the resonance occurs for $\omega = \pm\omega_0$, while in the case of the electron in crossed $\mathbf{E}_0$ and $\mathbf{B}_0$ the resonance occurs only for $\omega = +\omega_c$. The reason is that in the charged oscillator the electromagnetic field always resonates with the charge at $|\omega| = |\omega_0|$, while in the second case the circularly polarized wave resonates with the electron only if the wave field rotates in the same sense of the electron.

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Le Châtelier reciprocal relations and the mechanical analog

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(Received 10 March 1982; accepted for publication 17 August 1982)

Le Châtelier's principle is discussed carefully in terms of two sets of simple thermodynamic examples. The principle is then formulated quantitatively for general thermodynamic systems. The formulation is in terms of a perturbation-response matrix, the Le Châtelier matrix $[L]$. Le Châtelier's principle is contained in the diagonal elements of this matrix, all of which exceed one. These matrix elements describe the response of a system to a perturbation of either its extensive or intensive variables. These response ratios are inverses of each other. The Le Châtelier matrix is symmetric, so that a new set of thermodynamic reciprocal relations is derived. This quantitative formulation is illustrated by a single simple example which includes the original examples and shows the reciprocities among them. The assumptions underlying this new quantitative formulation of Le Châtelier's principle are general and applicable to a wide variety of nonthermodynamic systems. Le Châtelier's principle is formulated quantitatively for mechanical systems in static equilibrium, and mechanical examples of this formulation are given.

I. INTRODUCTION

It is amazing how well Le Châtelier's principle is known, yet how poorly it is treated in the literature of thermodynamics. Most thermodynamics treatises do not discuss it at all. Of those that do, about half claim it states that when a system is perturbed, it responds in the direction of the perturbation, the other half claiming the system will respond in the opposite direction. Rare is the treatise that makes a precise statement; rarer still one that makes a quantitative statement. No source at all considers responses among other than conjugate variables. The treatment of Le Châtelier's principle in the literature of thermodynamics is so deficient that it has been criticized in the literature of economics. Samuelson writes[1] that the statement of this principle usually "is given vague and even mystical formulation, couched in teleological language reminiscent of Adam Smith's beneficent 'invisible hand' that leads self-centered competition unwittingly to the social good. The following formulation is typical: 'If the external conditions of a thermodynamic system are altered, the equilibrium of the system will tend to move in such a direction as to oppose the change in external conditions.' " Samuelson quotes Fermi.[2]

There are two major sources of confusion surrounding Le Châtelier's principle:

(1) Does it describe the (a) direct response of a thermodynamic variable to a perturbation of its conjugate variable,[3] or the (b) indirect response to a perturbation, obtained by allowing secondary forces to operate?[4,5]

In the latter case

(2) Is the indirect response to the perturbation (a) larger than,[4] or (b) smaller than[5] the direct response?

For the first question, direct responses involve statements about partial derivatives of a thermodynamic variable with respect to its conjugate variable, such as $(\partial S/\partial T)_{\text{any}}$ or $(\partial T/\partial S)_{\text{any}}$. All such thermodynamic response functions are positive. This is a stability requirement of the second law of thermodynamics. This suggests that Le Châtelier's principle must be about indirect responses to perturbations. In fact, Le Châtelier's principle was intended to be the thermodynamic analog of Lenz's law[6]:

> When a force acting on a primary electric current induces a secondary current, the direction of the latter is such that its electrodynamical action opposes the acting force.

For the second question, two separate situations can occur.

(1) If an extensive variable is perturbed, the direct response of the conjugate intensive variable is larger than its indirect response.[4]

(2) If an intensive variable is perturbed, the direct response of the conjugate extensive variable is smaller than its indirect response.[5]

This dichotomy was first noticed by Ehrenfest,[7] who proposed that this principle should be stated separately for these two cases.

Le Châtelier's principle, as applied to perturbations of extensive variables, is illustrated by two simple thermodynamic examples in Sec. II. In Sec. III, this principle is illustrated for perturbations of intensive variables using two similar examples. In Sec. IV we present a precise formulation of Le Châtelier's principle, considering responses of nonconjugate as well as conjugate variables to perturbations of either an extensive or an intensive variable. This formulation, which is quantitative, is presented in terms of a perturbation-response matrix $[L_{\alpha\beta}]$. This matrix is symmetric and positive definite. The diagonal matrix elements describe Le Châtelier's principle and the off-diagonal matrix elements describe a new set of reciprocal relations. In Sec. V this generalized principle is used to illustrate the relationships among the two pairs of examples discussed in Secs. II and III.

The arguments leading to this perturbation-response formulation of Le Châtelier's principle are rather general, and therefore widely applicable. In particular, they are applicable to mechanical systems in stable static or dynamic equilibrium. This principle is formulated also for static mechanical systems in Sec. VI. Its application is illustrated by two simple examples: one (Sec. VII) for perturbation of a generalized displacement (extensive variable), the other (Sec. VIII) for perturbation of a generalized force (intensive variable).

II. PERTURBATION OF EXTENSIVE VARIABLES: TWO EXAMPLES

Example 1

We consider a gas contained within a cylinder sealed off by a heavy piston [Fig. 1(a)]. The cylinder is well insulated. Initially, the temperature and pressure of the gas within the cylinder are equal to the temperature and pressure of the surrounding reservoir. At time $t = 0$, the entropy of the gas within the cylinder is suddenly increased by a small amount (ΔS). A short time later ($t = 0^+$) the gas within the cylinder has reached a state of thermodynamic equilibrium with itself but not with its surroundings [Fig. 1(b)]. The pressure difference will eventually drive the piston outward until a new state of constrained equilibrium is reached as $t \to \infty$ [Fig. 1(c)]. In this new equilibrium state, the pressure difference vanishes, but the temperature difference does not, since the cylinder, including the piston, is insulated. However, the temperature difference between the insulated walls of the cylinder has decreased.

The responses of the four thermodynamic variables as a function of time are as follows:

ΔS: S suddenly is increased by ΔS at $t = 0$ and is constrained at $S + \Delta S$ for all $t > 0$ because the cylinder is insulated.

ΔV: $\Delta V(t = 0^+) \simeq 0$ because it takes a finite time for the force on the piston ($F \sim \Delta P$) to move the piston a finite distance. Eventually $\Delta V(t \to \infty) > 0$.

ΔP: $\Delta P(t = 0^+) > 0$ because the gas temperature suddenly rises at $t = 0$. Eventually $\Delta P(t) \to 0$ as $t \to \infty$.

ΔT: $\Delta T(0^+) > 0$ because $\Delta S > 0$. As $t \to \infty$, the temperature change $\Delta T(t)$ will decrease because the pressure decreases as the volume increases. Eventually $\Delta T(t)$ will approach a final constrained equilibrium value $\Delta T(\infty) > 0$. The long-term temperature change is positive because entropy has been added to the gas within the cylinder.

The four responses $\Delta S(t), \Delta V(t), -\Delta P(t), \Delta T(t)$ to the perturbation have been shown schematically in Fig. 1(d). The response $-\Delta P(t)$ has been shown instead of $+\Delta P(t)$ since $-P$ is the conjugate variable to V.

Le Châtelier's principle for this experiment is

$$\Delta T(0^+) > \Delta T(\infty) > 0 \quad (\Delta S > 0). \tag{1a}$$

Expressed in terms of thermodynamic partial derivatives (ΔS of either sign) it is

$$\left(\frac{\partial T}{\partial S}\right)_V > \left(\frac{\partial T}{\partial S}\right)_P > 0. \tag{1b}$$

Example 2

We consider now a gas contained within an uninsulated cylinder. The gas is initially in thermodynamic equilibrium with its surroundings [Fig. 2(a)]. At time $t = 0$, the volume of the cylinder is suddenly increased by a small amount (ΔV), and the piston is locked into its new position. A short time later ($t = 0^+$) the gas within the cylinder has reached a

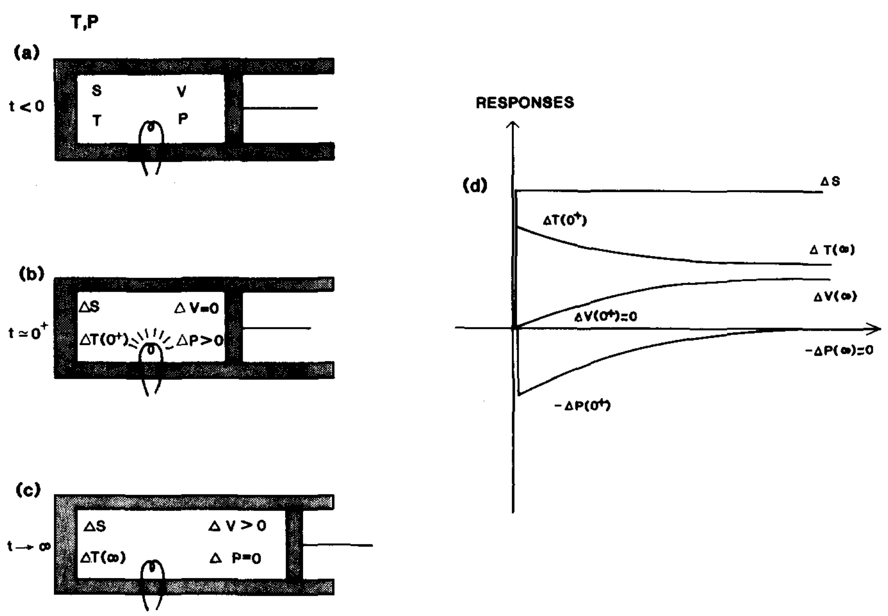

Fig. 1. (a) For $t < 0$ the gas within the insulated cylinder has the same temperature and pressure as the surrounding reservoir. (b) At $t = 0$, the entropy of the gas within the insulted cylinder is increased by ΔS, and a short time afterward, at $t = 0^+$, the gas within the cylinder has reached a state of internal thermodynamic equilibrium. (c) After a long time ($t \to \infty$), the gas within the cylinder has reached a state of constrained equilibrium with the reservoir, in which $\Delta T \neq 0$, $\Delta P = 0$. (d) The differences between the four thermodynamic variables and their initial ($t < 0$) values are shown as a function of time.

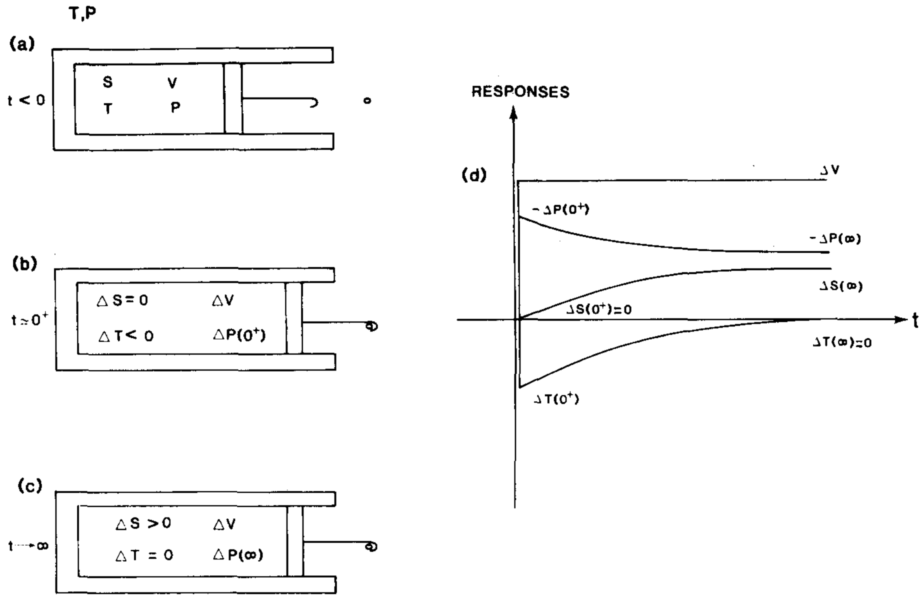

Fig. 2. (a) For $t<0$ the gas within the uninsulated cylinder has the same temperature and pressure as the surrounding reservoir. (b) At $t=0$ the volume of the cylinder is suddenly increased by ΔV, and a short time afterward, at $t=0^+$, the gas within the cylinder has reached a state of internal thermodynamic equilibrium. (c) After a long time ($t\rightarrow\infty$), the gas within the cylinder has reached a state of constrained equilibrium with the reservoir, in which $\Delta T=0, \Delta P\neq 0$. (d) The differences between the four thermodynamic variables and their initial ($t<0$) values are shown as a function of time.

state of thermodynamic equilibrium with itself, but not with its surroundings [Fig 2(b)]. The temperature difference will eventually drive a flow of heat into the cylinder until a new state of constrained equilibrium is reached as $t\rightarrow\infty$ [Fig. 2(c)]. In this new equilibrium state, the temperature difference vanishes, but the pressure difference does not, since the piston is locked into its new position. However, the external force required to hold the piston in its new position has decreased.

The responses of the four thermodynamic variables as a function of time are as follows:

ΔV: V suddenly is increased by ΔV at $t=0$ and is constrained at $V+\Delta V$ for all $t>0$.

ΔS: ΔS ($t=0^+$)$\simeq 0$ since the rapid expansion is adiabatic. The increase in entropy is driven by the temperature difference between the gas in the cylinder and the reservoir. Eventually $\Delta S\,(t\rightarrow\infty)>0$.

ΔT: ΔT $(t=0^+)<0$ because the volume suddenly increases (at constant entropy) at $t=0$. Eventually $\Delta T(t)\rightarrow 0$ as $t\rightarrow\infty$.

ΔP: $\Delta P(0^+)<0$ because $\Delta V>0$. As $t\rightarrow\infty$, the magnitude of the pressure change will decrease because of the rise in temperature. Eventually $\Delta P(t)$ will approach a final constrained equilibrium value $\Delta P(\infty)<0$. The long-term pressure change is negative because the volume of the cylinder has increased.

The four responses $\Delta V(t), \Delta S(t), \Delta T(t), -\Delta P(t)$ to the perturbation have been shown schematically in Fig. 2(d). The response $-\Delta P(t)$ has been shown instead of $+\Delta P(t)$ since $-P$ is the conjugate variable to V.

Le Châtelier's principle for this experiment is

$$-\Delta P(0^+) > -\Delta P(\infty) > 0 \quad (\Delta V>0). \tag{2a}$$

Expressed in terms of thermodynamic partial derivatives (ΔV of either sign) it is

$$-\left(\frac{\partial P}{\partial V}\right)_S > -\left(\frac{\partial P}{\partial V}\right)_T > 0. \tag{2b}$$

Comparison

In both these samples we see:

(1) A sudden small change in an extensive thermodynamic variable will produce a change in all remaining thermodynamic variables.

(2) The intensive variable conjugate to the perturbed extensive variable will initially experience a large response in the direction of the perturbation. This response will diminish in magnitude as the system relaxes to a new constrained equilibrium with its surroundings.

(3) The initial response of the "other" extensive variable, and the final response of the "other" intensive variable, are zero.

(4) As the system relaxes toward a constrained equilibrium, if the variable conjugate to the perturbation decreases, the "other" variables both increase, and vice versa.

(5) The initial change of the "other" intensive variable and the final response of the "other" extensive variable are opposite in sign.

III. PERTURBATION OF INTENSIVE VARIABLES: TWO EXAMPLES

Example 1′

We consider a gas contained within a cylinder sealed off by a heavy piston [Fig. 3(a)]. The cylinder is not insulated. Initially, the temperature and pressure of the gas within the cylinder are equal to the temperature and pressure of the surrounding reservoir. At time $t=0$ the cylinder is placed in thermal contact with a new reservoir at the same pressure, but at a slightly higher temperature (by ΔT). A short time later ($t=0^+$) the gas within the cylinder has reached a state of thermodynamic equilibrium with itself but not with its surroundings [Figs. 3(b)]. The pressure difference generated by the increased temperature will eventually drive the piston outward until a new state of constrained equilibrium is reached as $t\rightarrow\infty$ [Fig. 3(c)]. As the volume of the cylinder expands isothermally, the entropy increases further.

The responses of the four thermodynamic variables as a function of time are as follows:

ΔT: T is suddenly increased by ΔT at $t=0$ and is constrained at $T+\Delta T$ for all $t>0$ because the cylinder is in thermal contact with the new reservoir.

ΔV: $\Delta V(t=0^+)\simeq 0$ because it takes a finite time for the force on the piston to move the piston a finite distance.

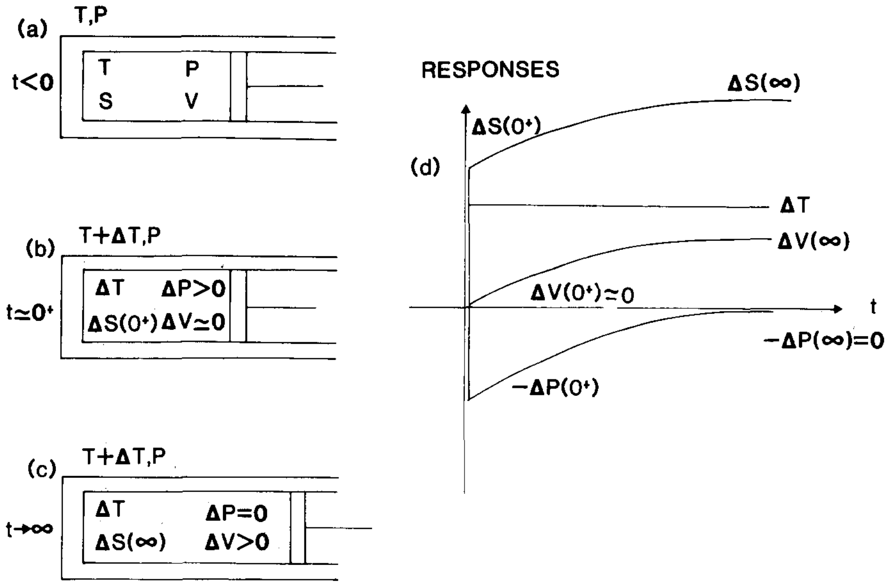

Fig. 3. For $t<0$ the gas within the cylinder is in equilibrium with its surroundings at temperature T and pressure P. (b) At $t=0$ the cylinder is placed in thermal contact with a new reservoir at temperature $T+\Delta T$ and pressure P. A short time afterward, at $t=0^+$, the gas within the cylinder has reached a state of internal thermodynamic equilibrium. (c) After a long time $(t\to\infty)$ the pressure difference has increased the volume and entropy of the cylinder, which is now in equilibrium with its surroundings with $\Delta T\neq 0$, $\Delta P=0$. (d) The differences between the four thermodynamic variables and their initial $(t<0)$ values are shown as a function of time.

Eventually $\Delta V(t\to\infty)>0$.

ΔP: $\Delta P\ (t=0^+)>0$ because the gas temperature suddenly rises at $t=0$ while the volume of the cylinder remains essentially unchanged. Eventually $\Delta P\to 0$ as $t\to\infty$.

ΔS: $\Delta S(0^+)>0$ because $\Delta T>0$. As $t\to\infty$, the entropy will further increase as the gas in the cylinder undergoes isothermal expansion.

The four responses $\Delta T(t), \Delta V(t), -\Delta P(t), \Delta S(t)$ to the perturbation have been shown schematically in Fig. 3(d).

Le Châtelier's principle for this experiment is

$$\Delta S(\infty)>\Delta S(0^+)>0 \quad (\Delta T>0). \tag{1a'}$$

Expressed in terms of thermodynamic partial derivatives (ΔT of either sign) it is

$$\left(\frac{\partial S}{\partial T}\right)_P > \left(\frac{\partial S}{\partial T}\right)_V > 0. \tag{1b'}$$

Example 2′

We consider the same cylinder as in the previous example [Fig. 4(a)]. Now, however, the cylinder is removed from contact with a reservoir at temperature T and pressure P with which it is in thermodynamic equilibrium, and placed in contact with a new reservoir at temperature T and pressure P-ΔP. A short time later $(t=0^+)$ the volume has increased and the temperature decreased while only a small amount of heat has entered the cylinder [Fig. 4(b)]. The temperature difference will eventually drive a flow of heat into the cylinder until a state of thermodynamic equilibrium is reached at $t\to\infty$ [Fig. 4(c)]. As the gas within the cylinder heats up, the volume increases further.

The responses of the four thermodynamic variables as a function of time are as follows:

ΔP: P is suddenly decreased by ΔP at $T=0$ and is constrained at P-ΔP for all $t>0$ because the cylinder is in mechanical contact with the new reservoir.

ΔS: $\Delta S(t=0^+)\simeq 0$ since the rapid expansion is adiabatic. The temperature difference between the gas in the cylinder and the reservoir drives an increase in entropy. Eventually $\Delta S(t\to\infty)>0$.

ΔT: $\Delta T(t=0^+)<0$ because the cylinder expands adiabatically at $t=0$. Eventually, $\Delta T\to 0$ as $t\to\infty$.

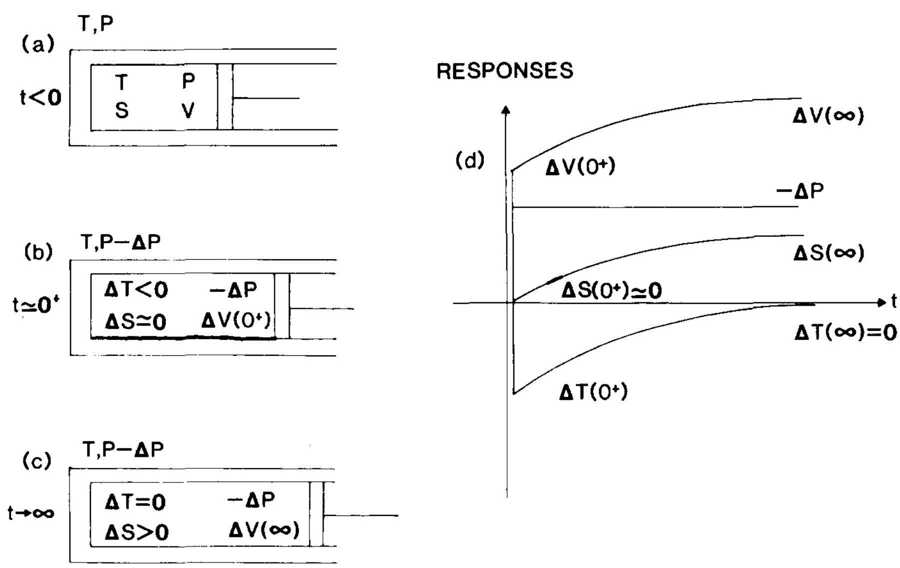

Fig. 4. (a) For $t<0$ the gas within the cylinder is in equilibrium with its surroundings at temperature T and pressure P. (b) At $t=0$ the cylinder is placed in mechanical contact with a new reservoir at temperature T and pressure P-ΔP. A short time afterward, at $t=0^+$, the gas within the cylinder has reached a state of internal thermodynamic equilibrium. (c) After a long time $(t\to\infty)$ the temperature difference has increased the entropy and volume of the cylinder, which is now in equilibrium with its surroundings with $\Delta T=0$, $-\Delta P\neq 0$. (d) The differences between the four thermodynamic variables and their initial $(t<0)$ values are shown as a function of time.

ΔV: $\Delta V(t=0^+)>0$ because $\Delta P<0$. As $t\to\infty$, the volume will further increase as the gas within the cylinder warms up at constant pressure.

The four responses $-\Delta P(t)$, $\Delta S(t)$, $\Delta T(t)$, $\Delta V(t)$ to the perturbation have been shown schematically in Fig. 4(d).

Le Châtelier's principle for the experiment is

$$\Delta V(\infty)>\Delta V(0^+)>0 \quad (-\Delta P>0). \tag{2a'}$$

Expressed in terms of thermodynamic partial derivatives (ΔP of either sign), it is

$$-\left(\frac{\partial V}{\partial P}\right)_T > -\left(\frac{\partial V}{\partial P}\right)_S >0. \tag{2b'}$$

Comparison

These two experiments, involving perturbation of intensive thermodynamic variables, can be compared in exactly the same way as were the two experiments (involving extensive variables) discussed in Sec. II. The five comparisons discussed for extensive variables (end of Sec. II) are valid for intensive variables, provided the following word changes are made:

extensive $\to$ intensive
diminish $\to$ increase

Another fruitful comparison can be made. This involves comparison of the experiment involving perturbation of S with that involving T (experiments 1 of Sec. II and 1′ of Sec. III). If the vertical scale of the graph in Fig. 1(d) is stretched by a scale factor depending on time in such a way that $\Delta T(t)$ is horizontal, then $\Delta S(t)$ will increase in time. In fact, this scaling transforms Fig. 1(d) into Fig. 3(d). Figure 2(d) can be transformed into Fig. 4(d) by a similar scale transformation. In this way, we easily see that a long-term decrease in an intensive thermodynamic variable for fixed value of its conjugate extensive variable [Fig. 1(d), Fig. 2(d)] is intimately related to a long-term increase in an extensive thermodynamic variable for fixed value of its conjugate intensive variable [Fig. 3(d), Fig. 4(d)]. These are the two faces of Le Châtelier's principle seen by Ehrenfest.

IV. FORMULATION OF THE GENERAL THERMODYNAMIC PRINCIPLE

In this section we present a unified and generalized formulation of Le Châtelier's principle (subsection D). To do this, we first introduce a useful notation (A) and discuss perturbations of extensive (B) and intensive (C) thermodynamic variables. The properties of the Le Châtelier perturbation-response matrix, introduced in (D) are then listed (E) and the connection with Le Châtelier's principle established (F).

A. Notation[8]

We consider a system initially in thermodynamic equilibrium with its surroundings. The system state is described by the values of its extensive thermodynamic variables E^α (e.g., S, V, N_j, ...). The system's intensive thermodynamic variables i_α (e.g., T, $-P$, μ_j,...) are equal to the corresponding intensive variables of the surrounding reservoir. The intensive thermodynamic variable i_α is conjugate to the extensive variable E^α:

$$i_\alpha=\left(\frac{\partial U}{\partial E^\alpha}\right)_E. \tag{3}$$

Here $U=U(E^\alpha)$ is the internal energy of the system and the subscript E means that all other extensive variables have been held constant. A small change δE^β in the extensive variables will produce a small change in the intensive variables:

$$\delta i_\alpha=\sum_\beta U_{\alpha\beta}\,\delta E^\beta, \tag{4a}$$

$$U_{\alpha\beta}=\left(\frac{\partial^2 U}{\partial E^\alpha\,\partial E^\beta}\right)_E=\left(\frac{\partial i_\alpha}{\partial E^\beta}\right)_E=\left(\frac{\partial i_\beta}{\partial E^\alpha}\right)_E =\left(\frac{\partial E^\beta}{\partial i_\alpha}\right)_E^{-1}. \tag{4b}$$

The relationship (4a) can be inverted

$$\delta E^\alpha=\sum_\beta U^{\alpha\beta}\,\delta i_\beta, \tag{5a}$$

$$U^{\alpha\beta}=\left(\frac{\partial E^\alpha}{\partial i_\beta}\right)_i=\left(\frac{\partial E^\beta}{\partial i_\alpha}\right)_i=\left(\frac{\partial i_\beta}{\partial E^\alpha}\right)_i^{-1}. \tag{5b}$$

The matrices $[U_{\alpha\beta}],[U^{\alpha\beta}]$ may conveniently be considered as susceptibility tensors. They are real, symmetric, inverses of each other, positive definite, and have positive diagonal matrix elements:

$$U_{\alpha\beta}=U_{\beta\alpha},\quad U^{\alpha\beta}=U^{\beta\alpha}; \tag{6a}$$

$$\sum_\beta U_{\alpha\beta}U^{\beta\gamma}=\delta_\alpha^\gamma; \tag{6b}$$

$$U_{\alpha\alpha}>0,\quad U^{\alpha\alpha}>0. \tag{6c}$$

In order to set the stage for a unified formulation of Le Châtelier's principle, we must first consider responses of a system to perturbations of extensive and intensive variables. This is done in the following two subsections.

B. Perturbation of an extensive variable

We make the following assumptions[9]:

(1) At time $t=0$, one of the system's extensive variables (primary extensive variable) is perturbed ($\Delta E^\alpha\neq 0$) and held fixed for $t>0$.

(2) A short time afterward ($t=0^+$) the system has reached a state of internal thermodynamic equilibrium, so that the susceptibility relations (4a) and (5a) are valid. In this time interval the remaining (secondary) extensive variables E^β ($\beta\neq\alpha$) have not had a chance yet to change.

(3) The only constraint imposed on the system is that which keeps ΔE^α fixed for $t>0$. This constraint also prevents i_α from returning to its initial equilibrium value.

(4) The generalized (secondary) forces Δi_β will drive the system to a new constrained equilibrium state in which $\Delta i_\beta=0$ ($\beta\neq\alpha$) and $\Delta E^\beta\neq 0$.

The near-term ($t=0^+$) responses of the thermodynamic variables are

$$\Delta E^\alpha(0^+)=\Delta E^\alpha, \tag{7a}$$

$$\Delta E^\beta(0^+)=0,\ \beta\neq\alpha, \tag{7b}$$

$$\Delta i_\alpha(0^+)=\left(\frac{\partial i_\alpha}{\partial E^\alpha}\right)_E\Delta E^\alpha=U_{\alpha\alpha}\Delta E^\alpha, \tag{7c}$$

$$\Delta i_\beta(0^+)=\left(\frac{\partial i_\beta}{\partial E^\alpha}\right)_E\Delta E^\alpha=U_{\beta\alpha}\Delta E^\alpha. \tag{7d}$$

The long-term ($t\to\infty$) responses of the thermodynamic variables are

$$\Delta E^{\alpha}(\infty) = \Delta E^{\alpha}, \quad (8a)$$

$$\Delta E^{\beta}(\infty) = \left(\frac{\partial E^{\beta}}{\partial E^{\alpha}}\right)_i \Delta E^{\alpha} = (U^{\beta\alpha}/U^{\alpha\alpha})\Delta E^{\alpha}, \quad (8b)$$

$$\Delta i_{\alpha}(\infty) = \left(\frac{\partial i_{\alpha}}{\partial E^{\alpha}}\right)_i \Delta E^{\alpha} = (1/U^{\alpha\alpha})\Delta E^{\alpha}, \quad (8c)$$

$$\Delta i_{\beta}(\infty) = 0, \quad \beta \neq \alpha. \quad (8d)$$

C. Perturbation of an intensive variable

We make the following assumptions:

(1) At time $t = 0$ one of the system's intensive variables (primary intensive variable) is perturbed ($\Delta i_{\alpha} \neq 0$) and held fixed for $t > 0$.

(2) A short time afterward ($t = 0^+$) the system has reached a state of internal thermodynamic equilibrium. In this time interval, the secondary extensive variables $E^{\beta} (\beta \neq \alpha)$ have not yet had a chance to change.

(3) The secondary forces Δi_{β} will drive the system to a new equilibrium state in which $\Delta i_{\beta} = 0 \, (\beta \neq \alpha)$ and $\Delta E^{\beta} \neq 0$.

The near-term responses of the thermodynamic variables are

$$\Delta i_{\alpha}(0^+) = \Delta i_{\alpha}, \quad (9a)$$

$$\Delta i_{\beta}(0^+) = \left(\frac{\partial i_{\beta}}{\partial i_{\alpha}}\right)_E \Delta i_{\alpha} = (U_{\beta\alpha}/U_{\alpha\alpha})\Delta i_{\alpha}, \quad (9b)$$

$$\Delta E^{\alpha}(0^+) = \left(\frac{\partial E^{\alpha}}{\partial i_{\alpha}}\right)_E \Delta i_{\alpha} = (1/U_{\alpha\alpha})\Delta i_{\alpha}, \quad (9c)$$

$$\Delta E^{\beta}(0^+) = 0, \ \beta \neq \alpha. \quad (9d)$$

The long-term responses of the thermodynamic variables are

$$\Delta i_{\alpha}(\infty) = \Delta i_{\alpha}, \quad (10a)$$

$$\Delta i_{\beta}(\infty) = 0, \quad \beta \neq \alpha, \quad (10b)$$

$$\Delta E^{\alpha}(\infty) = \left(\frac{\partial E^{\alpha}}{\partial i_{\alpha}}\right)_i \Delta i_{\alpha} = U^{\alpha\alpha}\Delta i_{\alpha}, \quad (10c)$$

$$\Delta E^{\beta}(\infty) = \left(\frac{\partial E^{\beta}}{\partial i_{\alpha}}\right)_i \Delta i_{\alpha} = U^{\beta\alpha}\Delta i_{\alpha}. \quad (10d)$$

D. Le Châtelier perturbation-response matrix

Since $\Delta i_{\beta}(\infty) = 0$ and $\Delta E^{\beta}(0^+) = 0$ ($\beta \neq \alpha$), it is useful to compare the product of secondary variables $\Delta i_{\beta}(0^+)$ $\Delta E^{\beta}(\infty)$, which has the dimensions of energy, with the product $\Delta i_{\alpha}(\infty)\Delta E^{\alpha}(0^+)$ of primary variables. This comparison defines a dimensionless constant of proportionality, $L_{\beta\alpha}$, as follows:

$$\Delta i_{\beta}(0^+)\Delta E^{\beta}(\infty) = L_{\beta\alpha}\Delta i_{\alpha}(\infty)\Delta E^{\alpha}(0^+). \quad (11)$$

The value of the constant $L_{\beta\alpha}$ can be derived from Eqs. (7) and (8) when the extensive variable is perturbed ($\Delta E^{\alpha} > 0$) or from Eqs. (9) and (10) when the intensive variable is perturbed ($\Delta i_{\alpha} > 0$). In either case we find

$$L_{\beta\alpha} = U_{\beta\alpha} U^{\beta\alpha}. \quad (12)$$

The set of n^2 coefficients $L_{\beta\alpha}$ (for a system with n degrees of freedom) can be written in matrix form. The perturbation-response matrix $[L_{\beta\alpha}]$ is called the Le Châtelier matrix.

E. Properties of the Le Châtelier matrix

(1) It is dimensionless because each matrix element is the ratio of two energies.

(2) It is symmetric because the susceptibility tensors $[U_{\alpha\beta}]$, $[U^{\alpha\beta}]$ are symmetric [cf. Eq. (6a)]:

$$L_{\alpha\beta} = U_{\alpha\beta} U^{\alpha\beta} = U_{\beta\alpha} U^{\beta\alpha} = L_{\beta\alpha}. \quad (13a)$$

(3) It is positive definite because the susceptibility tensors $[U_{\alpha\beta}]$, $[U^{\alpha\beta}]$, are positive definite.

(4) The sum of the elements of any row or column is equal to unity:

$$\sum_{\beta} L_{\beta\alpha} = \sum_{\beta} U_{\beta\alpha} U^{\beta\alpha} = \sum_{\beta} U_{\alpha\beta} U^{\beta\alpha} = \delta^{\alpha}_{\alpha} = 1. \quad (13b)$$

(5) The diagonal matrix elements all exceed unity. This follows most easily by applying the Schwartz or Bessel inequality to the metric geometry of thermodynamics.[8,10] The result is $U_{\alpha\alpha} \geqslant (1/U^{\alpha\alpha})$ or

$$L_{\alpha\alpha} = U_{\alpha\alpha} U^{\alpha\alpha} > 1. \quad (13c)$$

The inequality holds unless $[U_{\alpha\beta}]$ or $[U^{\alpha\beta}]$ is diagonal.

F. Le Châtelier's principle

The dual cases of Le Châtelier's principle studied by Ehrenfest are simultaneously contained in the diagonal elements $L_{\alpha\alpha}$ of the Le Châtelier matrix

$$L_{\alpha\alpha} = \frac{\Delta i_{\alpha}(0^+)\Delta E^{\beta}(\infty)}{\Delta i_{\alpha}(\infty)\Delta E^{\alpha}(0^+)} > 1. \quad (14)$$

Case 1: If the extensive variable is perturbed, $\Delta E^{\alpha}(0^+) = \Delta E^{\alpha}(\infty)$ and Eq. (14) reduces to

$$\Delta i_{\alpha}(0^+)/\Delta i_{\alpha}(\infty) = L_{\alpha\alpha} > 1 \quad (15a)$$

or

$$\left(\frac{\partial i_{\alpha}}{\partial E^{\alpha}}\right)_E > \left(\frac{\partial i_{\alpha}}{\partial E^{\alpha}}\right)_i > 0. \quad (15b)$$

Case 2: If the intensive variable is perturbed, $\Delta i_{\alpha}(0^+) = \Delta i_{\alpha}(\infty)$ and Eq. (14) reduces to

$$\Delta E^{\alpha}(\infty)/\Delta E^{\alpha}(0^+) = L_{\alpha\alpha} > 1 \quad (16a)$$

or

$$\left(\frac{\partial E^{\alpha}}{\partial i_{\alpha}}\right)_i > \left(\frac{\partial E^{\alpha}}{\partial i_{\alpha}}\right)_E > 0. \quad (16b)$$

Returning now to the two sources of confusion surrounding this principle, we may now state Le Châtelier's principle as follows:

(1) When a system is perturbed, it initially (after internal equilibrium is reached, before secondary forces have acted) responds in the direction of the perturbation. The responding variable is conjugate to the perturbed variable.

(2) Secondary forces subsequently act to "oppose" (extensive variable perturbed, intensive variable responding) or "relieve" (extensive variable responding) the perturbation.

Part (1) of this statement is essentially Newton's second law applied to generalized forces and displacements. Part (2) states the two cases of Le Châtelier's principle discerned by Ehrenfest.

V. THERMODYNAMIC EXAMPLE

For the simple single-component fluid considered in the examples of Secs. II and III, the susceptibility tensor

$[U_{\alpha\beta}]$ and its inverse $[U^{\alpha\beta}]$ are described in terms of the six standard linear response functions:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \quad C_P = T\left(\frac{\partial S}{\partial T}\right)_P,$$
$$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S, \quad \beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{17}$$
$$\Gamma_V = T\left(\frac{\partial S}{\partial P}\right)_V, \quad \alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

$$[U_{\alpha\beta}] = \begin{bmatrix} \dfrac{T}{C_V} & -\dfrac{T}{\Gamma_V} \\ -\dfrac{T}{\Gamma_V} & \dfrac{1}{V\beta_S} \end{bmatrix},$$

$$[U^{\alpha\beta}] = \begin{bmatrix} \dfrac{C_P}{T} & V\alpha_p \\ V\alpha_p & V\beta_T \end{bmatrix}. \tag{18}$$

The Le Châtelier matrix for this fluid is

$$[L_{\alpha\beta}] = \begin{bmatrix} \dfrac{C_P}{C_V} & -\dfrac{TV\alpha_p}{\Gamma_V} \\ -\dfrac{TV\alpha_p}{\Gamma_V} & \dfrac{\beta_T}{\beta_S} \end{bmatrix}. \tag{19}$$

The property $L_{\alpha\alpha} > 1$ of the Le Châtelier matrix leads immediately to the inequalities

$$C_P/C_V > 1 \quad \text{or} \quad C_P > C_V > 0,$$
$$\beta_T/\beta_S > 1 \quad \text{or} \quad \beta_T > \beta_S > 0. \tag{20}$$

The property that all row and column sums are + 1 leads to the equalities

$$\frac{C_P}{C_V} - \frac{TV\alpha_p}{\Gamma_V} = 1 = \frac{\beta_T}{\beta_S} - \frac{TV\alpha_p}{\Gamma_V}. \tag{21}$$

From the last result we immediately see that $C_P/C_V = \beta_T/\beta_S$. In fact, the Le Châtelier matrix (19) is completely determined by one number $(-TV\alpha_p/\Gamma_V)$, given its properties (Sec. IV. E).

The Le Châtelier matrix provides a deep understanding of the four experiments discussed in Secs. II and III, and the relations which exist among them. Relations exist among both direct and indirect responses. Table I summarizes these four experiments, the variable which is perturbed, and the response ratios for both direct and indirect responses.

We see from this table that the direct response ratios for examples 1 and 2 are equal $(C_V/C_P = \beta_S/\beta_T < 1)$ and less than unity, while the direct response ratios for examples 1′ and 2′ are their reciprocals. We also see that all four indirect (reciprocal) response ratios are equal $(-TV\alpha_p/\Gamma_V)$. Finally, in view of the equality (21) obtained from the property of $[L_{\beta\alpha}]$ that all row and column sums are + 1, we observe that any single indirect response ratio is sufficient to determine the remaining seven response ratios in this table.

VI. FORMULATION OF LE CHÂTELIER'S PRINCIPLE FOR MECHANICAL SYSTEMS

We consider now a mechanical system which can be described by n generalized coordinates (displacements) X^1, $X^2, \ldots, X^n$. The potential energy of this system is described by a function $U = U(X^\alpha)$. The generalized forces f_α conjugate to the generalized displacements X^α are defined by

$$f_\alpha = -\frac{\partial U}{\partial X^\alpha} = -U_\alpha. \tag{22a}$$

If the generalized displacements are changed slightly $(X^\beta \to X^\beta + \delta X^\beta)$ the generalized forces are also changed slightly $(f_\alpha \to f_\alpha + \delta f_\alpha)$, where

$$\delta f_\alpha = -\sum_\beta \frac{\partial^2 U}{\partial X^\beta} \partial X^\beta = -\sum_\beta U_{\alpha\beta}\, \delta X^\beta. \tag{22b}$$

At an equilibrium, $U_\alpha = 0$. If the equilibrium is stable, $[U_{\alpha\beta}]$ is positive definite:

$U_\alpha = 0$ (equilibrium condition) (23a)

$[U_{\alpha\beta}]$ positive definite (stability condition). (23b)

At an equilibrium, the change in potential energy due to a displacement δX from equilibrium is, to lowest nonvanishing order

Table I. Comparison of the direct and indirect responses of the thermodynamic variables for the four examples considered in Secs. II and III.

Section	Type of response	Experiment number	Perturbation	Response ratio
II	Direct	1	ΔS	$\Delta T(\infty)/\Delta T(0^+) = C_V/C_P < 1$
		2	ΔV	$\Delta P(\infty)/\Delta P(0^+) = \beta_S/\beta_T < 1$
	Indirect	1	ΔS	$-\Delta P(0^+)\Delta V(\infty) = -\dfrac{TV\alpha_P}{\Gamma_V}\Delta T(\infty)\Delta S$
		2	ΔV	$\Delta T(0^+)\Delta S(\infty) = -\dfrac{TV\alpha_P}{\Gamma_V}[-\Delta P(\infty)]\Delta V$
III	Direct	1′	ΔT	$\Delta S(\infty)/\Delta S(0^+) = C_P/C_V > 1$
		2′	$-\Delta P$	$\Delta V(\infty)/\Delta V(0^+) = \beta_T/\beta_S > 1$
	Indirect	1′	ΔT	$-\Delta P(0^+)\Delta V(\infty) = -\dfrac{TV\alpha_P}{\Gamma_V}\Delta T\Delta S(0^+)$
		2′	$-\Delta P$	$\Delta T(0^+)\Delta S(\infty) = -\dfrac{TV\alpha_P}{\Gamma_V}(-\Delta P)\Delta V(0^+)$

$$U = \tfrac{1}{2}\sum_{\alpha,\beta} U_{\alpha\beta}\,\delta X^\alpha \delta X^\beta = -\tfrac{1}{2}\sum_\alpha \delta f_\alpha\,\delta X^\alpha$$
$$= \tfrac{1}{2}\sum_{\alpha,\beta} U^{\alpha\beta}\,\delta f_\alpha\,\delta f_\beta. \tag{24}$$

The matrices $[U_{\alpha\beta}]$, $[U^{\alpha\beta}]$ are inverses. They are real, symmetric, and, if the system is stable, positive definite.

A mechanical system at equilibrium may be perturbed by suddenly changing one of its variables (primary variable), and holding the perturbation constant for all future times. The perturbed primary variable may be either extensive ($\Delta X^\alpha \neq 0$) or intensive ($\Delta f_\alpha \neq 0$). In either case, the secondary displacements ΔX^β will initially be small because of the inertia associated with extensive variables $[\Delta X^\beta(0^+) \simeq 0,\ \beta \neq \alpha]$. The nonzero secondary forces Δf_β will drive the system to a new constrained equilibrium in which they vanish $[\Delta f_\beta(\infty) = 0,\ \beta \neq \alpha]$. The initial ($t = 0^+$) and final ($t \to \infty$) responses of the generalized forces and displacements can be determined by making the identifications $(-f_\alpha, X^\alpha) \leftrightarrow (i_\alpha, E^\alpha)$ and following the arguments of Sec. IV. There results the following perturbation-response relation:

$$\Delta f_\beta(0^+)\Delta X^\beta(\infty) = L_{\beta\alpha}\Delta f_\alpha(\infty)\Delta X^\alpha(0^+), \tag{25}$$

where

$$L_{\beta\alpha} = U_{\beta\alpha} U^{\beta\alpha}. \tag{26}$$

The matrix $[L_{\beta\alpha}]$ has the properties described in Sec. IV. E.

For many mechanical systems, the stability matrix $[U_{\beta\alpha}]$ obeys the condition $U_{\beta\alpha} \leqslant 0$ ($\beta \neq \alpha$). Under these conditions, the Le Châtelier response matrix possesses an additional set of properties. These properties are summarized in the Appendix.

To illustrate Le Châtelier's principle for mechanical systems, we consider the simple mass–spring system shown in Fig. 5(a). We assume that the masses are large (see below) and the springs are slightly damped. The potential energy function can be expressed in terms of the generalized displacements X^1, X^2, X^3 from unconstrained equilibrium in both standard and matrix form:

$$U(X^1, X^2, X^3)$$
$$= \tfrac{1}{2}k(X^1)^2 + \tfrac{1}{2}k(X^1 - X^2)^2 + \tfrac{1}{2}k(X^2 - X^3)^2 + \tfrac{1}{2}k(X^3)^2 \tag{27a}$$

$$= \tfrac{1}{2}(X^1, X^2, X^3)\begin{bmatrix} 2k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & 2k \end{bmatrix}\begin{pmatrix} X^1 \\ X^2 \\ X^3 \end{pmatrix}. \tag{27b}$$

The generalized forces conjugate to the displacements are

$$\begin{bmatrix} f_1 \\ f_2 \\ f_3 \end{bmatrix} = -\begin{bmatrix} \dfrac{\partial}{\partial X^1} \\ \dfrac{\partial}{\partial X^2} \\ \dfrac{\partial}{\partial X^3} \end{bmatrix} U(X^1, X^2, X^3)$$
$$= -\begin{bmatrix} 2k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & 2k \end{bmatrix}\begin{bmatrix} X^1 \\ X^2 \\ X^3 \end{bmatrix}. \tag{28}$$

The inverse of the positive-definite matrix appearing in Eqs. (27b) and (28) is

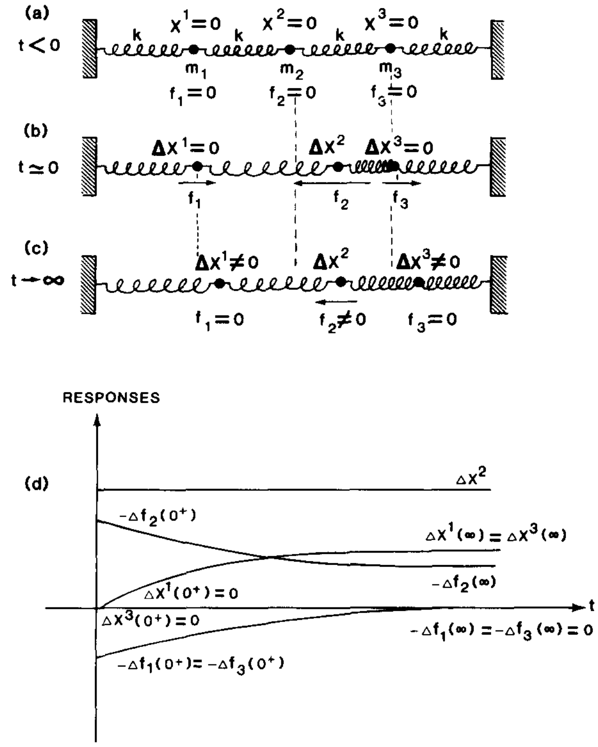

Fig. 5. (a) For $t < 0$ the mass–spring system is in static equilibrium. All masses are equal, as are all spring constants. (b) At $t = 0$ the middle mass m_2 is suddenly displaced by ΔX^2, creating nonzero forces on all masses but no displacements of m_1, m_3 at $t = 0^+$. (c) After a long time ($t \to \infty$) the system has reached a new constrained equilibrium in which $\Delta f_1 = \Delta f_3 = 0$, $\Delta f_2 \neq 0$. (d) The three displacements ΔX^α and forces $-\Delta f_\alpha$ are shown as a function of time. We have plotted $-\Delta f_\alpha$ instead of $+\Delta f_\alpha$ for two reasons: (i) $\partial U/\partial X^\alpha = -f_\alpha$ and (ii) to emphasize the close similarity with the thermodynamic cases [Figs. 1(d), 2(d)].

$$-\begin{bmatrix} 2k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & 2k \end{bmatrix}^{-1} = -\frac{1}{4k}\begin{bmatrix} 3 & 2 & 1 \\ 2 & 4 & 2 \\ 1 & 2 & 3 \end{bmatrix}. \tag{29}$$

The Le Châtelier matrix associated with this mechanical system is therefore

$$[L] = \begin{bmatrix} 3/2 & -1/2 & 0 \\ -1/2 & 2 & -1/2 \\ 0 & -1/2 & 3/2 \end{bmatrix}. \tag{30}$$

The matrix is dimensionless, real, symmetric, and positive definite. The diagonal matrix elements exceed $+1$, the off-diagonal matrix elements are nonpositive, and the sum of the elements in any row or column is $+1$.

VII. PERTURBATION OF AN EXTENSIVE VARIABLE: A MECHANICAL EXAMPLE

To see how the Le Châtelier matrix (30) is related to physical processes induced by perturbation of an extensive variable, we consider a displacement of mass m_2 from its unconstrained equilibrium position. This displacement $\Delta X^2 \neq 0$ must be carried out on a time scale much shorter than $\sqrt{m/k}$. The conditions at $t = 0^+$ are [cf. Fig. 5(b)] $\Delta X^1 = \Delta X^3 = 0$ and

$$t=0^+:\quad \begin{bmatrix}\Delta f_1\\ \Delta f_2\\ \Delta f_3\end{bmatrix} = -k\begin{bmatrix}2 & -1 & 0\\ -1 & 2 & -1\\ 0 & -1 & 2\end{bmatrix}\begin{bmatrix}0\\ \Delta X^2\\ 0\end{bmatrix}$$

$$= \begin{bmatrix}+k\Delta X^2\\ -2k\Delta X^2\\ +k\Delta X^2\end{bmatrix}. \tag{31}$$

After the oscillations have damped out ($t \to \infty$) the conditions are [cf. Fig. 5(c)] $\Delta f_1 = \Delta f_3 = 0, \Delta X^2 =$ constant and

$$t\to\infty:\quad \begin{bmatrix}\Delta X^1\\ \Delta X^2\\ \Delta X^3\end{bmatrix} = -\frac{1}{4k}\begin{bmatrix}3 & 2 & 1\\ 2 & 4 & 2\\ 1 & 2 & 3\end{bmatrix}\begin{bmatrix}0\\ \Delta f_2\\ 0\end{bmatrix}$$

$$= -\begin{bmatrix}2\Delta f_2/4k\\ 4\Delta f_2/4k\\ 2\Delta f_2/4k\end{bmatrix} = \begin{bmatrix}\frac{1}{2}\Delta X^2\\ \Delta X^2\\ \frac{1}{2}\Delta X^2\end{bmatrix}. \tag{32}$$

From Eqs. (31) and (32) we easily compute

$$\Delta f_2(\infty)\Delta X^2 = (-k\Delta X^2)(\Delta X^2) \tag{33a}$$

and

$$\Delta f_1(0^+)\Delta X^1(\infty) = (+k\Delta X^2)(\tfrac{1}{2}\Delta X^2) \quad L_{12} = -\tfrac{1}{2},$$

$$\Delta f_2(0^+)\Delta X^2(\infty) = (-2k\Delta X^2)(\Delta X^2) \quad L_{22} = +2, \tag{33b}$$

$$\Delta f_3(0^+)\Delta X^3(\infty) = (+k\Delta X^2)(\tfrac{1}{2}\Delta X^2) \quad L_{32} = -\tfrac{1}{2}.$$

The time evolution of the generalized displacements and forces is indicated schematically in Fig. 5(d). The oscillations in f_1, f_2, f_3, X^1, X^3 have been averaged over, assuming the decay time is sufficiently longer than the normal mode periods, and only the mean values of the forces and displacements have been shown. The initial response of the force $\Delta f_2(0^+) = -2k\Delta X^2$ conjugate to the perturbed variable ΔX^2 is twice the long-term response $\Delta f_2(\infty) = -k\Delta X^2$, or $\Delta f_2(0^+)/\Delta f_2(\infty) = L_{22} = 2$.

In this experiment when the middle mass is displaced to the right, a large restoring force Δf_2 will act toward the left on it. If its position is held fixed, this force will be diminished by the motion of the two satellite masses toward the right. The external force F_{ext} required to hold m_2 fixed with $\Delta f_2 \neq 0$ will be diminished by the motion of the satellite masses since $F_{ext} + \Delta f_2 = 0$ when m_2 is unaccelerated (at $t = 0^+$ and $t \to \infty$).

VIII. PERTURBATION OF AN INTENSIVE VARIABLE: A MECHANICAL EXAMPLE

To see how the Le Châtelier matrix (30) is related to physical processes induced by perturbation of an intensive variable, we apply a constant external force F_{ext} to the middle mass [Fig. 6(a)]. We will assume that m_2 is much less than the satellite masses m_1, m_3. An alternative assumption can be made that the masses m_1, m_3 are constrained in their original positions until m_2 has reached a new equilibrium position under $F_{ext} \neq 0$, and then are released. Either of these assumptions is sufficient to establish a clean separation of the time scales on which the responses to perturbation take place.

These responses can be computed using the matrix relations given in Sec. VII. The results are

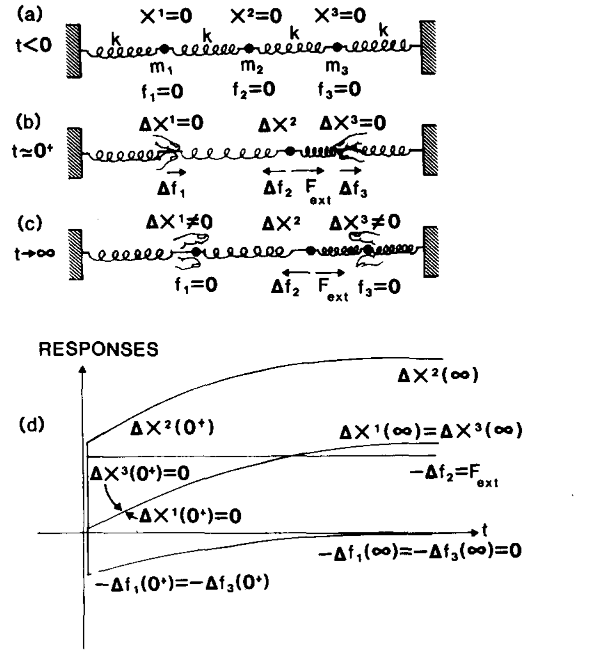

Fig. 6. (a) For $t<0$ the mass–spring system is in static equilibrium. (b) At $t=0$, a constant external force F_{ext} is applied to the middle mass m_2. If $m_2 \ll m_1, m_3$, then m_2 has moved to a new quasi equilibrium position before either of the other masses have moved ($t=0^+$). If the mass inequality is not satisfied, the masses m_1, m_3 may be held in place until m_2 has reached an equilibrium position ("$t=0^+$"). (c) After a long time ($t\to\infty$) the masses m_1, m_3 move to the right, allowing m_2 to move further to the right under the action of the constant external force F_{ext}. (d) The displacements ΔX^α and forces $-\Delta f_\alpha$ are shown as a function of time. During the interval $0^+ \leqslant t < \infty$ while m_2 is almost unaccelerated, the external force F_{ext} and the spring force Δf_2 on m_2 sum approximately to zero: $F_{ext} + \Delta f_2 \simeq 0$.

$$t=0^+:\quad \begin{aligned} &\Delta f_1 = \tfrac{1}{2}F_{ext}, && \Delta X^1 = 0\\ &\Delta f_2 = -F_{ext}, && \Delta X^2 = +\frac{1}{2k}F_{ext}\\ &\Delta f_3 = \tfrac{1}{2}F_{ext}, && \Delta X^3 = 0\cdot \end{aligned} \tag{34}$$

These responses are illustrated in Fig. 6(b).

$$t\to\infty:\quad \begin{aligned} &\Delta f_1 = 0, && \Delta X^1 = \frac{1}{2k}F_{ext}\\ &\Delta f_2 = -F_{ext}, && \Delta X^2 = \frac{2}{2k}F_{ext}\\ &\Delta f_3 = 0, && \Delta X^3 = \frac{1}{2k}F_{ext}. \end{aligned} \tag{35}$$

These responses are illustrated in Fig. 6(c). From Eqs. (34) and (35) we easily compute

$$\Delta f_2 \Delta X^2(0^+) = (-F_{ext})(1/2kF_{ext}) \tag{36}$$

and

$$\Delta f_1(0^+)\Delta X^1(\infty) = (1/2F_{ext})(1/2kF_{ext}) \quad L_{12} = -\tfrac{1}{2},$$

$$\Delta f_2(0^+)\Delta X^2(\infty) = (-F_{ext})(2/2kF_{ext}) \quad L_{22} = +2,$$

$$\Delta f_3(0^+)\Delta X^3(\infty) = (1/2F_{ext})(1/2kF_{ext}) \quad L_{32} = -\tfrac{1}{2}.$$

The time evolution of the generalized displacements and forces is indicated schematically (neglecting oscillations) in Fig. 6(d).

In both these experiments, the middle mass is displaced to the right by an external force F_{ext}. Initially, the satellite masses remain undisplaced ($t=0^+$), but the secondary forces which are generated by the changed position of the middle mass act on the satellite masses and move them to new equilibrium positions. In one case (Sec. VII) the position of the middle mass remains fixed, and motion of the remaining masses reduces the external force required to hold the middle mass in place. In the other case (this section) the external force $F_{\rm ext}$ on the middle mass ($F_{\rm ext}+\Delta f_2=0$ when m_2 is unaccelerated) is held constant. When the constraints holding the satellite masses in place are relaxed (e.g., by the passage of time, if $m_2 \ll m_1$, $m_2 \ll m_3$), these masses also move to the right, allowing the middle mass to move even further to the right. The experiments are in a sense dual, and the ratios of final to initial responses are reciprocals. For the case $\Delta X^2=\text{const}$, $\Delta f_2(\infty)/\Delta f_2(0^+)=1/2$ while for the case $F_{\rm ext}=\Delta f_2=\text{const}$, $\Delta X^2(\infty)/\Delta X^2(0^+)=2$.

IX. CONCLUDING REMARKS

Le Châtelier's principle has three main ingredients.

(1) A system is in static or dynamic equilibrium, and this equilibrium is stable. Small displacements of the system from equilibrium are returned to equilibrium by nonzero restoring forces which are usually (but not necessarily) assumed to be linear functions of the displacement [cf. Eqs. (4) and (22)].

(2) Constraints are imposed on the system after it is displaced from equilibrium. These constraints prevent the system from returning to the original unperturbed equilibrium configuration. As each constraint is removed, the system can approach closer to the original equilibrium.

(3) There is a dynamic response of the system to perturbation. The dynamic response involves two or more characteristic time scales. The characteristic times are widely separated.

Samuelson[1] gives a careful discussion of the response of a general locally stable system to a perturbation, and the approach to equilibrium as constraints are successively removed. His work presents a careful discussion of the first two ingredients, but is entirely devoid of dynamical considerations.

Formulations of Le Châtelier's principle in the literature of thermodynamics involve transitive verbs either explicitly or implicitly. The dynamical ingredient is therefore generally recognized, even if the separation of time scales and role of constraints is less well understood. It is, however, recognized that Le Châtelier's principle is a static, rather than dynamic, principle.[5(a),5(c)] We have suggested throughout that the physical parameters (massive pistons in Secs. II and III, relative size of k_i, m_i in Secs. VII and VIII) which govern the dynamical properties of these systems are such that a clear separation of time scales occurs. If this is not the case, as implied in Fig. 6, the Le Châtelier matrix can be used to describe the system as it undergoes a relaxation of constraints, from $\Delta X^\beta=0$ to $\Delta f^\beta=0$.

The ingredients of Le Châtelier's principle are rather general, and can be found in many fields. These include the thermodynamics of equilibrium and nonequilibrium processes alike, mechanical systems in static and dynamic equilibrium, passive multiport electrical networks involving resistors, capacitors, and inductors (Lenz's law), economic models of input–output and general equilibrium type, feedback and control systems of both linear and nonlinear type, and in all probability, biological, social, and political models as well. In all such systems the diagonal matrix elements

$$L_{\alpha\alpha}=\Delta f_\alpha(0^+)\Delta X^\alpha(\infty)/\Delta f_\alpha(\infty)\Delta X^\alpha(0^+)$$

describe the direct responses of the system to perturbation. These matrix elements include the dual cases first discussed by Ehrenfest:

$$L_{\alpha\alpha}=\Delta f_\alpha(0^+)/\Delta f_\alpha(\infty)>1$$

if ΔX^α is fixed, or

$$L_{\alpha\alpha}=\Delta X^\alpha(\infty)/\Delta X^\alpha(0^+)>1$$

if Δf_α is fixed. The off-diagonal matrix elements describe the indirect responses. If the system is described by a potential, $L_{\alpha\beta}=L_{\beta\alpha}$ and reciprocal relations between the primary and secondary variables hold. In such cases (thermodynamics, mechanics) the Le Châtelier matrix describes two kinds of reciprocal relations:

(1) The response ratios $\Delta f_\alpha(\infty)/\Delta f_\alpha(0^+)$ and $\Delta X^\alpha(\infty)/\Delta X^\alpha(0^+)$ for the dual cases described by Ehrenfest are reciprocals of each other.

(2) The response ratio of secondary to primary variables $\Delta f_\beta(0^+)\Delta X^\beta(\infty)/\Delta f_\alpha(\infty)\Delta X^\alpha(0^+)$ is unchanged under the reversal of roles: primary $\rightleftarrows$ secondary.

A precise qualitative statement of Le Châtelier's principle which avoids the confusions described in Sec. I is

(1) When a small external force is applied to a system in locally stable equilibrium, the system is initially displaced in the direction of the applied force.

(2) After the secondary forces generated by the perturbation have established a new equilibrium, (a) the external force is reduced if the displacement is held constant or (b) the displacement is increased if the external force is held constant.

APPENDIX

In many types of systems it happens that the stability matrix $[U_{\alpha\beta}]=[\partial^2U/\partial X^\alpha\,\partial X^\beta]$ is positive definite with respect to a natural coordinate system X^α, and that all off-diagonal matrix elements are nonpositive. When this is the case, its inverse $[U^{\alpha\beta}]$ is positive definite and all its matrix elements are non-negative:

$$U_{\alpha\beta}=U_{\beta\alpha},\quad U_{\alpha\alpha}>0,\quad U_{\alpha\beta}\leqslant 0,\quad \alpha\neq\beta,$$
$$U^{\alpha\beta}=U^{\beta\alpha},\quad U^{\alpha\alpha}>0,\quad U^{\alpha\beta}\geqslant 0,\quad \alpha\neq\beta.$$

For such systems the Le Châtelier response matrix $L_{\alpha\beta}=U_{\alpha\beta}U^{\alpha\beta}$ has the properties:

$$L_{\alpha\beta}=L_{\beta\alpha}, \tag{A1}$$

$$L_{\alpha\alpha}\geqslant 1, \tag{A2}$$

$$L_{\alpha\beta}\leqslant 0\quad \alpha\neq\beta, \tag{A3}$$

$$\sum_\alpha L_{\alpha\beta}=1=\sum_\beta L_{\alpha\beta}. \tag{A4}$$

This last expression can be written

$$\sum_{\substack{\beta\\ \beta\neq\alpha}} -L_{\beta\alpha}=L_{\alpha\alpha}-1\geqslant 0. \tag{A4$'$}$$

Since $-L_{\beta\alpha}\geqslant 0$ when $\beta\neq\alpha$ by Eq. (A3), if the sum in Eq. (A4′) extends over some, but not all, values of $\beta\neq\alpha$ (indicated by a prime in the summation below) the following inequalities are obtained:

$$0 < \sum_{\substack{\beta \\ \beta \neq \alpha}}^{r} - L_{\beta\alpha} < L_{\alpha\alpha} - 1. \quad \text{(A5)}$$

For systems in thermodynamic equilibrium, the off-diagonal matrix elements of the stability matrix $[U_{\alpha\beta}]$ are not constrained in sign. For very many thermodynamic systems, the matrix elements $U_{\alpha\beta}$ and $U^{\alpha\beta}$ $(\alpha \neq \beta)$ do have opposite signs. The second law of thermodynamics requires the inequalities (A2) but not the inequalities (A3). If inequalities of the form (A3) or (A5) were found to be universally satisfied by systems in thermodynamic equilibrium with respect to the natural thermodynamic variables, our understanding of the second law of thermodynamics would have to be sharpened.

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APL and the numerical solution of high-order linear differential equations

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(Received 12 April 1982; accepted for publication 18 September 1982)

An Nth-order linear ordinary differential equation is rewritten as a first-order equation in an $N \times N$ matrix. Taking advantage of the matrix manipulation strength of the APL language this equation is then solved directly, yielding a great simplification over the standard procedure of solving N coupled first-order scalar equations. This eases programming and results in a more intuitive algorithm. Example applications of a program using the technique are given from quantum mechanics and control theory.

INTRODUCTION

A task of a physics student, and that of a physicist in general, frequently leads to a differential equation. Some intuition about the nature of its solution is invariably very helpful. Working interactively with a computer that generates solutions and provides graphical output is an excellent way to develop such intuition. This note reports on a great simplification possible for high-order linear differential equations taking advantage of the matrix manipulation capabilities of the APL computer language. The matrix manipulation flexibility of APL allows an Nth-order linear ordinary differential equation to be solved numerically in terms of a single first-order equation in an $N \times N$ matrix, instead of the standard system of N first-order scalar equations. This greatly simplifies programming and results in more intuitively understandable algorithm. A program implementing this technique is described below, and examples are given from quantum mechanics and control theory.

MATRIX FORMULATION

The general form of the problem is

$$A_N(t)\frac{d^N z}{dt^N} + \cdots + A_1(t)\frac{dz}{dt} + A_0(t)z = F(t), \quad (1)$$

with initial conditions

$$\left.\frac{d^{N-1}z}{dt^{N-1}}\right|_{t=t_0} = K_{N-1}, \ldots, \left.\frac{dz}{dt}\right|_{t=t_0} = K_1, \; z(t_0) = K_0. \quad (2)$$

The standard method for numerically solving such an Nth-order initial-value problem entails converting it ot the system of N first-order equations