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Le Chatelier's principle with multiple relaxation channels

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Le Chatelier's principle is discussed within the constrained variational approach to thermodynamics. The formulation is general enough to encompass systems not in thermal (or chemical) equilibrium. Particular attention is given to systems with multiple constraints which can be relaxed. The moderation of the initial perturbation increases as additional constraints are removed. This result is studied in particular when the (coupled) relaxation channels have widely different time scales. A series of inequalities is derived which describes the successive moderation as each successive relaxation channel opens up. These inequalities are interpreted within the metric-geometry representation of thermodynamics.

I. INTRODUCTION

Le Chatelier's principle[1,2] comes close to making statements about the dynamics of thermodynamic processes without actually doing so.[3] Here we discuss the principle as determining an orbit[4] in the thermodynamic state space but not the actual trajectory of the system. We consider a system whose state is specified by a number of extensive variables (the "constraints" of the variational formulation[5,6]). The state is then perturbed and the system is allowed to relax. This description includes the familiar case when both the initial and final, relaxed, states of the system are those of thermodynamic equilibrium. Both the principle and our results apply, however, to a wider class of situations. Explicitly, the discussion below is valid whenever the state of the system is one of "constrained equilibrium." If the constraints are the usual additive constants of the motion we have the familiar equilibrium situation.[6] There may well, however, be additional constraints. It is easiest to think of those as effective constants of motion on a shorter time scale. For example, a gas of diatomic molecules will equilibrate the translational degrees of freedom some 4–5 orders of magnitude faster than the vibrational relaxation. Chemical relaxation will be even slower. It is therefore sensible to think of separation of time scales where some constraints have already fully relaxed while others have not yet departed from their initial value. Sometimes the successive relaxations can even be controlled from the outside, e.g., in making chemical relaxation proceed at a measurable rate by the introduction of a catalyst.

In the interpretation of the Le Chatelier principle it is assumed that the initial perturbation is imposed over a time scale which is far shorter than that for response of the system.[7,8] It is through this assumption that the principle appears to make statements about the dynamics of the response, without actually doing so: the principle serves only to establish the direction in which time's arrow points. When the system response to perturbation occurs on several separated time scales, a number of intermediate Le Chatelier ratios[8] can be constructed. As time unfolds and new relaxation channels open, the response of the system produces an *increased* moderation of the initial perturbation. The ratio of the system's response before and after each successive relaxation mechanism opens is always larger (less) than one for an initial perturbation of an extensive (intensive) variable.

One purpose of this paper is to demonstrate the enhanced moderation for systems with multiple coupled relaxation channels. This is particularly noteworthy for systems not initially in thermal and/or chemical equilibrium. The additional relaxation processes in such systems necessarily act so as to augment the moderation of an initial perturbation. Another purpose is more methodological in nature. It is to derive and discuss the principle within the framework of the constrained variational approach. The result is then the statement that the "potential" function whose unconstrained variation determines the state of the system[9,10] is everywhere convex.[10,11] To make the presentation as elementary as possible we shall, however, restrict the derivation to the linear-response regime where it is sufficient to retain terms only up to quadratic in the Taylor-series expansion of the potential. It is important, however, to stress that the conclusions remain valid also in the general case.

The Le Chatelier principle is a statement about the orbit, i.e., the direction along which the system will evolve. If the initial and final states of the system are those of complete equilibrium then we all agree on the constraints that are to be imposed. In the more general case it is always possible that a relevant constraint has been inadvertently omitted. It is essential therefore to point out that our derivation will show that the direction of the moderation is correctly given even if not all relevant constraints have been included. Explicitly, the ratio of the system response before and after the relaxation is larger (or less) than one even if some relaxation channels have been left out of consideration. The direction of the response is independent of the specific choice of relaxation channels (or, equivalently, of the constraints). In Sec. III below we shall, in fact, prove even a stronger version of this result, namely that the computed response ratio is always a bound on the observed one.

The paper presents a derivation of the orbit (Sec. II), a discussion of the sequence of inequalities for the extent of moderation (Sec. III), and two very simple examples (Sec. IV) followed by a summary of the main points (Sec. V). An appendix provides a discussion of the principle within the framework of metric geometry.[12,13] A key point is that the sequence of inequalities for the moderation can be cast as a Bessel inequality.

II. CONSTRAINED VARIATION WITH MULTIPLE TIME SCALES

We assume that the state of the system is described by n variables. The constrained variation (see below) will associate with each a conjugate variable (which one can think of as a Lagrange multiplier). Hence after the variation (i.e., in the state of constrained equilibrium) the system is described by n pairs of conjugate variables which we denote $(i_1,E^1),(i_2,E^2),\ldots,(i_n,E^n)$. For a macroscopic system $i_\alpha(E^\alpha)$ denotes an intensive (extensive) variable. Nowhere in the derivation do we assume, however, that the number n is the minimal number as required at complete thermal and chemical equilibrium. We shall, however, make one assumption, namely that different variables are associated with quite different relaxation times. This will enable us to readily derive Le Chatelier ratios at intermediate times and to demonstrate their increasing magnitude. As will become clear, our primary conclusion, namely, that additional relaxation pathways necessarily imply an increased moderation, is independent of the separation in time scales.

The constrained equilibrium state of the system is determined by maximizing the constrained entropy[9] or minimizing the constrained energy:[7,8]

$$\mathscr{S}=S(E^1,\ldots,E^n)-\sum_{\alpha=1}^{n}\lambda_\alpha E^\alpha\ , \tag{1a}$$

$$\mathscr{U}=U(E^1,\ldots,E^n)-\sum_{\alpha=1}^{n}i_\alpha E^\alpha\ . \tag{1b}$$

The conjugate variables λ_α (i_α) are determined at the stationary point of $\mathscr{S}$ ($\mathscr{U}$). Thus

$$\lambda_\alpha=(\partial S/\partial E^\alpha)_E\ , \tag{2a}$$

$$i_\alpha=(\partial U/\partial E^\alpha)_E\ . \tag{2b}$$

At complete equilibrium, Eqs. (2) are familiar results.

Displacements in the state of the system (e.g., changes in the E^α's) lead to changes in $\mathscr{S}$ or $\mathscr{U}$. To lowest order the change is given by

$$\delta\mathscr{S}\rightarrow\tfrac{1}{2}\sum_{\alpha,\beta=1}^{n}S_{\alpha\beta}\delta E^\alpha\delta E^\beta\ , \tag{3a}$$

$$\delta\mathscr{U}\rightarrow\tfrac{1}{2}\sum_{\alpha,\beta=1}^{n}U_{\alpha\beta}\delta E^\alpha\delta E^\beta\ . \tag{3b}$$

$S_{\alpha\beta}=\partial^2S/\partial E^\alpha\partial E^\beta$ is negative definite while $U_{\alpha\beta}=\partial^2U/\partial E^\alpha\partial E^\beta$ is positive definite[14] so that the extremum in (1) is a true maximum (minimum).

The displacement of state will also lead to new values for the conjugate variables. To lowest order, changes in the E^α's result in linear changes in their conjugates

$$\delta\lambda_\alpha=\sum_{\beta=1}^{n}S_{\alpha\beta}\delta E^\beta\ , \tag{4a}$$

$$\delta i_\alpha=\sum_{\beta=1}^{n}U_{\alpha\beta}\delta E^\beta\ . \tag{4b}$$

It is always possible that the set of n (extensive) variables does not suffice to fully specify the state of the system. Under such circumstances, we adopt the following interpretation[8] of (4). Say at time $t=0$ the state of the system is perturbed by the (small) change $E^\alpha\rightarrow E^\alpha+\delta E^\alpha$, $\alpha=1,\ldots,n$. Internal relaxation processes will then bring the system to a new state of constrained equilibrium. In that new state the changes in the conjugate variables have the magnitudes given by (4). We take the time required for the system to reach a state of constrained equilibrium consistent with the given values of the E^α's to be fast on our scale or, in other words, to be instantaneous. At every point in our time scale the system is therefore in a state of equilibrium constrained by the given values of the E^α's at that time.[9,15]

The system's orbit can now be determined as follows. We take as the perturbation the displacement of the extensive variable E^n to a new value $E^n\rightarrow E^n+\Delta E^n$ and E^n is then held fixed for all later times. As a result of this displacement the system "climbs up the side" of the energy paraboloid [given by (3b) and shown also in Fig. 1]. As each successive relaxation channel opens, the system slides lower down on the paraboloid until all channels have opened. In the entropy representation the description would simply be "inverted" since $S_{\alpha\beta}$ is negative definite. Upon perturbation, the system slides down the entropy paraboloid and each successive relaxation process brings it further up.

We assume that the time scale for the relaxation of the jth constraint is τ_j and that $\tau_1\ll\tau_2\ll\tau_3\ll\cdots\ll\tau_{n-1}\ll\tau_n\rightarrow\infty$, the last limit resulting from the condition that E^n is held fixed.

To determine the state of the system at time $\tau_l<t_l<\tau_{l+1}$ after the lth relaxation channel has opened up, the potential (3b) is minimized with respect to the δE^i's, $i=1,2,\ldots,l$ subject to the remaining $n-l$ constraints being unchanged in value, $\delta E^j=0$, $j=l+1,\ldots,n-1$, and $\delta E^n=\Delta E^n$:

$$\delta\left[\sum_{i,k=1}^{l}U_{ik}\delta E^i\delta E^k+2\sum_{i=1}^{l}U_{in}\delta E^i\Delta E^n+U_{nn}\Delta E^n\Delta E^n\right]=0\ . \tag{5}$$

The solution is

$$\Delta E^i(l)=-\sum_{k=1}^{l}[\mathbf{U}^{-1}(l)]^{ik}U_{kn}\Delta E^n\ . \tag{6}$$

where $\mathbf{U}(l)$ is the $l\times l$ square submatrix of $U_{\alpha\beta}$ consisting of the first l rows and columns and $\mathbf{U}^{-1}(l)$ is its inverse. By construction, (6) holds for $i\leq l$ while $\Delta E^j=0$ for $l<j\leq n-1$, and the same solution obtains for all possible l values, $l=1,\ldots,n-1$. The only difference is the order l of the inverse matrix $\mathbf{U}^{-1}(l)$ in (6) and hence the range of summation. To emphasize the dependence on l the summation convention is not used.

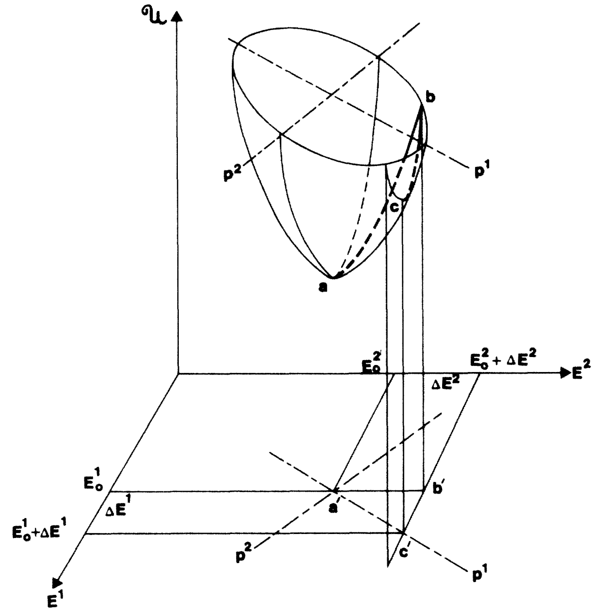

FIG. 1. Le Chatelier's principle is illustrated as a process of sliding down the side of a potential from an initial perturbed state b to a new constrained minimum c. The energy surface is shown as a two-dimensional paraboloid [cf. Eq. (3b)] in three-dimensional space with principal axes p^1, p^2 not parallel to the coordinate axes E^1, E^2. The initial equilibrium at state a is perturbed by changing E_0^2 to $E_0^2+\Delta E^2$, and keeping ΔE^2 fixed. The new restricted energy surface is now a one-dimensional parabola in the two-dimensional plane $E^2=\text{const}=E_0^2+\Delta E^2$. The initial perturbed state at point b sits on the side of the paraboloid; it will slide down the side of the paraboloid along the parabola in the plane $E^2=E_0^2+\Delta E^2$ until it reaches the minimum of the parabola. The projection of the perturbation $(a\to b)$ and response $(b\to c)$ orbit onto the plane of the independent extensive variables is the path $a'\to b'\to c'$. In the linear-response regime the segments $a'b'$, $b'c'$, and $a'c'$ are straight lines and $a'b'c'$ a right triangle.

III. MODERATION

The response of the intensive variable i_n which is conjugate to E^n is given, at the time t_l, $\tau_l < t_l < \tau_{l+1}$, in the linear regime by

$$\Delta i_n(l) = \left[U_{nn} - \sum_{i,k=1}^{l} U_{ni}[\mathbf{U}^{-1}(l)]^{ik} U_{kn} \right] \Delta E^n , \quad (7)$$

where we used (6) in (4b).

We now argue that moderation can only be enhanced upon opening of new relaxation channels or

$$\Delta i_n(0) \geq \Delta i_n(1) \geq \Delta i_n(2) \geq \cdots \geq \Delta i_n(n-1) . \quad (8)$$

In other words, all the Le Chatelier ratios satisfy $\Delta i_n(l)/\Delta i_n(l+1) \geq 1$. Here $\Delta i_n(0)$ is the initial response to the perturbation before any relaxation channel is open.

That the response is diminished for later times, Eq. (8), follows directly from the inequality

$$U_{nn} - \sum_{i,j=1}^{l} U_{ni}[\mathbf{U}^{-1}(l)]^{ik} U_{kn} \geq U_{nn} - \sum_{i,j=1}^{l'} U_{ni}[\mathbf{U}^{-1}(l')]^{ik} U_{kn} \quad \text{for } l < l' \quad (9)$$

which holds for positive-definite matrices $U_{\alpha\beta}$. While the result (9) is not new it is of interest to prove it within a metric geometry framework for it then provides new insights. We do so in the Appendix.

The physical intuitive interpretation of the mathematical inequality (9) is that the relaxation of each successive constraint ($\delta E^l = 0 \to \delta E^l \neq 0$) can only serve to lower the energy (increase the entropy) of the system.

The linear-response relation (4) together with (6) can be used to show that

$$\delta i_k = 0, \quad k = 1, 2, \ldots, l \quad (10)$$

for times t_l, $\tau_l < t_l < \tau_{l+1}$. Indeed, this condition can be used instead of the constraints imposed on (5) to derive (6) using (4) and (10).

The linear-response analysis can equally well be carried out for the complementary problem where the response of the extensive variables is being considered.[7,8,16] For example, if the intensive variable i_n is at time zero displaced to $i_n + \Delta i_n$ and then maintained constant for all later times, we find

$$\Delta E^n(0) \leq \Delta E^n(1) \leq \cdots \leq \Delta E^n(n-1) . \quad (11)$$

Note that the sense of the inequalities is opposite to that of (8).

Several relaxation time scales may, in a specific problem, be comparable. In such a case these relaxation channels must be treated simultaneously rather than successively. Under such conditions the appropriate intermediate inequalities are missing in (8). The extreme case is the familiar discussion of Le Chatelier's principle where all intermediate steps are missing and one concludes that $\Delta i^n(0)/\Delta i^n(n-1) \geq 1$. This observation also provides proof that the Le Chatelier ratio is given correctly even if some relevant intermediate constraint has been (inadvertently or intentionally) left out. One does not need to know the specific relaxation channels which opened up between $t=0$ and $t=t_l \geq \tau_l$ to conclude that $\Delta i^n(0)/\Delta i^n(l) \geq 1$. The *direction* of the change is irrespective of the mechanism.

It is, in fact, possible to formulate this result in stronger terms. If all of the relevant relaxation channels have not been included, the *observed* ratio of the initial response to the final response, $\Delta i(0)/\Delta i(l)$, may exceed, but can never be less than, that *computed* on the basis of an inadequate number of relaxation mechanisms. In the case of extensive variables responding to perturbation of an intensive parameter, the observed response ratio $\Delta E(0)/\Delta E(l)$ may be less than or equal to but never exceed the ratio computed on the basis of an inadequate number of relaxation channels. This discrepancy in response ratios can be used, in the sense of surprisal analysis,[10] to identify additional relaxation channels.

IV. EXAMPLES

In this section we discuss two examples to illustrate the Le Chatelier inequalities (8) and (11).

Example 1. We consider a thermally insulated hot air balloon in an isothermal atmosphere in thermodynamic equilibrium. Its state may be described by three independent thermodynamic variables from the three pairs of thermodynamic variables $(P,V),(F,Z),(T,S)$, where Z is the height of the balloon above ground level and F is the buoyancy force acting on it. For this system the metric matrix $U_{\alpha\beta}$ is

$$U_{\alpha\beta}\rightarrow\begin{bmatrix} U_{VV} & U_{VZ} & U_{VS} \\ U_{ZV} & U_{ZZ} & 0 \\ U_{SV} & 0 & U_{SS} \end{bmatrix} . \tag{12}$$

These matrix elements are related to standard linear-response coefficients; for example, $U_{SS}=T/C_{VZ}$. The matrix element U_{ZS} is negligible, since changing the entropy at constant volume has no effect on the buoyancy force.

Assume that heat ΔS is added to the air in the balloon. The initial temperature change is

$$\Delta T(0)=U_{SS}\Delta S . \tag{13a}$$

After a time $t\sim\tau(=\tau_P)$ the pressure difference between the air inside and outside the balloon causes the balloon to expand adiabatically. The temperature response is

$$\Delta T(1)=\left[U_{SS}-\frac{U_{VS}^2}{U_{VV}}\right]\Delta S . \tag{13b}$$

The expansion is assumed to have occurred on a time scale fast in comparison to the response to buoyancy forces: $\tau_1\ll\tau_2=\tau_F$. Since the balloon has expanded, buoyancy forces will drive it higher, and it will continue to rise until the buoyancy forces have vanished. The response $\Delta T(2)$ is

$$\Delta T(2)=\left[U_{SS}-\frac{U_{SV}^2}{U_{VV}-U_{VZ}^2/U_{ZZ}}\right]\Delta S . \tag{13c}$$

Thus even though there is no direct coupling between the entropy perturbation and buoyancy response mode, the indirect coupling through the (P,V) mode causes a further moderation in the response to the perturbation: $\Delta T(0)>\Delta T(1)>\Delta T(2)$.

Example 2. We consider the hot air balloon as described above. However, we now assume the temperature is raised by an amount ΔT and is maintained at the fixed new temperature for all later times. The temperature is raised initially by the addition of an amount of heat $\Delta S(0)$ to the air within the balloon during a time interval short in comparison with the time required for the balloon to expand. As the balloon expands, additional heat must be added to the air within the balloon in order to maintain a constant temperature. At the end of the expansion stage the total heat added is $\Delta S(1)$, where $\Delta S(1)>\Delta S(0)$. Finally, the enlarged balloon begins to ascend, experiencing a drop in atmospheric pressure as it does so. The drop in pressure will cause an additional increase in the volume of the balloon. In order to maintain a constant temperature during this additional enlargement, yet more heat must be supplied. As a result, the total heat added to the balloon after the new equilibrium height has been reached, $\Delta S(2)$, is larger than the total heat added after the expansion phase has been completed at constant altitude. The final set of inequalities

$$\Delta S(0)<\Delta S(1)<\Delta S(2) \tag{14}$$

is a particular case of the general result (11).

V. CONCLUDING REMARKS

This paper discussed the orbit of the system as consecutive relaxation channels open up. In the linear regime, as shown in Fig. 1, the orbit between any two successive relaxations is a straight line. The entire orbit in the system state space consists of $n-1$ connected straight line segments. The only modification in the nonlinear regime is that the orbit is a series of connected arcs. It is still determined by the constrained variational conditions (1), subject to the same set of constraints as used in (5). The inequalities (8) or (11) remain valid.

The orbit establishes the direction of the response of the system. It can be constructed for the general case when the system is in a state of constrained equilibrium. The evolution of the system is through a succession of such states where each consecutive state is not only of higher entropy (lower energy) but also more moderated. This is very evident in (7). The initial response $\Delta i_n(0)=U_{nn}\Delta E^n$ is in the direction of the displacement and is of the same sign. The relaxation channels act so as to oppose [second term in (7) which, using (9), is positive] this initial response. The more channels open up the more extensive is the moderation. That the discussion is not limited to systems in complete equilibrium is, in retrospect, not surprising. The direction of the response is independent of whichever relaxation channels are explicitly recognized.

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APPENDIX

In this appendix we prove the inequalities (9) for a positive-definite quadratic form using the Bessel inequality. We also point out how the proof is equivalent to minimizing the quadratic potential function subject to constraints.

Let $v_1, v_2, \ldots, v_n$ be a system of nonorthogonal basis vectors which span a linear vector space with positive-definite inner product: $(v_i, v_j) = U_{ij}$. The Bessel inequality for an arbitrary vector w in this space may be written

$$\min \left|\left| w - \sum_{i=1}^{k} x^i v_j \right|\right|^2 \geq \min \left|\left| w - \sum_{j=1}^{l} y^j v_j \right|\right|^2, \quad k \leq l \; . \tag{A1}$$

This inequality is valid because if the coefficient values x_0^i $(i = 1, 2, \ldots, k)$ minimize the norm on the left, the choice of coefficients $y^i = x_0^i$ $(i = 1, 2, \ldots, k)$, $y^j = 0$ $(j = k+1, \ldots, l)$ produces a norm with the same value but does not necessarily minimize the norm on the right-hand side of (A1). The square of the norm is easily minimized,

$$\delta \left[(w,w) - 2 \sum_{j=1}^{k} x^j (v_j, w) + \sum_{i,j=1}^{k} x^i x^j (v_i, v_j) \right] = 0 \; , \tag{A2}$$

$$x_0^j = - \sum_{i=1}^{k} [\mathbf{U}^{-1}(k)]^{ji} (v_i, w) \; . \tag{A3}$$

The minimum value of the square of the norm is

$$\min \left|\left| w - \sum_{i=1}^{k} x^i v_i \right|\right|^2 = (w,w) - \sum_{i,j=1}^{k} (w, v_i) [\mathbf{U}^{-1}(k)]^{ij} (v_j, w) \; . \tag{A4}$$

Now by choosing $w = v_n$ we obtain from (A1)

$$U_{nn} - \sum_{i,j=1}^{k} U_{ni} [\mathbf{U}(k)^{-1}]^{ij} U_{jn} \geq U_{nn} - \sum_{i,j=1}^{l} U_{ni} [\mathbf{U}(l)^{-1}]^{ij} U_{jn}, \quad k \leq l \; . \tag{A5}$$

Minimizing the inner product $||v_n - \sum_{i=1}^{j} x^i v_i||^2$ is equivalent to minimizing the quadratic form (3) subject to the constraints $\delta E^\alpha = 0$, $\alpha = j+1, \ldots, n-1$, as can be seen by writing out both quadratic forms. Each additional vector which is used to approximate $w = v_n$ in norm [cf. (A2)] reduces the length of the linear combination; each additional degree of freedom which is opened allows the potential $\mathscr{U}$ to decrease in value [cf. (5)].

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[4]By an orbit we mean specifying the variables of the state of the system in terms of a progress parameter. For a trajectory the parameter is time.

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