

Finite-time thermodynamics of a porous plug

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(Received 17 March 1986)

Three related systems, two of which describe diffusion of an ideal gas through a porous plug, are optimized so as to minimize the work required to move the plug from one equilibrium position to another equilibrium position in a given time τ . All systems follow a "turnpike" (i.e., boundary-singular-boundary branch) trajectory, and the dissipation (work required) is proportional to $(\Delta l)^2/\tau$, where Δl is the distance moved, at least for slow processes. The result is of interest as a lower bound for the separation of gases by diffusion.

I. INTRODUCTION

Diffusion at a nonvanishing rate is inherently dissipative. Nonetheless, it has been used to separate mixtures of gaseous compounds, e.g., containing different isotopes of the same element. Finite-time thermodynamics¹ has been developed to provide lower bounds on the dissipation in rate processes. In this paper we use one of the methods of finite-time thermodynamics, optimal control theory, to examine the minimum dissipation associated with finite-time passage of an ideal gas through a porous plug.

Two basically different physical situations are readily identified, one in which the system is closed and the total amount of gas thus constant (Fig. 1), and the other in which the system is open and diffusion occurs against a gas reservoir of constant pressure (Fig. 2). In both cases control is achieved by varying the position of the plug. The plug is assumed to be movable without friction or inertia, and it is further assumed that the process is done sufficiently slowly so that the gas is isothermal and in internal equilibrium on each side of the plug (i.e., diffusion through the plug is slow compared to internal equilibration and heat conduction to a surrounding heat bath). This assumption of separability of time scales is equivalent to endoreversibility (literally "reversible on the inside," meaning that all irreversibilities are located across the boundary to the environment²) and is justified by our intent to explore only that portion of the irreversibility associated with the passage of gas through the porous plug.

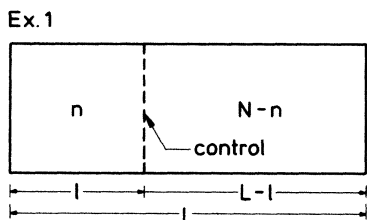


FIG. 1. Box of total length L , cross sectional area A , and containing N moles of an ideal gas at fixed temperature T is separated into two compartments by a porous plug permeable to the gas. The left compartment of length l contains n moles of gas. The rate of diffusion through the plug is proportional to the pressure difference across it. The position of the plug is used to control the system.

Under these assumptions the solutions turn out to be of the "turnpike" form previously observed in finite-time heat engines.³ (The expression turnpike solution is frequently used⁴ to indicate that the optimal path goes as fast as possible to the turnpike along which the system follows a solution of the Euler-Lagrange equations, and finally gets off the turnpike at the last moment which allows enough time to reach the final state.) While this turnpike property is difficult to prove even for these simplified examples, it is likely to be generally true for endoreversible systems in the absence of friction and inertia.

The solution of the optimal control problem for the example in Fig. 1 is quite difficult. This prompted us to explore the example in Fig. 2, which is of a very similar mathematical form, but is simpler to solve. The progression from the example in Fig. 1 to the example in Fig. 2 in fact suggested an even simpler problem of the same mathematical form, which has a physical counterpart shown in Fig. 3. This problem served mainly as the mathematical compass which provided direction for the progressively more difficult problems. Consequently, in the following our arguments will be given in parallel for the three examples termed Ex1 (Fig. 1), Ex2 (Fig. 2), and Ex3 (Fig. 3).

Section II will define the three examples in mathematical terms. Section III states a number of theorems for the optimal trajectories with the proofs given in the Appendix. This information is collected to form the actual trajectories and to calculate the dissipation along each one in Sec. IV. The physical examples are chosen as a means of obtaining a bound on the irreversibility in simple separation processes using semipermeable membranes; this is explored in Sec. V of the paper.

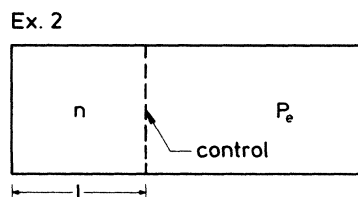


FIG. 2. Right compartment of Fig. 1 is replaced by an environment of constant pressure P_e .

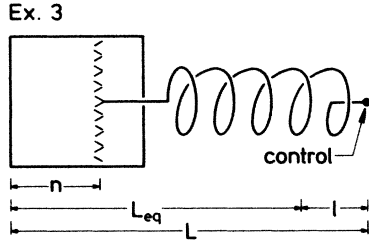


FIG. 3. Dashpot, whose resistive force is proportional to its velocity, is connected through a spring to a control. The position of the dashpot relative to some fixed point is n , that of the control is L , and the extension of the spring away from its equilibrium position is l .

II. PROBLEM FORMULATION

A. Example 3 (Fig. 3)

Given: An incompressible fluid in a cylinder containing a dashpot which is connected to an external control through a spring.

Find: The control trajectory necessary to move the dashpot from one equilibrium position $l(0)$ to another equilibrium position $l(\tau)$ in a given time τ with minimal work.

Assume: (i) The system is free of inertial effects, (ii) the resistance of the dashpot to movement is proportional to its velocity, and (iii) the tension in the spring is proportional to its displacement from its equilibrium length.

The variables used are shown in Fig. 3.

Since the system has no inertia, the force on the control must at all times equal both the tension in the spring and the resistance force on the dashpot,

$$\begin{aligned} F_{\text{control}} &= T_{\text{spring}} = F_{\text{dashpot}} \\ &= k_{\text{spring}}(l - n) = k_{\text{dashpot}}\dot{n}, \end{aligned} \quad (1)$$

where the dot indicates time derivative. To simplify the situation, we select units of distance such that $k_{\text{spring}} = 1$ and units of time so that $k_{\text{dashpot}} = 1$. Then the work done on the system by the control is

$$\begin{aligned} W &= \int_{l(0)}^{l(\tau)} F_{\text{control}} dl \\ &= \int_0^\tau (l - n)\dot{l} dt. \end{aligned} \quad (2)$$

In order to ensure the existence of a solution, we make the admissible set compact by constraining the velocity \dot{l} to be bounded. Thus the final mathematical statement of example 3 becomes the following: minimize

$$W = \int_0^\tau (l - n)\dot{l} dt,$$

subject to

$$\dot{n} = l - n, \quad (3)$$

$$|\dot{l}| \leq u_{\text{max}}, \quad (4)$$

$$n > 0, \quad (5)$$

$$n(0) = l(0), \quad (6)$$

$$n(\tau) = l(\tau). \quad (7)$$

B. Example 2 (Fig. 2)

Given: A rectangular box with the right side open to the environment through a porous plug which can be moved in order to control the system. The box and the environment contain an ideal gas.

Find: The trajectory necessary to move the plug from one equilibrium position $l(0)$ to another equilibrium position $l(\tau)$ in a given time τ with minimal work.

Assume: (i) The environment has constant pressure, (ii) the rate of diffusion of the gas through the plug is proportional to its concentration difference across the plug, (iii) the process is carried out isothermally, (iv) the system is free of inertial effects and friction, (v) internal degrees of freedom equilibrate rapidly compared to the time scale of diffusion through the plug, (vi) the velocity of the plug is bounded.

The variables used are shown in Fig. 2.

Using the ideal gas law, we find the work done on the system by the control

$$\begin{aligned} W &= \int_{V(0)}^{V(\tau)} \Delta P dV \\ &= \int_{l(0)}^{l(\tau)} \left[P_e - \frac{nRT}{lA} \right] A dl \\ &= RT \int_0^\tau \left[\frac{P_e A}{RT} - \frac{n}{l} \right] \dot{l} dt \end{aligned} \quad (8)$$

with

$$\dot{n} = \frac{k}{A} \left[\frac{P_e A}{RT} - \frac{n}{l} \right]. \quad (9)$$

As in example 3, we simplify the expressions by selecting units of distance such that $P_e A / RT = 1$, units of time such that $k/A = 1$, and units of energy such that $RT = 1$. Then the mathematical statement of example 2 becomes the following: minimize

$$W = \int_0^\tau (1 - n/l)\dot{l} dt, \quad (10)$$

subject to

$$\dot{n} = 1 - n/l = (l - n)/l, \quad (11)$$

$$|\dot{l}| \leq u_{\text{max}}, \quad (12)$$

$$n > 0, \quad (13)$$

$$l > 0, \quad (14)$$

$$n(0) = l(0), \quad (15)$$

$$n(\tau) = l(\tau). \quad (16)$$

C. Example 1 (Fig. 1)

Given: A rectangular box containing an ideal gas and a porous plug which divides the box into two compartments and which can be moved back and forth within the box to control the system.

Find: The trajectory necessary to move the plug from one equilibrium position $l(0)$ to another equilibrium position $l(\tau)$ in a given time τ with minimal work.

Assume: The assumptions as in example 2 except (i).

The variables used are shown in Fig. 1.

Using the ideal gas law we find the work done on the system by the control

$$\begin{aligned} W &= \int_{V(0)}^{V(\tau)} \Delta P dV \\ &= \int_{l(0)}^{l(\tau)} \left[\frac{(N-n)RT}{(L-l)A} - \frac{nRT}{lA} \right] A dl \\ &= RT \int_0^\tau \left[\frac{N-n}{L-l} - \frac{n}{l} \right] \dot{l} dt, \end{aligned} \quad (17)$$

with

$$\dot{n} = \frac{k}{A} \left[\frac{N-n}{L-l} - \frac{n}{l} \right]. \quad (18)$$

As before, we simplify the expressions by letting the length of the box be our unit of distance $L=1$, the total amount of gas in the box be our unit quantity of gas $N=1$, and selecting units of time such that $k/A=1$ and units of energy such that $RT=1$. This gives the following mathematical statement of example 1: minimize

$$W = \int_0^\tau \left[\frac{1-n}{1-l} - \frac{n}{l} \right] \dot{l} dt, \quad (19)$$

subject to

$$\dot{n} = \frac{1-n}{1-l} - \frac{n}{l} = \frac{l-n}{l(1-l)}, \quad (20)$$

$$|\dot{l}| \leq u_{\max}, \quad (21)$$

$$0 < n < 1, \quad (22)$$

$$0 < l < 1, \quad (23)$$

$$n(0) = l(0), \quad (24)$$

$$n(\tau) = l(\tau). \quad (25)$$

The similarity of the three examples now becomes clear since they all fit into the following format: minimize

$$W = \int_0^\tau \psi u dt \quad (26)$$

with the control

$$u = \dot{l} \quad (27)$$

and the forcing function

$$\psi = \dot{n}, \quad (28)$$

where

$$\dot{n} = \begin{cases} (l-n) & \text{(Ex3)} \\ (l-n)/l & \text{(Ex2)} \\ (l-n)/(1-l) & \text{(Ex1)}. \end{cases} \quad (3) \quad (11) \quad (20)$$

Their solution is accomplished by optimal control theory from which we know⁵ that the Hamiltonian

$$H(\lambda, \psi, u) = \lambda_0 \psi u + \lambda_1 \dot{\psi} + \lambda_2 u, \quad (29)$$

where the λ 's are Lagrange functions conjugate to Eqs. (26), (28), and (27), respectively, is constant along the optimal trajectory. This can be rewritten as

$$H = \sigma u + \lambda_1 \dot{\psi}, \quad (30)$$

where

$$\sigma = \lambda_0 \dot{\psi} + \lambda_2. \quad (31)$$

The conjugate function $\lambda_0(t)$ is actually⁵ a nonpositive constant, so if $\lambda_0 \neq 0$ we may divide the Hamiltonian by $-\lambda_0$, effectively rescaling the λ 's such that $\lambda_0 = -1$. Consequently, we have only two possibilities, $\lambda_0 = 0$ or $\lambda_0 = -1$. In either case, the optimal trajectory obeys the dynamical equations

$$\dot{n} = \psi, \quad (28)$$

$$\dot{l} = u, \quad (27)$$

$$\dot{\lambda}_1 = -\partial H / \partial n, \quad (32)$$

$$\dot{\lambda}_2 = -\partial H / \partial l, \quad (33)$$

valid for all three examples.

The Pontryagin maximum principle now states that, for all admissible values of the control u , the control corresponding to the optimal trajectory maximizes the Hamiltonian. Therefore, if σ is greater than zero, the optimal trajectory will require [cf. Eq. (30)] u to obtain its maximum admissible value (i.e., $u = u_{\max}$). Likewise, if σ is less than zero, u must obtain its largest admissible negative value (i.e., $u = -u_{\max}$). For this reason, σ is referred to as the switching function, since it determines when one may switch on or off a boundary trajectory. Thus the control is determined by the boundary constraints on u whenever $\sigma \neq 0$. For $\sigma \equiv 0$, u is obtained as the solution of Eqs. (27), (28), (32), (33) in optimal control theory or of the Euler-Lagrange equations in a calculus of variations approach. This trajectory is referred to as the singular trajectory.

III. OPTIMAL TRAJECTORIES

We now proceed to identify the possible solution trajectories and show that the required combination of these trajectories corresponds to the turnpike form. Without loss of generality, we may restrict our discussion to processes with $n(\tau) > n(0)$.

First we make some observations which hold for all three examples.

(i) The set of equilibrium points is the line $l = n$.

(ii) If $n < l$, then $\dot{n} > 0$.

(iii) If $n > l$, then $\dot{n} < 0$.

(iv) At all singular points ($\sigma = 0$), $\psi = \lambda_2$ and $H = \lambda_1 \lambda_2$.

(v) At all equilibrium points $\psi = 0$ and $H = \lambda_2 u$.

(vi) No equilibrium points are singular points.

The last statement is easily seen from the fact that, if any equilibrium point is also a singular point, then at that point $H = \psi u = 0$, implying $\dot{n} = \dot{l} = 0$, so that the entire trajectory must consist of only that one point.

Next note that, as the allowed time τ increases, the minimum work decreases monotonically. This is readily seen from the fact that if we accomplish the objective in a time τ with a certain amount of work, we can accomplish the objective in time $\tau + \epsilon$ with the same work by just sitting at the initial equilibrium position for the duration ϵ

and then following the same trajectory as before. Thus the minimal amount of work, given time $\tau + \epsilon$, must be no larger than the amount of work given time τ .

The shortest possible time for passage between two equilibrium states is achieved by increasing l as fast as possible (i.e., $u = u_{\max}$) until a point when the system can just return to equilibrium at the desired final state in the remaining time while moving at the maximum permissible compression rate ($u = -u_{\max}$). This is the "bang-bang" (boundary-boundary branch) solution^{4,5} which has a trivial trajectory. We can decrease the work by allotting additional time, so this is only the optimal solution if the given time τ is exactly equal to the minimum possible time. For this reason, we are not interested in the bang-bang solution.

We are now in a position to prove a number of lemmas—the actual proofs may be found in the Appendix—which will lead to the optimal trajectory.

Lemma 1. If $\lambda_0 = 0$ then the optimal trajectory is the bang-bang solution.

Since this solution is not of interest, we will consider only $\lambda_0 = -1$ for the rest of this paper and thus find the optimal trajectory from among the continuum of admissible trajectories which exist for values of τ larger than the minimum possible time. Then

$$\begin{aligned} H &= -\psi u + \lambda_1 \psi + \lambda_2 u \\ &= \lambda_1 \psi + \sigma u, \end{aligned} \quad (34)$$

where

$$\sigma = \lambda_2 - \psi \quad (35)$$

and

$$\dot{n} = \psi, \quad (28)$$

$$\dot{l} = u, \quad (27)$$

$$\dot{\lambda}_1 = -(\partial\psi/\partial n)(\lambda_1 - u), \quad (36)$$

$$\dot{\lambda}_2 = -(\partial\psi/\partial l)(\lambda_1 - u). \quad (37)$$

This set of equations has three possible types of trajectories, namely, the two boundary trajectories ($u = u_{\max}$ and $u = -u_{\max}$), and the singular trajectory ($\sigma \equiv 0$).

Here we recall the observation that the singular branch trajectory can never cross the equilibrium line, and we

realize that, if we start at equilibrium and move along any boundary branch, this will not take us to another equilibrium point. This tells us that if we are "left" of equilibrium (i.e., $l < n$), in order to reach another equilibrium point we must approach that equilibrium along the $u = u_{\max}$ boundary trajectory. Similarly, if $l > n$, to reach an equilibrium point we must approach it along a $u = -u_{\max}$ boundary trajectory. This leads to the following lemmas.

Lemma 2. The Hamiltonian is positive.

Lemma 3. The initial branch is the boundary branch toward the final state [i.e., $u = u_{\max}$ if $n(\tau) > n(0)$].

Since we limited our discussion to $n(\tau) > n(0)$, at least the initial part of the optimal trajectory will be "to the right of equilibrium" ($l > n$).

Lemma 4. If we reach an equilibrium point from the right (i.e., with $l > n$) it must be the final equilibrium point.

Thus the optimal trajectory can never cross the equilibrium line, and in our case the entire trajectory is to the right of equilibrium. Now to find the exact form of the solution trajectory, it is reasonable to assume that the form of this solution will be independent of the actual value of u_{\max} . Consequently, to make the calculations easier we set $u_{\max} = 1$. The general case of an unspecified u_{\max} will be discussed later.

Lemma 5. If we switch to a $u = -1$ trajectory from a point to the right of equilibrium ($l > n$), then we will never reach another point where the switching function allows us to switch (i.e., $\sigma = 0$).

Thus, once we switch to a $u = -1$ trajectory, we must continue to the final equilibrium and cannot cross the singular trajectory. This means that the overall trajectory must start along a $u = +1$ trajectory until a switching point from where we follow the singular trajectory to the point where the $u = -1$ trajectory will take us to the final equilibrium state. This is the turnpike form and it has been shown for $u_{\max} = 1$.

If we now look at $u_{\max} > 1$, it is easily seen that the technique used in the proof of lemma 5 will hold for examples 2 and 3, but for example 1 it is not clear that this is true. Nevertheless, it seems reasonable to assume that the turnpike form of the solution will be the optimal trajectory form regardless of the value of u_{\max} .

IV. SOLUTIONS OF INDIVIDUAL BRANCH TRAJECTORIES

Substituting the values for ψ , $\partial\psi/\partial n$, and $\partial\psi/\partial l$ from Eqs. (28), (A4), and (A5) into Eq. (A10) yields the singular trajectories

$$\begin{aligned} n &= \begin{cases} l - 2h & \text{(Ex3)} \\ l - 2lh[(1+h^2)^{1/2} - h] & \text{(Ex2)} \\ l - 2l(1-l)h(\{1+[h(1-2l)]^2\}^{1/2} - h(1-2l)) & \text{(Ex1)} \end{cases} \end{aligned} \quad \begin{aligned} (38a) \\ (38b) \\ (38c) \end{aligned}$$

where for convenience we have defined $h \equiv \sqrt{H}/2$. Further using the expressions for \dot{n} in Eqs. (3), (11), and (20) we find

$$\begin{aligned} \lambda_2 = \psi = \dot{n} &= \begin{cases} 2h & \text{(Ex3)} \\ 2h[(1+h^2)^{1/2} - h] \equiv h_2 & \text{(Ex2)} \\ 2h(\{1+[h(1-2l)]^2\}^{1/2} - h(1-2l)) \equiv h_1 & \text{(Ex1)} \end{cases} \end{aligned} \quad \begin{aligned} (39a) \\ (39b) \\ (39c) \end{aligned}$$

$$\lambda_1 = \frac{H}{\psi} = \begin{cases} 2h & \text{(Ex3)} \\ 2h[(1+h^2)^{1/2}+h] & \text{(Ex2)} \\ 2h(\{1+[h(1-2l)]^2\}^{1/2}+h(1-2l)) & \text{(Ex1)} \end{cases} \quad \begin{matrix} (40a) \\ (40b) \\ (40c) \end{matrix}$$

$$u = \dot{l} = \frac{\dot{n}}{(dn/dl)} = \begin{cases} 2h & \text{(Ex3)} \\ h_2/(1-h_2) & \text{(Ex2)} \\ h_1 / \left[1-h_1 \left[1-2l + \frac{2l(1-l)h}{\{1+[h(1-2l)]^2\}^{1/2}} \right] \right] & \text{(Ex1)} \end{cases} \quad \begin{matrix} (41a) \\ (41b) \\ (41c) \end{matrix}$$

These singular branch trajectories are shown graphically in Fig. 4.

The differential equations for the boundary branch trajectories in example 1 are greatly simplified by again choosing $u_{\max} = 1$. Then with $u = 1$,

$$\dot{l} = 1 \quad (42)$$

and

$$\psi = \dot{n} = \dot{n}/\dot{l} = dn/dl, \quad (43)$$

which for the three examples yields

$$n = \begin{cases} l-1+(n_0-l_0+1)e^{l_0-l} & \text{(Ex3)} \\ \frac{n_0 l_0}{l} + \frac{l^2-l_0^2}{2l} & \text{(Ex2)} \\ 1 + \frac{1-l}{l} \left[\ln \left[\frac{1-l}{1-l_0} \right] + \frac{l_0(n_0-1)}{1-l_0} \right] & \text{(Ex1)} \end{cases} \quad \begin{matrix} (44a) \\ (44b) \\ (44c) \end{matrix}$$

The Lagrange functions λ_1 and λ_2 are obtained by applying the identity $\dot{\lambda} = \dot{\lambda}/\dot{l} = d\lambda/dl$ to Eqs. (36) and (37), respectively,

$$\lambda_1 = \begin{cases} (\lambda_{10}-1)e^{l-l_0} + 1 & \text{(Ex3)} \\ (\lambda_{10}-1)\frac{l}{l_0} + 1 & \text{(Ex2)} \\ (\lambda_{10}-1)\frac{l(1-l_0)}{l_0(1-l)} + 1 & \text{(Ex1)} \end{cases} \quad \begin{matrix} (45a) \\ (45b) \\ (45c) \end{matrix}$$

$$\lambda_2 = \begin{cases} (\lambda_{10}-1)(1-e^{l-l_0}) + \lambda_{20} & \text{(Ex3)} \\ (\lambda_{10}-1)\frac{l_0-l}{2ll_0}(2n_0+l-l_0) + \lambda_{20} & \text{(Ex2)} \\ (\lambda_{10}-1) \left[\frac{1-l_0}{ll_0(1-l)} \ln \left[\frac{1-l}{1-l_0} \right] + (1-n_0) \left[\frac{1}{l_0(1-l_0)} - \frac{1}{l(1-l)} \right] - \frac{l_0-l}{l_0(1-l)} \right] + \lambda_{20} & \text{(Ex1)} \end{cases} \quad \begin{matrix} (46a) \\ (46b) \\ (46c) \end{matrix}$$

Similarly, for $u = -u_{\max} = -1$,

$$n = \begin{cases} l + 1 + (n_0 - l_0 - 1)e^{l-l_0} & \text{(Ex3)} \\ l \left[\frac{n_0}{l_0} + \ln \left(\frac{l_0}{l} \right) \right] & \text{(Ex2)} \\ \frac{l}{1-l} \left[\frac{n_0(1-l_0)}{l_0} + \ln \left(\frac{l_0}{l} \right) \right] & \text{(Ex1)} \end{cases} \quad (47a-c)$$

$$\lambda_1 = \begin{cases} (\lambda_{10} + 1)e^{l_0-l} - 1 & \text{(Ex3)} \\ (\lambda_{10} + 1) \frac{l_0}{l} - 1 & \text{(Ex2)} \\ (\lambda_{10} + 1) \frac{l_0(1-l)}{l(1-l_0)} - 1 & \text{(Ex1)} \end{cases} \quad (48a-c)$$

$$\lambda_2 = \begin{cases} (\lambda_{10} + 1)(1 - e^{l_0-l}) + \lambda_{20} & \text{(Ex3)} \\ (\lambda_{10} + 1) \left[\frac{l_0}{l} \ln \left(\frac{l}{l_0} \right) + \frac{(l_0-l)(l_0-n_0)}{ll_0} \right] + \lambda_{20} & \text{(Ex2)} \\ (\lambda_{10} + 1) \left[\frac{l_0}{l(1-l)(1-l_0)} \ln \left(\frac{l}{l_0} \right) + n_0 \left[\frac{1}{l_0(1-l_0)} - \frac{1}{l(1-l)} \right] + \frac{l_0-l}{l(1-l_0)} \right] + \lambda_{20} & \text{(Ex1)} \end{cases} \quad (49a-c)$$

These boundary branch trajectories are plotted in Figs. 5 and 6.

If we now allow u_{\max} to increase without bound, the porous plug will reach the singular branch trajectory before any of the gas has had time to diffuse through the plug. Since we are only interested in the irreversible dissipation associated with the passage of gas through the plug, we will ignore the work along this initial boundary branch as it will be recovered along the final boundary branch. Thus the dissipation of the process is equal to the work expended along the singular branch trajectory.

For example 3 \dot{n} is constant [Eq. (39a)], so that total duration is

$$\tau = \Delta n / \dot{n} = [n(\tau) - n(0)] / 2h \quad (50)$$

and

$$H = 4h^2 = \left[\frac{n(\tau) - n(0)}{\tau} \right]^2 \quad (51)$$

The work along this trajectory, Eq. (26), is then, by Eqs. (38a) and (39a),

$$\begin{aligned} W &= \int_0^\tau \psi \dot{l} dt \\ &= \int_{n(0)+2h}^{n(\tau)+2h} 2h dl \\ &= [n(\tau) - n(0)]^2 / \tau \end{aligned} \quad (52)$$

Example 2 is almost as simple because, again, the singular branch trajectory has a constant forcing function ψ [Eq. (39b)] and a constant velocity u [Eq. (41b)], so

$$\begin{aligned} \dot{n} &= [n(\tau) - n(0)] / \tau \\ &= (H + H^2/4)^{1/2} - H/2, \end{aligned} \quad (53)$$

$$H = \frac{[n(\tau) - n(0)]^2}{\tau \{ \tau - [n(\tau) - n(0)] \}}, \quad (54)$$

and

$$\begin{aligned} W &= \int_{l(0)}^{l(\tau)} [(H + H^2/4)^{1/2} - H/2] dl \\ &= \frac{[n(\tau) - n(0)]^2}{\tau - [n(\tau) - n(0)]} \end{aligned} \quad (55)$$

The exact solution to example 1 is quite difficult since n and u depend on l , but for long times an approximate solution is tractable. In this case, the singular trajectory will be close to the equilibrium line, i.e., $n \approx l$, and h is small. Then Eqs. (38c) and (39c) simplify to

$$n \approx l - 2l(1-l)h, \quad (56)$$

$$\psi = \dot{n} \approx 2h. \quad (57)$$

With \dot{n} now approximately a constant, the equations may be solved as before to yield

$$H \approx \left[\frac{n(\tau) - n(0)}{\tau} \right]^2, \quad (58)$$

$$l \approx n[1 + 2h(1-n)], \quad (59)$$

and

$$\begin{aligned} W &\approx \int_{l(0)}^{l(\tau)} 2h dl \\ &\approx [n(\tau) - n(0)]^2 / \tau \end{aligned} \quad (60)$$

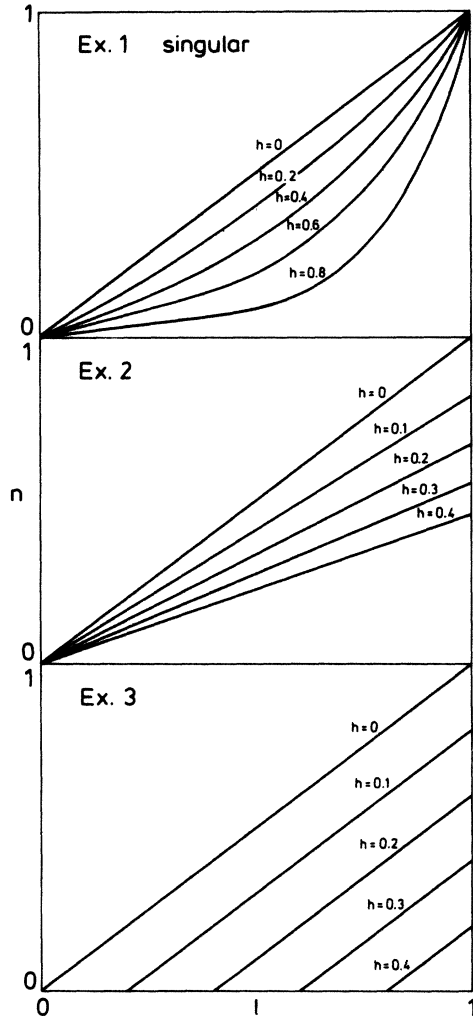


FIG. 4. Singular trajectories for example 1 (a), example 2 (b), and example 3 (c) for selected values of the Hamiltonian. The equilibrium line corresponds to $h = 0$.

In conclusion we see, for all three examples, that for large times the work is proportional to $(\Delta n)^2/\tau$, and from Eqs. (41) and (38) it is also clear that $h \ll 1$ and $l \approx n$ (i.e., we do not get very far from equilibrium). Consequently, we obtain the relationship that for large times work is proportional to $(\Delta l)^2/\tau$.

V. RELATIONSHIP TO SEPARATION PROCESSES

One of the applications of this result is the separation of a mixture of ideal gases by diffusion. This can be achieved by an arrangement of two concentric interlocking boxes of the same length, as shown in Fig. 7. The middle compartment contains a mixture of two ideal gases, A and B . The left end of the right-hand box is a semipermeable plug (a) which allows diffusion of gas A , but is impermeable to gas B , while conversely the right end of the left-hand box (b) is permeable to gas B but not to gas A . As in the previous examples the rate of diffusion through a plug of the gas to which it is permeable

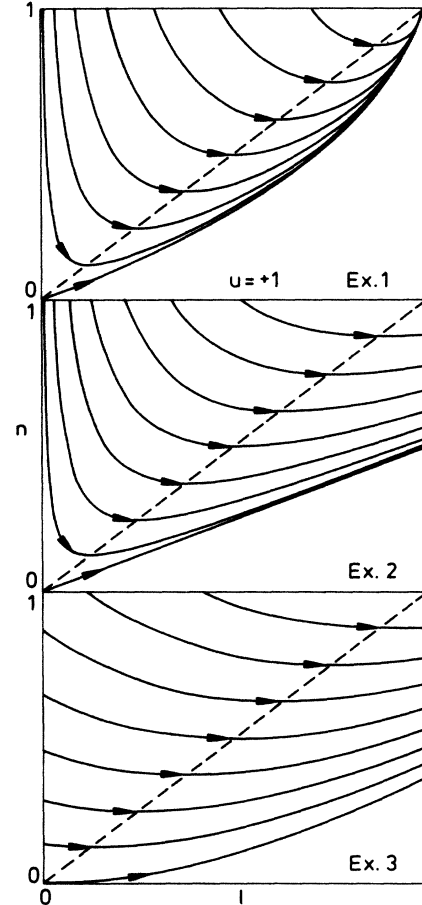


FIG. 5. $u = +1$ boundary trajectories for example 1 (a), example 2 (b), and example 3 (c) for different initial conditions. Time evolution is indicated by arrows, and the equilibrium line is dashed.

is proportional to the concentration difference of that gas across the plug. Then, with the same assumptions listed for examples 2 and 1 and the assumption that the external pressure on the box is zero, we get the following expressions for the flow rates and work (for notation see Fig. 7):

$$\dot{n}_A = \frac{k_A}{A} \left[\frac{N_A - n_A}{L - l} - \frac{n_A}{l} \right], \quad (61)$$

$$\dot{n}_B = \frac{k_B}{A} \left[\frac{N_B - n_B}{L - l} - \frac{n_B}{l} \right], \quad (62)$$

$$W = RT \int_0^\tau \left[\frac{(N_A + N_B) - (n_A + n_B)}{L - l} - \frac{n_A + n_B}{l} \right] i dt. \quad (63)$$

If now we construct the porous plugs such that $k_A = k_B$, we can again choose units such that $L = 1$, $N_A + N_B = 1$, $k_A/A = k_B/A = 1$, and $RT = 1$. This results in the following mathematical formulation: minimize

$$W = \int_0^\tau \left[\frac{1 - n}{1 - l} - \frac{n}{l} \right] i dt, \quad (64)$$

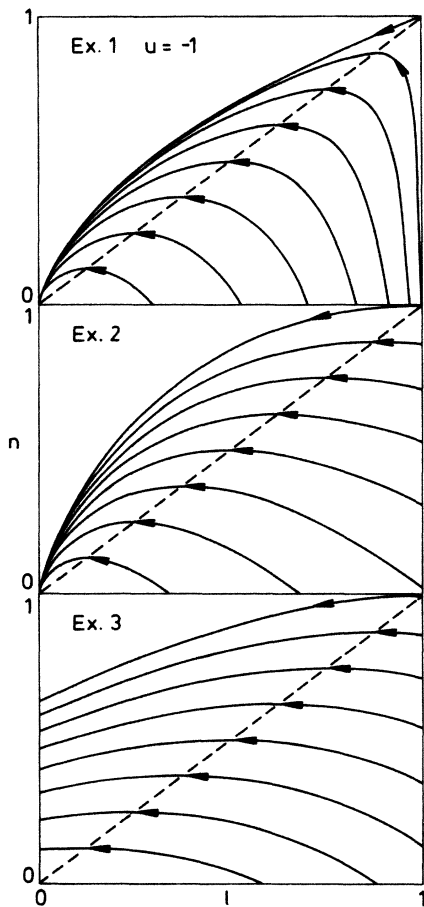


FIG. 6. $u = -1$ boundary trajectories for example 1 (a), example 2 (b), and example 3 (c) for different initial conditions. Time evolution is indicated by arrows, and the equilibrium line is dashed.

where

$$n = n_A + n_B$$

subject to

$$\dot{n} = \frac{1-n}{1-l} - \frac{n}{l}, \tag{65}$$

$$|\dot{l}| \leq u_{\max}, \tag{66}$$

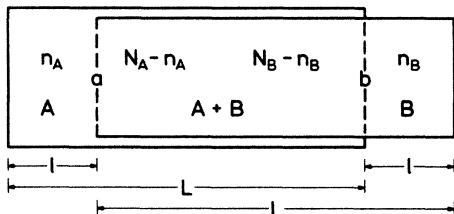


FIG. 7. Box arrangement similar to Fig. 1 in which a mixture of two ideal gases A and B is contained in the overlapping region of the two boxes. Porous plug a is permeable only to gas A and plug b only to gas B . The relative position of the two boxes is used to control the system.

$$0 < n < 1, \tag{67}$$

$$0 < l < 1, \tag{68}$$

$$n(0) = l(0), \tag{69}$$

$$n(\tau) = l(\tau). \tag{70}$$

Since this is the same mathematical problem as example 1 [Eqs. (19)–(25)] it tells us that, with the Fick's law diffusion constants equal for the two porous plugs, the irreversibility associated with the passage of gas through the plugs is only dependent on the total amount of gas passing through the plugs and not on the relative proportions of gas A and gas B . It also tells us that the overall dissipation will be approximately proportional to $(\Delta l)^2/\tau$. This supports the predictions of the theory of thermodynamic length.^{6,7}

ACKNOWLEDGMENTS

We acknowledge support from the Petroleum Research Fund administered by the American Chemical Society. B.A. acknowledges a grant from the Danish Natural Science Research Council. We are very grateful to Mary Ondrechen and Jim Nulton for helpful discussions.

APPENDIX

Proof of Lemma 1. If $\lambda_0 \equiv 0$, then by Eq. (29)

$$H = \lambda_1 \psi + \lambda_2 u, \tag{A1}$$

$$\dot{\lambda}_1 = -\partial H / \partial n = -\lambda_1 (\partial \psi / \partial n), \tag{A2}$$

$$\dot{\lambda}_2 = -\partial H / \partial l = -\lambda_1 (\partial \psi / \partial l). \tag{A3}$$

From the expressions for ψ , Eqs. (28), (3), (11), and (20), we see that

$$-\frac{\partial \psi}{\partial n} = \begin{cases} 1 & \text{(Ex3)} \\ 1/l & \text{(Ex2)} \\ 1/(1-l) & \text{(Ex1)}, \end{cases} \tag{A4a, A4b, A4c}$$

and

$$-\frac{\partial \psi}{\partial l} = \begin{cases} -1 & \text{(Ex3)} \\ -n/l^2 & \text{(Ex2)} \\ -[(1-n)/(1-l)^2 + n/l^2] & \text{(Ex1)}, \end{cases} \tag{A5a, A5b, A5c}$$

which are, respectively, positive,

$$-\partial \psi / \partial n > 0, \tag{A6}$$

and negative,

$$-\partial \psi / \partial l < 0, \tag{A7}$$

due to the constraints on n and l . This in turn makes $\dot{\lambda}_1$ of the same sign as λ_1 so that λ_1 never changes sign. It is also apparent that $\dot{\lambda}_2$ must have the opposite sign of λ_1 . Since the switching function in Eq. (A1) is $\sigma = \lambda_2$, $\lambda_1 = 0$ implies $\dot{\lambda}_1 = 0$ and $\lambda_2 = 0$, so that the switching function is a constant, which means we can never switch trajectories. This is impossible since we cannot reach the objective on a single boundary trajectory, and $\lambda_0 = \lambda_1 = \lambda_2 = 0$ is prohibited. If $\lambda_1 \neq 0$, then $\lambda_2 \neq 0$ and, since λ_2 is monotonic, it can

be equal to 0 on at most one point. Thus the switching function determines that the control u must always be on the boundary trajectories $u = u_{\max}$ or $u = -u_{\max}$ and can switch boundary trajectories at most once. Therefore, the only possible solution is the bang-bang solution. ■

Proof of Lemma 2. Along the singular trajectory $\sigma \equiv 0$, $\psi = \lambda_2 \neq 0$, and $H = \lambda_1 \lambda_2$ so that by Eqs. (36) and (37),

$$\lambda_1 = H / \lambda_2, \quad (\text{A8})$$

$$\begin{aligned} \dot{\lambda}_1 &= -\frac{H}{\lambda_2^2} \dot{\lambda}_2 \\ &= -\frac{\partial \psi}{\partial n} (\lambda_1 - u) = -\frac{H}{\lambda_2^2} \left[-\frac{\partial \psi}{\partial l} (\lambda_1 - u) \right], \end{aligned} \quad (\text{A9})$$

implying

$$-\frac{\partial \psi}{\partial n} = \frac{H}{\lambda_2^2} \frac{\partial \psi}{\partial l}. \quad (\text{A10})$$

The signs of the derivatives, Eqs. (A6) and (A7), finally make it clear that $H > 0$. ■

Proof of Lemma 3. Since the initial state is an equilibrium point, it cannot be on a singular trajectory. If $l(\tau) > l(0)$ and we initially follow a $\dot{l} = -u_{\max}$ boundary trajectory, we will be left of equilibrium ($l < n$), but from there one can never reach the final state since $n(\tau) > n(0)$, whereas $\dot{n} < 0$ by Eqs. (3), (11), and (20). Consequently, one must cross over to the right of equilibrium ($l > n$) on a $u = u_{\max}$ trajectory in order to get to the final state. At the point where this switch is made $\sigma = 0$ (a necessary condition to switch branches) and $\psi < 0$ (since we are left of equilibrium). This implies that $\lambda_1 \psi = H > 0$ or $\lambda_1 < 0$ at this point. The constraints Eqs. (A6) and (A7) further make $\dot{\lambda}_1 < 0$ so that λ_1 must remain negative and $\dot{\lambda}_2$ must be positive throughout this $u = u_{\max}$ trajectory. When it reaches equilibrium $H = \lambda_2 u_{\max} > 0$, so that $\lambda_2 > 0$, but since $\dot{\lambda}_2 > 0$ throughout this trajectory, λ_2 must remain positive for the remainder of the trajectory, and the system will never reach another singular point which would require $H = \lambda_1 \lambda_2 > 0$. Thus it must remain on the $u = u_{\max}$ trajectory which cannot lead to the final equilibrium state. Consequently, one cannot start along a $u = -u_{\max}$ branch from the initial point, and the only other possible branch trajectory is $u = u_{\max}$ which is the boundary trajectory toward the final state. ■

Proof of Lemma 4. Since we are right of equilibrium initially, the expressions for \dot{n} , Eqs. (3), (11), and (20), are clearly positive. The approach to equilibrium must be on a $u = -u_{\max}$ branch trajectory, and when the switch to this branch was made, $\sigma = 0$, $\psi > 0$, and $H = \lambda_1 \psi > 0$. Therefore, λ_1 was positive and, by Eq. (36), must remain positive throughout the rest of the branch. When it reaches equilibrium $H = -\lambda_2 u_{\max} > 0$ so that $\lambda_2 < 0$, but Eq. (37) implies that $\dot{\lambda}_2 < 0$ if this is not the final equilibrium state, so for the remainder of the branch $\lambda_2 < 0$. Again, this implies that the trajectory will never reach another singular point since that would require $H = \lambda_1 \lambda_2 > 0$, with $\lambda_1 > 0$ and $\lambda_2 < 0$. Therefore, one can never switch off of this branch which leads away from equilibrium, so if the equilibrium point which is reached along this $u = -u_{\max}$ branch is not the final equilibrium

point, then the system will never reach the final equilibrium point. ■

Proof of Lemma 5. For this proof we consider the three examples one at a time. In all cases at the switch to $u = -1$, $\lambda_2 > 0$, $\lambda_1 = H / \lambda_2 > 0$, and $\dot{\lambda}_1 > 0$. Thus, as in lemma 4, $\lambda_1 > 0$ along this branch. From the expression for σ , Eq. (35), we have

$$\dot{\sigma} = \dot{\lambda}_2 - \dot{\psi} = -\frac{\partial \psi}{\partial l} \lambda_1 - \frac{\partial \psi}{\partial n} \psi. \quad (\text{A11})$$

For example 3, using Eq. (3) for ψ , this yields

$$\dot{\sigma} = -\lambda_1 + \psi. \quad (\text{A12})$$

Now consider

$$\dot{\sigma} / \lambda_1 \psi = 1 / \lambda_1 - 1 / \psi. \quad (\text{A13})$$

This quantity must have the same sign as $\dot{\sigma}$ since ψ and λ_1 are both positive right of equilibrium. At the switch to $u = -1$, $\dot{\sigma} \leq 0$ as previously discussed for a switch to $u = -u_{\max}$. Consequently, $\dot{\sigma} / \lambda_1 \psi \leq 0$ at this switch. If we look at

$$\frac{d}{dt} \left[\frac{\dot{\sigma}}{\lambda_1 \psi} \right] = -\frac{1}{\lambda_1^2} \dot{\lambda}_1 + \frac{1}{\psi^2} \dot{\psi} \quad (\text{A14})$$

and recall $\dot{\lambda}_1 > 0$ and $\dot{\psi} = -\psi - 1 < 0$, we observe that $(d/dt)(\dot{\sigma} / \lambda_1 \psi) < 0$. Thus $\dot{\sigma}$ is never positive, and σ is monotonically decreasing from a value of 0 at the switch onto this trajectory. This means that the system can never again reach a point where the switching function σ allows it to leave the $u = -1$ branch.

Similarly for example 2 substituting Eq. (11) into Eq. (A11) yields

$$\dot{\sigma} = (\lambda_1 \psi - \lambda_1 + \psi) / l. \quad (\text{A15})$$

This time considering

$$\dot{\sigma} / \lambda_1 \psi = 1 / \lambda_1 - 1 / \psi + 1 \quad (\text{A16})$$

eliminates mixed terms to ease evaluation. This quantity is again of the same sign as $\dot{\sigma}$ and is initially nonpositive. The derivative

$$\frac{d}{dt} \left[\frac{\dot{\sigma} l}{\lambda_1 \psi} \right] = -\frac{1}{\lambda_1^2} \dot{\lambda}_1 + \frac{1}{\psi^2} \dot{\psi}, \quad (\text{A17})$$

with $\dot{\psi} = -\psi / l - n / l^2 < 0$ is clearly negative by the fact that ψ , n , and l are all positive. This again implies that the system will never again reach a switching point.

For example 1 the same equations give us

$$\dot{\sigma} = [\psi - \lambda_1 + (1 - 2l)\psi\lambda_1] / l(1 - l). \quad (\text{A18})$$

To eliminate the cross terms we consider

$$\dot{\sigma} l(1 - l) / \lambda_1 \psi = 1 / \lambda_1 - 1 / \psi + (1 - 2l), \quad (\text{A19})$$

which again has the same sign as $\dot{\sigma}$ and is initially nonpositive since $\psi > 0$ and $\lambda_1 > 0$. From

$$\frac{d}{dt} \left[\frac{\dot{\sigma}l(1-l)}{\lambda_1\psi} \right] = -\frac{1}{\lambda_1^2} \dot{\lambda}_1 + \frac{1}{\psi^2} \dot{\psi} + 2 \quad (\text{A20})$$

some algebraic manipulation leads to

$$\dot{\psi}/\psi^2 + 2 = -1/\psi^2 l(1-l) - 2n/(l-n), \quad (\text{A21})$$

which again proves that $(d/dt)[\dot{\sigma}l(1-l)/\lambda_1\psi] < 0$, so that here too the system never again reaches a switching point. ■

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¹See, e.g., B. Andresen, P. Salamon, and R. S. Berry, *Phys. Today* **37** (9), 62 (1984); B. Andresen, R. S. Berry, M. J. Ondrechen, and P. Salamon, *Acc. Chem. Res.* **17**, 266 (1984).

²M. H. Rubin, *Phys. Rev. A* **19**, 1272 (1979).

³M. H. Rubin, *Phys. Rev. A* **19**, 1277 (1979).

⁴See, e.g., G. Hadley and M. Kemp, *Variational Methods in Economics* (North-Holland, New York, 1971).

⁵See, e.g., H. Tolle, *Optimization Methods* (Springer-Verlag, New York, 1975); V. G. Boltyanskii, *Mathematical Methods of Optimal Control* (Holt, Reinhart, and Winston, New York, 1971).

⁶P. Salamon and R. S. Berry, *Phys. Rev. Lett.* **51**, 1127 (1983).

⁷J. Nulton, B. Andresen, and P. Salamon (unpublished).