ROLE OF RELAXATION IN AN ADIABATIC CHANGE

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Whenever rapid chanes of energy occur in polyatomic gases, the phenomenon of relaxation is called into play. This is because the internal degrees of freedom do not readily acquire the temperature of the external degrees of freedom but take an appreciable time, the relaxation time. The purpose of this note is to examine the possibility of using an adiabatic compression) (or expansion) of a gas for the study of relaxation.

Consider a polyatomic gas suddenly compressed adiabatically. It is reasonable to assume that the external degrees of freedom will attain equilibrium almost instantaneously with the external conditions thereby increasing the temperature. By external degrees we mean here the translational and all such degrees which instantaneously acquire equilibrium with the external conditions. On the other hand the internal degrees exibit a lag and it is only through some slow process that energy flows from external to internal degrees and equilibrium is attained. In this process the temperature of the external degrees falls while those of internal rises.

Let us also assume that the adiabatic change is quite fast and its duration is much smaller than the relaxation time of the gas. Under such conditions the total specific heat of the gas, C_v, is not effective and the energy transfer fails to follow the quick adiabatic change. We denote the contributions of the external degrees of freedom to the total specific heat of the gas by C'_e and C'_i, respectively. We have therefore

$$C'_v = C'_e + C'_i. \tag{1}$$

Let T_0 and V_0 be the initial temperature and volume of the gas respectively, and after the adiabatic compression the temperature rises to T_1 while the volume reduces to V_1. We also presume that this adiabatic change is so fast that only the external degrees participate and the internal degrees remain unexcited. However, as the time passes the exchange of energy occurs between the external and internal modes and finally they get into epuilibrium and at this stage let T_2 be the temperature of the gas. Applying the law of conservation of energy we get

$$C'_e(T_1-T_2) = C_i(T_2-T_0). \tag{2}$$

Further, for the adiabatic change

$$T_0 V_0^{\gamma-1} = T_1 V_1^{\gamma-1}. \qquad \ldots (3)$$

Here, γ is the ratio of the two specific heats of the gas with the internal degrees of freedom frozen and we take γ to be constant in the small temperature range, $(T_1 - T_0)$. In writing equation (3) it is assumed that the equation of state depends only on the temperature T_1. This, however, seems reasonable in view of the success of a similar assumption in the study of the dispersion and absorption of ultra-sonic waves. (Herzfeld, 1955). Eliminating T_1 from equations (2) and (3) we get,

$$C_i = C_v \left[1 + \frac{(T_2 - T_0) V_1^{-\gamma}}{(T_0 V^{\gamma-1} - V_1^{\gamma-1})} \right]. \qquad \ldots (4)$$

Thus, the knowledge of the initial temperature and volume of the gas and their values after the adiabatic change, will enable to estimate C_i and therefore the extent of participation of the internal modes at that temperature.

In the above treatment we have assumed the gas to be perfect which, however, is not true and therefore we replace the perfect gas equation by the following equation of state :

$$PV = RT[1 + B(T)/V]. \qquad \ldots (5)$$

Here, P, V and T represent the pressure, volume and temperature of the gas, respectively. R is the gas constant and $B(T)$ the second virial coefficient of the gas at the temperature T. Consideration of equation (5) modifies equation (3) to

$$T_0 V_0^{\gamma-1}[1 + B(T_0)/V_0]^{\gamma-1} = T_1 V_1^{\gamma-1}[1 + B(T_1)/V_1]^1 \qquad (6)$$

Combining equations (2) and (6) and eliminating T_1 we get

$$C_v = C_v \left[1 + \frac{(T_2 - T_0) V_0^{\gamma-1}[1 + B(T_0)/V_0]^{\gamma-1}}{T_0 V_0^{\gamma-1}(1 + B(T_1)/V_1)^{\gamma-1} - V_1^{\gamma-1}(1 + B(T_0)/V_0)^{\gamma-1}} \right]$$

instead of equation (4).

The slow energy exchange between the external and internal degrees of freedom is characterised by the relaxation time, τ. It is possible to derive an expression for τ adopting a treatment similar to that of Herzfeld (1955). However, unlike Herzfeld we prefer to express τ in terms of the temperature of the external degrees of freedom since it is directly measurable. The final result is :

$$T(t) = T_2 + \frac{C_i}{C_m - C_i}(T_2 - T_0)e^{-\frac{C_v}{C_i}\frac{t}{\tau}} \qquad (8)$$

In equation (8) $T(t)$ is the temperature of the external modes at a certain time t, and if its values be determined as a function of t, τ can be evaluated directly.

The application of equation (8) is in general handicapped because of the short relaxation times, which range between 10^{-3} to 10^{-9} sec. or so. A practical though indirect way to use it, is to study the changes in volumes corresponding

to the changes in temperatures at a constant pressure as a function of time. Such an experiment can be conducted making use of an apparatus technically called as ERMA (expansion rate measuring apparatus). This essentially consists of a hollow cylinder closed at one end, with a light piston. Through the wall of the barrel a number of electrical contacts are located whose position can be accurately determined. As the piston moves it shorts the electrical contacts one after the other and generates electrical signals. It had been possible to measure the position of the piston at intervals of a few microseconds with such an arrangement. (Siegel, 1952).

Another example where the theory developed here will find application is the study of the state of a gas in a weak shock wave. When a weak shock wave from an explosion or shock tube has passed a certain distance in a gas, the gas adiabatically to return to the original pressure. For such an expansion equation (4) will get modified to

$$C_i = C_v \left[1 - \frac{(T_0 - T_2)V_1^{\gamma-1}}{T_0(V_1^{\gamma-1} - V_0^{\gamma-1})} \right], \qquad \ldots (9)$$

or in an alternative form in terms of the pressure as

$$C_i = C_v \left[1 - \frac{(T_0 - T_2)}{T_0 \left\{ 1 - \left(\dfrac{p_1}{p_0} \right)^{\frac{\gamma-1}{\gamma}} \right\}} \right]. \qquad \ldots (10)$$

Here T_0, V_0 and p_0 represent the temperature, volume and the pressure of the gas in the presence of the shock wave and T_2, V_1 and p_1 the corresponding quantities after the adiabatic expansion had subsided.

The various quantities involved in the above equations are measurable. Such an experiment apart from being of practical value in the determination of C_i, will also be of great theoretical importance in verifying the assumption viz., the equation of state depends only on the temperature of the external degrees of freedom. This assumption, though successfully applied and tested to some extent from the study of ultrasonic waves, still awaits a more direct confirmation and support from as straightforward experiments as mentioned and proposed here.

REFERENCES

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