^\infty c^4 \cdot e^{-\frac{c^2}{v_p^2}} \cdot dc \pm 3\int_0^\infty w \cdot c^3 \cdot e^{-\frac{c^2}{v_p^2}} \cdot dc + 3\int_0^\infty w^2 \cdot c^2 \cdot e^{-\frac{c^2}{v_p^2}} \cdot dc \pm \int_0^\infty c \cdot w^3 \cdot e^{-\frac{c^2}{v_p^2}} \cdot dc \right)$$

The integrals in the parenthesis from the right member are gamma functions [7] of type: $\int_0^\infty x^m e^{-ax^n} dx = \frac{1}{na^{\frac{m+1}{n}}} \Gamma\left(\frac{m+1}{n}\right)$,wheree $n=2$ *and* $a = \frac{1}{v_p^2}$. Therefore:

$$P_p = \frac{m \cdot N}{3V} \cdot \frac{4}{\sqrt{\pi}} \cdot v_p^{-3} \cdot \left[\frac{v_p^5}{2} \cdot \Gamma\left(\frac{5}{2}\right) \pm 3 \cdot w \cdot \frac{v_p^4}{2} \cdot \Gamma(2) + 3 \cdot w^2 \cdot \frac{v_p^3}{2} \cdot \Gamma\left(\frac{3}{2}\right) \pm \frac{v_p^2}{2} \cdot 3 \cdot w^3 \cdot \Gamma(1) \right] =$$

$$= \frac{m \cdot N}{3V} \cdot \frac{3}{2} \cdot \frac{2}{3} \cdot C^2 \cdot \left(1 \pm \frac{4}{\sqrt{\pi}} \cdot \frac{\sqrt{3}}{\sqrt{2}} \cdot \frac{w}{C} + 2 \cdot \frac{3}{2} \cdot \frac{w^2}{C^2} \pm \frac{4}{3 \cdot \sqrt{\pi}} \cdot \frac{3}{2} \cdot \frac{\sqrt{3}}{\sqrt{2}} \cdot \frac{w^3}{C^3} \right) =$$

$$= P_g \cdot \left(1 \pm 2{,}764 \cdot \frac{w}{C} + 3 \cdot \frac{w^2}{C^2} \pm 1{,}382 \cdot \frac{w^3}{C^3} \right) \tag{21}$$

Based on this result we get a new equation for the calculation of the work in the compression and expansion processes with finite speed:

$\delta L_{ir} = p_{m,i} \cdot \left[1 \pm \frac{aw}{c} + \frac{bw^2}{c^2} \pm \frac{dw^3}{c^3} \right] \cdot dV$, where $a = 2{,}764;\ b = 3;\ d = 1{,}382$

As expected, the coefficients are identical to the ones from equation (3), which were obtained based on the same hypotheses. The coefficient of the third-order term in equation (21) cumulates the contributions of the third-order term and of all the terms of superior order in equation (3). Also, by comparing equations (5) and (21), we notice that the Maxwell-Boltzmann distribution facilitates the reduction of irreversibilities caused by the finite speed of the piston.

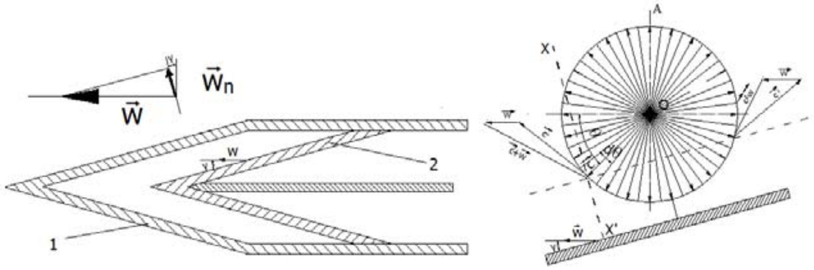
3. The finite speed gas-piston interaction at an γ angle from the movement trajectory

According to (1) and (4), the simplified mathematical expression of the first thermodynamic principle takes the following form:

$dU_{ir} = \delta Q_{ir} - \delta L_{ir} = \delta Q_{ir} - p_{m,i} \cdot \left[1 \pm \frac{aw}{c} \right] \cdot dV$ where $p_{m,i}$ is the average instantaneous pressure of the gas inside the cylinder and has the meaning of the pressure that would appear in the system at a certain moment if, in that instant, the piston suddenly stopped. This is one of the main operating parameters in the Thermodynamics with Finite Speed, which came to replace the equilibrium pressure *p*, typical to Classical Thermodynamics, and equation (21) is the equation that underlies this new branch of Irreversible Thermodynamics.

Based on Clausius' model described in the previous section, we will analyze how equation (21) can be applied to the interaction between the gas and the piston, when its surface is set at an inclined angle *γ*, as shown for the cone-shaped piston in Figure 6A. In this situation, the speed vector ***w***, with an axial direction, will have a normal component at the surface of the piston:

$w_n = w \cdot \cos\gamma$. Fig. 6B describes the uniform distribution, on all directions, for the speeds ***c*** of the gas molecules (by taking further the Clausius' model). The direction and the speed module of a molecule after collision with the piston are calculated as the vectorial sum of ***c'*** vector (corresponding to the speed direction after the collision with a stationary piston) and the speed vector of the piston.



(A) (B)

Fig. 6. The interaction between the gas and the sloped piston
(A) compressor: 1 cylinder cover, 2 cone shaped piston; (B) sphere of speed extremities

It should be noticed that the molecules following the same motion course as the piston towards an elementary surface δA crossed by an X-X' axis, perpendicular to the surface of the piston, will be accelerated after the collision (because the speed vector module will increase), while the molecules shifting towards this surface from the opposite direction will be slowed down (the speed vector module will decrease). In Figure 7 we highlighted one direction, offset to the left of O-X axis at an $\gamma+\beta$ angle, where the speed vector module does not suffer any changes after the collision (the speed vector for the molecules adopting this course will have, after collision, one extremity placed on the same sphere). The additional deviation β is caused by the speed of the piston motion and equals $\beta = \arcsin(w/2c)$. It is obvious that for $w \ll c$ the course of a molecule moving on a trajectory deviated to the left of the O-X axis at an γ angle will have, after collision, a similar direction as the O-A axis, perpendicular to the motion course of the piston, and the extremities of the speed

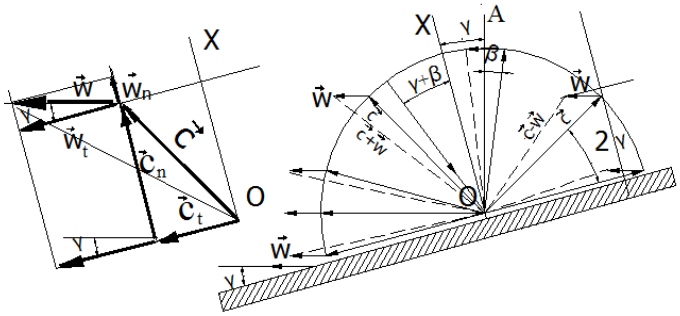


Fig. 7. The changes in the speed of the molecules depending on the angle of incidence

vectors will remain on the same sphere. Therefore, there are molecules slowed down from the collision with the piston, even during a compressing process, and these molecules have, before the collision, the direction angle included in the interval (0, $\pi/2-\gamma-\beta$). The other molecules are accelerated. For $w \ll c$, β converges to 0, therefore, the interval turns to (0, $\pi/2-\gamma$).

By decomposition of the vectors ***c*** and ***w*** along two axes, one normal to the surface of the piston, the other one tangent to it, the sum of the two speed values can be done by adding their components. It should be noticed that, for the molecules travelling towards the piston from the direction opposite its motion course at an angle from the surface of the piston smaller than $\pi/2-\gamma-\beta$, the normal components of the speeds are always oriented in the same direction (therefore, the component of the resultant is the sum of normal components of the two types of speed), while the tangential components have different directions (therefore, the component of the resultant will equal the difference between the components of the two types of speed). The pressure exerted by the gas on the piston is influenced only by the normal components of the speeds. The instantaneous pressure exerted by the gas on the piston at a certain moment in time is determined by the mean of the elementary pressures, exerted on all the elementary surfaces of the piston interacting with the gas at the same instant (conditioned by the impulse variations of all the molecules colliding against the corresponding elementary surface). Thus, for a surface of the piston at an γ angle from the motion course, the gas-piston interaction takes place in exactly the same way as when the compression is performed by a straight piston moving at a smaller speed (reduced by a $\cos\gamma$ coefficient), but with an area enlarged by the multiplication with a $1/\cos\gamma$ coefficient. As a result, all the conclusions drawn in the previous paragraph for an A area of the piston are valid for all the portions on the surface of any mobile organ where we can infer that the speed and the positioning to the motion course are not modified in the time unit taken into consideration, if the speed w is replaced by an equivalent speed $w\cdot\cos\gamma$:

$$P_{p,l} = P_{g,l}\cdot\left[1 \pm \frac{w\cdot\cos\gamma}{c}\right]^3, \text{ or, if } \alpha = \arcsin w/c: \tag{22}$$

$$P_{p,l} = P_{g,l}\cdot(1 \pm \sin\alpha\cdot\cos\gamma)^3 = P_{g,l}\cdot\left[1 \pm \frac{\sin(\alpha+\gamma)+\sin(\alpha-\gamma)}{2}\right]^3,$$

where $P_{p,l}$ and $P_{g,l}$ are the local pressures on an elementary surface of the piston and, respectively, from a gaseous area close to this surface, area where we can suppose a uniform gas pressure. For the compressor in Fig. 4, as well as for other types of compressors for witch the orientation of the piston to the direction of motion remains the same during the compression, or the expansion, relationship (22) is valid for the whole surface of the piston. Therefore :

$$P_p = P_g \cdot \left[1 \pm \frac{w \cdot \cos\gamma}{c}\right]^3 \tag{23}$$

These conclusions suggest one of the methods that the undesirable consequences of irreversibility due to finite speed of the piston can be reduced: building compressors with an uniform sloped piston surface or with a shaped surface.

Generally speaking, the surface of the mobile organ from rotating compressors is a curved surface (which can be represented in a three-dimensional system) whose area, orientation to the direction of motion, and speed, changes from one point to another and from one moment to another. In these circumstances, calculating the impact of the finite speed of the mobile organ on the development of processes inside the system is a difficult task that requires for solving, numerical methods. For high speed values of the piston, equation (22) must be included in the set of equations describing the behavior of the system.

When the surface of the piston is set at a γ angle from the motion course (Fig. 8), we have already stated, some of the gas molecules is accelerated, while another part is slowed down. For small speed values of the piston ($w \ll c$), the axis separating the directions of the molecules accelerated by the piston from the slowed down ones is normal to the motion course and set at an γ angle from the normal to the surface. For higher speed values of the piston, this angle increases by a $\beta=\arcsin(w/2c)$ value. The kinetic energy of the slowed down molecules decreases, which may lead to the formation of local regions with lower temperature. But, if we accept the hypothesis of chaotic molecular distribution, the kinetic energy of all the accelerated molecules surpasses the energy of the slowed down ones. As shown in Fig. 8, the courses of the molecules with a kinetic energy variation mutually compensated are settled on both sides of a direction offset to the left by a $\gamma+\beta$ angle from the normal to the surface of the piston.

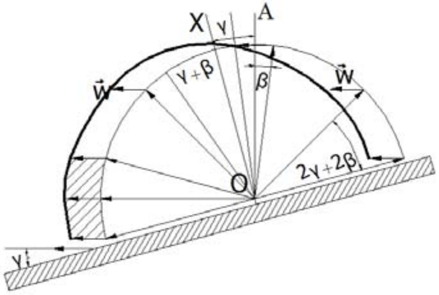


Fig. 8. The tire of speed extremities after interacting with a sloped piston

Therefore, all molecules with a kinetic energy remains unbalanced after the collision with the piston take a direction characterized by the angle θ included in the interval $(\pi-2\gamma-2\beta,\pi)$. For $w \ll c$, meaning that $\beta \to 0$, the interval shrinks and gets the opening 2 γ : $(\pi-2\gamma,\pi)$. The more pronounced the slope of the surface of the piston from the perpendicular on the motion course is (γ angle is narrowing), the less powerful the energy exchange between the gas system and the piston, which leads to a slower temperature increase for the system.

5. Conclusions

Even if it was conceived more than 150 years ago, Clausius' kinetic-molecular model is far from having exhausted all its potential. In the current study, we relied on this model to validate once more the accuracy of the equations underlying the development of the Thermodynamics with Finite Speed and we deduced, for the straight piston, two new formulas, easy to use. For the bent piston, the derived equations allow the analysis of irreversibilitis that arise, for the finite speed of the piston, in rotary compressors and in reciprocating compressors with shaped piston. The microscopic analysis made on the transformation of kinetic energy into thermal energy, offers the prospect of a better understanding of the processes taking place in thermoacoustic devices and in Hilsch-Ranke tubes.

REFERENCES

[1] *Stoicescu L., Petrescu S.,* Termodynamisce Zustandsanderungen die mit endlicher veranderlicher Geshwindigkeit durchlaufen werden, Buletinul Institutului Politehnic Bucuresti, nr.1/1965, tom 27.

[2] *Petrescu Stoian.,* Contributii la studiul unor interactiuni si procese termodinamice de neechilibru din masinile termice, (Contributions to the study of interactions and nonequilibrium thermodynamic processes of thermal machines), Teză de doctorat, Institutul Politehnic Bucuresti, 1969, (in romanian)

[3] *Petrescu Stoian.,* Tratat de inginerie termică, (Treaty thermal engineering), Editura AGIR, 2007. (in romanian)

[4] *Petrescu S., Costea M.,* Developement of thermodinamics with finite speed and direct method, Editura Agir, 2011.

[5] *Petrescu S., Harman C.,Costea M., Petre C., Dobre C.,* Irreversible finite speed thermodynamics (ifst) in simple closed systems. I. Fundamental Concepts, Revista Termotehnica 2/2009.

[6] *Petrescu S., Costea M., Charles H.*, Irreversible thermodynamics in complex systems: Irreversible Isothermal Processes with Finite Speed, Friction and Throttling, Revista Termotehnica, 2/2010.

[7] *Sommerfeld A.*, Thermodynamics and Statistical Mechanics, vol. 5, Academic Press, New York, 1967.

[8] *Macke W.*, Thermodynamik und Statistik, Leipzig, 1963.

[9] *Petrescu S.*, Kinetically Consideration Regarding the Pressure on a Movable Piston, Studii si Cercetări de Energetică si Electrotehnică, Academia Româna, Tom 21, Nr. 1, pp. 93-107, 1971

[10] *Onsager L.*, Phys. Rev.(a), 37, 405 (1931); 6, 38, 2265, 1931.

[11] *Prigogine I.*, Etude Termodinamique des Phenomenes Irreversibles, Desoer, Liege, 1947

[12] *Petrescu S.*, An Expression for Work in Processes with Finite Speed based on Linear Irreversible Thermodynamics, Cercetări de Energetică si Electrotehnică, Academia Româna,Tom 19, Nr2, pp. 1081-1086, 1974.

[13] *** Gamma functions, http://www.exampleproblems.com/wiki/index.php/SF12.