Thermodynamics of systems with internal adiabatic constraints: time evolution of the adiabatic piston

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Abstract

The equations for the time evolution of the controversial adiabatic piston problem are obtained using a very primitive model of the fluids. It thus shows that the 1st and 2nd laws of thermodynamics lead to equations of motion which determine uniquely the final equilibrium state, while this state cannot be predicted using the laws of thermostatics only.

1 Introduction: the adiabatic piston problem

For the last 30 years an "elementary" problem of thermostatics has raised a certain amount of controversy, and, as far as I know, no explicit solution has been given. This is the so called adiabatic piston problem described as follow [3]. The system is composed of two fixed cylinders containing two fluids separated by an *adiabatic* movable piston, as shown in figure 1. A brake maintains first the piston at rest and the two fluids are in equilibrium with pressure, temperature, and volume, respectively given by $(p_1^{(0)}, T_1^{(0)}, V_1^{(0)})$ and $(p_2^{(0)}, T_2^{(0)}, V_2^{(0)})$. At a certain time the brake is released and the problem is to find the final equilibrium state. (The similar problem but with a diathermic piston is straightforward).

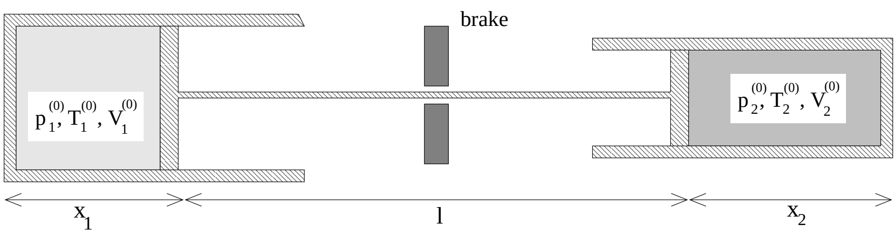

Figure 1: Initial state of the adiabatic piston problem: $x_1 + x_2 + l = D$; $l = \text{cst}, D = \text{cst}$. $V_i = A_i x_i$ with $A_i =$ area of the cylinders $i = 1, 2$

In Callen's word [3] "the movable adiabatic wall presents a unique problem with subtleties". However, within the framework of thermodynamics, it is neither unique (it appears in all systems with adiabatic walls, and adiabatic walls are at the basis of thermodynamics), nor subtle (since the adiabatic condition is expressed by the first and second laws and implies simply that the heat conduction is zero). On the other hand in the framework of thermostatics the problem is indeed more subtle since the constraints under which the entropy is maximum are given by inequalities ($\delta S_1 \geq 0, \delta S_2 \geq 0$), together with equalities ($\delta V_1 + \delta V_2 = 0, \delta U_1 + \delta U_2 = 0$), see ref. [11].

Assuming the area of the cylinders to be equal and using the principle of maximum of entropy Kubo [14], and Landau and Lifshitz [15], arrived at the conclusion that the condition for mechanical equilibrium is $\frac{p_1}{T_1} = \frac{p_2}{T_2}$, and they add that if heat transfer is also possible then $T_1 = T_2$. Callen [3], on the other hand, arrives at the conclusion that the final pressures will be equal ($p_1 = p_2$), but the final temperatures T_1, T_2 will depend on the relative viscosity of each fluid and can not be predicted; Nozière [18] gives the same conclusion, but writes that the final temperatures will depend on the ratio of viscosities; for Kestin [13], "the entropy produced is distributed over the two systems and can be computed only with the equations of fluid dynamics and, even then, with great difficulty"; for Carrington [4], "the maximum entropy production can tell us nothing about the equilibrium state".

It was then noted that Callen's argument, which was repeated by Leff [16], could not be correct since the equilibrium condition was derived from the first law, rather than the second law [7]. The correct proof of the equilibrium condition $p_1 = p_2$ was given by Curzon [6], and then later again by Chardin [5]. Indeed the controversy had started once more with an article by Barrat [1] (see also [2]) who claimed that the equality of temperatures follows from the definitions of work and heat. He then explained this result with a microscopic argument to conclude that movable adiabatic walls cannot exist. The error in this "proof" was pointed out in [5] and [12], where it was traced to a wrong application of the second law.

It seems that the controversy over this problem started because people were disturbed by the fact that thermostatics cannot always predict the final equilibrium, and arguments had to be found to explain such an "exceptional" result. This attitude is rather surprising since in classical mechanics, it is well known that the laws of statics, such as the principle of minimum potential energy (Lejeune-Dirichlet's theorem), do not always determine the equilibrium state to which the system will evolve under viscous friction: for the system in figure 2 (a), the minimum principle gives the equilibrium state $x = y = 0$; however for the system in figure 2 (b) the same minimum principle gives only the partial answer $y = 0$, and nobody is surprised: solving Newton's law of dynamics gives the unique solution.

In thermostatics the adiabatic piston is a mathematical problem of maximum with constraints. However the following type of arguments have been used:

1. Heat exchange and reversible processes. Gedanken experiments.

2. Real adiabatic movable walls can not exist from a microscopical point of view. Although this may be true, on can consider adiabatically closed systems as ideal systems (obtained as the limit where the heat conduction with the external environment

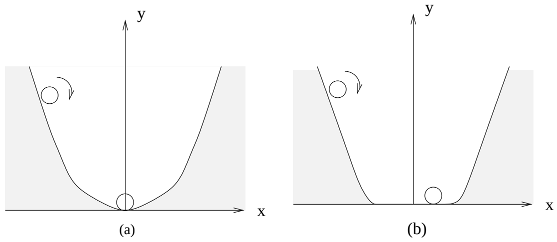

Figure 2: Ball rolling on a surface under the action of gravity and friction

tends to zero), just as frictionless systems are considered as ideal systems (obtained as the limit where the friction tends to zero). It is surprising to argue that such ideal systems do no exist since, from Carathéodory to Lieb and Yngvason [17], adiabatic processes form the basis for the axiomatic derivation of entropy and the second law of thermostatics. Therefore the real question is whether one can solve the adiabatic piston within the logic of thermodynamics.

3. Determinism was invoked to conclude that there "must" be another equation leading to $T_1 = T_2$. This claim is also surprising since determinism is associated with time evolution and not with equilibrium properties.

4. Unpredictability of the final temperatures is associated with boundary effects [9].

All these arguments are very surprising since none of them have been used for the one cylinder problem, or for the two-cylinders problem with diathermic piston, or for the special case of the two-cylinders problem with adiabatic piston for which one of the fluid is an ideal gas with no dissipation (thus $S_1 = \mathrm{cst}$ gives the necessary equation and leads to $T_1 \neq T_2$).

In the following, using a very primitive caricature of the fluids, I shall first derive the equations of motion for the one cylinder problem (Sect. 4), and then for the adiabatic piston problem (Sect. 5). Although the model is oversimplified, it gives an answer to the quesstions raised in the literature.

To avoid controversy, since the definitions and the statements of the two laws of thermodynamics differ very widely in the different textbooks, I will recall in Sect. 1 and 2, the formalism which is based on the book by Stueckelberg and Scheurer [8].

2 Framework of classical physics

In classical physics a *pure state* ρ of a given system can be entirely characterized by the values $(x_1, \dots, x_n)$ of a finite, or infinite, number of observables (or variables). For example, in classical mechanics the pure states of N point particles can be characterized either by $(\boldsymbol{x}_\alpha, \boldsymbol{v}_\alpha), \alpha = 1, \dots, N$, the position and the velocity of the particles (which may be submitted to further constraints), or by $(q_1, \dots, q_k, p_1, \dots, p_k)$ the generalized coordinates and momenta, or by any other set of variables such as angle-action variables,... For a one-component fluid, the state can be characterized by 5 fields, for example $(s(\boldsymbol{x}), m(\boldsymbol{x}), \boldsymbol{\Pi}(\boldsymbol{x}))$, the entropy density, the mass density, and the linear momentum density. A *state function* F is a physical property which depends only on the state of the system, i.e. $F = F[\rho]$ independent of the external world. Having chosen a set of variables $x_1, \dots, x_n$, the state function F is then represented by a function $F(x_1, \dots, x_n)$. For example the kinetic energy for N point particles will be represented either by $\sum_{\alpha=1}^{N} \frac{1}{2} m_\alpha \boldsymbol{v}_\alpha^2$ or by $\sum_{i,j=1}^{k} \frac{1}{2} a_{ij}(q) p_i p_j$.

For an *isolated system*, the determinism together with the homogeneity of time imply that the time evolution is described by a one-parameter group, or semi-group, of transformations. From those general assumptions follows that the time evolution of a classical system, described by the variables $(x_1, \dots, x_n)$, will be given by the solution of an ordinary differential equation:

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = f_i(x_1, \dots, x_n), \qquad i = 1, \dots, n \tag{1}$$

satisfying the initial conditions $x_i(t = 0) = x_i^{(0)}$.

Therefore, if the system is isolated then for any state function $F = F(x_1, \dots, x_n)$, the time derivative of F is again a state function. In fact we have:

$$\dot{F}(x_1, \dots, x_n) = \sum_i \left(\frac{\partial F}{\partial x_i} f_i \right) (x_1, \dots, x_n). \tag{2}$$

3 The two laws of thermodynamics

Following Stueckelberg and Scheurer, the two laws of thermodynamics are expressed in the following way.

First law For any system, there exists a state function, the *energy* E, which is extensive and conserved. Furthermore

$$\frac{\mathrm{d}E}{\mathrm{d}t} = P_W^{\mathrm{ext}}(t) + P_M^{\mathrm{ext}}(t) + P_Q^{\mathrm{ext}}(t) \tag{3}$$

where

$P_W^{\mathrm{ext}}(t)$ is the work-power done by the external world on the system by action on the work variables ξ_j, i.e.

$$P_W^{\mathrm{ext}}(t) = \sum_j F_j^{\mathrm{ext}}(t) \dot{\xi}_j \tag{4}$$

with $F_j^{\mathrm{ext}}(t)$ the generalized external force conjugate to ξ_j;

$P_M^{\mathrm{ext}}(t)$ is the power done by the external world on the system by transfer of matter; and

$P_Q^{\mathrm{ext}}(t)$, the remaining contribution, is the "heat-power" transferred from the external world to the system.

The system is then said to be *adiabatically closed* if both $P_Q^{\text{ext}}(t) = 0$ and $P_M^{\text{ext}}(t) = 0$ for all t. In other words the system is adiabatically closed if there is no exchange of matter with the outside and

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \sum_j F_j^{\text{ext}}(t)\dot{\xi}_j \tag{5}$$

Second law For any system there exists a state function, the *entropy* S, which is extensive, and satisfies the following two conditions:

a) if the system is *adiabatically closed*

$$\frac{\mathrm{d}}{\mathrm{d}t}S(t) \geq 0; \tag{6}$$

b) if the system is *isolated*

$$\lim_{t\to+\infty} S(t) = S_f = \max_{\rho \text{ compatible}} S[\rho] \tag{7}$$

where (7) means that $S(t)$ tends, in the distant future, towards a value S_f which is a local maximum of the state function $S[\rho]$ over all state ρ compatible with the constraints.

Let us recall that the constraints appear either as equalities (such as $g(x) = g(x^{(0)})$, or as inequalities (such as $dS_k \geq 0$, for adiabatic walls [11]).

It is not always fully appreciated that the above statements of the two laws yield as consequence all other statements which can be found in the literature concerning the second law. Moreover it should be stressed that no notion of "temperature" or "heat" appear in the statement of the 2nd law, except for the concept of adiabatically closed which is defined by the 1st law.

Part (a) of the 2nd law, together with the 1st law, gives the time evolution. On the other hand part (b), which defines the arrow of time, expresses the fact that the isolated system evolves towards a stable equilibrium state in the distant future. In this way $-S[\rho]$ appears as the Lyapunov's function associated with the equation of motion (1). Furthermore part (b) of the 2nd law, together with the 1st law, yields all the basic axioms of thermostatics, as well as the zeroth law of thermodynamics. (In the same way as in mechanics where the laws of statics are consequences of the laws of dynamics).

Let us remark that the above statement of the second law refers to ideal thermodynamical systems, i.e. systems for which the dissipation is such that the system will evolve toward an equilibrium state (which is part of the zeroth law of thermodynamics). On the other hand for ideal mechanical systems there is no dissipation and no approach toward equilibrium. It is possible however to modify the statement of the second law to include systems for which only some, or none, of the variables evolve toward equilibrium values. For such a generalisation, one should replace part (b) of the 2nd law by

(b′) the stable equilibrium states of the isolated system are strict local maxima of $S[\rho]$ over all states ρ compatible with the constraint.

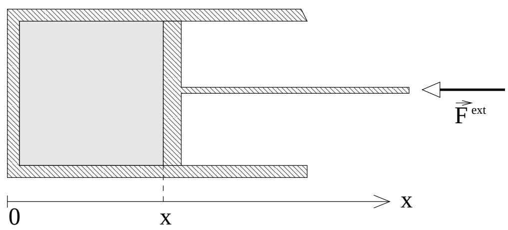

Figure 3: One-cylinder problem. $\boldsymbol{F}^{\text{ext}} = -p^{\text{ext}} A \boldsymbol{e}$ where A is the area of the cylinder

This statement (b′) is the extension to thermodynamics of the conjecture introduced in classical mechanics that the stable equilibrium states are strict local minima of the potential energy (i.e. the converse of Lejeune-Dirichlet's theorem). We shall come back on this point in the examples below.

4 Preliminary exercise: the one-cylinder problem

Let us first consider the one cylinder problem. The system is the fluid contained in the cylinder of figure 3. It is a closed system, i.e. there is no exchange of matter with the outside.

We shall assume that the state of the fluid can be entirely characterized by 3 variables (S, x, v) where $v = \frac{\mathrm{d}x}{\mathrm{d}t}$. It is of course a very primitive model of the fluid; however it is an improved version of the description usually introduced, where one assumes that the state of the fluid is defined by 2 variables only (S, x).

From the 1st law, there exists a state function $E = E(S, x, v)$ such that

$$\frac{\mathrm{d}E}{\mathrm{d}t} = F^{\text{ext}}(t)\dot{x} + P_Q^{\text{ext}}(t) \tag{8}$$

Introducing, as usual, the state functions

$$T(S, x, v) = \frac{\partial E}{\partial S} = \text{“temperature”} \tag{9}$$

and

$$F^{\text{int}}(S, x, v) = -\frac{\partial E}{\partial x} \qquad \text{or} \quad p = -\frac{1}{A}\frac{\partial E}{\partial x} = \text{“pressure”} \tag{10}$$

eq. (8) becomes

$$T\dot{S} - F^{\text{int}}\dot{x} + \frac{\partial E}{\partial v}\dot{v} = F^{\text{ext}}(t)\dot{x} + P_Q^{\text{ext}}(t). \tag{11}$$

In the following we shall assume that the "temperature" is positive [8] .

Case i) Consider first the case where the system is *isolated*, i.e. $F^{\text{ext}}(t) = 0$ and $P_Q^{\text{ext}}(t) = 0$. We have from eq. (11)

$$\dot{S} = \frac{1}{T}\left[F^{\text{int}} v - \frac{\partial E}{\partial v}\dot{v}\right]. \tag{12}$$

Since the system is isolated, $\dot{S}$ is a state function, i.e. there exists a state function $I(S, x, v)$ such that

$$I(S, x, v) = \frac{1}{T}\left[F^{\text{int}} v - \frac{\partial E}{\partial v}\dot{v}\right]. \tag{13}$$

Furthermore from the second law $I(S, x, v)$ is non negative, from which one concludes that there exist 4 state functions $\lambda_{\alpha\beta} = \lambda_{\alpha\beta}(S, x, v)$ such that

$$\begin{cases} F^{\text{int}} = \lambda_{xx} v + \lambda_{xv}\dot{v} & (14) \\ -\dfrac{\partial E}{\partial v} = \lambda_{vx} v + \lambda_{vv}\dot{v} & (15) \end{cases}$$

satisfying the conditions:

$$\lambda_{xx} \geq 0, \quad \lambda_{vv} \geq 0, \quad \left[4\lambda_{xx}\lambda_{vv} - (\lambda_{xv} + \lambda_{vx})^2\right] \geq 0. \tag{16}$$

We then have

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{1}{T}\sum_{\alpha\beta}\lambda_{\alpha\beta}\xi_\alpha\xi_\beta \geq 0, \qquad (\xi_1, \xi_2) = (x, v). \tag{17}$$

Case ii) One then considers the *adiabatically closed system*, i.e. $P_Q^{\text{ext}}(t) = 0$. In this case, we now have from (11):

$$\dot{S} = \frac{1}{T}\left[(F^{\text{ext}}(t) + F^{\text{int}})v - \frac{\partial E}{\partial v}\dot{v}\right]. \tag{18}$$

Since the system is adiabatically closed we must have from the 2$^{\text{nd}}$ law $\dot{S} \geq 0$. This inequality will then be satisfied if we replace (14) by

$$\begin{cases} F^{\text{ext}}(t) + F^{\text{int}} = \lambda_{xx} v + \lambda_{xv}\dot{v} & (19) \\ -\dfrac{\partial E}{\partial v} = \lambda_{vx} v + \lambda_{vv}\dot{v} & (20) \end{cases}$$

From (19) it is clear that $\dot{v}$ is not a state function (it depends on the outside through $F^{\text{ext}}(t)$). On the other hand in (20) all terms except $\dot{v}$ are state functions. We are thus forced to impose

$$\lambda_{vv} = 0 \tag{21}$$

and from (16)

$$\lambda_{xv} + \lambda_{vx} = 0. \tag{22}$$

Introducing the state function

$$m(S, x, v) = \lambda_{xv} = -\lambda_{vx} \tag{23}$$

we have from (20) and (21)

$$\frac{\partial E}{\partial v} = mv. \tag{24}$$

Going back to (18) we thus obtain from (24)

$$\dot{S} = \frac{1}{T}\left[F^{\text{ext}}(t) + F^{\text{int}} - m\dot{v}\right] v \tag{25}$$

and, in order to satisfy the condition $\dot{S} \geq 0$, one concludes that there exists a state function $\lambda(S, x, v)$ such that

$$\begin{cases} F^{\text{ext}}(t) + F^{\text{int}} - m\dfrac{\mathrm{d}v}{\mathrm{d}t} = \lambda v & (26) \\ \qquad\qquad\qquad\quad \dfrac{\mathrm{d}S}{\mathrm{d}t} = \dfrac{\lambda}{T}v^2 \qquad \text{with} \quad \lambda \geq 0. & (27) \end{cases}$$

We note that eq. (26) is Newton's equation of motion with friction force $-\lambda v$, while (27) expresses the fact that the entropy production $\dot{S}$ is the power dissipated by the friction force divided by the "temperature".

Let us also note that (23) is an expression of Onsager's relation, with the minus sign since x is invariant, while v changes sign, under time reversal.

Case iii) Finally let us consider the case where the closed system also exchanges heat with the outside. From (11) and the previous discussion we have

$$T\dot{S} = \left[F^{\text{ext}}(t) + F^{\text{int}} - m\dot{v}\right] v + P_Q^{\text{ext}}(t) \tag{28}$$

and from (27) we arrive at the *time evolution*

$$\begin{cases} m\dfrac{\mathrm{d}v}{\mathrm{d}t} = F^{\text{ext}}(t) + F^{\text{int}} - \lambda v & (29) \\ \dfrac{\mathrm{d}S}{\mathrm{d}t} = \dfrac{\lambda}{T}v^2 + \dfrac{1}{T}P_Q^{\text{ext}}(t), \qquad \lambda \geq 0 & (30) \end{cases}$$

Expressed in terms of pressures (29) would be (fig. 3 and eq. (9))

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = \left(p - p^{\text{ext}}(t)\right) A - \lambda v. \tag{31}$$

For example for a van der Waals fluid with N moles

$$p(T,x) = \frac{RT}{\frac{A}{N}x - b} - a\,\frac{N^2}{A^2}\frac{1}{x^2} \tag{32}$$

$$S(T,x) = NR\ln\left[\left(\frac{A}{N}x - b\right)T^{\frac{3}{2}}\right] + \text{constant}. \tag{33}$$

$\lambda(T,x,v) = \lambda(T,v)$ can be taken from the tables, and we can assume that m is the mass of the fluid.

Case iv) We consider again the *isolated system* with $F^{\text{ext}}(t) = F^{\text{ext}} = \text{cst}$ and $P_Q^{\text{ext}}(t) = 0$. It is seen from (30), (31) that for λ strictly positive the system will evolve toward an equilibrium state with $v = 0$ and $p = p^{\text{ext}}$. On the other hand using part (b) of the 2nd law, the condition of extremum of S under the constraints $E = \bar{E} =$ fixed implies

$$mv = 0 \qquad \text{and} \qquad F^{\text{ext}} + F^{\text{int}} = 0 \tag{34}$$

while the condition of maximum of S yields

$$m(S,x,v=0) \geq 0 \qquad \text{and} \qquad \frac{\partial^2 U}{\partial x^2} \geq 0 \tag{35}$$

where $U(S,x) = E(S,x,v=0)$.

In conclusion, assuming $T > 0$, part (a) of the 2nd law imposes the condition that the friction coefficient $\lambda(S,x,v)$ is strictly positive, while part(b) imposes the conditions that the mass m and the "spring constant" $k = \frac{\partial^2 U}{\partial x^2}$ are non negative state functions. In other words part (b) of the second law is the condition that the system evolves toward a stable equilibrium state.

We should remark that for $\lambda = 0$ (no friction), the isolated system will not reach equilibrium and part (b) is violated; however the statement (b$'$) will be valid.

Let us also remark that it is usually assumed that the state of the fluid is defined by only two variables $(S, x = \frac{V}{A})$. Under this assumption, the time evolution is

$$\begin{cases} \dfrac{\lambda}{A}\dfrac{\mathrm{d}x}{\mathrm{d}t} = p - p^{\text{ext}}(t) & (36) \\[2mm] \dfrac{\mathrm{d}S}{\mathrm{d}t} = \dfrac{\lambda}{T}v^2 + \dfrac{1}{T}P_Q^{\text{ext}}(t) & (37) \end{cases}$$

It should be stressed that as far as the final equilibrium state is concerned both description will give the same result $(p = p^{\text{ext}}, v = 0)$. One should also remark that in this case both the velocity v and the entropy production $\frac{\lambda}{T}v^2$ are not state functions.

5 The adiabatic piston

The system is composed of the two subsystems discussed in section 4 and the connecting rod (fig 1). As in section 4 we assume now that the state of the system can be entirely

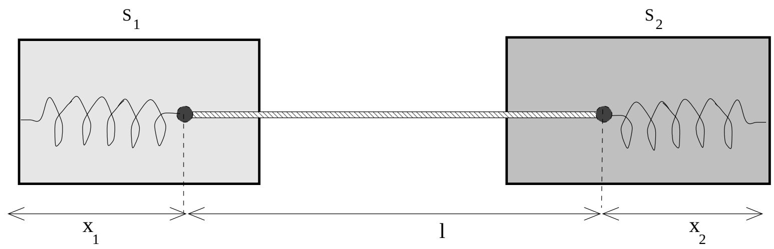

Figure 4: Two coupled damped oscillators

characterized by the 4 variables (S_1, S_2, x, v), where $x = x_1, x_1 + x_2 + l = D, v_1 = v, v_2 = -v$.

As we have already mentionned, it is a very primitive model for the problem under investigation. In fact this description would be more appropriate to the problem of two coupled, damped, oscillators represented on figure 4, which illustrates the same properties.

From the 1st law, we have

$$E(S_1, S_2, x, v) = E_1(S_1, x, v) + E_2(S_2, D - l - x, -v) + \frac{1}{2}\mu v^2 \tag{38}$$

where μ is the mass of the connecting rod. Since the system is isolated

$$\frac{\mathrm{d}E}{\mathrm{d}t} = T_1 \frac{\mathrm{d}S_1}{\mathrm{d}t} + T_2 \frac{\mathrm{d}S_2}{\mathrm{d}t} - \left(F_1^{\mathrm{int}} - F_2^{\mathrm{int}}\right)\dot{x} + Mv\dot{v} = 0 \tag{39}$$

where $M = (m_1 + m_2 + \mu)$ is non negative and $F_i^{\mathrm{int}}(S_i, x_i, v_i) = p_i A_i$. From the extensivity of the entropy and (39),

$$\begin{aligned} \frac{\mathrm{d}S}{\mathrm{d}t} &= \frac{\mathrm{d}S_1}{\mathrm{d}t} + \frac{\mathrm{d}S_2}{\mathrm{d}t} \\ &= \left[T_1 \frac{\mathrm{d}S_1}{\mathrm{d}t}\right]\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \left[\frac{1}{T_2}\left(F_1^{\mathrm{int}} - F_2^{\mathrm{int}} - M\dot{v}\right)\right] v \end{aligned} \tag{40}$$

Since the system is isolated $\dot{S}$ is a non-negative state function. Therefore from (40) one concludes that there exist 4 state functions $L_{\alpha,\beta} = L_{\alpha,\beta}(S_1, S_2, x, v)$, such that

$$\begin{cases} \frac{1}{T_2}\left(F_1^{\mathrm{int}} - F_2^{\mathrm{int}} - M\dot{v}\right) = L_{11} v + L_{12}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) & (41) \\ T_1 \frac{\mathrm{d}S_1}{\mathrm{d}t} = L_{21} v + L_{22}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) & (42) \end{cases}$$

with

$$L_{11} \geq 0, \quad L_{22} \geq 0, \quad 4L_{11}L_{22} - (L_{12} + L_{21})^2 \geq 0 \tag{43}$$

which then gives

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sum_{\alpha,\beta} L_{\alpha,\beta}\xi_\alpha\xi_\beta \geq 0, \quad (\xi_1, \xi_2) = (v, \frac{1}{T_1} - \frac{1}{T_2}) \tag{44}$$

Since both cylinders and the connecting rod are adiabatically closed, we must have (part (a) of the 2nd law)

$$\frac{\mathrm{d}S_1}{\mathrm{d}t} \geq 0 \quad \text{and} \quad \frac{\mathrm{d}S_2}{\mathrm{d}t} \geq 0 \tag{45}$$

and since L_{22} is non-negative (42), (43), (45) imply

$$L_{22} = 0 \quad \text{and} \quad L_{21} = -L_{12} = \lambda_1 v \tag{46}$$

(which is again the expression of Onsager relation since v changes sign, and $\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ is invariant under time reversal). Therefore:

$$\begin{cases} M\dfrac{\mathrm{d}v}{\mathrm{d}t} = F_1^{\text{int}} - F_2^{\text{int}} - \left[T_2 L_{11} - \lambda_1\left(\dfrac{T_2}{T_1} - 1\right)\right] v & (47) \\ T_1\dfrac{\mathrm{d}S_1}{\mathrm{d}t} = \lambda_1 v^2, \qquad \text{with} \quad \lambda_1 \geq 0 & (48) \end{cases}$$

where, from the model discussed in Sect. 3, we conclude that λ_1 is independent of S_2, i.e. $\lambda_1 = \lambda_1(S_1, x, v)$. Moreover from (39) and (46)

$$T_2\frac{\mathrm{d}S_2}{\mathrm{d}t} = \left(F_1^{\text{int}} - F_2^{\text{int}} - M\dot{v}\right) v - T_1\frac{\mathrm{d}S_1}{\mathrm{d}t} \tag{49}$$

$$= T_2\left(L_{11} - \frac{\lambda_1}{T_1}\right) v^2 \tag{50}$$

And the condition (45) implies that

$$L_{11} - \frac{\lambda_1}{T_1} = \frac{\lambda_2}{T_2} \geq 0 \tag{51}$$

From the model discussed in sect. 3 we conclude that λ_2 is independent of S_2.

In conclusion we have obtained the *equation of motion for the adiabatic piston problem*:

$$\begin{cases} M\dfrac{\mathrm{d}v}{\mathrm{d}t} = F_1^{\text{int}} - F_2^{\text{int}} - (\lambda_1 + \lambda_2)v, \qquad M \geq 0 & (52) \\ \dfrac{\mathrm{d}S_1}{\mathrm{d}t} = \dfrac{\lambda_1}{T_1}v^2 \qquad \lambda_1(S_1, x_1, v_1) \geq 0 & (53) \\ \dfrac{\mathrm{d}S_2}{\mathrm{d}t} = \dfrac{\lambda_2}{T_2}v^2 \qquad \lambda_2(S_2, x_2, v_2) \geq 0 & (54) \end{cases}$$

from which the total entropy production in the system is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \left(\frac{\lambda_1}{T_1} + \frac{\lambda_2}{T_2}\right) v^2 \tag{55}$$

It is thus seen that the *equilibrium states* must satisfy

$$v = 0, \qquad p_1 A_1 = p_2 A_2, \qquad U_1(S_1, x_1) + U_2(S_2, x_2) = \bar{E} \tag{56}$$

where $U_i(S_i, x_i) = E_i(S_i, x_i, v = 0), x_1 + x_2 = D - l$ and $p_i A_i = -\frac{\partial U_i}{\partial x_i}$. However there is no relation between T_1 and T_2. If both friction coefficients λ_1 and λ_2 are positive, the system will evolve toward the equilibrium state given by the solution of the equation of motion. If $\lambda_1 = 0$ and $\lambda_2 > 0$, the equilibrium state is given by (54) together with $S_1 = S_1^{(0)}$. If both λ_1 and λ_2 are zero, there is no dissipation and the piston will oscillate without damping.

It should be remarked that for this system, and for the system of figure 2b, the law of stable equilibrium (introduced in [11], p. 367, to generalize the second law of thermostatics), or the general form of the second law of thermostatics given in [14] (vol. II, p. 2) cannot be valid. Indeed the final equilibrium state is not unique and depends upon the order in which the constraints are removed (i.e. the way the brake is released). On the other hand the second law of thermodynamics given in sect. 3 [8] gives the time evolution and the final equilibrium state.

Let us finally note that for the *diathermic piston*, L_{22} is positive. In this case the equation of motion are

$$\begin{cases} M\dfrac{\mathrm{d}v}{\mathrm{d}t} = F_1^{\mathrm{int}} - F_2^{\mathrm{int}} - (\lambda_1 + \lambda_2)v & (57) \\ \dfrac{\mathrm{d}S_1}{\mathrm{d}t} = \dfrac{\lambda_1}{T_1}v^2 + L_{22}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)\dfrac{1}{T_1} & (58) \\ \dfrac{\mathrm{d}S_2}{\mathrm{d}t} = \dfrac{\lambda_2}{T_2}v^2 - L_{22}\left(\dfrac{1}{T_1} - \dfrac{2}{T_2}\right)\dfrac{1}{T_2} & (59) \end{cases}$$

and the total entropy production is now

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \left(\frac{\lambda_1}{T_1} + \frac{\lambda_2}{T_2}\right)v^2 + L_{22}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^2 \tag{60}$$

Let us now also note that (58), (59), together with (36) give

$$P_Q^{2\to 1} = L_{22}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = -P_Q^{1\to 2} \tag{61}$$

and thus L_{22} is the heat conductivity.

From the equation of motion for the *diathermic piston* (57-59) we conclude that if $(\lambda_1 + \lambda_2)$ is positive, the piston will evolve toward the equilibrium state

$$v = 0, \qquad T_1 = T_2, \qquad p_1 A_1 = p_2 A_2. \tag{62}$$

On the other hand if $\lambda_1 = \lambda_2 = 0$, the piston will oscillate without damping, but the temperatures will become equal in the distant future.

6 Conclusion

Using a very primitive caricature of the fluids, it has been shown that the laws of thermodynamics lead to ordinary differential equations (1), from which the final equilibrium state can be uniquely predicted. On the other hand this example illustrates the fact that the principle of extremalisation of entropy under specific constraints is equivalent to the condition that the right hand side of (1) is zero [8], i.e. it is equivalent to finding the equilibrium points of the O.D.E (1) (while the condition of maximalisation yields conditions on the sign of the phenomenological coefficients). In all cases where there is a finite or infinite number of such equilibrium points the laws of thermostatics will not be able to predict the final state of the system. It was seen in this model that this situation happens if the heat conductivity is exactly zero; moreover if both friction coefficients are exactly zero the system will oscillate. It should also be remarked that the equation of motions will remain valid in the case of solid friction (i.e. if $\lambda v = \mu \mathrm{sgn} v$), while no information can be obtained from thermostatics. In conclusion the beauty and the power of thermodynamics lies in the fact that it is the general theory describing the time evolution, and the equilibrium properties, of any macroscopical system, e.g. one can derive from the 1^{st} and 2^{nd} law the Lagrange equations of motion of classical mechanics, with or without friction [10].

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