# THE CONSTRAINED-EQUILIBRIUM APPROACH TO NONEQUILIBRIUM DYNAMICS

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## ABSTRACT

We review the constrained-equilibrium method for the description of the time-dependent behavior of dynamical systems in nonequilibrium states. The method is presented in a general mathematical framework that is relevant not only to thermodynamics and chemical kinetics, but also to economics, control theory and other sciences. We emphasize that a successful application of the method requires a deep understanding of the internal mechanisms governing the system dynamics and, in particular, their time scales and time invariants.

## INTRODUCTION

In thermodynamics, gas dynamics, chemical kinetics, control theory, information theory, economics and other sciences it is often necessary to determine the nonequilibrium time-dependent behavior of the state of a system for which the description of the equilibrium states is known and given by the solution of a constrained maximization problem. The conventional method of doing this consists of developing a fully detailed model of the nonequilibrium system, obtaining a full set of rate equations for all the state variables, and integrating this set of equations to yield the time-dependent behavior of the nonequilibrium state. This method can involve formidable modeling and computational tasks for it requires modeling of all the detailed mechanisms governing the dynamics of the system and it may require integration of a large number of possibly "stiff" differential equations.

An alternative method is particularly effective when it is possible to ascertain that the dynamics of the system is rate-controlled by a small number of "slow" mechanisms whereas the other mechanisms are all much faster than the time-scale of interest. The method, known as the "constrained equilibrium" method, consists of modeling the details of the slow rate-controlling mechanisms only, and assuming that all the other mechanisms are so fast that on the time-scale of interest, the system goes to equilibrium with respect to them in practically no time. This method can significantly reduce the modeling and computational efforts. It requires integration of the rate-controlling differential equations only, and the solution of a constrained maximization problem at each time step. However, it also requires a deeper understanding of the detailed dynamics of the system so as to be able to identify and model the rate-controlling mechanisms.

A familiar example of the constrained-equilibrium approach to the description of nonequilibrium dynamics is provided by the basic equations of fluid dynamics where the state of the fluid is assumed to be locally a state of thermodynamic equilibrium, therefore, with local temperature and pressure. This implies that the local internal equilibration mechanisms of the fluid are all much faster than the disequilibrating effects of the transport mechanisms and, indeed, the assumption breaks down if the transport mechanisms become extremely fast as, for example, across a shock wave.

In reacting gas dynamics, the constrained-equilibrium method has been applied successfully for the description and simplification of many specific nonequilibrium problems. Sugden and co-workers [1], Kaskan [2], Schott [3], and Franciscus and Lezberg [4] treated the hydrogen-oxygen combustion problem. Bray [5] developed the "sudden freezing" approximation for rapidly expanding nozzle flows. Keck and Gillespie [6] developed a general rate-controlled constrained-equilibrium method for reacting gas mixtures. Delichatsios and Keck [7], Sarofim and co-workers [8], and Morr and Heywood [9] applied the method to predict carbon monoxide and nitric oxide formation in hydrocarbon combustion. Galant and Appleton [10] further developed the method for open reacting systems. Levine [11] treated reactions in molecular beams. Ross [12] investigated the stability in highly nonequilibrium systems. Kerner [13] studied speciation in ecological systems.

We have not studied the literature in economics, control theory and other sciences, but we suspect that the same ideas have been applied in many specific applications. For example, Dornbush [14] developed a theory of exchange rate overshooting due to a changing monetary policy based on the notion that asset market prices including exchange rates adjust to the new equilibrium in practically no time whereas market prices of goods are "sticky", adjust in finite time and thus rate-control the relaxation of the system towards the new equilibrium state.

In this paper, we first review the general mathematical structure of the problem of describing the time evolution of nonequilibrium states and then we discuss the general ideas behind the constrained-equilibrium method.

## GENERAL NONEQUILIBRIUM PROBLEM

Let us denote by $\underline{x} = \{x_1,x_2,\dots,x_k,\dots\}$ the vector of variables describing the state of the system under study, and let us assume that the dynamics of the system is described by a rate equation of the form

$$\dot{\underline{x}} = \underline{D}(\underline{x}) + \underline{E}(\underline{x},t) \tag{1}$$

where $\underline{D}(\underline{x})$ represents the internal or endogenous dynamical mechanisms and $\underline{E}(\underline{x},t)$ the external or exogenous mechanisms. For example, if the system is a cell in a reacting fluid flow, the endogenous mechanisms are those responsible for the spontaneous relaxation towards a local equilibrium state whereas the exogenous mechanisms are those accounting for the transport of energy, momentum and matter across the boundaries of the cell.

The equilibrium states of the system are those that would not be changing in time if the system were isolated, i.e., if $\underline{E}(\underline{x},t) = 0$. Thus, a state $\underline{x}_{eq}$ is equilibrium if

$$\underline{D}(\underline{x}_{eq}) = 0 \tag{2}$$

In general, Equation 2 admits more than one solution, namely, the system admits more than one equilibrium state. For example, the second law of thermodynamics requires that a physical system has at least one equilibrium state for each of the possible values of the energy [15].

For many systems of practical interest, in particular, those of interest in thermodynamics and chemical kinetics, the internal dynamics of the system admits one or more nontrivial time-invariant functionals

$$C_i(\underline{x}) \tag{3}$$

namely, functionals such that

$$\underline{c}_i(\underline{x}) \cdot \underline{D}(\underline{x}) = 0 \tag{4}$$

for every state $\underline{x}$, where we defined the gradient vectors

$$\underline{c}_i(\underline{x}) = \frac{\partial C_i(\underline{x})}{\partial \underline{x}} \tag{5}$$

The functionals $C_i(\underline{x})$ are said to represent the constants of the motion of the system. For example, energy and the number of atomic nuclei of each type are constants of the motion for a chemically reacting system.

A particular class of trivial constants of the motion are functionals $B_k(\underline{x})$ such that $B_k(\underline{x}) = \beta_k$ for all the states $\underline{x}$ of the system, where $\beta_k$ are constants. These functionals generally specify restrictions on the geometry of the state space. For example, if the state variables $x_i$ represent probabilities then a geometrical constraint is $B_1(\underline{x}) = \sum_i x_i$ with $\beta_1 = 1$.

For a given state $\underline{x}$, it is interesting to identify a complete set of nontrivial constants of the motion $C_i(x)$ with linearly independent gradient vectors $\underline{c}_i(\underline{x})$ so that any other constant of the motion has a gradient vector which is a linear combination of the vectors $\underline{c}_i(\underline{x})$. If the state is an equilibrium state, then we see that Equations 2 and 4 yield

$$\underline{c}_i(\underline{x}_{eq}) \cdot \underline{D}(\underline{x}_{eq}) = 0 \qquad i = 1,\dots,r \tag{6}$$

implying that the equations in the set generated by Equation 2 are not all linearly independent and the solution depends on at least r arbitrary parameters. In other words, the equilibrium states form at least an r-parameter family.

For many systems of practical interest, there is a state functional

$$F(\underline{x}) \tag{7}$$

that is nondecreasing under the internal dynamics of the system, i.e., is such that

$$\underline{f}(\underline{x}) \cdot \underline{D}(\underline{x}) \geq 0 \tag{8}$$

for every $\underline{x}$, where we defined the gradient vector

$$\underline{f}(\underline{x}) = \frac{\partial F(\underline{x})}{\partial \underline{x}} \tag{9}$$

In thermodynamics and chemical kinetics, the entropy is such a state functional. Moreover, functional $F(\underline{x})$ is such that in the neighborhood of each one of the equilibrium states of interest (the stable equilibrium states, in thermodynamics), the functional

$$V(\underline{x}) = F(\underline{x}_{eq}) - F(\underline{x}) \tag{10}$$

when restricted to the subset of states

$$\{\underline{x} \text{ such that } C_i(\underline{x}) = C_i(\underline{x}_{eq}) \text{ for all constants of the motion}\} \tag{11}$$

is a Lyapunov functional [16] and, hence, each equilibrium state is conditionally stable [16] with respect to perturbations that do not alter the values of the constants of the motion.

Clearly, $V(\underline{x})$ can be a Lyapunov functional when restricted on the set 11 only if $V(\underline{x}) \geq \alpha(|\underline{x}-\underline{x}_{eq}|)$ where $\alpha$ is some strictly-increasing positive function with $\alpha(0) = 0$ and, hence, the equilibrium state $\underline{x}_{eq}$ is the unique state maximizing functional $F(\underline{x})$ on the set 11. It follows that these equilibrium states can be found by solving the following constrained maximization problem

$$\max F(\underline{x}) \tag{12}$$

subject to

$$B_k(\underline{x}) = \beta_k \qquad k = 1,\dots,q \tag{13}$$

$$C_i(\underline{x}) = \gamma_i \qquad i = 1,\dots,r \tag{14}$$

where the $\beta_k$ are the fixed values of the geometrical constraints and the $\gamma_i$ the values of the nontrivial constants of the motion. We have implicitly assumed that the functionals $B_k(\underline{x})$ and $C_i(\underline{x})$ form a complete set of geometrical constraints and nontrivial constants of the motion with linearly independent gradients $\underline{b}_1(\underline{x}),\dots,\underline{b}_q(\underline{x})$, $\underline{c}_1(\underline{x}),\dots,\underline{c}_r(\underline{x})$. The solution $\underline{x}_{eq}$ of the maximization problem satifies the set of equations

$$\underline{f}(\underline{x}_{eq}) = \sum_{k=1}^{q} \nu_k \, \underline{b}_k(\underline{x}_{eq}) + \sum_{i=1}^{r} \lambda_i \, \underline{c}_i(\underline{x}_{eq}) \tag{15}$$

which together with the constraints 13 and 14 yields an r-parameter family of equilibrium states

$$\underline{x}_{eq} = \underline{x}_{eq}(\gamma_1,\dots,\gamma_r) \tag{16}$$

which are stable with respect to all perturbations [16] if the function $\underline{x}_{eq}(\gamma_1,\dots,\gamma_r)$ is continuous in each $\gamma_i$.

If the internal dynamics is much faster than the external, we may asssume that for all practical purposes the system always passes through equilibrium states, namely,

$$\underline{x}(t) = \underline{x}_{eq}(\gamma_1(t),\dots,\gamma_r(t)) \tag{17}$$

where the values of the constants of the motion vary according to Equation 1, i.e., in view of Equation 4,

$$\dot{\gamma}_i(t) = \dot{C}_i(\underline{x}(t)) = \underline{c}_i(\underline{x}(t)) \cdot \underline{E}(\underline{x}(t),t) \tag{18}$$

For example, this is a reasonable assumption for the local description of nonreacting flow fields subject to moderate spatial gradients. But it would not be a reasonable assumption for reacting flows with some reaction time scales of the same order as some transport time scales.

## CONSTRAINED EQUILIBRIUM METHOD

In general, the time development of the state, $\underline{x}(t)$, is obtained by solving differential Equation 1 for given initial state $\underline{x}(0)$ and exogenous dynamics $\underline{E}(\underline{x},t)$. However, the modeling effort required to define the vector function $\underline{D}(\underline{x})$ may be a formidable task implying a full understanding of all the detailed mechanisms governing the internal dynamics of the system. Moreover, if the state variables are many, integration of Equation 1 may also be a formidable computational task.

Upon gaining a deeper understanding of the dynamics of a system, we often discover that many of the internal mechanisms that govern its time-dependent behavior are secondary in the sense that the final results are insensitive to changes in the modeling assumptions for such mechanisms. In other words, we conclude that the time-dependent behavior is relatively insensitive to such mechanisms, or that these are not the mechanisms which control the dynamics of the system on the time scale of interest. For example, in certain chemical kinetic computations it is often found that some chemical reaction mechanisms such as the two-body reactions are much faster than other mechanisms such as the three-body reactions and, therefore, the dynamics of the reacting system is controlled by the slow reactions and not by the fast ones.

Ideally, by scrutinizing all the features of the full endogenous dynamics of a system, we could classify the various governing mechanisms in a hierarchical structure based on their time scale as follows. We would single out all the internal mechanisms that act on a time scale shorter than a given scale $\tau$, and identify a complete set of nontrivial functionals

$$P_j^{\tau}(\underline{x}) \qquad j=1,\dots,s_\tau \tag{19}$$

with linearly independent gradient vectors $\underline{p}_j^{\tau}(\underline{x}) = \partial P_j^{\tau}(\underline{x})/\partial \underline{x}$ that are also linearly independent of the gradients $\underline{c}_i(\underline{x})$ of the constants of the motion of the system, and that would be constants of the motion if the internal dynamics of the system were determined only by those mechanisms with time scale shorter than $\tau$. Clearly, as $\tau$ increases, the number $s_\tau$ of such functionals decreases to reach $s_\infty = 0$. Conversely, as $\tau$ decreases and reaches the limit $\tau = 0$, at which time scale no mechanism can be active, the number $s_\tau$ increases to reach $s_0 = n - r - q$ where n is the number of state variables in vector $\underline{x}$, r is the number of nontrivial constants of the motion $C_i(\underline{x})$ with linearly independent gradients, and q the numbers of geometrical constraints $B_i(\underline{x}) = \beta_i$ with linearly independent gradients.

In principle, one would have to examine a hierarchy of dynamical equations of the form

$$\dot{\underline{x}} = \underline{D}^{\le\tau}(\underline{x}) \tag{20}$$

where $\underline{D}^{\le\tau}(\underline{x})$ accounts for all the internal mechanisms with time scale shorter than $\tau$. The functionals $P_j^{\tau}(\underline{x})$ are the constants of the motion for $\underline{D}^{\le\tau}(\underline{x})$ with gradients $\underline{p}_j^{\tau}(\underline{x})$ that are linearly independent of the gradients $\underline{c}_i(\underline{x})$ of the constants of the motion of the full internal dynamics $\underline{D}^{\le\infty}(\underline{x}) = \underline{D}(\underline{x})$. This means that no mechanism with time scale shorter than $\tau$ is capable of altering the value of the functionals $P_j^{\tau}(\underline{x})$.

If we are interested in describing the dynamics of the system only on a time scale longer than a certain scale $\tau$, then we are not interested in the details of the time evolution for time scales shorter than $\tau$. We may therefore assume that the fast mechanisms, described by $\underline{D}^{\le\tau}(\underline{x})$, contribute to the overall evolution by letting the functional $F(\underline{x})$ increase in practically no time to the highest value compatible with the instantaneous values of the functionals $C_i(\underline{x})$ -- which are constants of the motion for the overall dynamics -- and the functionals $P_j^{\tau}(\underline{x})$ -- which are constants of the motion for the fast dynamics. Thus, we only need to develop a detailed model of the dynamical mechanisms acting on time scales between $\tau$ and $\infty$, that we will denote by the symbol

$$\underline{D}^{>\tau}(\underline{x}) \tag{21}$$

In other words, we assume that for all practical purposes the system is at all times in some constrained-equilibrium state $\underline{x}_{ce}$ that can be found by solving the following constrained maximization problem

$$\max F(\underline{x}) \tag{22}$$

subject to

$$B_k(\underline{x}) = \beta_k \qquad k=1,\ldots,q \tag{23}$$

$$C_i(\underline{x}) = \gamma_i \qquad i=1,\ldots,r \tag{24}$$

$$P_j^\tau(\underline{x}) = \rho_j^\tau \qquad j=1,\ldots,s_\tau \tag{25}$$

The solution $\underline{x}_{ce}$ of the maximization problem satisfies the set of equations

$$\underline{f}(\underline{x}_{ce}) = \sum_{k=1}^{q} \nu_k\, \underline{b}_k(\underline{x}_{ce}) + \sum_{i=1}^{r} \lambda_i\, \underline{c}_i(\underline{x}_{ce}) + \sum_{j=1}^{s_\tau} \mu_j^\tau\, \underline{p}_j^\tau(\underline{x}_{ec}) \tag{26}$$

which together with the constraints 23, 24 and 25 yields an $(r+s_\tau)$-parameter family of constrained-equilibrium states

$$\underline{x}_{ce} = \underline{x}_{ce}(\gamma_1,\ldots,\gamma_r,\rho_1^\tau,\ldots,\rho_{s_\tau}^\tau) \tag{27}$$

If the exogenous dynamics, $\underline{E}(\underline{x},t)$, operates on a time scale larger than $\tau$, then we see that the evolution of the system can be described by modeling only those internal mechanisms with time scale longer than $\tau$. Indeed, we find

$$\dot{\gamma}_i(t) = \underline{c}_i(\underline{x}(t)) \cdot \underline{E}(\underline{x}(t),t) \tag{28}$$

$$\dot{\rho}_j^\tau(t) = \underline{p}_j^\tau(\underline{x}(t)) \cdot [\underline{D}^{>\tau}(\underline{x}(t)) + \underline{E}(\underline{x}(t),t)] \tag{29}$$

and, therefore, by assuming

$$\underline{x}(t) = \underline{x}_{ce}(\gamma_1(t),\ldots,\gamma_r(t),\rho_1^\tau(t),\ldots,\rho_{s_\tau}^\tau(t)) \tag{30}$$

where the function $\underline{x}_{ce}(\gamma_1,\ldots,\gamma_r,\rho_1^\tau,\ldots,\rho_{s\tau}^\tau)$ is that found in Equation 27 as a result of the maximization just discussed, we see that the set of Equations 28, 29 and 30 is closed and may be integrated to yield the time evolution of the state $\underline{x}$.

In particular, Equation 29 shows that the only internal mechanisms that determine the rates of change of the values of the functionals $P_j^\tau(\underline{x})$ are those acting on time scales between $\tau$ and $\infty$. Thus, the set of Equations 28, 29, and 30 is independent of the details of the dynamical mechanisms whose time scale is shorter than the given $\tau$.

It cannot be overemphasized that the effectiveness of the constrained equilibrium method hinges on a deep understanding of all the mechanisms governing the system dynamics because it requires classifying them on the basis of their time scale, understanding their time invariants, and predicting the rates at which the slower rate-controlling mechanisms vary the invariants of the faster mechanisms.

It is finally noteworthy that Relations 4 and 8 impose important restrictions on the expressions of $\underline{D}^{>\tau}(\underline{x})$ that can be adopted to model the rate-controlling slow endogenous dynamics of the system. The first condition, that we have already used in Equation 28, is that for every constrained-equilibrium state $\underline{x}_{ce}$,

$$\underline{c}_i(\underline{x}_{ce}) \cdot \underline{D}^{>\tau}(\underline{x}_{ce}) = 0 \qquad i=1,\ldots,r \tag{31}$$

namely, the functionals $C_i(\underline{x})$ must be constants of the motion of the endogenous dynamics also in the constrained-equilibrium scheme. The second, more demanding condition is that the state functional $F(\underline{x})$ must be nondecreasing under the endogenous dynamics. Combining Relation 26 and 29 (where we set the exogenous term $\underline{E}(\underline{x}(t),t) = 0$), this condition requires that

$$\sum_{j=1}^{s_\tau} \mu_j^\tau(\underline{x}_{ce})\, \underline{p}_j^\tau(\underline{x}_{ce}) \cdot \underline{D}^{>\tau}(\underline{x}_{ce}) \geq 0 \tag{32}$$

for every constrained-equilibrium state $\underline{x}_{ce}$, where

$$\mu_j(\underline{x}_{ce}) = \frac{\partial F(\underline{x}_{ce})}{\partial \rho_j^\tau} \tag{33}$$

The proof of Relation 33 is a standard result of nonlinear programming and is omitted [17].

## EXAMPLE. VIBRATIONAL AND TRANSLATIONAL TEMPERATURES

As an example of the constrained-equilibrium method we will consider the nonequilibrium state of a gas behind a shock wave. The main dynamical mechanisms that govern the relaxation of the gas towards equilibrium are: redistribution of energy between the translational and rotational modes of the molecules (with a characteristic time scale of order $10^{-9}$s), redistribution of energy between the vibrational modes (also with a time scale of order $10^{-9}$s), and transfer of energy between translational-rotational modes and vibrational modes (with a time scale of order ranging form $10^{-4}$s to $10^{-1}$s). For simplicity, we neglect the electronic modes of the molecules. If we are interested in describing the endogenous dynamics of the system only on a time scale longer than, say, $10^{-5}$s, then we do not need to model the details of the energy redistribution mechanisms because on this time scale their effect is to keep both the translational-rotational and the vibrational modes individually at their equilibrium distribution.

We will assume that the complete dynamics has the overall energy functional as the only constant of the motion, $E(\underline{x})$, where the state vector $\underline{x}$ lists the populations of all energy levels. The fast energy redistribution mechanisms have two additional constants of the motion: the translational-rotational energy functional, $E_{tr}(\underline{x})$, and the vibrational energy functional, $E_v(\underline{x})$.

More specifically, if $\varepsilon_i^t$ denotes the i-th translational energy level, $\varepsilon_j^r$ the j-th rotational level, and $\varepsilon_\ell^v$ the ℓ-th vibrational level, then the state variables, i.e., the population, may be denoted by $x_{ij\ell}$ and, assuming that the interaction energy between different modes is negligible, the three energy functionals just cited are

$$E(\underline{x}) = \sum_{ij\ell} x_{ij\ell}(\varepsilon_i^t + \varepsilon_j^r + \varepsilon_\ell^v) \qquad (34)$$

$$E_{tr}(\underline{x}) = \sum_{ij\ell} x_{ij\ell}(\varepsilon_i^t + \varepsilon_j^r) \qquad (35)$$

$$E_v(\underline{x}) = \sum_{ij\ell} x_{ij\ell}\varepsilon_\ell^v \qquad (36)$$

Clearly, only two of these functionals have linearly independent gradients, and the entropy functional

$$F(\underline{x}) = -k\sum_{ij\ell} x_{ij\ell} \ln x_{ij\ell} \qquad (37)$$

is nondecreasing under the endogenous dynamics. The constrained-equilibrium state obtained by maximizing $F(\underline{x})$ subject to the constraints $E(\underline{x}) = E$ and $E_v(\underline{x}) = E^v$, and the normalization condition $\sum_{ij\ell} x_{ij\ell} = 1$, can be written as

$$x_{ij\ell}^{ce} = \exp[\lambda - (\varepsilon_i^t + \varepsilon_j^r)/kT^{tr} - \varepsilon_\ell^v/kT^v] \qquad (38)$$

where the multipliers $T^{tr}$ and $T^v$ are determined by the values $E$ and $E^v$ of the constraints, and $\lambda$ by the normalization condition. Because Equation 38 can be rewritten as a product of two distributions, the multiplier $T^{tr}$ can be interpreted as the temperature of the translational-rotational system of energy levels, and $T^v$ as the temperature of the vibrational system of energy levels.

However, the translational-rotational system and the vibrational system are not decoupled, and they exchange energy on a slower time scale. Thus, according to the constrained equilibrium method (Equations 28 and 29) we need a rate equation for $dE^v/dt$, in addition to the rate equation for $dE/dt$ that would depend only on the exogenous dynamics (the energy balance equation). The rate equation for $dE^v/dt$ is usually written more indirectly in terms of the two temperatures $T^{tr}$ and $T^v$ as

$$\frac{d(T^{tr} - T^v)}{dt} = -\frac{T^{tr} - T^v}{\tau} \qquad (39)$$

where $\tau$ is a characteristic time constant of the endogenous dynamical mechanism by which energy is transferred between the translational-rotational modes and the vibrational modes.

## CONCLUSION

The constrained-equilibrium method is very useful in simplifying the description of nonequilibrium states and their tendency to relax towards equilibrium. We have discussed the general mathematical context and reviewed the philosophy of the method, and showed a simplest example of its application to a practical problem of physical chemistry.

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