On the Second Law of Thermodynamics and the Piston Problem

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The piston problem is investigated in the case where the length of the cylinder is infinite (on both sides) and the ratio m/M is a very small parameter, where m is the mass of one particle of the gaz and M is the mass of the piston. Introducing initial conditions such that the stochastic motion of the piston remains in the average at the origin (no drift), it is shown that the time evolution of the fluids, analytically derived from Liouville equation in a previous work, agrees with the Second Law of thermodynamics. We thus have a non equilibrium microscopical model whose evolution can be explicitly shown to obey the two laws of thermodynamics.

KEY WORDS: Nonequilibrium; thermodynamics; entropy; entropy production; piston; similarity flow.

1. INTRODUCTION

Recently the well-known "adiabatic piston problem" has attracted a lot of attention.[1–25] Most investigations have however concentrated on the motion of the piston and very few studies have been made concerning the time evolution of the fluids on the two sides of the piston. In our previous works[5,6] it was shown that the piston in a cylinder of finite length evolves with two different time scales. In a first time scale the motion of the piston can be considered as "deterministic" and "adiabatic", and the system evolves to a state of mechanical equilibrium where the pressures on both sides are approximately equal, but the temperatures differ. Then on a much larger time scale (if $m \ll M$), the piston evolves "stochastically" and

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with "heat transfer" to a state of thermal equilibrium, where the temperatures (and the pressures) on both sides of the piston are equal. It was shown in ref. 5a that in the first time scale the relaxational motion of the piston can be either weakly damped or strongly damped depending on whether the parameter $R = M_{\text{gas}}/M_{\text{piston}}$ is small ($R < 1$) or large ($R > 1$) where M_{gas} is the total mass of the gas.

A microscopical analysis of this model was given in ref. 5a,b. In the first paper in ref. 5a, we derived the general time evolution of the system starting from Liouville equation, and then we investigated its solutions in the thermodynamic limit ($M \to \infty$, area of the piston $A \to \infty$, M/A finite), which will correspond to the first time-scale evolution of the finite-mass piston. Then in ref. 5b, introducing three "reasonable" assumptions (which were not necessary in the thermodynamic limit) and using a singular two-scale perturbation approach with respect to m/M, we were able to describe the two-time scale evolution of the piston, but we never analyzed the evolution of the fluids. It was shown that the results obtained were qualitatively in good agreement with those observed on a very large number of numerical simulations, except for the observed damping coefficient which appears a lot smaller than the predicted value. It was realized that the underlying damping mechanism must be related to the propagation of sound waves bouncing back and forth between the boundaries of the cylinder and the piston. Unfortunately the effect of such a wave propagation could not be taken into account in our previous analysis, because of the "average assumption" we had used (i.e., the values of density, pressure, temperature on the right/left surface of the piston can be replaced by the average of these quantities in the right/left compartment), which is in fact the usual assumption introduced to analyze experimental measurements.[26] Therefore to understand how the damping effect can be generated by purely elastic collisions on the piston surface and cylinder walls, we are forced to investigate the propagation of shock waves through the ideal and out-of-equilibrium fluids (in the sense of Landau–Lifshitz.[27])

Although this work was motivated by the damping properties observed in the first time scale, which is the most relevant for real experiments and also a challenging issue to understand, we have restricted the following consideration to the analysis of the wave propagation in the fluids, which had not been done so far. Moreover, from thermodynamics, it is expected that damping is associated with dissipation and thus with entropy production. Therefore, another motivation for this work is to understand "entropy production" in the piston problem, and more generally to investigate the compatibility of the time evolution obtained from the microscopic laws with the laws of non-equilibrium thermodynamics. The same question has been recently investigated by Gaspard *et al.*, for another model.[28]

To simplify our investigation on the shock waves in the fluids, we shall consider the case where the length of the cylinder is infinite on both sides and all velocities (of the particles and the piston) are parallel to the axis of the cylinder. Initially the fluids on the left and on the right of the piston are each in thermal equilibrium with densities $n_0^\pm$, temperatures $T_0^\pm(T_0^+ > T_0^-)$ and pressures $p_0^\pm$, where the index $+/-$ refer to the right/left of the piston. To simplify the problem further we have chosen the pressures $p_0^\pm$ (given $T_0^\pm$) in such a manner that the piston, which evolves stochastically under the elastic collisions with the particles, remains on the average at the origin (for a time sufficiently short to neglect the Brownian deviation—a second-order contribution to the piston motion). With these initial conditions no work will be done by the right side on the left side and there will be only heat transfer (from the right to the left since $T_0^+ > T_0^-$) induced by the stochastic motion of the piston around the origin. It should be stressed that since the size of the compartments is infinite the fluids will remain for all time out of equilibrium and the asymptotic state of any finite region, in particular near the piston surface, will be a non-equilibrium stationary state (with heat flux).

Following the analysis in ref. 5b, which is a singular perturbative approach in powers of the small parameter m/M, we shall derive, for these initial conditions, the distribution function for the velocity of the piston, in the stationary state (of the piston), to first order in $\sqrt{m/M}$. Using the fact that we have only elastic collisions in our model, we shall then derive the distribution function $\rho(x, v; t)$ for the fluids. Finally we shall obtain from the well-known relations of kinetic theory the density fields $n(x, t)$, the velocity fields $w(x, t)$, the stress (tensor) $\tau(x, t)$ and the "heat" flux $j_Q(x, t)$. In other words we will obtain the time evolution of our microscopical model, considered as a fluid out of equilibrium.

The next problem we shall discuss in the following is whether the evolution thus obtained obeys the laws of non-equilibrium thermodynamics. In particular the question will be whether it is possible to find a microscopically rooted entropy $s(x, t)$, entropy flux $j_S(x, t)$, entropy production $i(x, t)$, temperature $T(x, t)$, pressure $p(x, t)$, from which we recover the above time evolution of the fluids.

It will be shown that whatever is the definition of entropy $s(x, t)$, it is impossible to define the entropy flux by $j_Q = T j_S$, as usual in thermodynamics, with $j_Q(x, t)$ and $T(x, t)$ given by the kinetic theory formulae: this leads to an entropy production $i(x, t)$ which becomes negative around the front of the shock wave. On the other hand if we take Boltzmann's definition for $s(x, t)$ and $j_S(x, t)$, then we are forced to define the temperature by $T = j_Q/j_S$ to be in agreement with the Second

Law, and in this case we do not recover the well-known thermodynamic relations (such as $T = \frac{\partial u}{\partial s}$). However, we shall see that it is possible to consider our fluid as a two-component simple fluid described by a fundamental equation $s = s(u, n_1, n_2)$. It will be shown that it is possible from this starting point to recover our fluid equations, together with the well-known phenomenological equations of thermodynamics, and an entropy production which is strictly positive. Moreover this entropy function will coincide with the Boltzmann entropy at those points where the fluid is in a stationary state (i.e., at $\pm\infty$ and on the right/left surface of the piston).

In Section 2 we shall recall the thermodynamic equations of the 1-component and the 2-component simple fluids. We then recall in Section 3 the microscopical definitions introduced in kinetic theory for the thermodynamical variables. The piston problem and the distribution function for the velocity of the piston in the stationary state are presented in Section 4. We then discuss the properties of the fluids at the surface of the piston in Section 5, and the general evolution of the fields in Section 6. The problem of entropy and entropy production is discussed in Sections 7 and 8 and numerical graphs of the different fields are presented for a specified set of initial conditions. Finally, general conclusions are presented in the last section.

2. THERMODYNAMICS OF 1-DIMENSIONAL SIMPLE FLUIDS

It is well known that the conservation of the number of particles, the linear momentum, and the energy, i.e., the First Law of thermodynamics, give for a single component fluid in 1-dimension the following equations for the density of particles $n(x, t)$, the fluid velocity $w(x, t)$ and the energy density $e(x, t)$:

$$\partial_t n + \partial_x(nw) = 0, \tag{1}$$

$$mn[\partial_t w + w\partial_x w] - \partial_x \tau = 0, \tag{2}$$

$$\partial_t e + \partial_x(ew + j_e) = 0, \tag{3}$$

where m is the mass of one particle, τ is the stress (tensor) and j_e is the energy current, adding to the "convective" contribution ew. We have also assumed that the fluid is not submitted to external forces. Furthermore, the Second Law of thermodynamics yields for the entropy density $s(x, t)$:

$$\begin{aligned} \partial_t s + \partial_x(sw + j_S) &= i, \\ i = i(x, t) &\geqslant 0 \quad \text{for all } (x, t), \end{aligned} \tag{4}$$

where $j_S(x, t)$ is the entropy current and $i(x, t)$ the "internal entropy production" or "irreversibility".

A simple fluid is defined by the condition that there exists a function $u = u(s, n)$, independent of x and t, such that:

$$e = \tfrac{1}{2} mnw^2 + u(s, n),\tag{5}$$

and in this case, one introduces the temperature $T(x, t)$ and the pressure $p(x, t)$ by the thermodynamical definitions:

$$T = \frac{\partial u}{\partial s}, \qquad \mu = \frac{\partial u}{\partial n}, \qquad p = Ts + \mu n - u.\tag{6}$$

It follows from Eqs. (1–6) that:

$$j_e = -\tau w + j_Q,\tag{7}$$
$$j_Q = Tjs,\tag{8}$$
$$i = j_Q \partial_x \left(\frac{1}{T}\right) + \frac{1}{T}(\tau + p)\partial_x w.\tag{9}$$

The description of a two-component fluid involves an additional equation, for the density $n_1(x, t)$ of the first component and the associated current $j_1(x, t)$:

$$\partial_t n_1 + \partial_x (n_1 w + j_1) = 0.\tag{10}$$

Assuming that the particles of the two components have all the same mass, the simple fluid is now defined by the condition that there exists a function $u = u(s, n_1, n_2)$ such that:

$$e = \tfrac{1}{2} mnw^2 + u(s, n_1, n_2) \qquad \text{with } n = n_1 + n_2.\tag{11}$$

Again one introduces the temperature $T(x, t)$ and the pressure $p(x, t)$ by the thermodynamical definitions:

$$T = \frac{\partial u}{\partial s}, \qquad \mu_i = \frac{\partial u}{\partial n_i}, \qquad p = Ts + \mu_1 n_1 + \mu_2 n_2 - u.\tag{12}$$

In that case we obtain

$$j_e = -\tau w + j_Q,\tag{13}$$
$$j_Q = Tjs + j_1(\mu_1 - \mu_2),\tag{14}$$
$$i = j_Q \partial_x \left(\frac{1}{T}\right) + \frac{1}{T}(\tau + p)\partial_x w + j_1 \partial_x \left(\frac{\mu_2 - \mu_1}{T}\right).\tag{15}$$

Let us stress that the "heat current" is not a uniquely defined concept in the case of a two-component fluid. One can either introduce the heat current by the condition that the sum of the "heat" current plus the "work" current $-\tau w$ yields the "energy" current j_e, so that j_Q defined above by Eq. (13) is interpreted as the heat current. Alternatively one can define a heat current j_H by the condition that Eq. (8), written above for a one-component fluid, remains the phenomenological relation between the "heat" and the "entropy" currents, i.e.,

$$j_H = T j_S = j_Q - j_1(\mu_1 - \mu_2). \tag{16}$$

With this definition the entropy production is expressed by

$$i = j_H \partial_x \left(\frac{1}{T} \right) + \frac{1}{T}(\tau + p)\partial_x w + \frac{1}{T} j_1 \partial_x (\mu_2 - \mu_1), \tag{17}$$

which is the usual form in thermodynamics.

The irreversibility $i(x, t)$ is thus a sum of products ["current" times "force"] and usually one introduces at this point phenomenological relations between forces and currents to ensure that the irreversibility is non-negative for all (x, t). Indeed, whereas the First Law Eqs. (1–3) can be understood from any microscopic viewpoint and has the status of an exact and inviolable necessity, the Second Law Eq. (4), which is of fundamental importance for non-equilibrium macroscopical physics, is a statement concerning concepts, "entropy" and "entropy production", for which there seems to be no agreement on a microscopical definition, except for equilibrium states, and whose necessity for non-equilibrium situations is even subject to controversy [29,30].

In the following we shall consider this issue for the piston problem described in the introduction. For this problem we are led to consider the special case where

$$u = \frac{1}{2} n k_B T = -\frac{\tau}{2}. \tag{18}$$

It then follows that:

$$s(u, n_1, n_2) = n k_B \left[\frac{1}{2} \left(1 + \ln \frac{4\pi u}{mn^3} \right) + g(n_1, n_2) \right], \tag{19}$$

where $g = g(n_1, n_2)$ is so far undetermined and:

$$p = nk_B T \left(1 - n_1 \frac{\partial g}{\partial n_1} - n_2 \frac{\partial g}{\partial n_2} \right). \tag{20}$$

In that case the viscous-stress (tensor) τ_{fr} is given by:

$$\tau_{fr} = \tau + p = -nk_B T \left(n_1 \frac{\partial g}{\partial n_1} + n_2 \frac{\partial g}{\partial n_2} \right). \tag{21}$$

Note that if the two fluids are identical and in equilibrium, then using the definition of Boltzmann entropy (Section 3) for $s(x, t)$, we have $g(n_1, n_2) \equiv 0$.

3. KINETIC THEORY

To obtain a microscopical definition of the entropy density $s(x, t)$, we consider the kinetic framework underlying the above fluid description. We consider a system of point particles, with mass m, in a semi-infinite cylinder $x \leqslant 0$. We assume that all velocities are parallel to the axis of the cylinder (i.e., the x-axis) and that the particles interact through pure elastic collisions only. In kinetic theory, this "one-dimensional" system is described by a distribution function $\rho(x, v, t)$ solution of the continuity equation:

$$(\partial_t + v\partial_x)\rho(x, v, t) = 0 \quad \text{for } x < 0 \tag{22}$$

together with the boundary condition at $x = 0$:

$$\int_{-\infty}^{+\infty} dv\, \rho(x, v, t)v = 0. \tag{23}$$

It is well known that one recovers the conservation equations for the one-component fluid Eqs. (1–3) by means of the following definitions:

$$n(x, t) = \int_{-\infty}^{+\infty} dv\, \rho(x, v, t), \tag{24}$$

$$w(x, t) = \frac{1}{n(x, t)} \int_{-\infty}^{+\infty} dv\, \rho(x, v, t)v, \tag{25}$$

$$\tau(x, t) = -m \int_{-\infty}^{+\infty} dv\, \rho(x, v, t)(v - w(x, t))^2, \tag{26}$$

$$j_Q(x, t) = \frac{m}{2} \int_{-\infty}^{+\infty} dv\, \rho(x, v, t)(v - w(x, t))^3, \tag{27}$$

$$e = \tfrac{1}{2} nmw^2 + u, \tag{28}$$

$$u = -\tfrac{1}{2}\tau, \tag{29}$$

$$j_e = -\tau w + j_Q. \tag{30}$$

We would like to complete these equations with a continuity equation for the entropy. In other words we want to define the fields entropy density, current of entropy, production of entropy, as well as the temperature and pressure fields.

One can introduce for example the *Boltzmann entropy*:

$$s_B(x,t) = -k_B \int_{-\infty}^{+\infty} dv\, \rho(x,v,t) \ln\, \rho(x,v,t), \tag{31}$$

which obeys the equation

$$\partial_t s_B + \partial_x (s_B w + j_B) = 0 \tag{32}$$

with

$$j_B(x,t) = -k_B \int_{-\infty}^{+\infty} dv\, \rho(x,v,t)[v - w(x,t)] \ln\, \rho(x,v,t). \tag{33}$$

However we do not have a standard definition of the "temperature". If we identify j_B with the current of s_B, then to obtain the fluid Eqs. (4) and (8), we are led to define:

$$T_B(x,t) = \frac{j_Q(x,t)}{j_B(x,t)}, \qquad i_B(x,t) = 0. \tag{34}$$

The condition $i_B = 0$ is understood from kinetic theory where the internal entropy production is induced by the collision term which is zero in our case. The problem with the above definition of temperature is that we do not know whether thermodynamic relations between n, u, s_B, T_B such as Eq. (6) will be satisfied.

If on the other hand, we adopt the usual definition of temperature as related to the thermal energy, i.e., for non-interacting particles in 1-dimension:

$$u = \tfrac{1}{2} nk_B T, \tag{35}$$

and the relation:

$$j_Q = T j_s \tag{36}$$

then we have

$$\partial_t s_B + \partial_x \left(s_B w + \frac{j_Q}{T} \right) = i_B \tag{37}$$

with $i_B(x,t)$ given by

$$i_B = \partial_x \left(\frac{j_Q}{T} - j_B \right) \tag{38}$$

but we cannot conclude at this point that $i_B(x,t)$ will be non-negative. Furthermore we do not have in general the thermodynamic relation $1/T = \partial s_B / \partial u$.

We could also consider that the fluid defined by $\rho(x,v,t)$ is a simple 1-component fluid with temperature given by the thermal temperature Eq. (35). In that case we have for the thermodynamic entropy, pressure, and viscous stress:

$$s(x,t) = n k_B \left[\frac{1}{2} \left(1 + \ln \frac{4\pi u}{mn^3} \right) + g(n) \right], \tag{39}$$

$$p = n k_B T - n^2 k_B T g'(n), \qquad \text{hence } \tau_{fr} = \tau + p = -n^2 k_B T g'(n). \tag{40}$$

We would have to find at this point an appropriate function $g(n)$ such that $i(x,t)$, Eq. (9), is non-negative. The simplest choice would be $g = 0$ in order that s coincide with s_B at equilibrium.

In the example presented in the introduction (piston problem, see also Section 4) the entropy at point (x,t) must depend on three parameters (n_0, T_0, T_P) where n_0, T_0 are the density and temperature at $x = -\infty$ and T_P the piston temperature. It is thus not possible to consider the fluid as a simple one-component fluid described by 2-state variables, i.e., $s = s(u,n)$. However, we shall see that it is possible to consider the system as a 2-component fluid with an entropy function:

$$s(x,t) = s[u(x,t), n_1(x,t), n_2(x,t)], \tag{41}$$

which coincide with the Boltzmann entropy at $x = -\infty$ and $x = -0$, where the fluid is in a stationary state. In that case we are led to introduce a temperature T_s by the thermodynamic definition:

$$\frac{1}{T_s} = \frac{\partial}{\partial u} s(u, n_1, n_2) \tag{42}$$

a current j_1 satisfying the continuity equation Eq. (10) and an entropy flux now given by Eq. (14). Again with this choice we have to verify whether $i(x, t)$ given by Eq. (15) is actually non-negative.

The purpose of the following sections is to explore what these different definitions imply for the piston problem, and whether we can arrive for this model at a description consistent with the thermodynamics of fluids, i.e., the two laws of thermodynamics.

4. PISTON PROBLEM

We consider an infinite cylinder of area A containing two gases separated by a movable piston. The gases are made of point particles with mass m, while the piston is a rigid solid with mass $M \gg m$ and no internal degrees of freedom. The particles and the piston interact through purely elastic collisions only. We assume that all velocities are parallel to the x-axis (the axis of the cylinder) which reduces the system to one dimension. Initially the piston is at rest and the two gases are homogeneous and in thermal equilibrium described by Maxwellian distributions of velocities with temperatures $T_0^\pm$, hereafter denoted $\varphi_{T_0^\pm}$, and densities $n_0^\pm$ respectively on the left $(-)$ and on the right $(+)$ of the piston. We shall take initial conditions $n_0^\pm$, $T_0^\pm$ such that the piston evolves toward an equilibrium state with $\langle V \rangle = 0$, and for clarity we choose $T_0^+ > T_0^-$. Using the results of ref. 5b, this requires that the initial pressures $p_0^\pm = n_0^\pm k_B T_0^\pm$ satisfy the condition:

$$p_0^+ - p_0^- = \frac{m}{2M}(p_0^+ + p_0^-)\left(\sqrt{\frac{T_0^+}{T_0^-}} - \sqrt{\frac{T_0^-}{T_0^+}}\right) + \mathcal{O}\left[\left(\frac{m}{M}\right)^2\right] > 0. \quad (43)$$

Using a singular perturbative approach to first order in m/M, it was shown that the piston will reach an equilibrium state $\Phi(V)$, with $\langle V \rangle = 0$ and temperature T_P where

$$k_B T_P \equiv M \langle V^2 \rangle = k_B \sqrt{T_0^+ T_0^-} \quad (44)$$

in a time t_1 which is proportional to M/A and can be made arbitrary small. In this equilibrium state of the piston, the heat passing through the piston per unit time is given by ref. 5b:

$$P_Q^{(+) \to (-)} = \frac{Am}{2M}\sqrt{\frac{8k_B}{m\pi}}(p_0^+ + p_0^-)\left(\sqrt{T_0^+} - \sqrt{T_0^-}\right) + \mathcal{O}\left[\left(\frac{m}{M}\right)^2\right] > 0. \quad (45)$$

In the present paper, we take this equilibrium state of the piston and $X = 0$ as the initial conditions for the piston and Maxwellian distribution with $T_0^{\pm}$ for the gases. The piston will henceforth diffuse around $X = 0$, but this diffusive motion is very slow compared to the relaxation phenomena inside the gases (damping oscillations) and it can be neglected on the time scale here considered.

In ref. 3, the velocity distribution function of the piston $\Phi(V)$ in the stationary state was obtained to first order in $\sqrt{m/M}$ for the case $p_0^+ = p_0^-$. The same analysis was conducted for the case $p_0^+ \neq p_0^-$ in ref. 7. For our considerations where p_0^+ and p_0^- satisfy the condition Eq. (43), one obtains:

$$\Phi(V) \sim e^{-\beta_P V^2} \left\{ 1 + \frac{1}{2}\sqrt{m/M}\, a_1 \sqrt{\beta_P}\, V - \frac{1}{3}\sqrt{m/M}\, a_1 \left(\sqrt{\beta_P}\, V \right)^3 + \mathcal{O}\left(\frac{m}{M} \right) \right\}$$
(46)

with

$$\beta_P = \frac{M}{2k_B\sqrt{T_0^+ T_0^-}} = \frac{M}{2k_B T_P}, \quad a_1 = \sqrt{\pi}\left(\eta - \frac{1}{\eta} \right), \quad \eta = \left(\frac{T_0^+}{T_0^-} \right)^{1/4}. \quad (47)$$

Assuming that we can neglect the recollisions of particles on the piston, or better, introducing a cutoff in the velocity distribution such as was done in refs. 9–11 and 14–16 to ensure that this condition is satisfied, one can thus compute the velocity distribution of the particles at the surface of the piston. The distribution of velocities of the particles before $(P(v))$ and after $(\widetilde{P}(v))$ a collision on the piston are given respectively by:

$$P^-(v) \sim \int_{-\infty}^{v} dV\; \varphi_{T_0^-}(v)\Phi(V), \quad \widetilde{P}^-(v) \sim \int_{v}^{\infty} dV\; \varphi_{T_0^-}(v')\Phi(V') \quad (48)$$

on the left-hand side and

$$P^+(v) \sim \int_{v}^{\infty} dV\; \varphi_{T_0^+}(v')\Phi(V'), \quad \widetilde{P}^+(v) \sim \int_{-\infty}^{v} dV\; \varphi_{T_0^+}(v)\Phi(V) \quad (49)$$

on the right-hand side where:

$$\begin{aligned} v' &= -(1-\alpha)v + (2-\alpha)V \\ V' &= (1-\alpha)V + \alpha v \end{aligned} \qquad \alpha = \frac{2m}{M+m} \ll 1. \qquad (50)$$

Introducing the boundary condition at the surface of the piston

$$\int_{-\infty}^{+\infty} dv \; \rho^{\pm}(0, v, t)v = 0,$$ (51)

and using the fact that $\Phi(V)$ is peaked in $V = 0$, of width $(k_B T_P/M)^{1/2}$ far smaller than typical v, we obtain the distribution function of the particles on the left surface of the piston:

$$\rho^-(0, v, t) = \theta(v)\rho^-(v) + \theta(-v)\tilde{\rho}^-(v),$$ (52)

where

$$\rho^-(v) = n_0^- \sqrt{\frac{\beta^-}{\pi}} \, e^{-\beta^- v^2},$$
$$\tilde{\rho}^-(v) = \frac{1}{1 + \delta^-} \, n_0^- \sqrt{\frac{\beta^-}{\pi}} \, e^{-\tilde{\beta}^- v^2}$$ (53)

with

$$\beta^- = \frac{m}{2k_B T_0^-},$$
$$\tilde{\beta}^- = \frac{\beta^-}{1 + \delta^-},$$
$$\delta^- = \alpha(2 - \alpha)\left(\frac{T_P}{T_0^-} - 1\right) = \mathcal{O}\left(\frac{m}{M}\right) > 0.$$ (54)

Similarly the distribution function on the right surface of the piston is given by

$$\rho^+(0, v, t) = \theta(-v)\rho^+(v) + \theta(v)\tilde{\rho}^+(v)$$ (55)

together with Eq. (53) where β^-, $\tilde{\beta}^-$ and δ^- are replaced by

$$\beta^+ = \frac{m}{2k_B T_0^+},$$
$$\tilde{\beta}^+ = \frac{\beta^+}{1 + \delta^+},$$
$$\delta^+ = \alpha(2 - \alpha)\left(\frac{T_P}{T_0^+} - 1\right) = \mathcal{O}\left(\frac{m}{M}\right) < 0.$$ (56)

Strictly speaking the distributions (52) and (55) are valid only for $|v| \gg (k_B T_P/M)^{1/2}$, because of the error functions which appear in (48) and (49). Indeed, in (48) and (49), we replaced $\int_{-\infty}^{v} dV$ by $\theta[v] \int_{-\infty}^{+\infty} dV$, and $\int_{v}^{+\infty} dV$ by $\theta[-v] \int_{-\infty}^{+\infty} dV$, which is valid only if $|v|$ is far larger than the width of $\Phi(V)$, namely $|v| \gg \sqrt{\langle V^2 \rangle} = (k_B T_P/M)^{1/2}$. However in the following, we shall be interested only in thermodynamic quantities defined by averages with respect to $\rho^{\pm}(0, v, t)$ and since $M \gg m = 1$ (typically $M = 10^3$–10^6 in our simulations), the corrections due to error functions will be negligible.

5. THERMODYNAMICAL QUANTITIES AT THE SURFACE OF THE PISTON

Given the distributions (52) and (55), the thermodynamical quantities defined in Section 3 are immediately obtained at the surface of the piston $(x = 0)$. On the left-hand side we have

$$n^-(0, t) = \frac{1}{2} n_0^- \left(1 + \frac{1}{\sqrt{1 + \delta^-}} \right), \tag{57}$$

$$2u^-(0, t) = -\tau^-(0, t) = \frac{1}{2} p_0^- \left(1 + \sqrt{1 + \delta^-} \right) = p_0^- \left(1 + \frac{m}{M} \left(\frac{T_P}{T_0^-} - 1 \right) \right)$$
$$+ \mathcal{O}\left[\left(\frac{m}{M} \right)^2 \right], \tag{58}$$

$$T^-(0, t) = \frac{2u^-(0, t)}{k_B n^-(0, t)} = T_0^- \sqrt{1 + \delta^-}, \tag{59}$$

$$j_Q^- = -\frac{1}{2} \delta^- p_0^- \sqrt{\frac{2 k_B T_0^-}{m \pi}} < 0, \tag{60}$$

and similarly for the right side, with corresponding quantities n_0^+, p_0^+, T_0^+ and δ^+, except for j_Q where an additional sign change is involved:

$$j_Q^+ = +\frac{1}{2} \delta^+ p_0^+ \sqrt{\frac{2 k_B T_0^+}{m \pi}} < 0. \tag{61}$$

As can be seen from (58), the (mechanical) equilibrium condition of the piston, i.e., the equality of the forces on both side (since $\langle V \rangle = 0$):

$$\tau^-(0, t) = \tau^+(0, t) \quad \text{for all } t \tag{62}$$

is to first order in m/M identical with the condition Eq. (43) previously obtained at this order (in the framework of kinetic theory). Moreover, from the stationarity condition expressed by

$$j_Q^-(0, t) = j_Q^+(0, t) = j_Q(0, t) \quad \text{for all } t, \tag{63}$$

we recover at lowest order in m/M our previous results Eqs. (44) and (45), i.e.,

$$T_P = \sqrt{T_0^+ T_0^-} + \mathcal{O}\left(\frac{m}{M}\right) \quad (\text{hence } T_0^- < T_P < T_0^+), \tag{64}$$

$$j_Q = -\frac{1}{A} P_Q^{(+) \to (-)} + \mathcal{O}\left[\left(\frac{m}{M}\right)^2\right] < 0. \tag{65}$$

For the Boltzmann entropy Eqs. (52) and (31) give:

$$s_B(0, t) = n(0, t) k_B \left\{ \frac{1}{2}\left(1 + \ln\frac{4\pi}{m}\right) + \frac{1}{2}\ln\frac{u(0, t)}{n^3(0, t)} + C(\delta) \right\},$$

$$C(\delta) = \left(\frac{1}{1 + \sqrt{1+\delta}} - \frac{3}{4}\right)\ln(1+\delta) + \ln\left(1 + \sqrt{1+\delta}\right) - \ln 2$$

$$= -\frac{3}{32}\delta^2 + \mathcal{O}\left[\left(\frac{m}{M}\right)^3\right], \tag{66}$$

where the subscript $(+/-)$ for right/left have been omitted and the currents $j_B^\pm$ of Boltzmann entropy (33) are

$$j_B^\pm(0, t) = \pm \frac{1}{2}\ln(1 + \delta^\pm) n_0^\pm k_B \sqrt{\frac{2k_B T_0^\pm}{m\pi}} < 0. \tag{67}$$

Finally integrating the continuity equation (32), the Boltzmann entropy $S_B^\pm$ on the right/left compartment satisfies equation :

$$\frac{d}{dt} S_B^\pm(t) = \pm A \frac{j_Q(0, t)}{T^\pm(0, t)} \sqrt{1+\delta} \frac{\ln(1+\delta)}{\delta} \qquad (\delta = \delta^\pm). \tag{68}$$

From (65) and (67), the "Boltzmann temperature" (34) is

$$T_B(0, t) = T(0, t) \frac{\delta}{\ln(1+\delta)} \frac{1}{\sqrt{1+\delta}} = T(0, t) \left(1 + \frac{\delta^2}{24} + \mathcal{O}\left[\left(\frac{m}{M} \right)^3 \right] \right) \quad (69)$$

i.e., both definition of temperatures coincide at order m/M on the surface of the piston.

If we identify $T_B(0, t)$ with the thermodynamic temperature then (68) is the well known expression of the Second Law and the entropy production $I^\pm(t)$ on the right/left of the piston is strictly zero. Thus we must conclude that $i(x, t) = 0$ and the increase of the total entropy is entirely due to heat transfer. However, with this definition of temperature, we do not recover the usual thermodynamical relations.

If on the other hand we want to identify $T(0, t)$, Eq. (59), with the thermodynamic temperature, we obtain for the entropy production:

$$\begin{aligned}
I^\pm &= \frac{d}{dt} S_B^\pm(t) \mp \frac{1}{T^\pm(0, t)} A j_Q^\pm(0, t) \\
&= \pm \left[\frac{\ln(1+\delta)}{\delta} \sqrt{1+\delta} - 1 \right] \frac{A}{T^\pm(0, t)} j_Q(0, t) \\
&= \mp \frac{[\delta^\pm]^2}{24} \frac{A}{T^\pm(0, t)} j_Q(0, t) + \mathcal{O}\left[\left(\frac{m}{M} \right)^4 \right].
\end{aligned} \quad (70)$$

Since j_Q is order of m/M, we thus conclude that $i(x, t)$ is zero to second order in m/M; but $j_Q(0, t)$ being negative, the definitions $s_B(x, t)$ and $T(0, t)$ are not compatible at order $\mathcal{O}[(m/M)^3]$ since they lead to an entropy production which will be negative for some (x, t).

5.1. Conclusion

The distribution functions at the surface of the piston $\rho^\pm(0, v, t)$, Eqs. (52) and (55), yield thermodynamic properties which are consistent to first order in m/M with previous results and with the laws of thermodynamics. In particular, the forces on both sides of the piston are equal, the "heat flux" j_Q is continuous, the different definitions of "temperature" and "entropy" coincide at this order on the surface of the piston. Moreover the viscous stress $\tau + p$ is zero. If we adopt the Boltzmann's definition of entropy, then the total entropy production:

$$I(t) = \frac{dS_B}{dt} = \frac{dS_B^-}{dt} + \frac{dS_B^+}{dt}$$

$$= \frac{mA}{2M} \sqrt{\frac{8k_B}{m\pi}} (p_0^+ + p_0^-) \left(\frac{\sqrt{T_0^+} + \sqrt{T_0^-}}{T_0^- T_0^+} \right) \left(\sqrt{T_0^+} - \sqrt{T_0^-} \right)^2$$
$$+ \mathcal{O}\left[\left(\frac{m}{M} \right)^2 \right] \tag{71}$$

is entirely due to heat transfer. However with this definition of entropy, we are forced to take T_B as definition of temperature, at least if we want to go at order $(m/M)^2$, and we do not recover the usual thermodynamical relations.

6. PROPAGATION THROUGH THE FLUID: SIMILARITY FLOW

So far we have investigated only the thermodynamical properties of the fluids near the surfaces of the piston. In that case the fluids are in a non-equilibrium but stationary state. In this section, we want to analyze the local properties of the fluids at any point x where the fluids are truly in non-equilibrium state and we want to discuss whether it is possible to introduce thermal definitions which imply the macroscopic equation of fluid dynamics.

Since the effect of purely elastic collisions between the particles is identical to the non-interating case, we consider that the distribution function $\rho(x, v, t)$ for the gas is the solution of the continuity equation (32), given by

$$\rho(x, v, t) = \rho^-(x, v, t) + \rho^+(x, v, t) \tag{72}$$

with

$$\rho^-(x, v, t) = \theta(-x)[\theta(vt - x)\rho^-(v) + \theta(x - vt)\widetilde{\rho}^-(v)],$$
$$\rho^+(x, v, t) = \theta(x)[\theta(x - vt)\rho^+(v) + \theta(vt - x)\widetilde{\rho}^+(v)], \tag{73}$$

where

$$\rho(v) = n_0\varphi(v) \quad \text{with} \quad \varphi(v) = \sqrt{\frac{\beta}{\pi}} e^{-\beta v^2},$$
$$\widetilde{\rho}(v) = n_0\widetilde{\varphi}(v) \quad \text{with} \quad \widetilde{\varphi}(v) = \frac{1}{1+\delta} \sqrt{\frac{\widetilde{\beta}}{\pi}} e^{-\widetilde{\beta} v^2}, \tag{74}$$
$$\beta = \frac{m}{2k_B T_0}, \quad \widetilde{\beta} = \beta(1+\delta)^{-1}$$

with δ given by Eq. (54) and the subscripts $(+/-)$ corresponding to $(x > 0)$ resp. $(x < 0)$ have been omitted. We thus have a similarity flow, i.e., for

all field $f(x, t)$ we have:

$$f(x, t) = f(\xi), \qquad \text{where } \xi = \frac{x}{t}. \tag{75}$$

Notice that ξ is negative on the left and positive on the right of the piston.

From now on we consider Eq. (72) as an exact solution of Boltzmann equation (for a system when the only collisions are on the piston) and we investigate the thermodynamic properties at the lowest order in m/M, which is relevant for these properties. In particular since j_Q and $\nabla(1/T)$ are of order one in m/M, the contribution to the entropy production i will be of order $(m/M)^2$.

From the expression $\rho(x, v, t)$, Eq. (72), we can compute the thermo-dynamical quantities defined in Section 3. We shall detail the computations only for the left side of the piston ($\xi \leqslant 0$ and $\delta^- > 0$) and shall drop the $(-)$ subscript. The different fields are represented on Figs. (1–5) for special values of $n_0^\pm$ and $T_0^\pm$. From the definition of density $n(x, t) = n(\xi)$:

$$n(\xi) = \int_\xi^{+\infty} dv \, \rho(v) + \int_{-\infty}^\xi dv \, \widetilde{\rho}(v) \tag{76}$$

follows that

$$\partial_\xi n(\xi) = \widetilde{\rho}(\xi) - \rho(\xi). \tag{77}$$

Defining $\bar{\xi}$ (in fact $\bar{\xi}^-$ but we have omitted the subscript $(-)$ in this whole section) by $\widetilde{\rho}(\bar{\xi}) = \rho(\bar{\xi})$, which gives (note that $\bar{\xi} < 0$):

$$\beta\bar{\xi}^2 = (1 + \delta) \frac{\ln(1 + \delta)}{\delta} \qquad \text{hence} \qquad \bar{\xi} = -\sqrt{\frac{2k_B T_0^-}{m}} + \mathcal{O}\left(\frac{m}{M}\right), \tag{78}$$

we have

$$\begin{aligned} \widetilde{\rho}(\xi) < \rho(\xi) \quad &\text{for } \bar{\xi} < \xi \leqslant 0, \\ \widetilde{\rho}(\xi) > \rho(\xi) \quad &\text{for } \xi < \bar{\xi}, \end{aligned} \tag{79}$$

and $n(\xi)$ reaches a maximum at $\xi = \bar{\xi}$ (see Fig. 1). For the velocity field we have (Fig. 2):

$$n(\xi) w(\xi) = n_0 \sqrt{\frac{\beta}{\pi}} \frac{1}{2\beta} \left(e^{-\beta\xi^2} - e^{-\widetilde{\beta}\xi^2} \right). \tag{80}$$
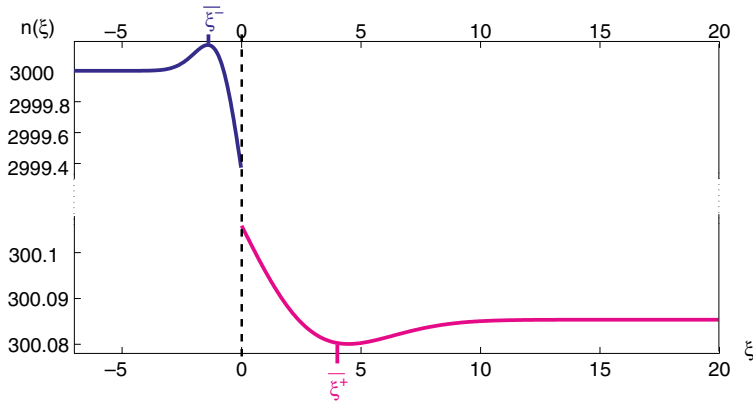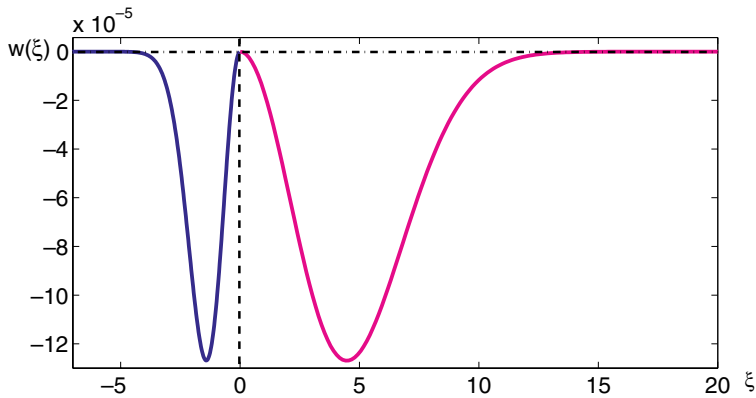
Fig. 1.   Density of particles $n(x,t) = n(\xi)$.

Fig. 2.   Fluid velocity $w(x,t) = w(\xi)$.

Therefore, $w(\xi)$ is negative for $\xi < 0$, zero for $\xi = 0$ and is minimum for $\xi = \bar{\xi}$. For the stress tensor $\tau(x,t) = -2u(x,t)$ we have (Fig. 3):

$$- \partial_\xi \tau(\xi) = m[\widetilde{\rho}(\xi) - \rho(\xi)][\xi - w(\xi)]^2 \tag{81}$$

i.e., the only points where $\partial_\xi \tau = 0$ are $\xi = 0$ and $\xi = \bar{\xi}$. For the heat flux we have (Fig. 4):

$$j_Q(\xi) = \frac{mn_0}{2} \sqrt{\frac{\beta}{\pi}} \frac{1}{2\beta^2} \left\{ \left[e^{-\beta\xi^2} - e^{-\widetilde{\beta}\xi^2} \right] \left[1 + \beta\xi^2 - \frac{3}{2} \frac{T(\xi)}{T_0} \right] - \delta e^{-\widetilde{\beta}\xi^2} \right\}$$
$$- \frac{m}{2} n(\xi) w(\xi)^3, \tag{82}$$
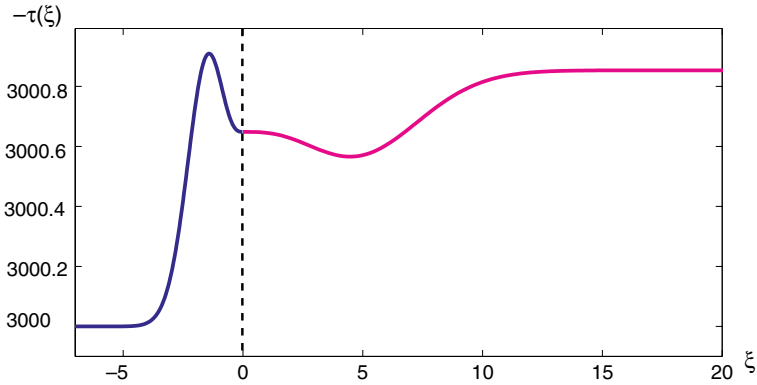
Fig. 3.   Pressure $p(x,t) = p(\xi) = -\tau(\xi)$.
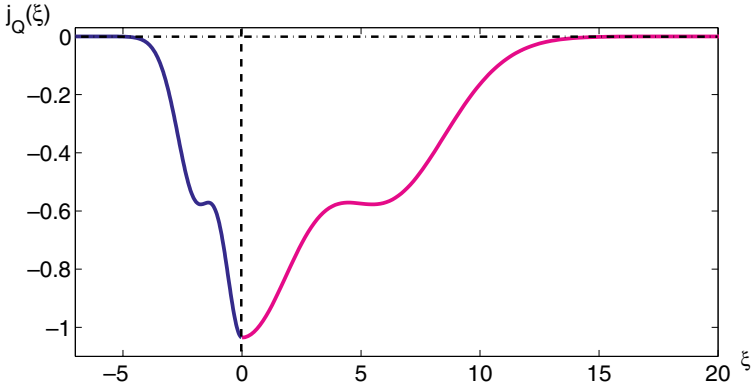
Fig. 4.   Heat current $j_Q(x,t) = j_Q(\xi)$.

$$\partial_\xi j_Q(\xi) = \frac{1}{2}[\tilde\rho(\xi) - \rho(\xi)][\xi - w(\xi)]\left[m[\xi - w(\xi)]^2 - 6\frac{u(\xi)}{n(\xi)}\right], \qquad (83)$$

and thus $\partial_\xi j_Q = 0$ for $\xi = 0$, $\xi = \bar\xi$ and $\xi = \widehat\xi^-$ where

$$\widehat\xi^- = -\sqrt{\frac{3k_B T_0^-}{m}} + \mathcal{O}\left(\frac{m}{M}\right). \qquad (84)$$

If we adopt the thermal definition of temperature, i.e., $k_B T = 2u/n$, we find that (Fig. 5a):

$$\partial_\xi[k_B T(\xi)] = \frac{1}{n(\xi)}[\tilde\rho(\xi) - \rho(\xi)]\left\{m[\xi - w(\xi)]^2 - k_B T(\xi)\right\}, \qquad (85)$$

(a)

(b)
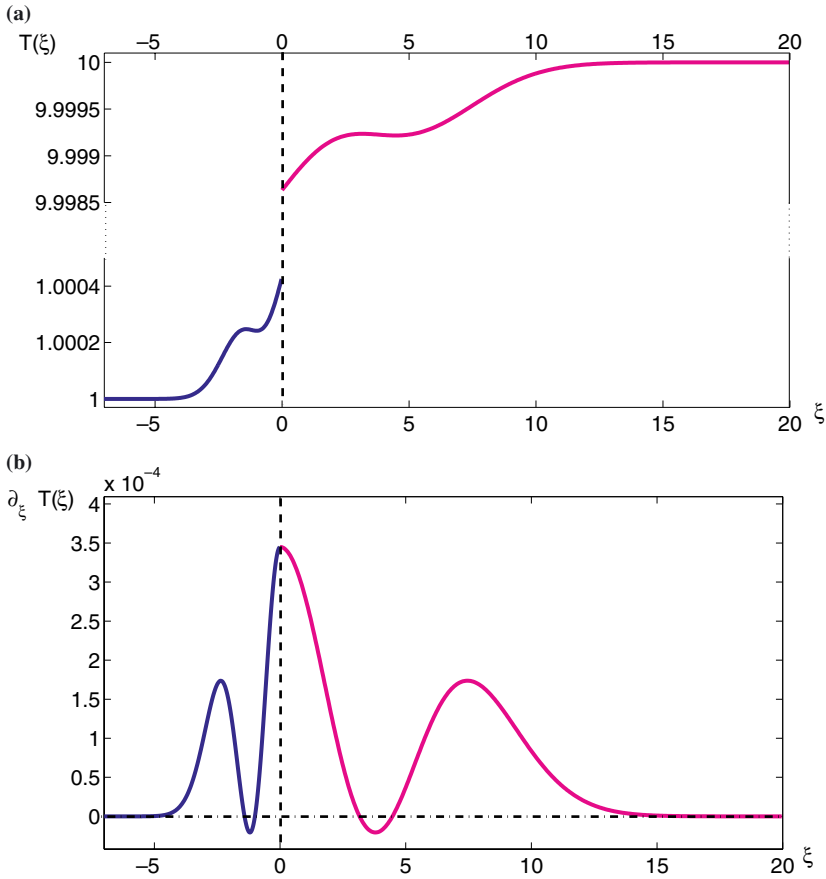
Fig. 5.   (a) Temperature $T(x, t) = T(\xi)$; (b) gradient $\partial_\xi T(\xi)$.

and thus $\partial_\xi T = 0$ if $\xi = \bar{\xi}$ and $\xi = \widetilde{\xi}$ where:

$$\widetilde{\xi} = -\sqrt{\frac{k_B T_0^-}{m}} + \mathcal{O}\left(\frac{m}{M}\right). \tag{86}$$

Therefore $\partial_\xi T$ is negative for $\xi = x/t \in]\bar{\xi}, \widetilde{\xi}[$ and positive if $\xi \notin]\bar{\xi}, \widetilde{\xi}[$ (Fig. 5b).

   In conclusion with the thermal definition of temperature, the contribution $j_Q \partial_\xi (1/T)$ to the irreversibility is non-negative if $\xi \notin]\bar{\xi}, \widetilde{\xi}[$ but negative for $\xi = x/t \in]\bar{\xi}, \widetilde{\xi}[$. Therefore, whatever is the definition of entropy
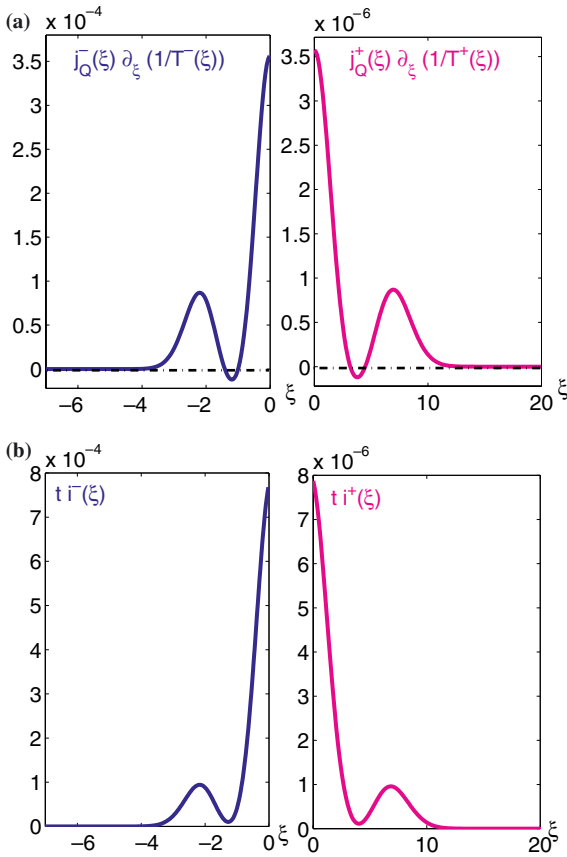
Fig. 6. Entropy production: (a) Contribution $j_Q \, \partial_\xi (1/T)$; (b) $i(x,t) = t i(\xi)$.

and of j_S, it is impossible to obtain an equation of the form

$$\partial_t s + \partial_x (sw + j_S) = i \tag{87}$$

with $i = j_Q \partial_\xi (1/T)$ without violating the Second Law (Fig. 6a). Of course if we take Boltzmann's definition, Eq. (31), and $j_S = j_B$, then $i(x,t) = 0$.

7. ENTROPY AND ENTROPY PRODUCTION

Whatever is the definition of entropy, from the Second Law

$$\partial_t s + \partial_x (sw + j_S) = i, \qquad i(x,t) \geqslant 0 \tag{88}$$

and the similarity of the flow, i.e.,

$$s(x,t)=s(\xi), \qquad t.i(x,t)=t.i(\xi), \qquad \xi=\frac{x}{t}, \tag{89}$$

it follows that (denoting the product $t\,i$, coming from the introduction of the variable ξ, under the form $t.i$ for the sake of clarity)

$$t.i(x,t)=t.i(\xi)=(w-\xi)\partial_\xi s+s\partial_\xi w+\partial_\xi j_S, \tag{90}$$

and

$$\frac{d}{dt}S^-(t) = A\left\{\int_{-\infty}^{0}d\xi\, t.i(\xi)-j_S(\xi=0)\right\}$$
$$= I^-(t)-Aj_S(\xi=0). \tag{91}$$

If we take Boltzmann's definition of entropy,

$$s_B^-(x,t)=s_B^-(\xi)=\theta[-\xi]\left\{s_B^-(-\infty)+k_B\int_{-\infty}^{\xi}dv\,[\rho^-\ln\rho^--\widetilde{\rho}^-\ln\widetilde{\rho}^-]\right\},$$
$$s_B^-(-\infty)=n_0^-\,k_B\,\frac{1}{2}\left[1+\ln\frac{2\pi k_BT_0^-}{m(n_0^-)^2}\right]. \tag{92}$$

then, as mentionned in Section 3, if we define the entropy current by Eq. (30), i.e., $j_S=j_B$, we will have $i(x,t)=0$ and to obtain the Second Law in the usual form (with $I^-(t)=0$), i.e.,

$$\frac{d}{dt}S_B^- = \frac{1}{T(0,t)}P_Q^{(+)\rightarrow(-)}(t), \tag{93}$$

we have to introduce a "Boltzmann temperature" defined by

$$T_B(x,t) = \frac{j_Q(x,t)}{j_B(x,t)}. \tag{94}$$

However with such a definition we do not recover the usual phenomenological equations of thermodynamics.

On the other hand, if we take Boltzmann's definition of entropy and define the entropy current by the usual phenomenological equation $j_Q=$

$T j_S$, where $T = 2u/nk_B$ is the thermal temperature, then $i(x, t) \neq 0$ given by Eq. (90). However from Eqs. (68) and (70)

$$I^-(t) = A \frac{j_Q(0, t)}{T(0, t)} \left(1 - \sqrt{1 + \delta^-} \frac{\ln(1 + \delta^-)}{\delta^-} \right) \tag{95}$$

is negative. In other words, as already noticed in Section 6, $i(x, t)$ cannot be non-negative (see Fig. 6a) which is not compatible with the Second Law.

If we adopt the definition of entropy given by the local equilibrium condition of a simple one-component fluid, i.e.

$$s(\xi) = n_0(\xi) \, k_B \frac{1}{2} \left\{ 1 + \ln \frac{4\pi \, u(\xi)}{mn^3(\xi)} \right\} \tag{96}$$

then

$$T(\xi) = \frac{2u(\xi)}{k_B n(\xi)} \quad \text{and} \quad i(\xi) = j_Q \partial_\xi \left(\frac{1}{T} \right). \tag{97}$$

As discussed in Section 6 this leads again to the conclusion that the Second Law is violated.

8. TWO-COMPONENT FLUID DESCRIPTION

To show that the time evolution of the piston problem satisfies the laws of thermodynamics, we first remark that the fluid on the left-hand side is characterized by three parameters (n_0^-, T_0^-, T_P). This leads us to look at our problem as a two-component fluid.

At the surface $x = 0$, introducing

$$n_1(0, t) = \frac{n_0}{2}, \qquad n_2(0, t) = \frac{n_0}{2\sqrt{1 + \delta}}, \qquad n = n_1 + n_2, \tag{98}$$

the Boltzmann entropy Eq. (66) can be expressed as

$$s_B(0, t) = s(u(0, t), n_1(0, t), n_2(0, t)), \tag{99}$$

$$s(u, n_1, n_2) = n \, k_B \left\{ \frac{1}{2}(1 + \ln(4\pi)) + \frac{1}{2} \ln \frac{u}{(n_1 + n_2)^3} + g(n_1, n_2) \right\}, \tag{100}$$

and

$$g(n_1, n_2) \equiv C(\delta) = 2 \left(\frac{n_2}{n_1 + n_2} - \frac{3}{4} \right) \ln \frac{n_1}{n_2} + \ln \left(1 + \frac{n_1}{n_2} \right) - \ln 2. \quad (101)$$

We note that $g(n_1, n_2) = g(n_1/n_2)$ implies

$$n_1 \frac{\partial g}{\partial n_1} + n_2 \frac{\partial g}{\partial n_2} = 0. \tag{102}$$

From (100) we obtain for the temperature $T_s = \partial u / \partial s$ and the pressure p, Eq. (8), at the surface of the piston:

$$T_s(0, t) = 2 \frac{u(0, t)}{k_B n(0, t)} = T(0, t) = T_0 \sqrt{1 + \delta},$$
$$p(0, t) = n(0, t) k_B T(0, t), \quad \text{i.e.,} \quad \tau_{fr} = \tau + p = 0, \tag{103}$$

where the subscript $(+/-)$ for right/left have been here omitted.

In the bulk $(x \neq 0)$ we shall assume that for all ξ one can express the variables $\{n_0, T_0, T_P\}$ in function of $\{u, n_1, n_2\}$, $n = n_1 + n_2$ as was the case for $x = 0$. The thermal temperature will then be of the form

$$T(\xi) \equiv \frac{2u}{nk_B} = T(\xi, u, n_1, n_2), \tag{104}$$

and thus if we want to identify the temperature Eq. (104) with the thermodynamic temperature $T_s = \partial u / \partial s$ the thermodynamic entropy must be given by

$$s(\xi) = s(\xi, u, n_1, n_2)$$
$$= n(\xi)k_B \left\{ \frac{1}{2} \left(1 + \ln \frac{4\pi}{m} \right) + \frac{1}{2} \ln \frac{u}{n^3} + g(\xi, n_1, n_2) \right\}, \tag{105}$$

where at this point $g(\xi, n_1, n_2)$ is undetermined. For simplicity we choose g independent of ξ, thus given by Eq. (101), i.e.,

$$g(n_1, n_2) = 2 \left(\frac{n_2}{n_1 + n_2} - \frac{3}{4} \right) \ln \frac{n_1}{n_2} + \ln \left(1 + \frac{n_1}{n_2} \right) - \ln 2. \tag{106}$$

Note that if $n_1(\xi)$ is chosen such that $n_1(\xi = \pm\infty) = \frac{1}{2}n_0^{\pm}$ then we will have $s = s_B$ for $\xi = \pm\infty$ and for $\xi = \pm 0$, i.e., at those points where the fluids are in a stationary state. Moreover since $g(n_1, n_2) = g(n_1/n_2)$ we have $n_1 \partial g/\partial n_1 + n_2 \partial g/\partial n_2 = 0$ which implies

$$p = n k_B T, \quad \text{i.e.,} \quad \tau_{fr} = \tau + p = 0. \tag{107}$$

In that case it follows from (17) that

$$i = j_Q \partial_x \left(\frac{1}{T}\right) + j_1 \partial_x \left(\frac{\mu_2 - \mu_1}{T}\right), \tag{108}$$

and from (12) and (100) that

$$\mu_2 - \mu_1 = k_B T \left(2 \ln \frac{n_2}{n_1} + \frac{1}{2}\left(\frac{n_2}{n_1} - \frac{n_1}{n_2}\right)\right) = \mathcal{O}\left(\frac{m}{M}\right), \tag{109}$$

which yields

$$t.i(\xi) = -\frac{1}{T_0^2} j_Q \partial_\xi T + 6k_B \frac{j_1}{n_0}(\partial_\xi n - 2\partial_\xi n_1) + \mathcal{O}\left[\left(\frac{m}{M}\right)^3\right]. \tag{110}$$

Note that the equations are consistently written at leading order in (m/M); terms in $(m/M)^2$ here arise from the product of two terms of leading order m/M.

Moreover, the continuity equation for n_1

$$-\xi \partial_\xi n_1 + \partial_\xi(n_1 w + j_1) = 0 \tag{111}$$

together with the boundary conditions

$$\lim_{\xi \to -\infty} j_1(\xi) = 0, \qquad \lim_{\xi \to -\infty} n_1(\xi) = \frac{n_0}{2} \tag{112}$$

implies (for $\xi < 0$)

$$j_1(\xi) = \xi(n_1 - \frac{n_0}{2}) - n_1 w - \int_{-\infty}^{\xi} d\xi \left(n_1 - \frac{n_0}{2}\right). \tag{113}$$

Guided by numerical investigations, let us then look for a solution of the form

$$n_1(\xi) = \frac{n_0}{2}\left(1 + \frac{\lambda_1}{\xi}\,w + \lambda_2\,\partial_\xi w\right), \tag{114}$$

where at this stage λ_1 and λ_2 are unspecified constants. With this ansatz, and introducing $x = -\sqrt{\beta}\xi > 0$, we have for the left compartment

$$j_1(\xi) = \delta n_0 \sqrt{\frac{\beta}{\pi}}\frac{e^{-x^2}}{4\beta}\left(x^2 + \lambda_2 x^2(2x^2 - 1) - \lambda_1\left(x^3 + \frac{1}{2}x + \frac{1}{2}e^{x^2}\int_x^\infty du\,e^{-u^2}\right)\right)$$
$$+\mathcal{O}\left[\left(\frac{m}{M}\right)^2\right], \tag{115}$$

and

$$\partial_\xi(n - 2n_1) = \delta n_0\sqrt{\frac{\beta}{\pi}}\,e^{-x^2}\{(x^2 - 1)[1 - \lambda_1 x + \lambda_2(2x^2 - 1)] - 2\lambda_2 x^2\}$$
$$+\mathcal{O}\left[\left(\frac{m}{M}\right)^2\right]. \tag{116}$$

We thus have to find λ_1 and λ_2 such that $t\,i(\xi)$, Eq. (110), is non-negative, where

$$j_Q(\xi)\partial_\xi\frac{1}{T} = \delta^2 n_0 k_B\frac{e^{-2x^2}}{4\pi}(x^2 - 1)(2x^2 - 1)[2 + x^2(2x^2 - 1)]$$
$$+\mathcal{O}\left[\left(\frac{m}{M}\right)^3\right]. \tag{117}$$

Moreover, we will have

$$\frac{d}{dt}S^-(t) = A\int_{-\infty}^0 d\xi\,t.i(\xi) - \frac{A}{T(-0,t)}[j_Q(0,t) + j_1(\mu_2 - \mu_1)(-0,t)] \tag{118}$$

with

$$j_Q(0,t) + j_1(\mu_2 - \mu_1)(-0,t) = j_H(-0,t)$$
$$= j_Q(0,t)\left\{1 - \frac{1}{8}\lambda_1\sqrt{\pi}\right.$$

$$\left[\ln\left(1+\delta^-\right)+\frac{1}{2}\frac{\delta^-}{\sqrt{1+\delta^-}}\right]\right\}$$

$$= j_Q(0,t)\left[1-\delta^--\frac{3}{16}\lambda_1\sqrt{\pi}\right]$$

$$+\mathcal{O}\left[\left(\frac{m}{M}\right)^3\right] \qquad (119)$$

and $j_Q(0)$ is given by Eq. (60). Using numerical computation, we see that choosing $\lambda_1=1$ and $\lambda_2=0.1$ the entropy production Eq. (110) will be strictly positive (Fig. 6b). For the right compartment $(\xi>0)$, we have

$$j_1(\xi)=\xi\left(n_1(\xi)-\frac{n_0}{2}\right)-n_1(\xi)w(\xi)$$

$$+\int_\xi^\infty d\xi\left(n_1(\xi)-\frac{n_0}{2}\right) \quad (\xi>0), \qquad (120)$$

$$\frac{d}{dt}S^+(t)=A\int_0^\infty d\xi\, t.i(\xi)$$

$$+\frac{A}{T(+0,t)}[j_Q(0,t)+j_1(\mu_2-\mu_1)(+0,t)], \qquad (121)$$

$$j_Q(0,t)+j_1(\mu_2-\mu_1)(+0,t)=j_Q(0,t)\left[1-\delta^++\frac{3}{16}\lambda_1\sqrt{\pi}\right]$$

$$+\mathcal{O}\left[\left(\frac{m}{M}\right)^3\right], \qquad (122)$$

and Eqs. (115)–(117) will remain valid with $x=\sqrt{\beta^+}\xi$. Therefore with $\lambda_1=1$ and $\lambda_2=0.1$ the entropy production $i(x,t)$ is strictly positive for all (x,t), and all phenomenological equations of thermodynamics will hold (Fig. 6a).

Remarks

1. With the choice $\lambda_1=1$ and $\lambda_2=0.1$ the density $n_1(x,t)$ corresponds approximately to the density $n_w(x,t)$ of particles with velocity larger than the average velocity of the fluid $w(x,t)$ (see Fig. 7).

2. We note that both definitions of heat current, (see Section 2) j_Q or $j_H=j_Q+j_1(\mu_2-\mu_1)$ are quantities of order (m/M), which differ by a factor of order $(m/M)^2$ (see Eqs. (115) and (116), or (119)). However j_Q is continuous at the surface of the piston (as it should since it is the energy current), while j_H is not continuous (see Fig. 9).
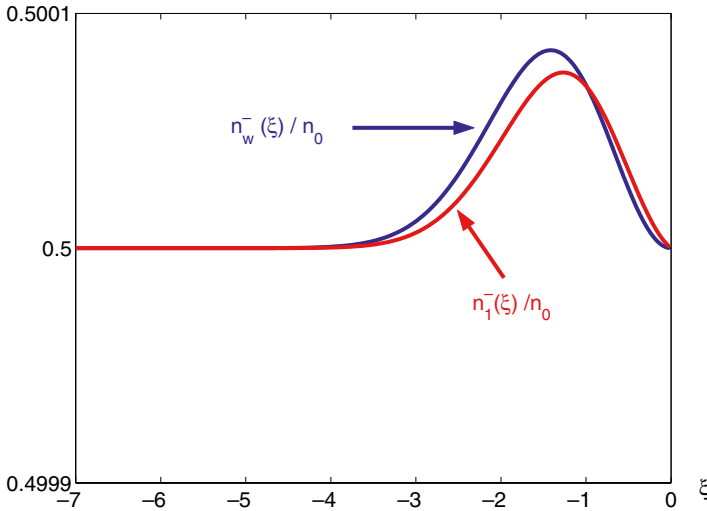
Fig. 7.   Density $n_1(x,t)/n_0 = n_1(\xi)/n_0$ and density of particles $n_w(x,t)/n_0 = n_w(\xi)/n_0$ with velocity larger than $w(x,t)$.

3.   From Eqs. (115) and (116) follows that the possible choice of λ_1, λ_2, leading to a positive entropy production, will be independent of the choice of the initial conditions $(T_0^{\pm}, n_0^{\pm})$. In all the numerical computations (Figs. 1–9) the following parameters have been chosen.

$$m = 1, \qquad M = 10.000, \qquad k_B = 1,$$
$$T_0^- = 1, \qquad T_0^+ = 10, \qquad n_0^- = 3000, \qquad n_0^+ = 300.085,$$
$$\text{i.e.,} \qquad p_0^- = 3000, \qquad p_0^+ = 3000.85, \tag{123}$$

4.   Let us note that the difference between the entropy densities $s(x,t)$ and $s_B(x,t)$ is very small of order $(m/M)^2$ (Fig. 8b).

5.   We recall that for one-dimensional ideal fluid the velocity of sound is $\sqrt{3k_B T/m}$ which coincide with $\widehat{\xi}^-$, Eq. (84).

6.   If we consider the stationary states of our model, then the left compartment is an homogeneous fluid in a stationary state characterised macroscopically by its temperature T (i.e., T^-) its density n (i.e., n^-), its velocity $w(x,t) = 0$ and the heat flux j_Q. Microscopically this fluid is described by the density function

$$\rho(x,v;t) = \theta[-x]\left[\theta[v]\,2n_1\sqrt{\frac{\beta}{\pi}}e^{-\beta v^2} + \theta[-v]\,2n_2\sqrt{\frac{\widetilde{\beta}}{\pi}}e^{-\widetilde{\beta}v^2}\right], \tag{124}$$
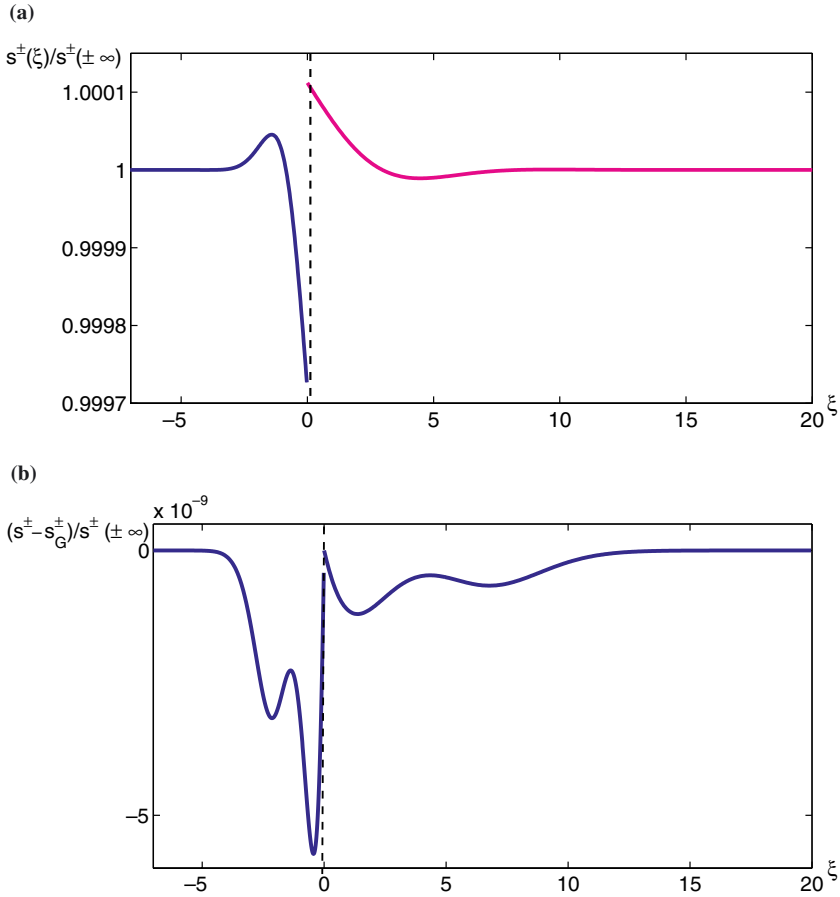
(a)

(b)

Fig. 8. (a) Entropy density $s^{\pm}(x,t)/s^{\pm}(\pm\infty)$; (b) $[s(x,t)-s_B(x,t)]/s^{\pm}(\pm\infty)$.

where, using the previous results,

$$\beta = \frac{m}{2k_BT}\frac{n_1}{n_2}, \qquad \widetilde{\beta} = \frac{m}{2k_BT}\frac{n_2}{n_1},$$

$$j_Q = -k_BT\left(\frac{n_1}{n_2}-\frac{n_2}{n_1}\right)\sqrt{\frac{n_2}{n_1}}\sqrt{\frac{2k_B}{m\pi}}, \qquad n=n_1+n_2, \qquad (125)$$

and the temperature of the piston is

$$T_P = T\left\{\frac{n_2}{n_1}+\frac{(M+m)^2}{4mM}\left(\frac{n_1}{n_2}-\frac{n_2}{n_1}\right)\right\}. \qquad (126)$$
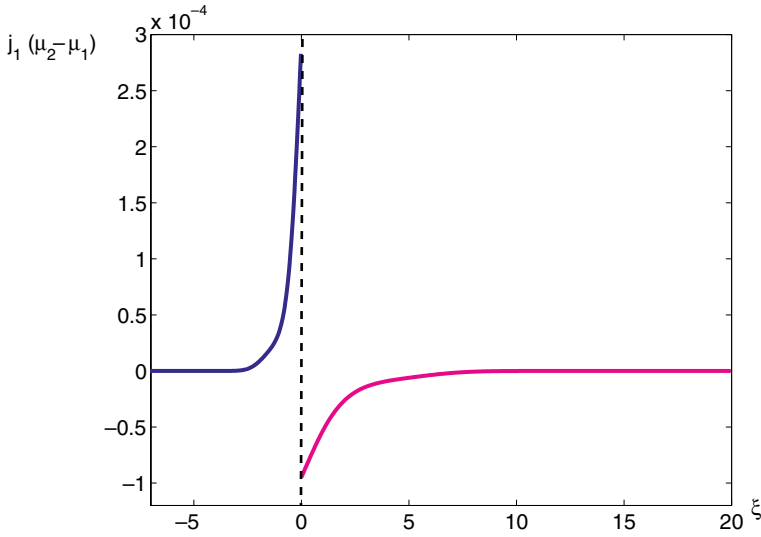
Fig. 9.   Contribution $[j_1(\mu_2 - \mu_1)](x, t) = [j_1(\mu_2 - \mu_1)](\xi)$ to the entropy current. Note that it is of the order $10^{-4} \cdot j_Q(x, t)$.

The system is furthermore characterised by its entropy function $s = s(u, n_1, n_2)$, given by Eq. (105) and we have:

$$u = \tfrac{1}{2} n k_B T, \qquad p = n k_B T = -\tau,$$
$$s[u(x, t), n_1(x, t), n_2(x, t)] = s_B(x, t). \tag{127}$$

Moreover in this stationary state $j_1 = 0$ implies

$$\frac{d}{dt} S^-(t) = -A \, \frac{j_Q}{T}, \qquad I = 0. \tag{128}$$

We obtain similar expressions for the right compartment and the stationary condition of the state is expressed by the relations

$$p^- = p^+, \qquad T_P^- = T_P^+, \qquad j_Q^- = j_Q^+. \tag{129}$$

Finally the total entropy production in the stationary state of this isolated system

$$\frac{d}{dt} S = -A \, j_Q \left(\frac{1}{T^-} - \frac{1}{T^+} \right) \tag{130}$$

is entirely due to the heat transfer from the subsystem at temperature T^+ to the subsystem at temperature T^- which reflects the fact that the fluids are ideal. (Let us note that $S = \infty$ and thus only the entropy production is relevant in such non-equilibrium stationary states.)

We should stress that the fluid in the stationary state is not locally in equilibrium (see Eq. (124)), which is a general property of far-from-equilibrium stationary states, but is a two-component simple fluid.

9. CONCLUSIONS AND OPEN PROBLEMS

Taking initial conditions such that on the average the piston remains at the same point so that there is only heat transfer from the right to the left compartment $(T_0^+ > T_0^-)$, but no work done, we have first derived the time evolution of the fluids on both sides of the piston.

We have then shown that this fluid out of equilibrium can be considered as a 2-component simple fluid described by an entropy function $s = s(u, n_1, n_2)$, and all the properties of the fluid will obey the laws of thermodynamics. In particular the two laws of thermodynamics are satisfied with

$$e = \tfrac{1}{2} mnw^2 + u(s, n_1, n_2),$$
$$T = \frac{\partial u}{\partial s} = \frac{2u}{nk_B},$$
$$p = sT + n_1\mu_1 + n_2\mu_2 - u = nk_B T = -\tau,$$
$$j_e = -\tau w + j_Q, \tag{131}$$

where n, w, u, τ, j_Q are defined by the usual relations of kinetic theory, $\mu_i = \partial u / \partial n_i$

$$T j_s = j_Q + j_1(\mu_2 - \mu_1), \tag{132}$$

and

$$i = j_Q \partial_x \left(\frac{1}{T} \right) + j_1 \partial_x \left(\frac{\mu_2 - \mu_1}{T} \right) \tag{133}$$

is strictly positive.

Moreover the entropy function which we have introduced coincides with the Boltzmann entropy in those domains where the fluids are in a stationary state. It was also shown that other natural definitions of entropy, temperature, irreversibility, which one could consider led to results violating the Second Law. Since the evolution is a similarity flow, one cannot expect to obtain phenomenological relations of the form

$$
\begin{aligned}
j_Q &= C_{11}\, \partial_x \left(\frac{1}{T}\right) + C_{12}\, \partial_x \left(\frac{\mu_2 - \mu_1}{T}\right), \\
j_1 &= C_{21}\, \partial_x \left(\frac{1}{T}\right) + C_{22}\, \partial_x \left(\frac{\mu_2 - \mu_1}{T}\right)
\end{aligned}
\tag{134}
$$

with C_{ij} a state function (indeed $\partial_x = 1/t\partial_\xi$).

However usual relations such as

$$
\begin{aligned}
\frac{d}{dt} S^-(t) &= I^-(t) + \frac{P_Q^{(+)\to(-)}}{T^-(0,t)}, \\
\frac{d}{dt} S^+(t) &= I^+(t) - \frac{P_Q^{(+)\to(-)}}{T^+(0,t)}
\end{aligned}
\tag{135}
$$

with

$$
I^\pm(t) > 0,
\tag{136}
$$

and

$$
P_Q^{(+)\to(-)} = \kappa (T_0^+ - T_0^-).
\tag{137}
$$

are satisfied with

$$
\kappa = A\, \frac{m}{M} \sqrt{\frac{8k_B}{m\pi}}\, \frac{1}{2} \left(\frac{p_0^- + p_0^+}{T_0^- + T_0^+}\right) + \mathcal{O}\left[\left(\frac{m}{M}\right)^2\right] \quad > 0.
\tag{138}
$$

It is however an open problem to understand what is the physical meaning of the decomposition of the density as a sum of two densities. It is also to be understood whether there is a physical argument which would lead to a uniquely defined decomposition of n as $n_1 + n_2$, and whether one could find a microscopical definition of our entropy function.

ACKNOWLEDGMENTS

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