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Application of thermodynamic extremum principles

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A simple system is used to illustrate the application of different extremum principles in thermodynamics. The system consists of an ideal gas contained in an adiabatically isolated cylinder interacting with a constant-pressure work device through an adiabatic movable piston. A kinetic model is also used to analyze the time evolution of the system toward the final equilibrium state. © *2001 American Association of Physics Teachers.*
[DOI: 10.1119/1.1397456]

I. INTRODUCTION

The thermodynamic extremum principles were formulated by Gibbs in essentially two versions.[1]

I. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative* (entropy maximum principle):

$$(\delta S)_{U,V,n} \leqslant 0. \qquad (1)$$

II. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive* (internal energy minimum principle):

$$(\delta U)_{S,V,n} \geqslant 0. \qquad (2)$$

Clearly, these theorems refer to hydrostatic closed systems where the volume V and the mole number n remain constant. These constraints, constant V and n, were not originally in these statements, but were later added as *equations of condition* by Gibbs.[1] Gibbs also proved the equivalence between the statements by showing that a violation of one leads to a violation of the other. A discussion of the above extremum principles, including proofs of their equivalence, can be found in most thermodynamics textbooks.[2–5] A less known third extremum principle, not considered by Gibbs, can be formulated.

III. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy and its energy, the variation of its volume shall either vanish or be positive* (volume minimum principle):

$$(\delta V)_{S,U,n} \geqslant 0. \qquad (3)$$

Kazes and Cutler[6] have demonstrated the validity of this volume minimum principle (see, also, Refs. 7 and 8).

The thermodynamic extremum principles can only be fully understood through the concept of a *composite system*, first introduced by Carathéodory.[9] A composite system is a set of two or more subsystems separated by *walls* avoiding the transfer of work and/or heat and/or matter. The subsystems must be *simple*, i.e., homogeneous, isotropic, and without surface, electric, magnetic, or gravitational effects. The walls provide internal constraints. Then, assuming the additivity principle for the entropy, it is possible to associate an entropy value with the equilibrium states of a composite system. The relaxation of any internal constraint, keeping fixed the external ones (conservation laws and environmental conditions), leads the composite system, by means of a spontaneous evolution through nonequilibrium states, from an initial equilibrium state to a less restrictive final equilibrium state, i.e., to a final equilibrium state defined by a number of independent variables smaller than in the initial state. Both the initial and the final states have a well-defined entropy. Therefore, in a composite system, the entropy change between two equilibrium states linked by a spontaneous process is also well defined. In these spontaneous processes the entropy of an isolated composite system must always increase (a particular case of the *weak Clausius evolution principle*[10]).

At this point, one should be aware of the difference between *evolutionary* and *variational* changes. An evolutionary change brings the system from an initial equilibrium state to a less restrictive final equilibrium state when an internal constraint is released, and energy or matter can flow between subsystems during the process. However, the Gibbs statements refer to *variational* (or *virtual*) changes. Variational changes compare states of a system and can never involve energy or matter flows. As Bailyn[5] has pointed out, a variational change does not mean that the system interacts with the environment; it means only that a comparison is to be made between the variables of one state with those of other *possible* states. Such variational changes are used to illustrate the extremum principles.

Although the extremum principles are equivalent, we remark that it is not always possible to use them independently; i.e., they are related. For instance, a previous calculation of the entropy value of the final equilibrium state by means of the entropy maximum principle is necessary for using the internal energy minimum principle. This is shown in Fig. 1 over the plane $V = V_{eq} = $ constant. One can see that, given the initial state, one can reach different final equilibrium states if one fixes $U_{eq} = U_i$ for the entropy maximum principle, or $S_{eq}^* = S_i$ for the internal energy minimum principle.

The aim of this work is to clarify, using a simple example, the rather abstract ideas underlying the extremum principles in thermodynamics. The example has the pedagogical value of being mathematically tractable since the system consid-
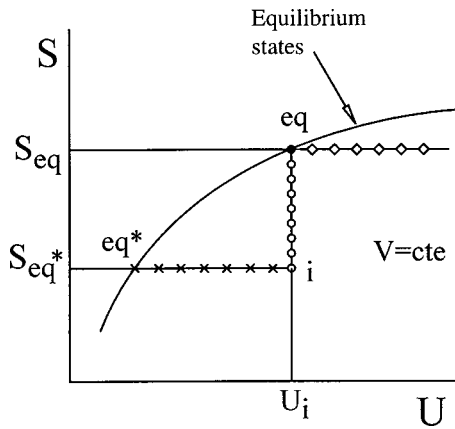
Fig. 1. Constrained states with $U = U_{eq} = U_i = $ constant ($\bigcirc$). Constrained states with $S = S_{eq*} = S_i = $ constant ($\times$). Constrained states with $S = S_{eq}$ = constant ($\diamond$). The equivalence between the entropy maximum principle and the internal energy minimum principle is only supported for the processes denoted by ($\bigcirc$) and by ($\diamond$).

ered needs only one variable for describing its equilibrium states. The work is structured as follows. In Sec. II the system is described from a thermodynamic viewpoint. In Sec. III we apply the extremum principles for the entropy (I), the internal energy (II), and the volume (III) in order to identify the different equilibrium states. This allows us to obtain the final equilibrium state and to analyze its extremum character. Numerical results are reported for a particular case, illustrating the behavior of the system with different processes. In Sec. IV we present a simple kinetic model for the system. This model predicts the same final equilibrium state reported in Sec. III and allows one to analyze the time evolution of the system toward this equilibrium state.

II. BAZAROV'S PROBLEM

Let us consider the system proposed by Bazarov,[11] consisting of one mol of an ideal gas contained in an adiabatically isolated cylinder with a movable, frictionless, adiabatic piston under constant external pressure P_w, as illustrated in Fig. 2. The following expressions are assumed for the pressure, P_g, the internal energy, U_g, and the entropy, S_g, of the gas:

$$P_g = \frac{RT_g}{V_g}, \tag{4}$$

$$U_g = U_{g,0} + c_v T_g, \tag{5}$$

$$S_g = S_{g,0} + c_v \ln T_g + R \ln V_g, \tag{6}$$

where T_g is the temperature of the gas, V_g its volume, c_v its molar heat capacity at constant volume, and $U_{g,0}$ and $S_{g,0}$ are constants. Furthermore, we assume that the environment acts
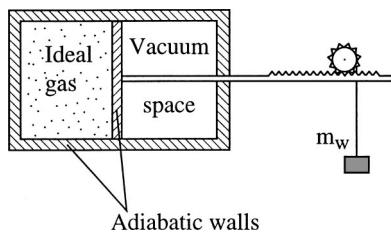

Fig. 2. The system under study.

as a constant-pressure work device, i.e., an adiabatic system whose pressure, P_w, and entropy have constant values.[12] On the other hand, since the internal energy of the work device, U_w, refers to the gravitational potential energy associated with the hanging mass in Fig. 2, one has

$$dU_w = \frac{m_w g}{\mathcal{A}} \mathcal{A} dh_w = -P_w dV_w, \tag{7}$$

where $m_w g$ is the weight of the hanging mass, h_w is its height, $\mathcal{A}$ is the area of the piston, and V_w is the volume of the right side in Fig. 2. Therefore, the internal energy, U_w, and the entropy, S_w, of the work device are given by

$$U_w = U_{w,0} - P_w V_w, \tag{8}$$

$$S_w = S_{w,0}, \tag{9}$$

where $U_{w,0}$ and $S_{w,0}$ are constants.

Bazarov proposed to determine the equilibrium conditions for the gas and to show that under such conditions the entropy is a maximum. The solution of this problem was also given by Bazarov.[13] However, as we shall see below, the system considered (gas plus work device) has only one independent variable, while Bazarov's work used two independent variables.

III. APPLICATION OF THE EXTREMUM PRINCIPLES

Let us assume that the gas is found in an initial equilibrium state with temperature $T_{g,i}$ and volume $V_{g,i}$, the piston being in a fixed position. If $P_{g,i} \neq P_w$, by removing the constraint fixing the piston, the gas evolves toward a final equilibrium state with a pressure

$$P_{g,eq} = \frac{RT_{g,eq}}{V_{g,eq}} = P_w. \tag{10}$$

Our aim is to analyze this final equilibrium state from the viewpoint of the extremum principles for the total entropy, internal energy, and volume.

A. Entropy maximum principle

From Eqs. (6) and (9), the entropy of the total system is given by

$$S = S_g + S_w = S_0 + c_v \ln T_g + R \ln V_g, \tag{11}$$

where $S_0 = S_{g,0} + S_{w,0}$ is a constant. Furthermore, since the internal energy and the volume of the total system remain constant one has

$$U_g + U_w = \text{constant}, \tag{12}$$

$$V_g + V_w = \text{constant}. \tag{13}$$

Substituting Eqs. (5) and (8) into Eq. (12), and taking into account Eq. (13), one obtains

$$c_v T_g + P_w V_g = A, \tag{14}$$

where A is a constant that can be calculated from the initial equilibrium state: $A = c_v T_{g,i} + P_w V_{g,i}$. Equation (14) shows that the equilibrium states of the composite system can be described by means of only one internal variable, i.e., in the maximization process for the entropy (11) under external constraints (12) and (13) there is only one independent vari-

able. Let us take the gas volume V_g as this variable. Then, from Eq. (14) one has

$$T_g = \frac{A - P_w V_g}{c_v}, \tag{15}$$

which substituted into Eq. (11) gives

$$S_{U,V} = S_0 + c_v \ln\left(\frac{A - P_w V_g}{c_v}\right) + R \ln V_g. \tag{16}$$

In order to investigate the behavior of $S_{U,V}$ near the equilibrium state, we shall denote $\delta V_g \equiv V_g - V_{g,\mathrm{eq}}$, and expand Eq. (16) in a Taylor series around the equilibrium state,

$$(\delta S)_{U,V} \equiv S_{U,V}(V_g) - S_{U,V}(V_{g,\mathrm{eq}})$$
$$= \left(\frac{dS}{dV_g}\right)_{\mathrm{eq}} \delta V_g + \frac{1}{2}\left(\frac{d^2 S}{dV_g^2}\right)_{\mathrm{eq}} (\delta V_g)^2 + \cdots, \tag{17}$$

where, from Eqs. (15) and (16),

$$\left(\frac{dS}{dV_g}\right)_{\mathrm{eq}} = -\frac{c_v P_w}{A - P_w V_{g,\mathrm{eq}}} + \frac{R}{V_{g,\mathrm{eq}}} = -\frac{P_w}{T_{g,\mathrm{eq}}} + \frac{R}{V_{g,\mathrm{eq}}}, \tag{18}$$

$$\left(\frac{d^2 S}{dV_g^2}\right)_{\mathrm{eq}} = -\frac{c_v P_w^2}{(A - P_w V_{g,\mathrm{eq}})^2} - \frac{R}{V_{g,\mathrm{eq}}^2}$$
$$= -\frac{P_w^2}{c_v T_{g,\mathrm{eq}}^2} - \frac{R}{V_{g,\mathrm{eq}}^2}. \tag{19}$$

Condition (10) assures that the first derivative (18) is zero in equilibrium, consistent with the extremum principle. Furthermore, substituting (10) into the second derivative (19) one obtains

$$\left(\frac{d^2 S}{dV_g^2}\right)_{\mathrm{eq}} = -\frac{\gamma R}{V_{g,\mathrm{eq}}^2}, \tag{20}$$

where we have used the Mayer relation $c_p - c_v = R$, c_p being the molar heat capacity at constant pressure, and $\gamma = c_p / c_v$ is the adiabatic coefficient of the gas. The second derivative (20) is clearly negative, consistent with the extremum character (maximum) for the entropy.

From Eqs. (15) and (10) one obtains

$$T_{g,\mathrm{eq}} = \frac{A - P_w V_{g,\mathrm{eq}}}{c_v} = \left(c_v + R\frac{P_w}{P_{g,i}}\right)\frac{T_{g,i}}{c_p}. \tag{21}$$

Substitution of Eq. (21) into Eq. (10) yields

$$V_{g,\mathrm{eq}} = \frac{R T_{g,\mathrm{eq}}}{P_w} = \left(c_v + R\frac{P_w}{P_{g,i}}\right)\frac{R T_{g,i}}{c_p P_w}. \tag{22}$$

Equations (21) and (22) give, respectively, the temperature and the volume of the gas in the final equilibrium state in terms of the pressure and the temperature of the gas in the initial equilibrium state and the equilibrium condition (10), i.e., the external pressure P_w. Results (21) and (22) can also be obtained by applying the first law to the gas for an adiabatic process under a constant external pressure P_w and by assuming that the initial and final states of the process are equilibrium states.

B. Internal energy minimum principle

In order to apply the extremum principle for the internal energy, it is necessary to know at least one state of the set of equilibrium states where the minimization process is done. This is the final equilibrium state obtained from the entropy maximum principle and is given by Eqs. (21) and (22). Then we can proceed in the following way. From Eqs. (5) and (8), the internal energy of the total system is given by

$$U = U_g + U_w = U_0 + c_v T_g - P_w V_w, \tag{23}$$

where $U_0 = U_{g,0} + U_{w,0}$ is a constant. Now the external constraints fix the total entropy and volume. The closure relation for the volume is given by Eq. (13) while the conservation law for the entropy follows directly from Eq. (11),

$$T_g V_g^{R/c_v} = B, \tag{24}$$

where B is a constant that can be calculated from the final equilibrium state: $B = T_{g,\mathrm{eq}} V_{g,\mathrm{eq}}^{R/c_v}$, where $T_{g,\mathrm{eq}}$ and $V_{g,\mathrm{eq}}$ are given by Eqs. (21) and (22), respectively. Equation (24) shows that in the minimization process for the internal energy (23) under external constraints (13) and (24), there is only one independent variable. Taking the gas volume V_g as this variable, from Eqs. (13), (23), and (24), one has

$$U_{S,V} = U_0^* + \frac{c_v B}{V_g^{R/c_v}} + P_w V_g, \tag{25}$$

where U_0^* is a constant. By expanding Eq. (25) in a Taylor series around the equilibrium state, one obtains

$$(\delta U)_{S,V} \equiv U_{S,V}(V_g) - U_{S,V}(V_{g,\mathrm{eq}})$$
$$= \left(\frac{dU}{dV_g}\right)_{\mathrm{eq}} \delta V_g + \frac{1}{2}\left(\frac{d^2 U}{dV_g^2}\right)_{\mathrm{eq}} (\delta V_g)^2 + \cdots, \tag{26}$$

where, from Eqs. (10), (24), and (25),

$$\left(\frac{dU}{dV_g}\right)_{\mathrm{eq}} = -\frac{RB}{V_{g,\mathrm{eq}}^\gamma} + P_w = -\frac{R T_{g,\mathrm{eq}}}{V_{g,\mathrm{eq}}} + P_w, \tag{27}$$

$$\left(\frac{d^2 U}{dV_g^2}\right)_{\mathrm{eq}} = \frac{RB\gamma}{V_{g,\mathrm{eq}}^{\gamma+1}} = \frac{R\gamma T_{g,\mathrm{eq}}}{V_{g,\mathrm{eq}}^2}. \tag{28}$$

From the preceding discussion, the first derivative (27) is clearly zero in equilibrium, while the second derivative (28) is positive, consistent with the existence of a minimum.

C. Volume minimum principle

As in the above case, the application of the extremum principle for the volume requires one known state from the set of equilibrium states where the minimization process is done. Again, this is the final equilibrium state obtained from the entropy maximum principle. Now the function to be considered is the total volume

$$V = V_g + V_w, \tag{29}$$

while the external constraints fix the total entropy and internal energy. The constraint for the entropy gives Eq. (24) and, taking into account Eq. (23), the constraint (12) for the internal energy leads to

$$c_c T_g - P_w V_w = C, \tag{30}$$

where C is a constant. Substituting Eqs. (24) and (30) into Eq. (29), one obtains

$$V_{S,U} = -\frac{C}{P_w} + V_g + \frac{c_v B}{P_w V_g^{R/c_v}}, \tag{31}$$

where B is given by Eq. (24). By expanding Eq. (31) in a Taylor series around the equilibrium state, one obtains

$$(\delta V)_{S,U} \equiv V_{S,U}(V_g) - V_{S,U}(V_{g,\text{eq}})$$
$$= \left(\frac{dV}{dV_g}\right)_{\text{eq}} \delta V_g + \frac{1}{2}\left(\frac{d^2V}{dV_g^2}\right)_{\text{eq}} (\delta V_g)^2 + \cdots, \tag{32}$$

where, from Eqs. (24) and (31),

$$\left(\frac{dV}{dV_g}\right)_{\text{eq}} = 1 - \frac{RB}{P_w V_{g,\text{eq}}^{\gamma}} = 1 - \frac{RT_{g,\text{eq}}}{P_w V_{g,\text{eq}}}, \tag{33}$$

$$\left(\frac{d^2V}{dV_g^2}\right)_{\text{eq}} = \frac{RB\gamma}{P_w V_{g,\text{eq}}^{\gamma+1}} = \frac{R\gamma T_{g,\text{eq}}}{P_w V_{g,\text{eq}}^2}. \tag{34}$$

The first derivative (33) is clearly zero in equilibrium, while the second derivative (34) is positive, consistent with the existence of a minimum.

In summary, for the composite system considered (ideal gas plus work device), the extremum principles for the entropy, internal energy, and volume consist in finding the extrema of three one-dimensional functions. By taking the gas volume V_g as the independent variable, these functions are:

$$S_{U,V} - S_0 = c_v \ln\left(\frac{A - P_w V_g}{c_v}\right) + R \ln V_g, \tag{35}$$

$$U_{S,V} - U_0^* = \frac{c_v B}{V_g^{R/c_v}} + P_w V_g, \tag{36}$$

$$V_{S,U} + \frac{C}{P_w} = V_g + \frac{c_v B}{P_w V_g^{R/c_v}}, \tag{37}$$

with

$$A = c_v T_{g,i} + P_w V_{g,i} = \left(c_v + R\frac{P_w}{P_{g,i}}\right)T_{g,i} = c_v T_g + P_w V_g, \tag{38}$$

and

$$B = T_{g,\text{eq}} V_{g,\text{eq}}^{R/c_v} = T_g V_g^{R/c_v}, \tag{39}$$

where $P_{g,i}$ and $T_{g,i}$ are the pressure and the temperature of the gas in the initial equilibrium state, P_w is the external pressure, and $T_{g,\text{eq}}$ and $V_{g,\text{eq}}$ are given by Eqs. (21) and (22), respectively.

In Fig. 3 we have plotted Eqs. (35)–(37) for the case of one mol of a monoatomic ideal gas ($c_v = 3R/2$) with $P_{g,i} = 2$ bar and $T_{g,i} = 300$ K, and a constant-pressure work device with $P_w = 1$ bar. In this case, Eqs. (21) and (22) give $T_{g,\text{eq}} = 240$ K and $V_{g,\text{eq}} = 0.02$ m^3, while Eqs. (38) and (39) give $A = 4988.4$ J and $B = 17.66$ m^2 K. One can see that the entropy function (35) has a maximum at $V_g = V_{g,\text{eq}} = 0.02$ m^3, while the internal energy function (36) and the volume function (37) present a minimum for the same value of the gas volume.

In Fig. 4 we have plotted in the (T_g, V_g) plane the gas states through which the maximization process for the en-
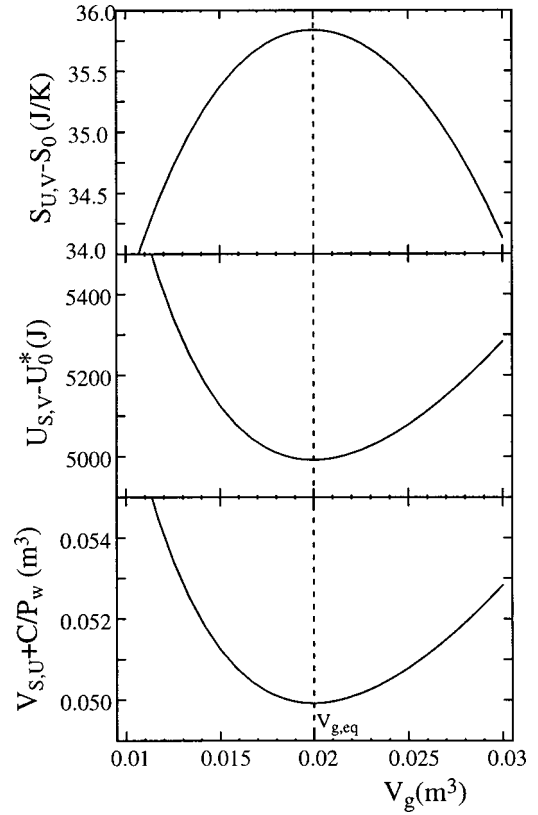

Fig. 3. Behavior of the functions $S_{U,V} - S_0$ [Eq. (35)], $U_{S,V} - U_0^*$ [Eq. (36)], and $V_{S,U} + C/P_w$ [Eq. (37)] for the system of Fig. 3 with 1 mol of a monoatomic ideal gas at initial conditions of 2 bar and 300 K, and an external pressure of 1 bar.

tropy is made, Eq. (38), and through which the minimization processes for the internal energy and for the volume are made, Eq. (39). Both functions share a common point, the final equilibrium state $(T_{g,\text{eq}}, V_{g,\text{eq}})$, and the straight line (38) is tangent to the curve (39) at this point. We remark that these are the gas states, but not the states of the composite system (gas plus work device), along the different extremum processes. We remember that the thermodynamic description of the composite system is made in the space (T_g, V_g, V_w). Therefore, in this space, the maximization process for the entropy is made along the curve defined by Eqs. (13) and (38), the minimization process for the internal energy is
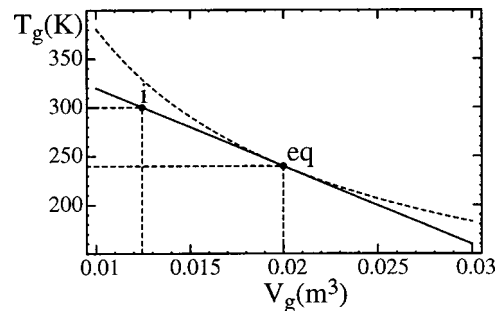

Fig. 4. States of the gas through the process of maximization of the total entropy (solid line) for the system of Fig. 3 with 1 mol of a monoatomic ideal gas at initial conditions of 2 bar and 300 K and an external pressure of 1 bar, and through the processes of the minimization of the total internal energy and the minimization of the total volume with $S_g = S_{g,\text{eq}}$ (dashed line).

made along the curve defined by Eqs. (13) and (39), and the minimization process for the volume is made along the curve defined by Eqs. (31) and (39).

IV. A KINETIC MODEL

In the previous section we have solved, from a purely thermodynamic viewpoint, the problem of predicting the final equilibrium state of the composite system. In the present section we solve the same problem from a microscopic viewpoint by using a simple kinetic model that can help students to visualize the time evolution of the temperature and volume of the gas toward the final equilibrium state given by Eqs. (21) and (22). The present model is based on the one proposed by Crosignani et al.[14] for the problem of two ideal gases separated by an internal adiabatic movable piston. A macroscopic approach to the time evolution of the piston in the one-cylinder problem has been reported by Gruber.[15]

Let us consider the system of Fig. 2. There are N_A, where N_A is Avogadro's number, identical point particles of mass m inside an adiabatic cylinder with an adiabatic movable piston of mass M and area $\mathcal{A}$. A constant force $F_w = P_w \mathcal{A}$ acts on the right face of the piston. We denote by x the piston position, so that the gas volume is given by $V_g = \mathcal{A}x$. We assume that the collisions between gas particles and between gas particles and the piston are elastic. Furthermore, we assume that the gas particles reach a Maxwellian molecular velocity distribution on a time scale negligible in comparison with that of the piston motion. Therefore, at any instant the temperature $T_g(t)$ is well defined, and the pressure and the internal energy of the gas are given, respectively, by Eqs. (4) and (5).

The dynamics of the piston is described by

$$M \frac{d^2x}{dt^2} = F_g - F_w = (P_g - P_w)\mathcal{A}, \tag{40}$$

where F_g is the force exerted on the piston by the gas. On the other hand, the energy conservation law reads

$$\frac{dK}{dt} + \frac{dU_g}{dt} + \frac{dU_w}{dt} = M \frac{dx}{dt}\frac{d^2x}{dt^2} + c_v \frac{dT_g}{dt} + P_w \mathcal{A} \frac{dx}{dt} = 0, \tag{41}$$

where $K = (M/2)(dx/dt)^2$ is the kinetic energy of the piston, and we have used Eqs. (5) and (8) and taken into account that $dV_w = -dV_g = -\mathcal{A}\,dx$. Now, following Bauman and Cockerham's kinetic model, which explicitly takes into account the influence of the finite piston velocity on the momentum change of the gas molecules,[16,17] the gas pressure P_g is given by

$$P_g = \frac{mN_A}{V_g}\left(\frac{1}{3}\langle v^2 \rangle - \langle v \rangle \dot{x} + \dot{x}^2\right)$$

$$= \frac{mN_A}{\mathcal{A}x}\left(\frac{k_B T_g}{m} - \sqrt{\frac{8k_B T_g}{\pi m}}\dot{x} + \dot{x}^2\right), \tag{42}$$

where the average values $\langle v^2 \rangle$ and $\langle v \rangle$ for the molecular velocity are obtained from Maxwell's velocity distribution law, and k_B is Boltzmann's constant. Substituting Eq. (42) into Eq. (40), and Eq. (40) into Eq. (41), the complete set of time evolution equations is

$$M \frac{d^2x}{dt^2} = -P_w \mathcal{A} + \frac{RT_g}{x} - \sqrt{\frac{8R\mathcal{M}}{\pi}}\frac{\sqrt{T_g}}{x}\left(\frac{dx}{dt}\right)$$

$$+ \frac{\mathcal{M}}{x}\left(\frac{dx}{dt}\right)^2, \tag{43}$$

$$c_v \frac{dT_g}{dt} = -\frac{RT_g}{x}\frac{dx}{dt} + \sqrt{\frac{8R\mathcal{M}}{\pi}}\frac{\sqrt{T_g}}{x}\left(\frac{dx}{dt}\right)^2$$

$$- \frac{\mathcal{M}}{x}\left(\frac{dx}{dt}\right)^3, \tag{44}$$

where $\mathcal{M} = mN_A$ is the molar mass of the gas. Equation (43), up to the first order in the piston velocity, is similar to the one reported by Gruber.[15]

Equations (43) and (44) allow one to obtain the equilibrium values of x and T_g, once the corresponding initial values are known. By setting both $d^2x/dt^2 = 0$ and $dx/dt = 0$ in Eq. (43), which corresponds to the final rest position, one has

$$P_w = \frac{RT_{g,\text{eq}}}{\mathcal{A}x_\text{eq}} = P_{g,\text{eq}}, \tag{45}$$

independent of the mass of the piston. The result (45) is in agreement with the mechanical equilibrium condition (10). Furthermore, assuming that the piston is initially at rest $[(dx/dt)_i = 0]$, integration of the energy conservation law (41) allows one to obtain

$$c_v T_{g,\text{eq}} + P_w \mathcal{A}x_\text{eq} = c_v T_{g,i} + P_w \mathcal{A}x_i, \tag{46}$$

from which, taking into account Eqs. (4) and (45), one obtains

$$T_{g,\text{eq}} = \left(c_v + R\frac{P_w}{P_{g,i}}\right)\frac{T_{g,i}}{c_p}, \tag{47}$$

in agreement with Eq. (21).

Introducing the dimensionless variables $\xi = x/x_i$, $\theta = T_g/T_{g,i}$, and $\tau = t/t_a$, with $t_a = (Mx_i^2/RT_{g,i})^{1/2} = (MRT_{g,i})^{1/2}/(P_{g,i}\mathcal{A})$, Eqs. (43) and (44) can be rewritten as

$$\ddot{\xi} = -\alpha + \frac{\theta}{\xi} - \delta\sqrt{\theta}\frac{\dot{\xi}}{\xi} + \frac{\pi\delta^2}{8}\frac{\dot{\xi}^2}{\xi}, \tag{48}$$

$$\dot{\theta} = -(\gamma - 1)\theta\frac{\dot{\xi}}{\xi} + (\gamma - 1)\delta\sqrt{\theta}\frac{\dot{\xi}^2}{\xi} - \frac{\pi\delta^2}{8}(\gamma - 1)\frac{\dot{\xi}^3}{\xi}, \tag{49}$$

where $\alpha = P_w/P_{g,i}$, $\delta = (8\mathcal{M}/\pi M)^{1/2}$, $\gamma = c_p/c_v$, and the dot stands for differentiation with respect to τ. From Eqs. (47) and (45), the equilibrium values of θ and ξ are

$$\theta_\text{eq} = \frac{c_v + R\alpha}{c_p}, \tag{50}$$

$$\xi_\text{eq} = \frac{\theta_\text{eq}}{\alpha} = \frac{c_v + R\alpha}{c_p\alpha}, \tag{51}$$

which are independent of the mass of the piston.

Figure 5 shows the numerical solution of Eqs. (48) and (49) for the case of 1 mol of gas Ar ($c_v = 3R/2$, $c_p = 5R/2$, $\mathcal{M} = 40 \times 10^{-3}$ kg/mol), $M = 10$ kg, and $P_{g,i} = 2P_w$. In this case, $\alpha = 0.5$, $\delta = 0.1$, $\theta_\text{eq} = 0.8$, and $\xi_\text{eq} = 1.6$. We note that we have chosen a piston mass so that the assumption $\delta \ll 1$
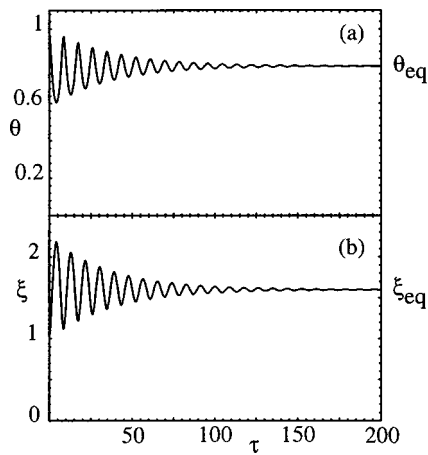
Fig. 5. Plot of $\theta(\tau)$ (a) and $\xi(\tau)$ (b) for $\theta(0)=1$, $\xi(0)=1$, $\dot{\xi}(0)=0$, $\alpha = P_w/P_{g,i}=0.5$, and $\delta=(8\mathcal{M}/\pi M)^{1/2}=0.1$, with $\theta=T_g/T_{g,i}$, $\xi=x/x_i$, and $\tau=t(RT_{g,i}/Mx_i^2)^{1/2}$.

underlying the kinetic model is verified.[14] Since our equations were derived for 1 mol of gas a large value of M is required. One can see that both the dimensionless gas temperature and the dimensionless piston position exhibit damped oscillations toward the equilibrium position with very similar relaxation times. The parameter δ governs this relaxation time and one can easily check that it decreases as δ increases, i.e., as the piston becomes less massive and the molar mass of the gas increases. In order to give a numerical meaning to the τ values involved (see Fig. 5), suppose that $P_{g,i}=2$ bar and $T_{g,i}=300$ K. Then, considering a cylinder with radius $r=0.1$ m and cross-sectional area $\mathcal{A}=3.14 \times 10^{-2}$ m², one obtains $t_a=0.025$ s. In this case, a value of $\tau=200$ (the time scale in Fig. 5) corresponds to $t=t_a\tau = 5$ s.

V. SUMMARY

In this paper we have applied three different thermodynamic extremum principles to analyze the equilibrium state in an isolated composite system consisting of an ideal gas interacting with a constant-pressure work device through an adiabatic movable piston. It is worth noting, however, that the system considered here differs from the so-called *adiabatic piston problem* (APP) that is a composite system consisting of two gases separated by an internal adiabatic movable wall.[14,15,18–20] In both cases, thermodynamics establishes the equality of the final pressures. However, by using only the laws of thermostatistics, while in the first case the final gas temperature and volume can be obtained from the initial conditions, in the second case, the final temperatures and volumes cannot be determined. (The calculation of the final volume and temperature in the APP is done in Ref. 14 using a microscopic model.) Mathematically, the difference between these systems lies in the fact that in the first case there is only one independent internal variable, while in the second case there are two independent internal variables.

We have also obtained the equilibrium state for the system considered by means of a simple kinetic model. This model does not take into account microscopic fluctuations in the gas pressure. The role played by these fluctuations is an intriguing question.[21] It is worth mentioning that this role in the APP has been very recently studied by Gruberg and

Frachebourg[22] and, in the mesoscopic regime, by Crosignani and Di Porto.[23] It has been argued that the stochastic motion of the piston, induced by the pressure fluctuations, drives the gas toward a final equilibrium state with the same pressure and the same temperature in both sides,[22,24,25] so that the mechanical equilibrium state must be considered as a quasi-equilibrium state. However, the time scale for this thermalization process is very long (unobservable, in practice) for macroscopic pistons.

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