Pressure-volume work exercises illustrating the first and second laws

William G. Hoover and Bill Moran
Department of Applied Science, University of California Davis-Livermore and University of California Lawrence Livermore Laboratory, Livermore, California 94550
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We present two exercises involving rapid compression and expansion of ideal gases. The exercises are useful teaching tools and illustrate the first and second laws of thermodynamics. The first problem involves the conversion of gravitational energy into heat through mechanical work. The second involves the mutual interaction of two gases through an adiabatic piston. Both local and global versions of the second law can be applied to this second exercise. Both problems are also treated by numerical fluid dynamics.

I. INTRODUCTION

Graduate students in applied science, both at Davis and at Livermore, must complete a core program of coursework in numerical methods, properties of matter, quantum mechanics, electricity and magnetism, nuclear science, and mathematics. The properties of matter course includes thermodynamics, statistical mechanics, kinetic theory, and a preliminary treatment of continuum mechanics.

In the properties of matter course, we have found that exercises distinguishing heat and work in irreversible processes are particularly useful teaching tools. Two such problems are discussed here. Both problems can be treated in the classroom at the macroscopic equilibrium level of the first and second laws of thermodynamics. Because both problems involve one-dimensional flow of viscous ideal gases, it is possible to analyze the details of the irreversible processes at a level of sophistication well suited to the small computers available at most colleges and universities.

The first exercise illustrates energy conservation. Gravitational potential energy is converted into thermal energy by allowing a weight to fall upon a piston confining gas to a chamber. The question is "from what height must the weight be dropped such that the gas volume is unchanged." Thermodynamics can answer this question, although it cannot detail the process through which the weight's potential energy becomes heat. The details of this process depend not only on the equation of state but also upon the mass density of the gas and its viscosity. A solution to this problem, with a viscosity high enough to simplify the calculation, is presented in Sec. II.

The second exercise illustrates entropy increase.[1] Two gases linked by an adiabatic movable piston approach mechanical equilibrium. Here entropy of the final state of the system must exceed the initial entropy. This problem differs from the first one in that energy conservation does not tell us the final location of the piston. Thermodynamics does provide a series of increasingly good bounds as the first law is supplemented by global and local versions of the second law. Again we carry out a numerical calculation to illustrate the irreversible process.

II. PROBLEM ONE: THE FALLING WEIGHT

Consider an ideal classical monatomic gas confined by a piston of mass m in the gravitational field g. The pressure, volume, and temperature of the N atoms comprising the gas obey the ideal gas law

$$P_0V_0 = NkT_0, \tag{1}$$

where k is Boltzmann's constant. Now suppose that a weight, with the same mass m as the piston, is dropped onto the piston (see Fig. 1). The resulting energy transfer to the gas increases the pressure and the temperature (at final equilibrium). The pressure doubles (because the supported mass doubles) and the temperature increases by an amount depending upon the height through which the weight falls

$$\Delta E = 1.5Nk(T - T_0) = mgh. \tag{2}$$

From the standpoint of teaching thermodynamics the most interesting situation is that in which the final piston position, after equilibration of the gas (and making the assumption that neither the piston nor the weight is heated) is the same as the initial position

$$\Delta V = V' - V_0 = 0. \tag{3}$$

The student is then required to (1) calculate the necessary height h and (2) find the resultant energy change ΔE, work done ΔW, and heat gained ΔQ for the gas.

The first law, $\Delta E = \Delta Q - \Delta W$, holds with $\Delta Q = 0$ because the piston is adiabatic. Thus both the energy change and minus the work done are mgh. The work done on the gas, $-\Delta W$, is also the integral of $-P_{zz}dV$ (where P_{zz} is the pressure exerted on the confining piston). Accordingly this integral must be mgh for the process even though the in-

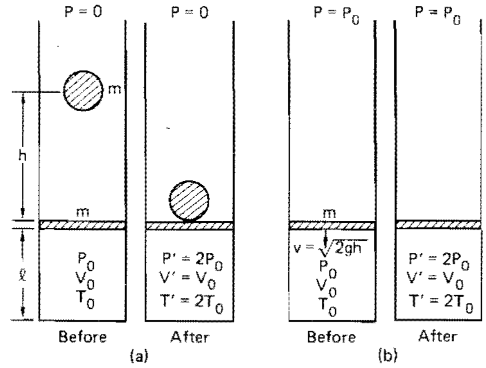

Fig. 1. Schematic diagram for problem I. (a) Exact treatment includes elastic bouncing of the weight on the piston. (b) Weight-piston interactions replaced by an averaged downward pressure P_0.

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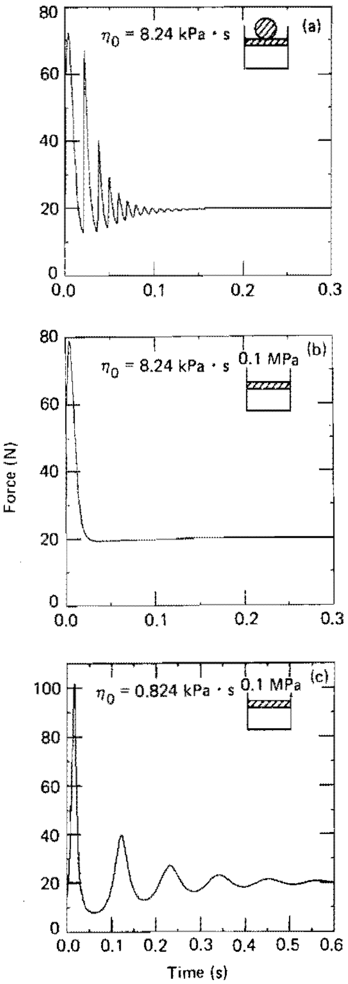

Fig. 2. Force-time history on the confining piston. (a) Calculation includes bouncing of the weight on the piston. (b) and (c) Weight-piston interaction replaced by an average downward pressure of 0.1 MPa.

tegral of dV vanishes; this appears paradoxical to many students.

In order to understand the process through which the falling weight transmits its energy to the gas it is useful to consider a particular problem numerically. We analyze the following example with a molecular weight of 40 (argon) for the confined gas:

$$P_0 = 0.1\ MPa = 1\ \text{bar},\ T_0 = 300\ \text{K},\ l = 0.01\ \text{m},$$
$$h = 0.015\ \text{m},\ m = 1.019\ \text{kg},\ g = 9.81\ \text{m/sec}^2, \quad (4)$$

cross sectional area $A = 10^{-4}\ \text{m}^2$.

Numerical hydrodynamic solutions can be obtained by integrating the continuum equation of motion. (Gravity is ignored in the gas phase.)

$$\rho \ddot{Z} = -(\nabla \cdot \mathbf{P})_z = -\frac{dP_{zz}}{dz}, \quad (5)$$

where z is the vertical space coordinate in the gas, ρ is the mass density, and the pressure tensor $\mathbf{P}$ contains, in addition to the equilibrium pressure a linear viscosity

$$P_{zz} = \frac{NkT}{V} - \eta_L \frac{du_z}{dz}. \quad (6)$$

The longitudinal viscosity η_L in (6) is equal to $4/3$ times the shear viscosity for a dilute gas without bulk viscosity.[2] We describe the temperature dependence of the viscosity with a power law:

$$\eta_L = \eta_0 (T/300)^\alpha. \quad (7)$$

For gases, α varies between 0.5 and 1.0. We use $\alpha = 0.8$ to represent argon. A more sophisticated calculation would include heat conduction too.

The interaction between the falling weight and the confining piston could be treated in three ways: (i) exactly, including the elastic bouncing of the weight on the piston; (ii) as an inelastic collision with the weight attached to the piston on collision; or (iii) as an averaged interaction, with the weight providing a downward constant pressure following the collision. The first possibility, an exact treatment, is feasible, but has the drawback of producing complex results. The second possibility is qualitatively incorrect, in that the initial velocity of the lower piston is reduced (by the square root of 2) if the two masses move together. The use of an average pressure together with an initial piston velocity conserving momentum and energy is the best choice. Here we present results from methods (i) and (iii) using two different values of η_0 in the latter case. Replacing the weight-piston collisions by an average pressure smooths out irregularities in the solution and simplifies the calculation.

The form of the hydrodynamic solution also depends upon the number of regions ("zones") in the spatial grid dividing up the gas. If the gas is represented by a single hydrodynamic zone, the viscous dissipation throughout the gas is uniform, and the resulting force per unit area on the

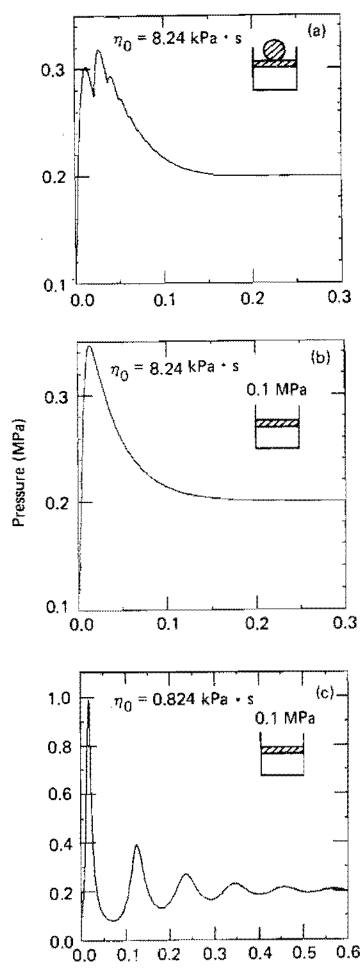

Fig. 3. Time variation of the mean pressure NkT/V in the gas. (a) Calculation includes bouncing of the weight on the piston. (b) and (c) Weight-piston interactions replaced by an average downward pressure of 0.1 MPa.

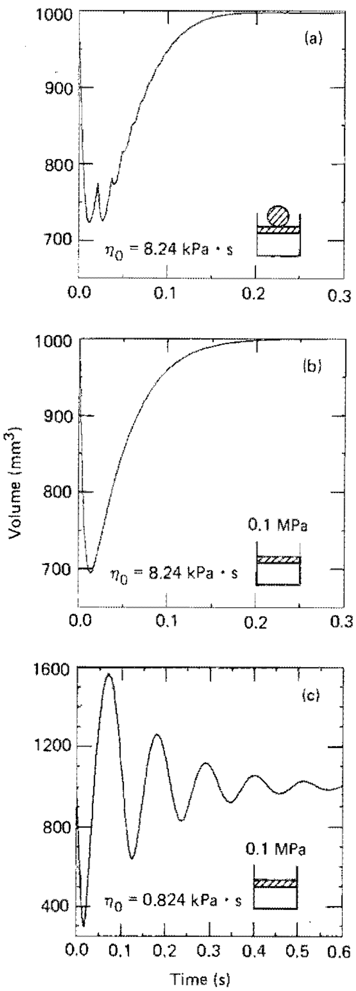

Fig. 4. Volume-time history. (a) Calculation includes bouncing of the weight on the piston. (b) and (c) Weight-piston interactions replaced by an average downward pressure of 0.1 MPa.

confining piston is the same as the zz component of the pressure tensor in the gas interior. Figures 2 and 3 illustrate the time variation of the force on the piston and the mean pressure NkT/V in this one-zone approximation. The gas behaves as a nonlinear spring plus dashpot combination; thus, by varying the ratio of dissipation to modulus, the range of conditions from underdamped to overdamped oscillations can be reproduced. Critical damping occurs when

$$\eta_L/l = 2\,(Km)^{1/2}/A, \tag{8}$$

where K is the effective spring constant of the gas. At the first impact, critical damping occurs with a viscosity of 8.24 kilopascal seconds (kPa sec), about eight orders of magnitude larger than the actual viscosity of argon gas at 300 K.

A large viscosity decreases the computational time required to reach final equilibrium but also changes the maximum compression $(V_0/V)_{\max}$ in the gas. For a viscosity η_0 of 8.24 kPa sec $(V_0/V)_{\max}$ is 1.4, for η_0 equals 0.824 kPa sec $(V_0/V)_{\max}$ is 3.3 and in the limit of zero viscosity, $(V_0/V)_{\max}$ is 4.0. The time variation of the volume is shown in Fig. 4.

The thermodynamics is conveniently summarized in Fig. 5 where the force on the piston versus the volume of the gas is mapped out. The circuitous route by which the gas state point travels from the initial to the final state depends upon the dissipation properties of the gas, but the net area under the curve does not. Figure 6 illustrates the pressure volume history of the gas.

Energy conservation [Eq. (2)] combined with the ideal gas law [Eq. (1)] shows that the final volume equals the initial volume if $h = 1.5l$. In our numerical example, l equals 0.01 m and the maximum piston speed is 0.54 m/sec or about 0.18% of the speed of sound in argon. This relatively slow motion produces no detectable shocks and a single hydrodynamic zone describes the gas adequately. However, as the height h increases, the maximum piston velocity also increases (as the square root of h) and a single hydrodynamic zone is no longer adequate. In such a case, the average pressure in the gas differs from the pressure felt at the piston. For a height $h = 150$ m the maximum piston velocity is 54 m/sec (about 18% of the sound speed) and the initial pressure felt at the piston after the first impact is 33% higher than the average pressure in the gas. With fine zoning, the passage of shock waves through the system can be followed and the final equilibrium state (without heat conduction) consists of zones at slightly different temperatures but with uniform energy density.

III. PROBLEM TWO: THE PRESSURE-DRIVEN HORIZONTAL PISTON

Consider again an ideal classical monatomic gas, but this time in a horizontal cylinder divided into two chambers by an adiabatic piston, as shown in Fig. 7. We assume that initially equal masses of gas, at identical temperatures, occupy the two chambers, so that there is an r-fold pressure

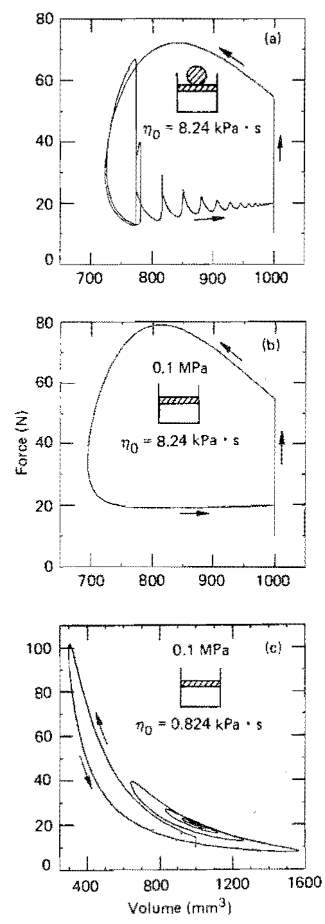

Fig. 5. Force on the piston versus volume of the gas. The area under each curve is $-mghA$. (a) Calculation includes bouncing of the weight on the piston. (b) and (c) Weight-piston interactions replaced by an average downward pressure of 0.1 MPa.

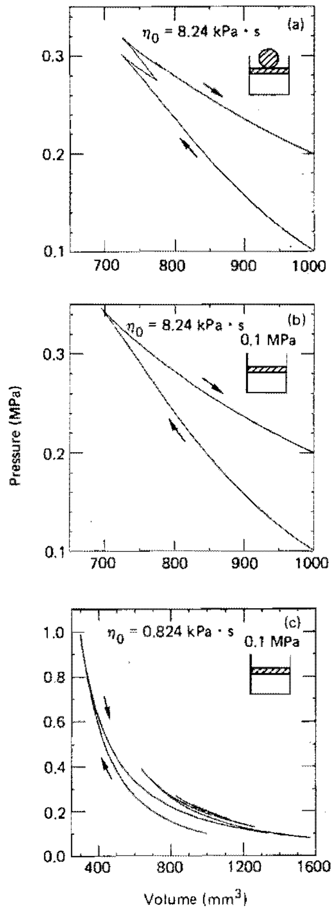

Fig. 6. Pressure-volume diagram. (a) Calculation includes bouncing of the weight on the piston. (b) and (c) Weight-piston interactions replaced by an average downward pressure of 0.1 MPa.

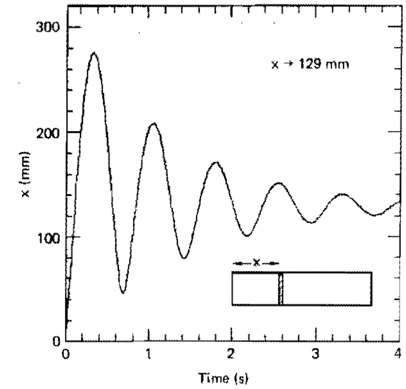

Fig. 8. Piston position as a function of time. m = 0.1 kg, η_0 - 0.2 kPa sec, α = 0.8.

difference across the piston, proportional to the number-density difference between the two chambers.

From the standpoint of thermodynamics this system is far from equilibrium. The maximum entropy state would correspond to a piston location at the center of the cylinder with identical gas temperatures and pressures in the two chambers. The student can be asked to analyze the irreversible behavior of this system once the piston is released. It is worthwhile to consider the problem from several points of view. In each case we assume that the total energy is conserved (first law of thermodynamics): (a) mechanical equilibrium; (b) global entropy increase; (c) local entropy increase; (d) simulation of the irreversible equilibrium process. Each of these points of view is discussed separately below.

First, it is apparent that at equilibrium the pressures on the two sides of the piston must match. Because the gas is ideal this means that the final energy density in each chamber must be identical to the overall energy density

$$3P_1/2 = 3P_2/2 = 3P/2 = E_1/V_1 = E_2/V_2 = E/V, \quad (9)$$

where subscripts 1 and 2 refer to the left- and right-hand sides, respectively. Because mechanical equilibrium can occur for *any* partitioning of the cylinder into two chambers (provided that the energy is proportionately partitioned) the mechanical equilibrium condition [Eq. (9)] tells us *nothing* as to the final position of the piston. Energy conservation does reveal that the final pressure is $2E/3V$, because the total system is insulated.

The global principle that the entropy of an isolated system (both chambers plus the piston in this case) must increase does provide definite bounds on the piston location. To show this, express the monatomic ideal gas entropy in terms of pressure and volume

$$\Delta S/Nk = (3/2)\ln(P/P_0) + (5/2)\ln(V/V_0). \quad (10)$$

The second law of thermodynamics states that the entropy of an isolated system must increase in an irreversible process. We can write this global entropy increase inequality as follows:

$$\Delta S/Nk = (3/2)\ln[4r/(1+r)^2] + (5/2)\ln[R(1+r)^2/r(1+R)^2] > 0, \quad (11)$$

where r is the initial volume ratio and $R = V_2/V_1$ is the final volume ratio. Let us find the two extreme values of R, bounding the range in which ΔS is positive. Equation (11) reduces to a quadratic equation for R when ΔS is zero.

Consider a particular numerical example,[1] with the initial volume ratio r equal to 50 (total volume of length 510 mm).

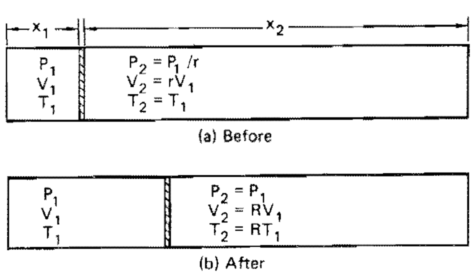

Fig. 7. Schematic diagram for problem II. Solutions for the case r = 50 are illustrated in Figs. 8–13.

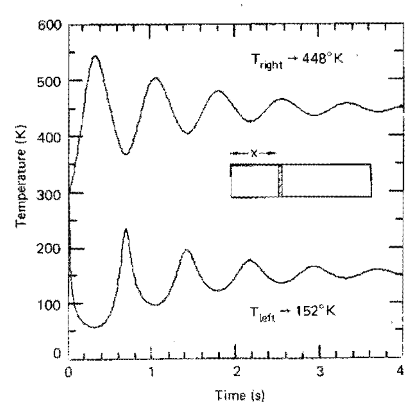

Fig. 9. Temperature of the gas on both sides of the piston as a function of time. m = 0.1 kg, η_0 = 0.2 kPa sec, α = 0.8.

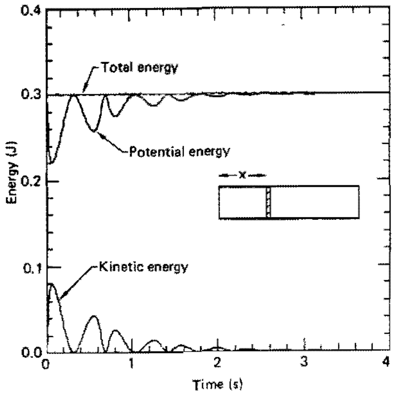

Fig. 10. Energy partition as a function of time. m = 0.1 kg, η_0 = 0.2 kPa sec, α = 0.8.

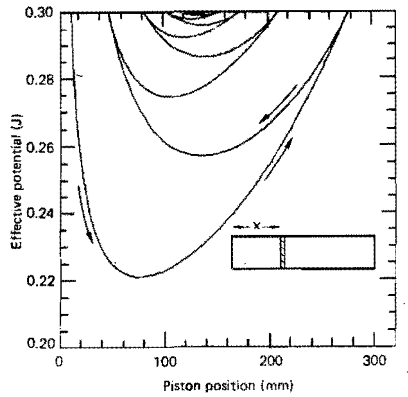

Fig. 12. Effective potential for piston motion.

Then the piston location X (in millimeters) is bounded as follows:

$$51 < X < 459. \quad (12)$$

Throughout this range of piston locations ΔS is positive, but the individual contributions, ΔS_1 and ΔS_2, of the two chambers can be positive and negative.

The second law of thermodynamics can be applied in a more powerful local form. Note that each of the two chambers can itself be treated as an adiabatic system upon which external work is being performed. Because this work is not reversible ΔS_1 and ΔS_2 must both be positive. Thus bounds on the piston position can be computed from the isentropic equation of state for the two sides

$$V > V_{\text{isen}} = V_0\,[(P_0/P)^{3/5}], \quad (13)$$

where isen represents isentrope. In our numerical example this markedly improves upon the bounds found in Eq. (12). We find

$$70 < X < 176. \quad (14)$$

Equilibrium thermodynamics can take us no closer to the truth. To discover the actual piston location requires a simulation of the nonequilibrium flows in the two chambers. In the limit that the piston is very heavy (so that the motion is quasistatic) the two chambers can be treated as single hydrodynamic zones. Otherwise it is necessary to use several zones in order to treat the shock and rarefaction waves moving through the two chambers. We have explored the problem for the following system $P_1 = 50P_2 = 0.1$ MPa, $T_1 = T_2 = 300$ K, $m = 0.1$ kg, $X_2 = 50X_1 = 500$ mm, $\eta_0 = 0.2$ kPa sec, $\alpha = 0.8$, cross-sectional area equals 100 mm^2. Several of the results are shown in Figs. 8–12.

If dissipation were absent then both chambers of gas would expand and contract isentropically with the extra energy being taken up by the piston

$$E = E_1 + E_2 + mv^2/2. \quad (15)$$

Thus the piston can be viewed as a point mass moving in the external potential $E_1(X) + E_2(X)$, where X is the piston location. The piston undergoes periodic nonlinear oscillations. By adding the effects of gas viscosity (and, to a lesser extent, thermal conductivity) the dissipation leading to an increase in the effective potential can be calculated.

It is interesting to note first that the entropy increase (Fig. 11) takes place more rapidly in the *small* initially expanding chamber despite the fact that this chamber is undergoing rarefaction while the larger one is shock compressed. This apparent anomaly can be understood by noting that the entropy production varies as the inverse of the volume. This inverse relationship comes about because entropy production per unit volume varies as the square of the velocity gradient. Thus the piston comes to rest a bit to the right of the minimum of the initial effective potential plotted in Fig. 12.

It is interesting to note next that the final position of the piston depends not just on the equilibrium properties of the gas, but also on the transport properties. Figure 13 shows the final piston position for two different dependences of viscosity on temperature: the square-root dependence ($\alpha = 0.5$) characteristic of hard spheres and the linear dependence ($\alpha = 1$) characteristic of Maxwellian molecules (inverse fourth power repulsive potential).

The limits imposed by thermodynamics on the final piston position are reproduced from the hydrodynamic calculations by allowing all the dissipation to occur in the

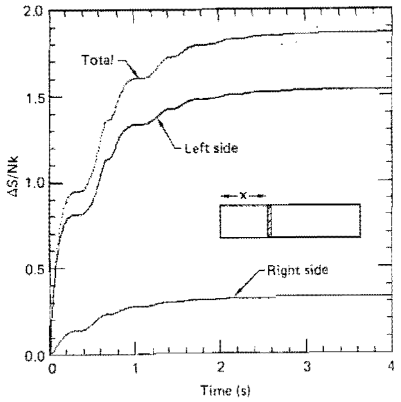

Fig. 11. Entropy increases as a function of time.

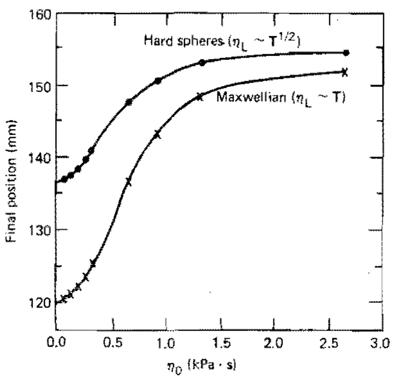

Fig. 13. Dependence of the final position on the transport properties.

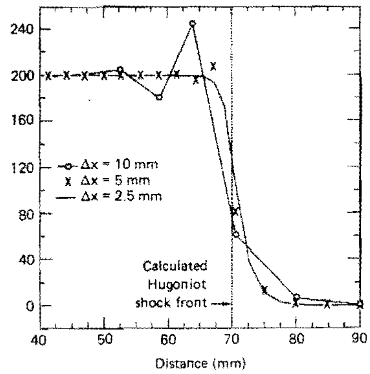

Fig. 14. Stream velocity profile within the shock front.

gas on only one side of the piston. This can be conveniently accomplished by taking the limit as α approaches plus or minus infinity. For α approaching plus infinity, all the dissipation occurs on the right side (see Fig. 7) of the piston and the piston comes to rest at $X \simeq 70$ mm. For α approaching minus infinity, all the dissipation occurs on the left-hand side and $X \simeq 176$ mm.

Several zones are required to treat the shockwaves arising in the case of a light piston. We use an explicit finite-difference hydrodynamic code without heat conduction[3] (HEMP) to investigate the case of a moderately massive piston ($m = 10^{-5}$ Kg = 1.8 times mass of gas), $\eta_0 = 1$ Pa sec. The maximum piston velocity is then 120 m/sec (about 0.4 times the speed of sound in argon) and the final piston position shifts from 128 mm in the one-zone approximation to 126 mm in the limit of a large number of zones. The calculation, which does not include heat conduction, shows that at equilibrium there is a 20% temperature variation among the hydrodynamic zones on the left side of the piston and a 5% temperature variation on the right side. On both sides the gas is coldest near the piston. We also investigated the case of a massless piston and found that it comes to rest with X about 90 mm.

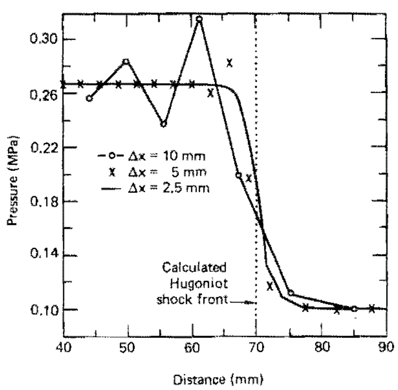

Fig. 15. Pressure profile within the shock front.

In conjunction with solving this problem, we studied the structure of a single shock as a function of zone size. Figure 14 shows the stream velocity profile within the shock front for three different zone sizes. The calculation uses the HEMP code with $\eta_0 = 0.5$ kPa sec, $\alpha = 0.8$ and a uniform piston speed compressing argon gas at the rate of 200 m/sec. For this particular shock, we obtain a smooth shock front if the shock spans six or more zones. (The shock speed is 466 m/sec and P/P_0 is 2.67 as calculated from sections 67–69 in Ref. 4.) Coarser zones produce an overshoot in the pressure as shown in Fig. 15.

The work done by a piston compressing a gas is proportional to the pressure at the gas zone adjacent to the piston. We found that for coarse zoning the time averaged value of that pressure converges linearly with zone size to the exact Hugoniot pressure. The time-averaged value of the pressure is always underestimated for a finite zone size. In our previous example, and at a time corresponding to a piston displacement of 20 mm, the time-averaged value of the pressure was underestimated by 14% for $\Delta X = 20$ mm, by 7% for $\Delta X = 10$ mm and by 3% for $\Delta X = 5$ mm. A computer simulation of a shock tube problem using finite element techniques is reported by Donea *et al.*[5]

ACKNOWLEDGMENT

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