

LeChatelier Dynamics

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Dynamics of the relaxation of a perturbed thermodynamic system to equilibrium is determined by the generalized eigenvalue equation $(\tilde{K}^{\alpha\beta} + \lambda S^{\alpha\beta})y_\beta = 0$. Here $S^{\alpha\beta}$ is a matrix of linear response coefficients and $\tilde{K}^{\alpha\beta}$ is a matrix of kinetic coefficients. We describe LeChatelier's Principle and both its static and dynamical symmetries, and treat cases in which there are multiple relaxation channels. The treatment simplifies when the relaxation channels have widely separated time scales.

I. INTRODUCTION

LeChatelier's Principle is a statement about how a system in thermodynamic equilibrium responds to a perturbation. In brief, after the perturbation the system relaxes back to an equilibrium. This equilibrium is the highest possible entropy state, or the lowest possible energy state, that is available to the system under the constraints that have been imposed. If one or more relaxation channels are closed, the new equilibrium will be different from the original equilibrium.

LeChatelier's Principle is usually stated in qualitative terms. When it is described quantitatively it is almost always in terms of responses to a perturbation from equilibrium when a single reaction channel opens up [1, 2]. The case of intermediate responses when there is a succession of relaxation channels with widely separated time scales has been discussed quantitatively in [3]. In this work we describe the *dynamical* response of a system with any number of relaxation channels to an *arbitrary* perturbation. The relaxation time constants are determined from a generalized eigenvalue equation. This equation involves the static linear response functions and their dynamic counterparts, the kinetic coefficients. The eigenvalues are well-defined functions of both sets of coefficients.

The generalized eigenvalue equation is first expressed in the entropy representation. In this representation the entropy, $S(t)$, continuously increases after the perturbation until the new equilibrium is reached. We then transform to the energy representation using what is for all practical purposes a similarity transformation. In this representation the internal energy, $U(t)$, continuously decreases after the perturbation until the new equilibrium is reached. Constraints that prevent the system from returning to its original equilibrium configuration are expressed naturally in this eigen-representation. Such constraints are represented by vanishing eigenvalues.

Natural extensive variables, and their conjugate intensive variables, are summarized in Table I for the two ther-

TABLE I: Natural conjugate variable pairs (Extensive, intensive) in the entropy and energy representations.

Representation			
Entropy		Energy	
X^α	y_α	E^α	i_α
U	$1/T$	S	T
V	P/T	V	$-P$
N	$-\mu/T$	N	μ

modynamic representations. Throughout we use contra- ($^\alpha$) and co- ($_\alpha$) variant notation for extensive and intensive thermodynamic variables. This notation is based on the geometric formulation of classical thermodynamics [4, 5, 6, 7].

In Sec. II we briefly review the properties of the matrices of static and dynamic coefficients, and then write down and justify the generalized eigenvalue equation that describes LeChatelier dynamics. In Sec. III we transform to the more familiar energy representation. We illustrate how constraints are handled in Sec. IV in terms of a simple example with a single relaxation channel. In Sec. V we review the symmetries that exist in single channel processes. They are of two types. One involves the ratios of asymptotic responses under dual perturbations. The other involves a single relaxation time constant, also under dual perturbations. In Sec. VI we treat the case in which there are multiple relaxation channels with widely separated time scales. The results are summarized in Sec. VII.

II. ASSUMPTIONS AND EQUATIONS - ENTROPY REPRESENTATION

Two fundamental equations describe the dynamics of LeChatelier's Principle. In the entropy representation these are

$$\delta X^\alpha = S^{\alpha\beta} \delta y_\beta \quad (\text{Statics}) \quad (1)$$

$$\frac{d}{dt} \delta X^\alpha = \tilde{K}^{\alpha\beta} \delta y_\beta \quad (\text{Dynamics}) \quad (2)$$

These equations describe very different physical processes.

The first equation describes “static” or “adiabatic” (meaning very slow) equilibrium processes. At equilibrium the entropy is a function of its natural extensive variables X (c.f., Table I). We assume there is an equilibrium for values X_0^α of the extensive thermodynamic variables, and $y_\alpha(X_0) = \frac{\partial S}{\partial X^\alpha}(X_0)$ are the values of the conjugate intensive thermodynamic variables at this equilibrium. If the extensive variables are changed to new values $X_0^\alpha + \delta X^\alpha$ slowly, so that the system moves on the equilibrium surface $S = S(X)$, the intensive variables will slowly change to new values $y_\alpha(X_0) + \delta y_\alpha$. For small displacements the linear relation between the displacements of extensive and intensive thermodynamic variables is given by Eq. (1). The $n \times n$ real symmetric matrix $S^{\alpha\beta}$ of static susceptibilities is the inverse of the matrix $S_{\alpha\beta} = \left(\frac{\partial^2 S(X)}{\partial X^\alpha \partial X^\beta} \right)_{X_0}$. This matrix is negative definite at equilibrium, since the entropy is a maximum at equilibrium. The susceptibilities $S^{\alpha\beta}$ and $S_{\alpha\beta}$ are *intrinsic* to the thermodynamic system: they are independent of the container holding the material.

The second equation above relates “forces” to fluxes”. The generalized forces are the differences in the intensive variables, δy_β , across some sort of barrier separating the system of interest (A) from the outside world (B). The generalized fluxes, $\frac{d}{dt} \delta X^\beta$, are the time rates of change of displacements of the extensive variables as the system tries to relax to equilibrium: the highest available entropy state. Eq. (2) is a linearization of the general equation $\delta \dot{X}^\alpha = F^\alpha(\delta y)$ near the equilibrium manifold [8]. The matrix $\tilde{K}^{\alpha\beta}$ of kinetic coefficients obeys the Onsager symmetry $\tilde{K}^{\alpha\beta}(t) = \tilde{K}^{\beta\alpha}(-t)$ [9] and is positive semidefinite. The kinetic coefficients $\tilde{K}^{\alpha\beta}$ are *extrinsic*: they depend on the container holding the material and can be changed from one experiment to another.

The positivity property of the matrix of kinetic coefficients can be seen by computing the time rate of change of the combined entropy of the two systems $A + B$:

$$\begin{aligned} \frac{d}{dt}(S_A + S_B) &= \frac{\partial S_A}{\partial X_A^\alpha} \frac{dX_A^\alpha}{dt} + \frac{\partial S_B}{\partial X_B^\alpha} \frac{dX_B^\alpha}{dt} \\ &= ((y_A)_\alpha - (y_B)_\alpha) dX_A^\alpha / dt \\ &= \delta y_\alpha \tilde{K}^{\alpha\beta} \delta y_\beta \geq 0 \end{aligned} \quad (3)$$

We have exploited conservation of extensive quantities: $X_A^\alpha + X_B^\alpha = X_{Tot}^\alpha = \text{const.}$, so that $\dot{X}_A^\alpha = -\dot{X}_B^\alpha$.

We point out here that by simple dimensional considerations, the dimensions $([*])$ of the kinetic coefficients

are closely related to the dimensions of the corresponding equilibrium linear response coefficients: $[\tilde{K}^{\alpha\beta}] = [S^{\alpha\beta}] (\text{time})^{-1}$.

We now assume that under a sudden perturbation from equilibrium $X_0^\alpha \rightarrow X_0^\alpha + \Delta X^\alpha$, the subsystem remains homogeneous (no sound waves) and the relation between the extensive and intensive variables given in Eq. (1) remains valid. In this case we can write Eq. (2) as

$$\frac{d}{dt} S^{\alpha\gamma} \delta y_\gamma = \tilde{K}^{\alpha\beta} \delta y_\beta \quad (4)$$

Since this is a linear equation we can assume an exponential time dependence of the form $\delta y_\beta(t) = \delta y_\beta(0^+) e^{-\lambda t}$. This leads directly to a generalized eigenvalue equation

$$(\tilde{K}^{\alpha\beta} + \lambda S^{\alpha\beta}) \delta y_\beta(0^+) = 0 \quad (5)$$

The eigenvalues λ are nonnegative because $S^{\alpha\beta}$ is negative definite and $\tilde{K}^{\alpha\beta}$ is positive semi-definite. These are thermodynamic stability conditions.

The number of independent decay channels is the number of nonzero eigenvalues of this generalized eigenvalue equation. Equivalently, it is the number of nonzero eigenvalues of the matrix $\tilde{K}^{\alpha\beta}$. The number of vanishing eigenvalues is the number of independent constraints preventing decay.

The eigenvectors $\mathbf{v}_i$ with eigenvalues λ_i and components $v_{\alpha i}$ of this generalized eigenvalue equation are mutually orthogonal with respect to the metric $-S^{\alpha\beta}$ and can be normalized as follows:

$$\begin{aligned} v_{\alpha i} (-S^{\alpha\beta}) v_{\beta j} &= \delta_{ij} \\ v_{\alpha i} (+\tilde{K}^{\alpha\beta}) v_{\beta j} &= \lambda_i \delta_{ij} \end{aligned} \quad (6)$$

They evolve in time like $v_{\alpha i} e^{-\lambda_i t}$. The time evolution of the intensive displacements is given by

$$\delta y_\alpha(t) = \sum_{j=1}^n a_j v_{\alpha j} e^{-\lambda_j t} \quad (7)$$

The coefficients a_j are determined in the usual way - by matching initial conditions:

$$S_{\alpha\beta} \delta X^\beta(0^+) = \delta y_\alpha(0^+) = v_{\alpha j} a_j \quad (8)$$

and inverting this matrix relation.

Equation (5) shows how the relaxation time scales λ_i^{-1} are determined as functions of both the static and kinetic coefficients. Equation (8) describes how the initial conditions enter into the dynamics.

III. ENERGY REPRESENTATION

The entropy and more familiar energy representation are related by something like a similarity transformation. Specifically, the matrix transformation relating displacements of the independent extensive variables in the two representations (c.f., Table I) is

$$dE^\alpha = R^\alpha{}_\beta dX^\beta \quad \text{eg.} \quad \begin{bmatrix} dS \\ dV \\ dN \end{bmatrix} = \begin{bmatrix} \frac{1}{T} & \frac{P}{T} & -\frac{\mu}{T} \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} dU \\ dV \\ dN \end{bmatrix} \quad (9)$$

The intensive variables are related by $dy = -\frac{1}{T}R^t di$. In the energy representation the static and dynamic equations are

$$\begin{aligned} \delta E^\alpha &= U^{\alpha\beta} \delta i_\beta & U &= -\frac{1}{T} R S R^t \\ \frac{d}{dt} \delta E^\alpha &= K^{\alpha\beta} \delta i_\beta & K &= -\frac{1}{T} R \tilde{K} R^t \end{aligned} \quad (10)$$

The generalized eigenvalue equation in this representation is

$$(K^{\alpha\beta} + \lambda U^{\alpha\beta}) \delta i_\beta(0) = 0 \quad (11)$$

The more familiar linear response coefficients in the energy representation are $U^{\alpha\beta} = \left(\frac{\partial^2 U(E)}{\partial E^\alpha \partial E^\beta} \right)^{-1}$. This matrix is positive definite, since U is a minimum at equilibrium. Similarly, the kinetic coefficients K in this representation form a negative semidefinite matrix, by arguments similar to those surrounding Eq. (4).

Since U^{**} and K^{**} are related to S^{**} and $\tilde{K}^{**}$ by identical transformations, the eigenvalue spectrum is the same in both representations. This must be true on the basis of physical arguments. The eigenvectors differ by the transformations in Eq. (10) involving the nonsingular change of basis matrix $R^\alpha{}_\beta$.

IV. CONSTRAINTS

We illustrate what happens when constraints are placed on the system by considering a simple gas in a cylinder [2]. The generalized eigenvalue problem in the energy representation has the form

$$\left\{ \begin{bmatrix} -K^{11} & -K^{12} \\ -K^{21} & -K^{22} \end{bmatrix} + \lambda \begin{bmatrix} U^{11} & U^{12} \\ U^{21} & U^{22} \end{bmatrix} \right\} \begin{pmatrix} \Delta T(0) \\ -\Delta P(0) \end{pmatrix} = 0 \quad (12)$$

The standard linear response functions are

$$\begin{bmatrix} U^{11} & U^{12} \\ U^{21} & U^{22} \end{bmatrix} = \begin{bmatrix} C_P/T & V\alpha_P \\ V\alpha_P & V\beta_T \end{bmatrix} \quad (13)$$

and

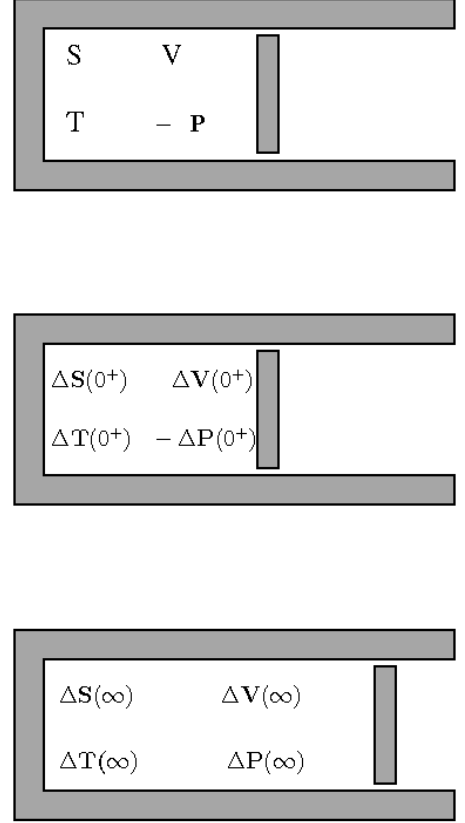


FIG. 1: The entropy is suddenly increased inside a cylinder that is thoroughly insulated ($K^{SS} = 0$). The temperature, pressure, and volume evolve in time as shown in Fig. 2.

$$\begin{bmatrix} U^{11} & U^{12} \\ U^{21} & U^{22} \end{bmatrix}^{-1} = \begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix} = \begin{bmatrix} T/C_V & 1/V\alpha_S \\ 1/V\alpha_S & 1/V\beta_S \end{bmatrix} \quad (14)$$

We have exhibited the negative signs explicitly for the negative semidefinite matrix of kinetic coefficients K , and we further take K to be diagonal. The matrix element $K^{11} = K^{SS}$ is measured in entropy flux per unit temperature increase and $K^{22} = K^{VV}$ defines the rate of volume change per unit decrease in pressure.

If the piston separating the gas in the cylinder from the reservoir is a good insulator (Fig. 1), $K^{11} = 0$, there is one constraint and one vanishing eigenvalue. The unnormalized eigenvector with $\lambda_1 = \lambda_S = 0$ is $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$. The second eigenvalue is $\lambda_2 = \lambda_V = K^{22}U_{22}$ and the corresponding unnormalized eigenvector is $\begin{pmatrix} -U^{12} \\ U^{11} \end{pmatrix}$. These two eigenvectors are orthogonal under the metric U^{**} .

The intensive variables evolve in time like

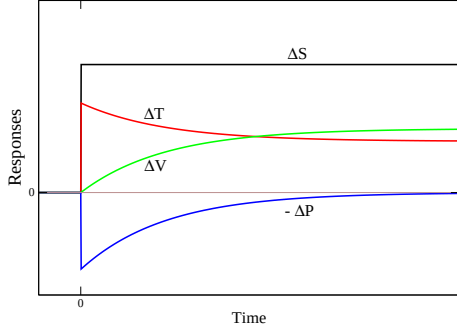


FIG. 2: Response of the perturbations to the experiment shown in Fig. 1. The single decay time scale is determined by $\lambda_2 = K^{22}U_{22}$.

$$\begin{bmatrix} \Delta T(t) \\ -\Delta P(t) \end{bmatrix} = a_1 e^{0t} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + a_2 e^{-\lambda_2 t} \begin{bmatrix} -U^{12} \\ U^{11} \end{bmatrix} \quad (15)$$

For this case $\Delta S(0^+) = \Delta S$, $\Delta V(0^+) = 0$ and Eq. (8) is explicitly

$$\begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix} \begin{bmatrix} \Delta S \\ 0 \end{bmatrix} = \begin{bmatrix} \Delta T(0^+) \\ -\Delta P(0^+) \end{bmatrix} = \begin{bmatrix} 1 & -U^{12} \\ 0 & U^{11} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \quad (16)$$

The coefficients are $a_1 = \Delta S/U^{11}$, $a_2 = \Delta S U_{21}/U^{11}$. The values of the two pairs of conjugate variables, under the no heat flow constraint $K^{11} = 0$, are given at $t = 0^+$ and $t \rightarrow \infty$ in Table II. The evolution of these perturbations is shown in Fig. 2. All variables except ΔS have the same characteristic decay time λ_V^{-1} , since there is only one decay channel.

The dual constraint is illustrated in Fig. 3. In this case the piston is suddenly displaced and maintained fixed at its new position. This constraint is represented by setting $K^{22} = 0$: the rate of volume change per negative unit pressure change is zero. In this case the zero eigenvalue is $\lambda_V = 0$ and the nonzero eigenvalue is $\lambda_S = K^{11}U_{11}$. The solution is computed as before, subject to initial conditions $\Delta V(0^+) = \Delta V$ fixed and $\Delta S(0^+) = 0$. The asymptotic behavior ($t = 0^+, t \rightarrow \infty$) is summarized in Table II. As for the case shown in Fig. 1, all variables except ΔV have the same characteristic decay time λ_S^{-1} , since there is only one decay channel. The time evolution of these four variables is similar to that shown in Fig. 2, with the exchange $(\Delta S, \Delta T) \leftrightarrow (\Delta V, -\Delta P)$. If the decay times are identical (λ_V in Fig. 1 and λ_S in Fig. 3) the two processes exhibit dynamical symmetry as well as the asymptotic symmetry described in the next section.

V. SYMMETRIES

It is possible to compare products of extensive variables with their conjugate intensive variables, since all

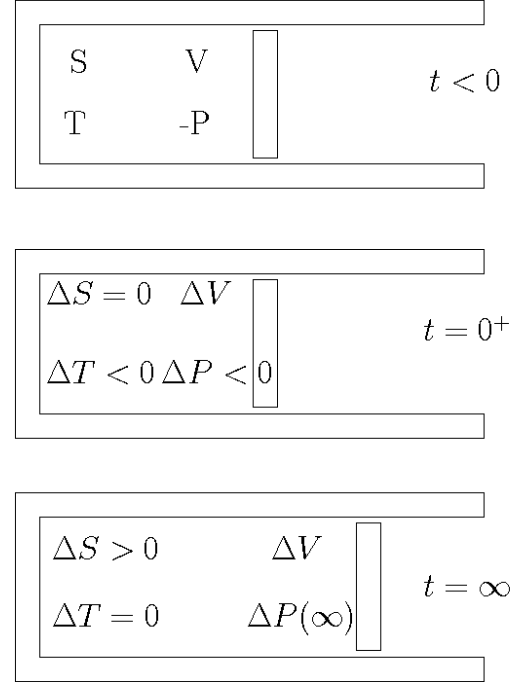


FIG. 3: The volume of a cylinder is suddenly increased and the piston is glued at its new position ($K^{VV} = 0$).

such products have the dimensions of energy. Table II shows that the only nontrivial product of the responding variables is $\Delta E^r(\infty)\Delta i_r(0^+)$. This can be compared with the “cross product” of the forcing variables $\Delta E^f(0^+)\Delta i_f(\infty)$. The result in the two cases above is

$$\frac{\Delta E^r(\infty)\Delta i_r(0^+)}{\Delta E^f(0^+)\Delta i_f(\infty)} = U^{fr}U_{fr} \quad (17)$$

This is true in general. The ratios of all such products are given by the elements of the LeChatelier matrix $L_{\alpha\beta} = U^{\alpha\beta}U_{\alpha\beta} = L_{\beta\alpha}$ [1, 2, 3]. This matrix is real and symmetric. Its diagonal matrix elements are greater than one [1, 2, 3, 7]. These are thermodynamic stability conditions. They provide quantitative expressions for LeChatelier’s Direct Principle. If an extensive forcing variable is suddenly changed and held constant, $\Delta i_f(0^+)/\Delta i_f(\infty) \geq 1$. Dually, if an intensive variable is suddenly changed and held constant, $\Delta E^f(\infty)/\Delta E^f(0^+) \geq 1$ [1, 2, 3]. Further, the sum of the matrix elements $L_{\alpha\beta}$ in each row and in each column is equal to 1. Finally, if the forcing and responding variables are interchanged, the cross ratios as given in Eq. (17) are equal, as seen in Table II.

Further symmetries are present for systems with two degrees of freedom. In such cases the constraint requires one of the two eigenvalues to vanish. The two systems have identical relaxation time scales provided the nonzero

TABLE II: Values of the thermodynamic variables under constraints for a gas in a cylinder.

Fig.1	Forcing Channel		Responding Channel	
	ΔS	ΔT	ΔV	$-\Delta P$
	$\lambda_S = 0$	—	$\lambda_V = K^{22}U_{22}$	—
$t = 0^+$	ΔS	$\Delta S \times U_{11}$	0	$\Delta S \times U_{21}$
$t \rightarrow \infty$	ΔS	$\Delta S/U^{11}$	$\Delta S \times U^{21}/U^{11}$	0

Fig.3	Responding Channel		Forcing Channel	
	ΔS	ΔT	ΔV	$-\Delta P$
	$\lambda_S = K^{11}U_{11}$	—	$\lambda_V = 0$	—
$t = 0^+$	0	$\Delta V \times U_{12}$	ΔV	$\Delta V \times U_{22}$
$t \rightarrow \infty$	$\Delta V \times U^{12}/U^{22}$	0	ΔV	$\Delta V/U^{22}$

eigenvalues are equal. The condition is that the nonzero kinetic coefficient K^{jj} multiplied by the corresponding covariant matrix element U_{jj} is the same for both experiments.

Finally, if the initial perturbations, ΔS in Fig. 1 and ΔV in Fig. 3, obey $(\Delta S)^2/U^{11} = (\Delta V)^2/U^{22}$, the time dependence of the internal energy, $U(t)$, is exactly the same for both experiments.

VI. CASCADING CONSTRAINTS

When there are multiple relaxation channels with widely differing time scales, the general solution that mixes the static and dynamic coefficients given in Eq. (5) simplifies. For specificity we consider a system with three degrees of freedom for which the matrix of kinetic coefficients is diagonal with $K^{11}/K^{22} \ll 1$ and $K^{22}/K^{33} \ll 1$. The equation determining the eigenvalues/eigenvectors of this problem is

$$\left\{ - \begin{bmatrix} K^{11} & 0 & 0 \\ 0 & K^{22} & 0 \\ 0 & 0 & K^{33} \end{bmatrix} - \lambda \begin{bmatrix} U^{11} & U^{12} & U^{13} \\ U^{21} & U^{22} & U^{23} \\ U^{31} & U^{32} & U^{33} \end{bmatrix} \right\} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} = 0 \quad (18)$$

The matrix of eigenvectors is upper triangular:

$$V = [v_{\alpha j}] = \begin{bmatrix} v_{11} & v_{12} & v_{13} \\ 0 & v_{22} & v_{23} \\ 0 & 0 & v_{33} \end{bmatrix} \quad (19)$$

The three eigenvalues satisfy

$$K^{jj} v_{jj}^2 = \lambda_j \mathbf{v}_j^t U^{**} \mathbf{v}_j = \lambda_j \sum_{\alpha, \beta=1}^j v_{\alpha j} U^{\alpha \beta} v_{\beta j} \quad (20)$$

to an excellent approximation. The components $v_{\alpha j}$ of the j th eigenvector $\mathbf{v}_j$ can be constructed directly from the $j \times (j-1)$ submatrix in the upper left-hand corner of the matrix U^{**} of susceptibilities. The component $v_{\alpha j}$ is the minor of this submatrix obtained by removing row α . The three eigenvectors of Eq. (19) are, to a very good approximation

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \begin{bmatrix} -U^{21} \\ U^{11} \\ 0 \end{bmatrix} \quad \begin{bmatrix} +(U^{21}U^{32} - U^{31}U^{22}) \\ -(U^{11}U^{32} - U^{31}U^{12}) \\ +(U^{11}U^{22} - U^{21}U^{12}) \end{bmatrix} \quad (21)$$

The eigenvalues are easily determined from these eigenvectors

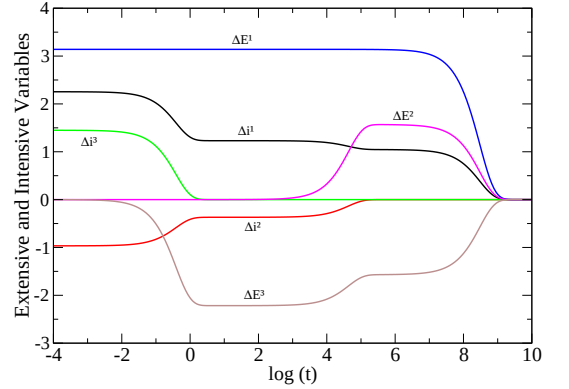


FIG. 4: Response of all thermodynamic variables when three channels have widely separated time scales and the slowest extensive variable is perturbed.

In Fig. 4 we illustrate the dynamics when there are three channels with widely separated relaxation time scales $T_3 \simeq 10^0$, $T_2 \simeq 10^4$ and $T_1 \simeq 10^8$, with $T_j = 1/\lambda_j$. In this figure the extensive variable with the longest relaxation time, E^1 , is initially perturbed. Immediately following the perturbation all three intensive variables assume nonzero values while the remaining two extensive variables remain zero.

As t passes through the shortest time scale, $T_3 \simeq 10^0$, all three intensive variables relax to new values; the force with the shortest time scale, Δi_3 , drops to zero. Its conjugate extensive variable ΔE^3 , rises to a nonzero value. Although Δi_1 and Δi_2 relax to new values, ΔE^1 and ΔE^2 remain unchanged at the initial value and zero, respectively. As t passes through the intermediate time scale T_2 , the force Δi_2 drops to zero and its conjugate extensive variable, ΔE^2 , becomes nonzero. The extensive variable ΔE^3 with the shorter time scale relaxes to a new value while the extensive variable ΔE^1 with the longer time scale continues to remain unchanged. Finally, as (if) t exceeds the longest time scale T_1 the corresponding force Δi_1 also drops to zero. At this point, all perturbations have relaxed to zero when no eigenvalues of the generalized eigenvalue equation are zero.

The succession of steps is summarized in Table III. This table also includes cases for which the extensive variables E^2 with intermediate time scale, and E^3 with shortest time scale are initially perturbed.

Throughout this relaxation process the linear relation Eq. (1) between extensive and intensive thermodynamic variables is maintained. In the quiet regimes between time scales $T_{j+1} \ll t \ll T_j$ the three thermodynamic variables (labeled with *) can be determined from the three that are given explicitly in Table III by simple matrix methods previously introduced to simplify the computation of thermodynamic partial derivatives [5, 6].

When “faster” extensive thermodynamic variables are initially perturbed the relaxation takes place faster, as shown in Table 3. This comes about because the faster variables do not have sufficient time to feed into the slower extensive variables before they relax to zero.

VII. CONCLUSIONS

The dynamical aspects of LeChatelier’s Principle are described by the generalized eigenvalue equation Eq. (5) in the linear response regime. The number of closed and open relaxation channels is determined by the number of zero and nonzero eigenvalues of the matrix of kinetic coefficients. The nonzero eigenvalues are complicated functions of the matrices of static and dynamic (kinetic) coefficients determined through the generalized eigenvalue equation. These equations were constructed in both the entropy (Eq. (5)) and energy (Eq. (11)) representations. There is, as usual, a clean separation of the dynamics into the equations of motion and the initial conditions (Eq. 8).

When there is a single relaxation channel there is only one decay time scale. Under such conditions the LeChatelier symmetries are exhibited [1, 2, 3]. These symmetries relate products of conjugate variables in the asymptotic limits $t = 0^+$ and $t \rightarrow \infty$. If the nonzero kinetic coefficients are properly adjusted, so that the responding time scales in dual experiments are equal, there is also a dynamical symmetry.

When two or more relaxation channels exist and are well-separated in time, the successive relaxations through each of the widely separated time scales can be treated as if each was a single channel relaxation with a single time scale. In such cases the asymptotic and even the dynamical symmetries exist on each side of the newly-opened relaxation channel, as shown in Fig. 4 and Table III.

Acknowledgment: It is a pleasure to acknowledge the inspiration afforded by Prof. R. D. Levine for this problem.

TABLE III: Succession of steps as t increases when $\lambda_1 \ll \lambda_2 \ll \lambda_3$ or $T_3 \ll T_2 \ll T_1$ and the initial perturbation is in the extensive variable corresponding to the longest (top), intermediate (middle) and shortest (bottom) time scale. Each matrix contains three pairs of extensive and conjugate intensive variables ($\Delta E^\alpha, \Delta i_\alpha$), ordered by relaxation time scale from slowest (top) to fastest (bottom).

$t = 0^+ \ll T_3$	$\ll t \ll T_2$	$\ll t \ll T_1$	$\ll t$
$\begin{bmatrix} \Delta E^1, * \\ 0, * \\ 0, * \end{bmatrix}$	$\begin{bmatrix} \Delta E^1, * \\ 0, * \\ *, 0 \end{bmatrix}$	$\begin{bmatrix} \Delta E^1, * \\ *, 0 \\ *, 0 \end{bmatrix}$	$\begin{bmatrix} 0, 0 \\ 0, 0 \\ 0, 0 \end{bmatrix}$
$\begin{bmatrix} 0, * \\ \Delta E^2, * \\ 0, * \end{bmatrix}$	$\begin{bmatrix} 0, * \\ \Delta E^2, * \\ *, 0 \end{bmatrix}$	$\begin{bmatrix} 0, 0 \\ 0, 0 \\ 0, 0 \end{bmatrix}$	
$\begin{bmatrix} 0, * \\ 0, * \\ \Delta E^3, * \end{bmatrix}$	$\begin{bmatrix} 0, 0 \\ 0, 0 \\ 0, 0 \end{bmatrix}$		

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