Passivity Based Control of Transport Reaction Systems

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Inventory control is based on the idea manipulating process flows so that the inventories follow their set points. The operator mapping flows to inventories in a coarse grained (macroscopic) system is passive and any input strictly passive (ISP) feedback controller can, therefore, be used to achieve input-output stability. Examples of ISP controllers include the PID controller, parameter adaptive feedforward control, optimal controllers and many nonlinear and gain scheduling controllers. Input-output stability and convergence of inventories, such as total mass and energy can be used to show that other internal state variables are bounded and belong to an invariant set. However, this does not necessarily imply convergence of all state variables to stationary valves because a stabilizability condition, known as strict state passivity, must be satisfied. The 2nd law of thermodynamics is used to develop sufficient conditions for strict state passivity in the space of intensive variables. The theory relies on following two assumptions concerning nonequilibrium systems: (1) The hypothesis of local equilibrium, and (2) That a local entropy is defined using semiclassical statistical mechanics. These assumptions allow us to define a local entropy function for the coarse grained system which is homogeneous degree one, concave, and has positive temperature. Subject to these conditions stability theory is developed for conjugate variables, such as temperature, pressure and chemical potential in infinite dimensional reaction-diffusion-convection systems. In classical irreversible thermodynamics this type of analysis assumes linearity and symmetry of transport relations. The use of Gibbs tangent plane condition allows us to define a Lyapunov like storage function for passivity design, which gives stability criteria for nonlinear problems. The resulting sufficient condition for stability can be expressed in terms of dimensionless groups, similar to the (second) Damkohler number. Simple simulation examples illustrate the application of the theory.
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Introduction

In the context of control of distributed parameter systems in chemical engineering, four main categories of control problems and their applications were reviewed by Christofides (2001).[1] They included (1) control of spatial profiles with application to packed-bed reactors, CVD and etching, (2) control of size distributions with applications in aerosol production, crystallization and emulsion polymerization, (3) control of fluid flows with application in fluid mixing, wave suppression and drag reduction, and (4) control of material microstructures with applications for thin film growth and nanostructured coatings.

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This work expands on the list since the objective is to control inventories by adjusting flows. The inventory of a transport-reaction process (TRP) is an integral measure that represents physical properties like total mass, energy or the holdup of a chemical constituent. The inventory is controlled by adjusting the flows at the boundary or the reaction rate. Inventory control is closely related to mass and energy balance control (Buckley, 1964; Shinskey, 1967),[2,3] and extensive variable control (Georgakis, 1986).[4] The method was developed to its final form by Farschman et al. (1998)[5] who used Lyapunov theory to show that inventory control systems with PID feedback are indeed input-output stable.

In this current article we show that the inventory control method can be applied to coarse-grained TRPs using strictly input passive feedback control. We also show that latent (intensive) variables like temperature, pressure and chemical potentials converge. A distinctive feature of the control problem at hand is that control may only be possible at one or only a few points at the boundary. Examples where this type of control may find application include: plasma etching for microelectronics processing, moving and fixed-bed reactors for chemical and metallurgical processes, bioreactors, membrane and hollow fiber reactors for nanoprocessing.

Many methods have been proposed for control of TRPs (Ray, 1978; Christofides, 2001).[6,1] In one approach the partial differential equations are spatially discretized to form large systems of ordinary differential equations using the method of lines. Controllers can then be synthesized using classical theory like pole placement, linear quadratic or model predictive control. However, neglecting the infinite dimensional nature of the original system may lead to erroneous conclusions concerning the stability, controllability and observability properties of the system since the number of modes required to derive a finite dimensional ODE systems that yields a desired degree of approximation can in fact be very large (Aling et al., 1998; Balas, 1986; Christofides, 2000).[7,8,9]

Methods have been developed to reduce the dimensionality of the system before the controllers and observers are synthesized to reduce the complexity of the controller design. One very natural framework for deriving low-dimensional ODE systems that accurately reproduce their solution is based on the concept of inertial and approximate inertial manifolds (IM/AIM). The IM appears as the dominant solution to a high-dimensional input-output system under feedback when all but very few modes are heavily damped. In such systems the high-order dynamics dissipate and control only need to take effect in a low dimensional space. For example, the dynamics of a parabolic PDE system is restricted on an inertial manifold described by a set of ODEs (Temam, 1988; Brown et al., 1990; Smoller, 1996).[10,11,12] Systematic methods for the derivation of the inertial form has been proposed by Deane et al., 1991; Christofides and Daoutides (1997), and Kazantzis and Good (2003).[13,14,15]

The Lyapunov method for control system design is based on the idea of defining an energy related function which captures the dynamics of the state and choosing a controller to make the energy function decrease. A review of this approach applied to finite dimensional systems can be found in the books by Slotine and Li (1992) and Sontag (1998).[16,17] The method has been applied to control for robust control of PDE systems (Christofides and Daoutidis, 1998, and Christofides, 1998).[18,19] More recently El-Farra (2003)[20] extended the method to cover systems with input constraints, whereas Kazanzis and Kravaris (1999)[21] related the energy based method to predictive control.

Sliding mode control (Palazoglu and Owens, 1987; Hanczyc and Palazoglu, 1995; Sira-Ramirez, 1989)[22,23,24] has been applied to control TRPs. The main idea behind this technique is to let a discontinuous feedback controller define a so-called sliding surface on which the system has desirable behavior. A Lyapunov-like stability condition guarantees that the distance to the sliding surface decreases exponentially along all system trajectories. Application of sliding mode control, a form of high gain feedback (the feedback gain is infinitely large), requires that the input-output pairing (or transformations thereof) are passive. Finally, Godasi et al. (2002)[25] develop a symmetry group representation which they use to develop control methods for PDE systems.

The inventory approach for stabilization of TRPs distinguishes itself from the methods mentioned previously in that we develop stabilizing controllers using macroscopic (integrated) properties for feedback. The method is related to the averaging methods used to study nonlinear systems and stochastic processes since the use of inventories leads to "smearing" of the detailed structure of the dynamics. However, in the inventory approach we obtain the reduced order model by averaging over space rather than time. This gives a coarse grained view of the system dynamics and in this way the method can be linked to the classical methods of irreversible thermodynamics and statistical mechanics. The resulting manifold is described by a small number of ODE's (one for each control objective) derived from the macroscopic conservation equations. The final control design is achieved using either Lyapunov or passivity design techniques. A description of this approach and its application to finite dimensional systems with and without input constraints is given by Farschman et al. (1998).[5] Ydstie and Jiao (2004)[26] applies inventory and flow control to a float glass production system and Ruszkowski et al. (2005)[27] applied inventory and flow control to real-time optimization of a silicon furnace.

Passivity, a concept derived from electrical circuit theory, is encountered in many scientific disciplines (Desoer and Vidyasagar, 1975).[28] The fundamental idea is based on dissipation of useful work by irreversible transformations and input-output pairings with phase shift no more than $\pi/2$. Willems (1972a,b)[29,30] developed a systems perspective for dissipativity and linked the concept to state space representations. Byrnes et al. (1991)[31] showed that passivity and Lyapunov stability is equivalent for a class of feedback systems using geometric methods. Van der Schaft (1996)[32] developed control methods linking passivity and L_2 stability, while Slotine and Li (1992)[16] and Ortega et al. (1998, 2001)[33,34] stressed passivity based on physical arguments following from the law of conservation of energy. Krstic et al (1995)[35] linked passivity and nonlinear adaptive control. Ydstie and Alonso (1997)[36] advanced the idea of combining thermodynamics and passivity and showed that passivity could be motivated using a storage function related to the available work, and Gibbs tangent plane criteria for phase stability. Alonso and Ydstie, (2001)[37], Ydstie (2002)[38], and Coffey et al. (2000)[39] highlighted the importance of concavity of the entropy function, and used the Poincare inequality to estimate the impact of the size on stability of the system.

The main objectives of the current article are: (1) to give a tutorial overview of passivity based control, and (2) to show that passivity based methods are effective in stabilizing infinite dimensional transport reaction systems. We develop this result using a Lyapunov-like "energy" function, which exploits macroscopic, as well as microscopic system properties. An important technical contribution of the article is that we exploit the homogeneity of the entropy function more fully than we have achieved in previous articles.

Classical Thermodynamics

Let Σ, a convex subset of $\mathbf{R}_+^{n+2}$, be called the space of extensive variables and let Z denote an arbitrary point. We can for example have $Z = (U,V,M_1,\ldots,M_n,X)^T$ where U is the internal energy, V is the volume, M_i is mass or moles of chemical component i and X can correspond to the charge, degree of magnetization, area, momentum *et cetera*.

Assumption A1 (The structure of equilibrium thermodynamics): There exists a $\mathbf{C}^2$ function, $S : \Sigma \mapsto \mathbf{R}_+$, called the entropy so that[1]:

1. For any positive constant λ we have $S(\lambda Z) = \lambda\, S(Z)$ (S is positively homogeneous of degree one).
2. For all points $Z_1, Z_2 \in \Sigma$ and any positive constant λ we have

$$S(\lambda Z_1 + (1-\lambda) Z_2) \geq \lambda S(Z_1) + (1-\lambda) S(Z_2)$$

(S is concave).

3. $T = (\partial U/\partial S) > 0$(the temperature is positive).

The developments below do not depend on a particular definition of S since we do not actually need to evaluate the entropy function numerically. It suffices that there exists an entropy function which satisfies the axioms given earlier. We also want to note that the assumption of concavity is not needed for passivity design. It suffices that the entropy is over-bounded by a concave function. This is demonstrated in the first part of the article by Ydstie and Alonso (1997).[36]

To make the discussions precise, consider the example of semiclassical statistic mechanics. The microcanonical partition function for a single component system of N structureless particles is defined so that (Ruelle, 1969)[40]

$$\Omega(U, V, N) = \frac{\varepsilon}{\hbar^{3N} N!} \int \delta(U - H(p^{3N}, q^{3N}))\, dp^{3N} dq^{3N}$$

where H the Hamiltonian, $\hbar$ is Planck's constant (divided by 2π), p and q are the momenta and positions, ε is a scaling constant with units of energy and $\delta(\cdot)$is the Dirac delta function. The entropy is now defined using Boltzman's principle so that

$$S = k_B \ln \Omega(U, V, N)$$

Together these expressions give an entropy function which is (1) first-order homogeneous, (2) concave, and (3) has positive temperature. All these properties are due to the definition of the logarithm and Assumption A1 is, therefore, satisfied (Kestin and Dorfman, 1971).[43] Methods to evaluate $\Omega(U, V, N)$ numerically have recently been developed by Wang and Landau (2001) and Shell et al. (2002).[41,42]

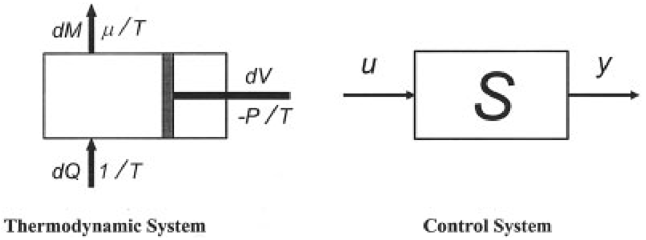

Figure 1. Equilibrium thermodynamics can be viewed as an input-output theory of systems.

Three actions (change of volume, heat and mass) provide the inputs to the system. The system response is observed by a change in the conjugate variables (pressure, temperature and chemical potential). By defining the corresponding input vector u and output vector y we can represent the thermodynamic processes as a control system as shown in the figure on the right.

The implied function relating $Z = (U,V,N)$ to S given by the two equations earlier is called a fundamental relation. In the case of an ideal gas with constant heat capacity the result is very clear since we get an explicit formula for the entropy so that

$$S_2 - S_1 = c_V \ln\left(\frac{U_2}{U_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$$

In more general cases it can be quite difficult to evaluate S numerically. In nonequilibrium systems it may not be possible to define a unique entropy function since the concept of an equilibrium state loses its precise interpretation. It is possible to make good approximations, and the use of classical thermodynamic variables in nonequilibrium settings gives excellent predictions in all but very extreme cases, however. We will follow an approximate approach to nonequilibrium theory called "coarse graining via the hypothesis of local equilibrium" (HLE). In this approach we grid the system into sub-regions and make the assumption that Boltzman's principle holds for each sub-region. The results of the article are based on the premise that Assumption A1 and HLE hold.

A mapping $\mathbf{P}$: $\Sigma \mapsto \Sigma$ is called a *thermodynamic process* (Figure 1). For control purposes, it is useful to represent the thermodynamic process by the input output operator $\mathbf{S}$ so that

$$y = \mathbf{S}u$$

We may, for example, have $u = (\Delta V, \Delta Q, \Delta M)^T$ and $y = ((1/T), (P/T), -(\mu/T))^T$. Thus, we are interested in modeling how intensive variables respond to a finite change in volume, heat and mass flow. The fundamental equation provides the key for constructing the operator $\mathbf{S}$ since it contains all information needed to characterize how the variables y change in response to a given action u. In the coarse grained approach we model systems distributed in time and space by cascading simple systems while making the assumption that each unit cell still obeys the assumptions A1.1 – A1.3. A coarse grained system with an input-output operator $\boldsymbol{S}$ and dynamics constrained by a

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[1] We follow the approach espoused by Caratheodory and Callen. This approach to thermodynamics is based on a limited number postulates expressed in mathematical form. The requirement that the entropy is twice differentiable is convenient but not necessary to obtain the main results of the paper. In general it suffices that S is $\mathbf{C}^1$.

fundamental relation satisfying axioms A1.1 – A1.3 is called a *process system* (Ydstie and Alonso, 1997).[36]

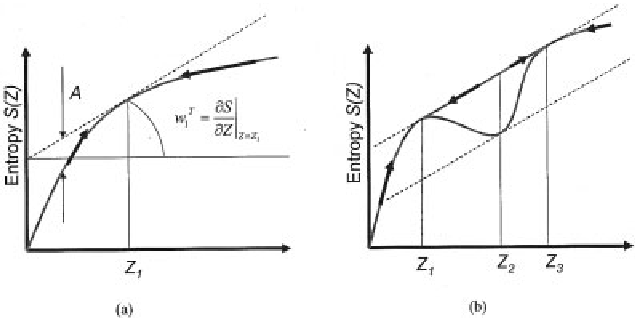

Figure 2. (a) Shows a projection of an entropy function and a unique point of stability indicated at the point Z_1. The slope of the tangent line, w_1 defines the intensive variables at that point, and (b) shows a projection, as it might arise in a cubic equation of state like the Van der Waals equation.

In this case the EOS gives three points where the slope, and, hence, the intensive variables are the same. The actual entropy is defined to be the smallest concave relaxation as indicated by the straight line segment. Entropy functions below the line are in violation of the second law.

Consider now two points Z_1, Z_2 and let $Z_3 = Z_1 + Z_3$. The second law of thermodynamics for a simple system can now be stated in the following, and maybe more familiar manner (Callen, 1985; Sandler, 1999)[44,45]

$$\text{The Second Law: } S(Z_3) \geq S(Z_1) + S(Z_2)$$

This expression states that the entropy of combined systems at equilibrium is never smaller than the sum of the entropies of the subsystems. The following result shows that the classical definition of the second law and Assumption A1.2 are in fact equivalent.

Result R1 (Equivalence of concavity and the second law): The entropy *S(Z)* is concave if and only if for all $Z_1, Z_2 \in \mathbf{Z}$

$$S(Z_1 + Z_2) \geq S(Z_1) + S(Z_2)$$

Proof: For any positive constant λ

$$S(\lambda Z_1 + (1 - \lambda) Z_2) \geq S(\lambda Z_1) + S((1 - \lambda) Z_2)$$

Using homogeneity gives

$$S(\lambda Z_1 + (1 - \lambda) Z_2) \geq \lambda S(Z_1) + (1 - \lambda) S(Z_2)$$

It follows that S is concave. The reverse argument follows immediately.

We now introduce the set of conjugate variables

$$w = \frac{\partial S}{\partial Z} \tag{1}$$

called the vector of intensive variables. For a simple system, we can make the assignment

$$w = \left(\frac{1}{T}, \frac{P}{T}, -\frac{\mu_1}{T}, \ldots, -\frac{\mu_n}{T}\right)^T$$

where the negative signs are introduced to follow the standard notation. The intensive variables therefore define the slope of the entropy as shown in Figure 2. Using these definitions we can also generate the Legendre transform of S so that

$$S^*(w) = w^T Z - S(Z)$$

Z is now regarded as a function of w and S^*. We see that the variables Z and w are dual. The space $\mathbf{\Sigma}^* = \{w\colon Z \in \mathbf{\Sigma}\}$ is called the space of intensive variables. Alonso and Ydstie (2001)[37] showed that taking the Legendre transform of *S(w)* does not yield unique results due to the homogeneity of S. This simply means that we can scale "size of the system"without changing the intensive variables.

From Eq. 1 we now have the Gibbs equation $dS = w^T dZ$, which for a simple system we write out term by term so that

$$dS \equiv \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu_1}{T} dM_1, \ldots, -\frac{\mu_n}{T} dM_n \tag{2}$$

Euler's theorem for homogeneous functions gives[2]

$$S(Z) = w^T Z \tag{3}$$

Using Eq. 3, and the chain rule we can now write $(\partial S/\partial Z) = (\partial w/\partial Z) Z + w^T$. It follows from Eq. 1 that

$$\mathbf{M} Z = 0 \tag{4}$$

where

$$\mathbf{M}_{ij} = \frac{\partial^2 S}{\partial Z_i \partial Z_j} \leq 0$$

The matrix $\mathbf{M}$ of second derivatives of S is symmetric and nonpositive, as indicated. The symmetry gives rise to the Maxwell relations, and the nullspace of $\mathbf{M}$ defines invariant sub-spaces $\mathbf{\Sigma^0}$ of $\mathbf{\Sigma}$ (Figures 2 and 3). Gibbs showed that $\dim(\mathbf{\Sigma^0})$ is equal the number of phases present is a nonreactive, simple system.

Equation 4 is often written on the form

$$0 = dw^T Z \tag{5}$$

For a simple system this gives the Gibbs-Duhem equation (Sandler, 1999)[45]

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[2] Euler's theorem asserts that if $f(\lambda x) = \lambda f(x)$ then we must have $f(x) = (\partial f/\partial x) x$.

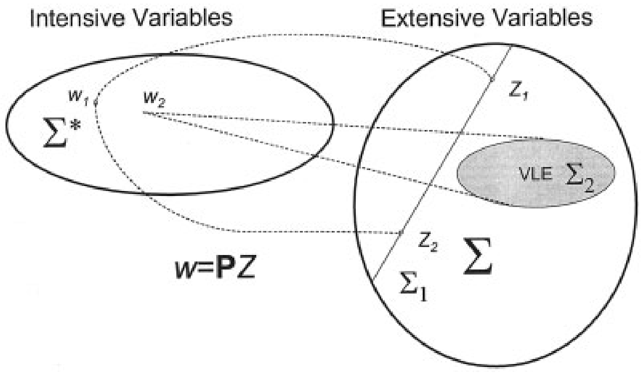

Figure 3. The mapping w = PZ from the space of extensive to the space of intensive variables is not one to one.

The line $\boldsymbol{\Sigma}_1$, corresponds to uniform scaling of the extensive variables. Such a line maps a point w_1 in $\boldsymbol{\Sigma}^*$, indicating that pressure, temperature and chemical potential remain invariant. Subregions with positive measure (regions in $\boldsymbol{\Sigma}$ with phase or reaction equilibrium) map to points with zero measure (in $\boldsymbol{\Sigma}$ *). Controlling intensive variables neither guarantees stability or convergence in the space of the extensive variables.

$$0 = dw^T\hat{Z} = d\left(\frac{P}{T}\right)\hat{V} + d\left(\frac{1}{T}\right)\hat{U} - d\left(\frac{\mu_1}{T}\right)\hat{M}_1, \ldots, -d\left(\frac{\mu_n}{T}\right)\hat{M}_n \qquad (6)$$

which turns out to play a particularly important role in our developments. The specific (or molar) properties are defined so that

$$\hat{Z} = Z/M = (\hat{V}, \hat{U}, \hat{M}_1, \ldots, \hat{M}_n)^T \qquad (7)$$

and $M = \sum_{i=1}^{n} M_i$ denotes the total mass (moles).

Neither the Helmholtz function $F = U-TS$, which is based on fixing the micro-canonical ensemble *(U,V,N)* nor Gibbs function $G = H - TS$, which is based on fixing the canonical ensemble *(T,P,N)*, provide convenient starting points for the development of process control theory. Both functions fail for similar reasons. The Helmholtz function fails because here is no way to guarantee that N and U are fixed unless the system already is well controlled. The Gibbs function fails because we need to develop methods to stabilize pressure and temperature before we can use the stability theory. In practice these problems show up as a problem of lower-boundedness of G and F in unconstrained systems (Coleman and Owen, 1974).[46]

Ydstie and Alonso (1997)[36] proposed to overcome the problem of lower-boundedness by defining a Lyapunov function which measure distance to a fixed reference point in a stationary, open system. They used the microcanonical ensemble description, and the concavity of the entropy as their point of departure. This theory led to definition a Lyapunov function related to thermodynamic availability and exergy defined so that for any pair of points Z_1, Z_2 in $\boldsymbol{\Sigma}$ we have

$$A_1(Z_2) = S(Z_1) + w_1^T(Z_2 - Z_1) - S(Z_2) \geq 0 \qquad (8)$$

That A_1 (Z_2) is non-negative is easy to verify geometrically as shown in Figure 2. From Eq. 8 and the Euler identity (Eq. 3) we have

$$A_1(Z_2) = w_1^T Z_2 - S(Z_2)$$

Thus, we see that A is closely related to S^* only that we have fixed w_1. From the Gibbs tangent plane condition we have that two points Z_1 and Z_2 are in equilibrium if and only if A_1 $(Z_2) = 0$. It is easy to to see that this condition is equivalent to $w_1 = w_2$. The function A, therefore, measures distance from an arbitrary, fixed reference point $w_1 \in \boldsymbol{\Sigma}^{*3}$.

Coarse Graining, Transport and Reaction

In order to introduce the theory of transport reaction systems we must deal with the following problem: Classical thermodynamics does not consider the spatial dependency of the system. One way to overcome this problem is to use coarse graining. In this approach, we tessellate physical space into N subregions. Assumption A1 is assumed to be valid for each subregion provided that the tessellation is sufficiently fine.

The macroscopic balances for each sub-region, independent of scale, can be written on the form (Hangos and Cameron, 2001[47])

$$\frac{dv}{dt} = \phi + p$$

v is here the vector of coarse grained variables (inventories) corresponding to the total internal energy, volume and number of moles (mass) of each species so that

$$v^T = (V_t, U_t, M_{1t}, \ldots, M_{nt})$$

The subscript t refers to "total" in order to distinguish the inventories from extensive variables. The state of the subregions, as well as the overall system may then change continuously. The flows between the subregions will be governed by classical transport theory so that

$$\phi = \sum_{i=1}^{m} f_i$$

where f_i gives the net rate of transport. The vector p represents the rate of production. We then get the following (very nice) decomposition for the thermodynamic process

$$v(t) = v(0) + \int_0^t \phi + p\,ds$$

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[3] Note that A does not define a metric on the space Σ^* since we do not necessarily have symmetry. Consider two arbitrary points Z_1 and Z_2. We may then have $A_1(Z_2) \neq A_2(Z_1)$, indicating that the distance measured in one direction is not equal to the distance measured in the opposite direction.

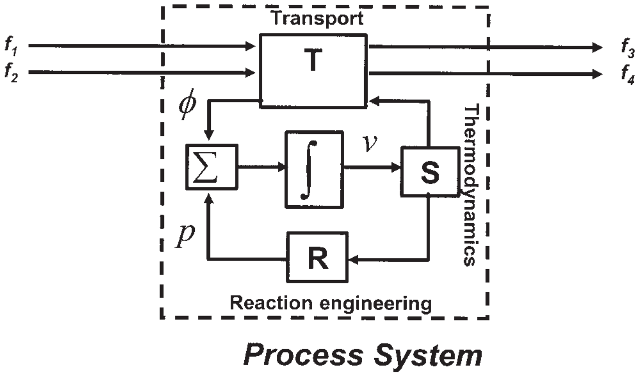

Figure 4. Hypothesis of local equilibrium leads directly to the separation of thermodynamics, transport and reaction engineering into distinct subfields of process systems engineering.

As illustrated in Figure 4 we see that in order to predict the evolution of a process from its initial condition we need to evaluate a line integral (the action) involving three classical branches of chemical engineering: thermodynamics, transport and reaction engineering.

In the coarse-grained system we have

$$v = \sum_{i=1}^{N} Z_i$$

By letting N → ∞ we can then define the density of the inventory *i* so that

$$v_i(t) = \int_{V_t} \rho(x, t) z_i(x, t) dV_t \quad i = 1, \ldots, n + 2$$

where ρ is the molar or mass density, z_i is the local state, and dV_t is the measure of V_t (Kestin and Dorfman, 1971).[43] In order to maintain clarity of presentation we consider processes distributed in one spatial dimension only. We let x represent the spatial dimension, let dx represent dV_t, and we assume furthermore that functions of x and t defined on the domain $\Omega = [0, L] \times [0, \infty)$ exist and are continuous.

Assumption A2: (The hypothesis of Local Equilibrium (HLE)): For every $\varepsilon > 0$, there exists $\delta > 0$, so that if $|V_t| < \delta$ then $\|z(x, t) - \hat{Z}(x, t)\| < \varepsilon$.

This is the essence of HLE (Kreuzer, 1981; Astarita, 1990; Ottinger, 2005).[46,49,50] The main importance of HLE is that we can make the substitution

$$z(x, t) = \hat{Z}(x, t) \tag{13}$$

This means that the local state *z(x,t),* and the specific properties $\hat{Z}$ are equivalent on small enough scales. We can then use statistical/quantum mechanics to develop fundamental equations that link the energy and mass conservation laws with thermodynamic quantities like temperature, pressure and chemical potentials. In course grained systems we can furthermore calculate the gradients of intensive variables which are needed to estimate the rate of energy and mass flow between the subregions. HLE is very well tested and holds even at very small scales and quite sharp gradients.

According to the definitions above we can approximate the coarse grained system locally (Eq. 9) by a system of partial-differential equations on the form

$$\frac{\partial \rho z}{\partial t} + \frac{\partial f}{\partial x} = \sigma \tag{14}$$

where *f(x,t)* represents the flux density, and *σ(x,t)* represents the density of production. These variables are connected to the macroscopic balances via the relationships

$$\phi(t) = f(L, t) + f(0, t) \quad \text{and} \quad p(t) = \int_0^L \sigma(x, t) dx$$

where the sign chosen so that it is positive for flow into the system and negative for flow out. We normally divide the flux density into orthogonal components (in the sense of Gibbs-Duhem) so that

$$f = f_{\text{conv}} + f_{\text{diff}} \quad \text{where} \quad f_{\text{conv}} = \rho u z \tag{15}$$

u is the center of mass velocity. The division into diffusive and convective terms can be motivated on physical grounds and corresponds to a separation into Eulerian and Lagrangian components.

Consider now a process system with first-order reaction to illustrate application of HLE, and the balances given earlier. Following the notation of Sandler (1999),[45] we can make the following assignments in Eqs. 14 and 15

$$z = \begin{pmatrix} \hat{U} \\ \hat{V} \\ \hat{M}_1 \\ \hat{M}_2 \end{pmatrix}, \quad f_{\text{conv}} = \dot{m}\begin{pmatrix} \hat{U} \\ \hat{V} \\ \hat{M}_1 \\ \hat{M}_2 \end{pmatrix}, \quad f_{\text{diff}} = \begin{pmatrix} \dot{Q} \\ 0 \\ \dot{F}_{D1} \\ \dot{F}_{D2} \end{pmatrix}, \quad \sigma = \begin{pmatrix} -P\dfrac{\partial u}{\partial x} + 2\mu\left(\dfrac{\partial u}{\partial x}\right)^2 \\ \dfrac{\partial u}{\partial x} \\ \sigma_1 \\ \sigma_2 \end{pmatrix} \tag{16}$$

We note that $\dot{m} = \rho$ denotes the center of mass flow, $\dot{Q}$ the heat flow $\dot{F}D_i$ the rate of diffusion, μ is the viscosity as used in the Navier-Stokes equations and σ_i is the local rate of chemical reaction. The conservation law corresponding to volume (the second entry) does not add information and is only introduced for convenience[4]. The term $P(\partial u/\partial x)$ is the generation of internal energy due to compression. This term is reversible and

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[4] The corresponding conservation law is given by $(\partial \rho\hat{V}/\partial x) + (\partial \dot{m}\hat{V}/\partial x) = (\partial u/\partial x)$ which is true but uninteresting.

cancels in the 1D entropy balance as shown in Appendix[5]. The term $2\mu(\partial u/\partial x)^2 \geq 0$ represents the irreversible generation of heat due to viscous dissipation.

The chemical potential of a mixture can be expressed so that

$$\mu_i(x, t) = \mu_{i0}(T, P) + k_B T \ln(a_i z_i)$$

where a_i is the activity coefficient. A continuous relationship, therefore, exists among concentrations, pressures, temperatures and chemical potentials. Reaction rates expressed in terms of concentrations can, therefore, be related to the chemical potentials and more generally to the affinities as shown in the Appendix. For example, the first-order reaction $A \rightarrow B$ with Arrhenius rate expression can be written so that

$$\sigma(x, t) = k_0 \exp(-E/RT(x, t)) c_A(x, t) \tag{17}$$

The HLE allows us to express concentrations as continuous functions of the intensive variables except across phase boundaries. It follows that expression Eq. 17 is (Lipschitz) continuous in the intensive variables w. If instead we consider a bioreactor with substrate inhibition model, then we have

$$\sigma(x, t) = \frac{\mu_m c_S}{K_s + c_S + c_S^2/K_i}$$

where μ_m is the maximum growth rate, c_s is the concentration of substrate in the reactor, and K_m and K_i are the growth constants and continuity still holds. More generally, for continuous functions $\sigma(w)$ we can write

$$\|\sigma(w_1) - \sigma(w_2)\| \leq k_0 \|w_1 - w_2\|$$

It follows that

$$(\sigma(w_1) - \sigma(w_2))^T (w_1 - w_2) \geq -k_0 \|w_1 - w_2\|^2$$

for some constant k_0.

We now investigate the stability properties of the conservation laws (Eq. 14) using the potential A (defined by Eq. 8) as an energy function. For this development is convenient to define the "natural set of driving forces"

$$X = \frac{\partial w}{\partial x} \tag{18}$$

We see that according to HLE we have $X(x,t)$ equal to zero if the system is at equilibrium. It is also convenient to define the deviation variables

$$\begin{aligned} \tilde{f} &= f_1 - f_2 \\ \tilde{\sigma} &= \sigma_1 - \sigma_2 \\ \tilde{w} &= w_1 - w_2 \\ \tilde{X} &= X_1 - X_2 \end{aligned} \tag{19}$$

where subscript 2 refers to the time invariant reference system. We can analyze stability by studying the trajectories of the deviation system derived from Eq. 14 defined so that

$$\frac{\partial \rho \tilde{z}}{\partial t} + \frac{\partial \tilde{f}}{\partial x} = \tilde{\sigma}$$

using the function A as a Lyapunov like storage function. This theory can be extended using the idea of contraction analysis as introduced by Lohmiller and Slotine (1998)[51].

Lemma L1 (Evolution equation for A): Suppose that assumptions A1 and A2 are satisfied. We then have

$$\frac{\partial A}{\partial t} = \frac{\partial(\tilde{f}^T \tilde{w})}{\partial x} - \tilde{f}^T_{\text{diff}} \tilde{X} - \tilde{w}^T \tilde{\sigma}$$

Proof: Since A1 and A2 are satisfied we can use Eq. 13 and set $z(x, t) = \hat{Z}(x, t)$. We can now write

$$\frac{\partial A}{\partial t} = -(w_1 - w_2)^T \frac{\partial(\rho_1 z_1 - \rho_2 z_2)}{\partial t}$$

By using the conservation laws Eq. 14, and the deviation variables (Eq. 19) we get

$$\frac{\partial A}{\partial t} = -\tilde{w}^T \left(-\frac{\partial \tilde{f}}{\partial x} + \tilde{\sigma} \right)$$

We now use the identity $(\partial(\tilde{f}^T \tilde{w})/\partial x) = \tilde{f}^T(\partial \tilde{w}/\partial x) + \tilde{w}^T(\partial \tilde{f}/\partial x)$ and Eqs. 18 and 19 to give

$$\frac{\partial A}{\partial t} = \frac{\partial(\tilde{f}^T \tilde{w})}{\partial x} - \tilde{f}^T \tilde{X} - \tilde{w}^T \tilde{\sigma}$$

$$W(t) = \int_0^L A(x, t)\,dx \geq 0 \tag{21}$$

This gives the following key result.

Corollary C1 (Dissipation equality for process systems):

$$\frac{dW}{dt} = \tilde{f}^T \tilde{w}\Big|_0^L - \int_0^L (\tilde{f}^T \tilde{X} + \tilde{w}^T \tilde{\sigma})\,dx$$

Proof: Follows from Lemma L2 by integration.

We see from Corollary C1 that the storage function W decreases if the righthand side is negative. We furthermore notice that the righthand side consists of three distinct terms.

1. The term $\tilde{f}^T \tilde{w}|_0^L$ is due to deviations in boundary conditions.
2. The term $\tilde{f}^T \tilde{X}$ represents deviations due to convection diffusion and heat conduction.

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[5] In the general case the right hand side of the energy balance consists of additional terms $-\mathbf{P}: \nabla \mathbf{u} + \sum_{i-1}^{n} f_{\text{diff}\,i} \mathbf{F}_i$ where the first term represents the conversion of kinetic energy to internal energy through compression and viscous dissipation, and the second term represents the conversion potential energy to internal energy through diffusion.

3. The term $\tilde{w}^T\tilde{\sigma}$ represents deviations due to chemical reaction and power of compression.

We will now review very briefly the substance of linear irreversible thermodynamics (LIT). LIT is based on modeling diffusion flow, heat conduction and chemical reaction using linear relations so that

$$f = \mathbf{L}X \quad \text{and} \quad \sigma = \mathbf{K}w$$

where **L** and **K** are symmetric with nonnegative and all positive eigenvalues, respectively. The entropy production due to diffusion and heat-conduction can now be written as $X^T\mathbf{L}X$ which defines the Riemannian metric, often referred to as the Rayleigh-Onsager dissipation function. Using linearity we can write

$$\tilde{f}_{\text{diff}}^T\tilde{X} = \tilde{X}^T\mathbf{L}\tilde{X} \geq \alpha_0\tilde{X}^T\tilde{X} \quad \text{and} \quad \tilde{w}^T\tilde{\sigma} = \tilde{w}^T\mathbf{K}\tilde{w} \geq 0$$

where α_0 is smallest eigenvalue of **L**. From Corollary C1 we then have

$$\frac{dW}{dt} \leq \tilde{f}^T\tilde{w}\big|_0^L - \alpha_0\int_0^L \tilde{X}^T\tilde{X}dx$$

Using the Poincare inequality (Straughan, 1992; Struwe, 1992)[52,53] we can write

$$\frac{dW}{dt} \leq \tilde{f}^T\tilde{w}\big|_0^L - \alpha_0\frac{\pi^2}{L^2}\int_0^L \tilde{w}^T\tilde{w}dx$$

From Result R2, we can now conclude that there exists a constant ϑ_0 so that $\tilde{w}^T\tilde{w} \geq A(\tilde{Z})$.. Hence

$$\frac{dW(t)}{dt} \leq \tilde{f}^T\tilde{w}\big|_0^L - \vartheta_0\alpha_0\frac{\pi^2}{L^2}W(t)$$

It follows that *W(t)* is a (control) Lyapunov function (Sontag, 1990)[54] for the intensive variables $\tilde{w}$, and stability follows by choosing the boundary conditions so that $\tilde{f}^T\tilde{w}\big|_0^L \leq 0$.

Prigogine developed a similar stability result using the second variation of entropy as a Lypunov function. His approach gives local results and it cannot be applied to phase equilibria since the stability conditions obtained from the second-order variation, δS^2 are not topologically equivalent to those obtained from the Gibbs tangent-plane method across phase boundaries due to discontinuities in *S*. A further discussion of the framework of classical equilibrium thermodynamics, linear laws and stability is given in the Appendix.

The remainder of the article does not rely on linearity and symmetry. Instead we derive a broader class of stability conditions which can be tried for nonlinear problems.

Result R3 (Stability of Process Systems): Suppose that there exists positive β_0 so that

$$\int_0^L \tilde{f}^T\tilde{X} + \tilde{w}^T\tilde{\sigma}dx - \tilde{f}^T\tilde{w}\big|_0^L \geq \beta_0\tilde{w}^T\tilde{w}$$

Then we have $(dW(t)/dt) \leq -\vartheta_0W(t)$ for some positive constant ϑ_0.

Proof: Follows from Corollary C1 by integration and using the fact that according the Result R2 and HLE we a positive constant ϑ_0. so that $W(t) \geq \vartheta_0\tilde{w}^T\tilde{w} \geq 0$.

W(t) is radially bounded and positive definite on $\mathbf{\Sigma}^*$. It follows that *W* is a Lyapunov function for the intensive variables in the finite dimensional case. This theory is explored more fully in the context of process networks by Jillson and Ydstie (2005).[59] We also note that if the conditions above are satisfied then we use the theory to establish the existence of an inertial manifold. We now introduce the following assumption.

Assumption A3 (Sufficient conditions for dissipativity): There exists constants k_L and $\alpha_0 > 0$ so that

$$(1)\ \ \tilde{w}^T\tilde{\sigma} \geq k_L\tilde{w}^T\tilde{w} \quad \text{and} \quad (2)\ \ \tilde{f}^T\tilde{X} \geq \alpha_0\tilde{X}^T\tilde{X}$$

We see that condition (1) of Assumption A3 is satisfied if $\sigma = \hat{\sigma}(w)$ is Lipschitz continuous in *w*. The conditions are satisfied if we use the Arrhenius or substrate inhibition rate described above and Fourier-Fick theory for heat conduction and diffusion.

Corollary C2 (Sufficient condition for dissipativity): Suppose that Assumption A3 is satisfied. The dissipation condition of Result 3 holds true if α_0 and k_L defined in Assumption A3 satisfy the inequality

$$\alpha_0\frac{\pi^2}{L^2} + k_L > 0$$

where *L* is the length.

Proof: The Poincare inequality for homogeneous boundary conditions gives

$$\int_0^L \tilde{X}^T\tilde{X}dx \geq \alpha_0\frac{\pi^2}{L^2}\int_0^L \tilde{w}^T\tilde{w}dx$$

and the result follows from Result R3 using

$$\beta_0 = \alpha_0\frac{\pi^2}{L^2} + k_L$$

By rearranging the inequality in Result 4 we see that the process system with homogeneous boundary conditions is stable if

$$k_L > -\alpha_0\frac{\pi^2}{L^2}$$

This expression shows that the process system is always stable if k_L is positive. Autocatalytic, coupled systems like the van der Vusse system and exothermic reactions may give k_L negative.

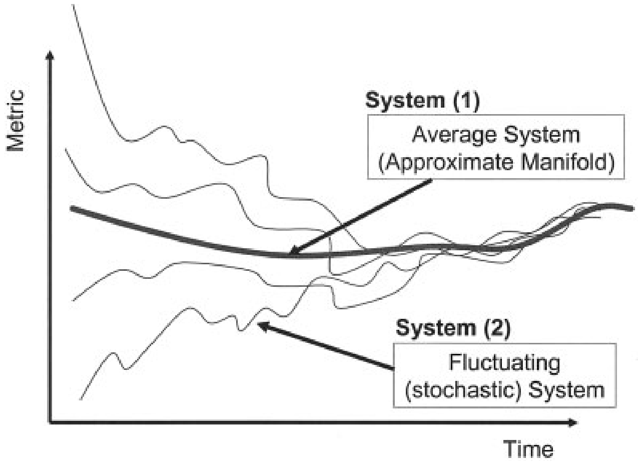

Figure 5. Trajectories of passive process systems with different initial conditions, and the same boundary conditions converge to a single trajectory in the mean square sense.

In such cases it is possible to achieve stability in distributed reaction diffusion systems by counterbalancing reaction by diffusion and heat conduction if L is not too large (Alonso and Ydstie, 2001).[37] In order to develop spatiotemporal patterns in reaction diffusion equations we, therefore, need to satisfy certain limiting size constraints as might be expected.

There are many ways to interpret deviation variables as illustrated in Figure 5. One way is to view System 2 as a stationary reference for System 1. Convergence results then show that all trajectories converge to stationary behavior determined by the reference system. Another way is to view deviations as spontaneous/stochastic fluctuations that die out after period of time.

Passivity of Input Output Systems

It is quite easy to develop "counter examples" to control. For example, the linear transfer function

$$G(s) = \frac{(s+3)(s-0.5)}{(s+10)(s-0.5)(s+4)} \tag{22}$$

is impossible to stabilize because there is an unstable pole-zero cancellation. The Bode plot of *G(s)* shown in Figure 6 reveals one aspect of the input output behavior of the system however. The plot shows that the phase shift of *G(s)* is never more than 90°. Systems that display this kind of behavior are said to be passive. Passivity provides a counterpart to small gain stability theory. In the small gain theory we ignore phase and rely on gain margin for stability. In passivity theory, we ignore the gain and we use instead the phase margin for stability.

The classical example of a passive system is an electrical circuit made op of resistors, capacitors, and inductors connected in parallel with resistors. In this case the input u in Figure 1 represents the applied voltage and the output y represents the current. Independently of the complexity of the circuit we can now write

$$W(t) \leq W(0) + \int_0^t uyds$$

where W represents the stored electrical energy and product uy represents the power supply. The inequality shows that the electrical energy stored in circuit at time t is less or equal to what initially stored plus the integrated power supply. The difference has been dissipated as heat in the resistors. A linear transfer function *G(s)* is passive if

1. *G(s)* is real for real s.
2. Re[G(s)] $\geq$ for all Re(s) >0.

We note that there is a close connection between passivity and Lyapunov stability theory which can be expressed through the Kalman-Yakubovich-Popov type stability theory. Let *G(s)* have the controllable state space realization $\{C,A,B\}$ with A having all its eigenvalues in the closed left half plane. It then follows that *G(s)* is passive if and only if there exists a positive definite matrix P and vector d so that

$$A^TP + PA = -dd^T$$
$$PB - C = 0$$

The function $V = X^T Px$ turns out to be a Lyapunov function for the unforced system. More generally and assuming that *W(t)* is differentiable we have the following definitions for nonlinear systems.

Definition D1: Consider system **S** in Figure 1 with input u and output y. Suppose that there exists a nonnegative $\mathbf{C}_1$ function *W(t)*, so that

$$\frac{dW}{dt} \leq u^Ty - \beta\|\xi\|_2^2$$

.

The system **S** is

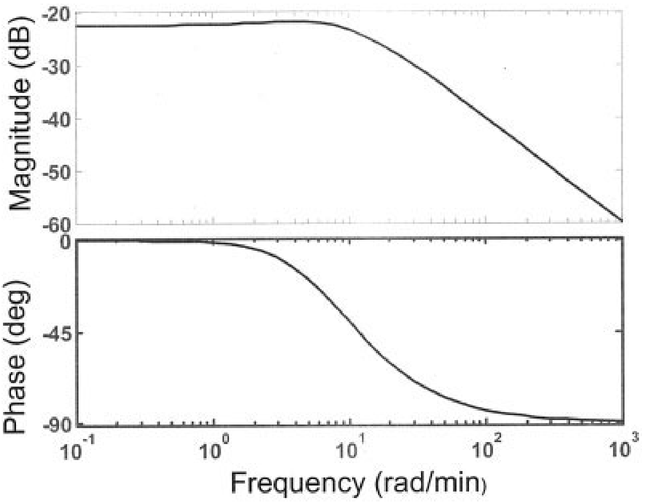

Figure 6. Bode diagram of the transfer function shown in Eq. 22 generated by MATLAB.

Note the Bode stability criterion does not apply due to the presence of the unstable pole.

1. *passive* if $\beta = 0$.
2. *strictly input passive* if $\xi = u$ and $\beta > 0$.
3. *strictly output passive* if $\xi = y$ and $\beta > 0$.
4. *strictly state passive* if ξ represents the state and $\beta = 0$.

The notation $\|\cdot\|_2$ denotes the L_2 norm for a function defined on a domain Ω so that for square integrable vectors ξ we have

$$\|\xi\|_2^2 = \int_\Omega \xi^T \xi d\Omega < \infty$$

In this article Ω is defined by the semiclosed set $[0, \infty) \times [0, L]$, and subsets thereof.

Willems (1972b)[30] proved that if W has a strong local minimum then there is an intimate connection between dissipativity and Lyapunov stability. In this case, W is convex, and it is also a Lyapunov function. Byrnes et al. (1991)[31] developed these ideas further and established conditions for stabilizability of nonlinear, finite dimensional systems using passivity. It was shown that a finite dimensional system is stabilizable if it is feedback equivalent to a passive system. These results suggest a close relation between passivity and the methods of irreversible thermodynamics.

Result R3 shows that process systems are strictly passive if Assumptions A1-A3 are satisfied, and if L is sufficiently small. We can then write

$$\frac{dW(t)}{dt} \leq u^T y - \beta_0 \int_0^L \tilde{w}(t, x)^T \tilde{w}(t, x) dx \tag{23}$$

where we made the assignments

$$u = \begin{pmatrix} \tilde{f}(t, 0) \\ \tilde{f}(t, L) \end{pmatrix} \quad y = \begin{pmatrix} \tilde{w}(t, 0) \\ \tilde{w}(t, L) \end{pmatrix}$$

Thus, the input vector consists of flow deviations at the boundary and the measurement consists of intensive variable deviations at the boundary. Strict state passivity (in the space of intensive variables) follows when we make the assignment $\tilde{w} = \xi$. We note that passivity has a very nice intuitive interpretation which is evident from inequality (Eq. 23). *The input and the output in the average have the same sign*. In other words, if u is positive then y should be positive "most of the time". Conversely, if u is negative then y should be negative "most of the time". In the nonlinear case this translates into a sector condition which plays a crucial role in nonlinear stability theory.

One aspect concerning passive systems is that they are easy to control. This can be observed by defining a proportional control

$$u = -Ky, \quad K > 0$$

Substituting this control law into expression Eq. 23 convinces us that the storage function decreases according to

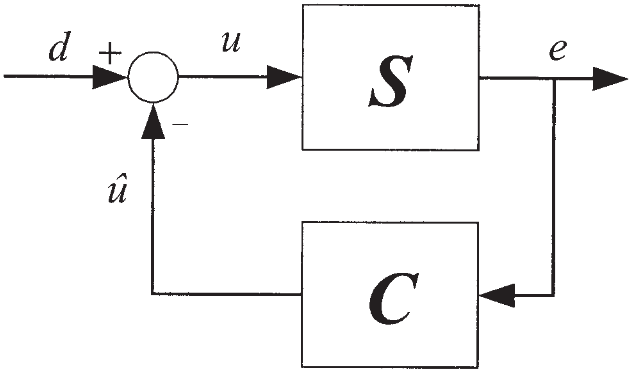

Figure 7. Feedback interconnection between a passive system S, and a strictly passive controller C.

$$W(t) \leq W(0) - \int_0^T Ky^2 dt - \beta_0 \int_0^T \int_0^L \tilde{w}^T \tilde{w} dt$$

Thus, the stored energy never increases under negative output feedback, and it is in fact decreasing if either of the vectors y or $\tilde{w}$ is not identically equal to zero for some finite period of time. This gives convergence of y and $\tilde{w}$ since $W(t)$ cannot decrease indefinitely[6].

The central result of passivity aimed at stability analysis of interconnected systems is the *passivity theorem.* The following result is most useful for out purposes.

Lemma L2 (Stability of feedback systems): Consider a passive system **S** and an input strictly passive controller **C** connected in feedback as shown in Figure 7. The respective storage functions $W_\mathbf{S}$ and $W_\mathbf{C}$ have dissipation rates $\beta_\mathbf{S} = 0$ and $\beta_\mathbf{C} > 0$. The interconnected feedback system with input d and output e has L_2 gain $g = 1/\beta_\mathbf{C}$.

Proof: The proof is instructive so we give it here for completeness. First we note that we have

$$\frac{dW_\mathbf{S}}{dt} \leq u^T e$$

and

$$\frac{dW_\mathbf{C}}{dt} \leq e^T \hat{u} - \beta_\mathbf{C} e^T e$$

where $\hat{u}$ is defined in Figure 7. By adding the two storage functions, defining $W = W_\mathbf{S} + W_\mathbf{C}$ and setting $u = d - \hat{u}$ we get

$$\frac{dW}{dt} \leq e^T d - \beta_\mathbf{C} e^T e$$

We now integrate over the interval *[0,T]* to give

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[6] Note that convergence is in the L_2 sense, meaning that the error signals are square integrable. This result can be strengthened to one of asymptotic stability of the signals have uniformly bounded first derivative. It turns out that it it quite easy to establish that this is the case if the smallest eigenvalue of **L** is bounded away from zero.

$$W(t) \leq W(0) + \int_0^T (e^T d - \beta_C e^T e) dt$$

Since W is nonnegative we can re-arrange this so that

$$\beta_C \int_0^T e^T e dt \leq W(0) + \int_0^T e^T d dt$$

Using the Schwartz-inequality we get

$$\beta_C \int_0^T e^T e dt \leq W(0) + \sqrt{\int_0^T d^T d dt} \sqrt{\int_0^T e^T e dt}$$

Hence

$$\beta_C \sqrt{\int_0^T e^T e dt} \leq \frac{W(0)}{\sqrt{\int_0^T e^T e dt}} + \sqrt{\int_0^T d^T d dt}$$

By ignoring the effect of initial conditions we can write

$$\sqrt{\int_0^T e^T e dt} / \sqrt{\int_0^T d^T d dt} \leq \frac{1}{\beta_C}$$

The result then is established by letting T → ∞.

The passivity theorem, Lemma L2, shows that the gain from the disturbance input d to the error e is finite and bounded by the constant $1/\beta_C$. Other results concerning the interconnection of passive systems can be found in the books by Desoer and Vidyasagar (1975) and Khalil (1996).[28,55]

Inventory and Flow Control

Farschman et al. (1998)[5] used the macroscopic balance

$$\frac{dv}{dt} = \phi(m, z, d) + p(m, z, d) \tag{24}$$

to derive control structures for chemical processes. We have indicated that the flux and production variables depend on vectors of manipulated variables m, state variables z, and disturbances d. We furthermore note that (Eq. 24) is a "positive system" since the state consists of elements that are nonnegative. All states of the system are stabilized (in the sense of Lyapunov) if the total energy and total mass is bounded. We now have the following result.

Result R4: Let v^* denote a time-varying reference. The synthetic input and output pair

$$u = \phi + p + \frac{dv^*}{dt} \quad e = (v - v^*)$$

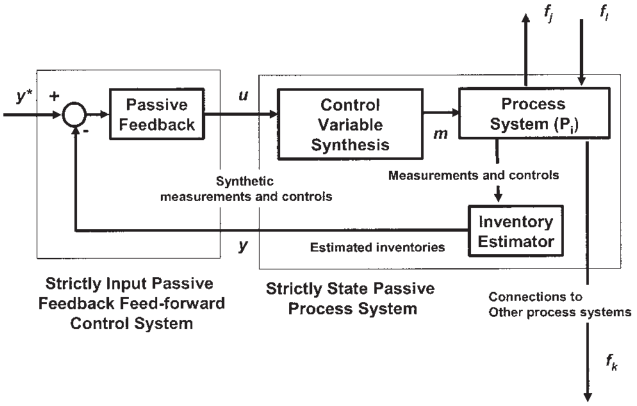

Figure 8. Inventory controller acts on transformed measurements and generates a set of synthetic control outputs which need to be transformed to real process inputs through control variable synthesizers (CVs).

This structure is similar to the extensive variable controller proposed by Georgakis (1986).[4]

is passive.

Proof: Let

$$V = \frac{1}{2}(v - v^*)^T (v - v^*) \tag{25}$$

That the vectors u and e are related in a passive manner is now easily verified. By differentiating V we get

$$\dot{V} = e^T \dot{e} = e^T(\dot{v} - \dot{v}^*) = e^T u$$

Passivity follows.

The input output pair is called synthetic since it does not necessarily correspond to what is directly measured and manipulated in the real process.

Definition D2 (Inventory Control): A control strategy which ensures that an inventory asymptotically tracks a desired set point is called inventory control.

It follows from Lemma L2 and Result R4 that inventory control is input/output stable when we use feedback-feedforward control in the form

$$u = \hat{\phi}(m, z, d) + \hat{p}(m, z, d) + \frac{dv^*}{dt} = -\mathbf{C}(e) \tag{26}$$

In this expression $\hat{\phi}$ denotes the estimate of the net flow, and $\hat{p}$ denotes the estimate of the net production. Furthermore, let $\tilde{\phi} = \phi - \hat{\phi}$ and $\tilde{p} = p - \hat{p}$. The operator $\mathbf{C}(e)$, which maps errors into synthetic controls, should be strictly input passive. We can then use Lemma L2 to show that the gain from the error $d = \tilde{\phi} + \tilde{p}$ to set point errors is given by the inverse of the L_2 gain of the operator $\mathbf{C}$. The structure of the control system is shown in Figure 8. What we see here is that we distinguish between two types of inputs and outputs to the process system. One type of inputs and outputs concern the physical flows. These flows connect with other process systems

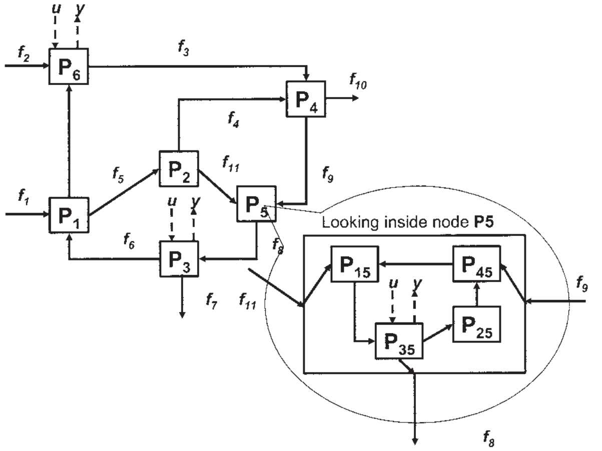

Figure 9. Process systems can be connected together to form large networks.

Each node corresponds to a passive system and inventory controllers may be used to control the node in a decentralized fashion by acting on inputs *u* using measurements *y*. The nodes themselves may consist of more devices connected together as indicated.

and boundary conditions, and can be used to define large and very complex networks of process systems as indicated in Figure 9. The beginnings of a theory for how such systems are connected, and the stability can be analyzed is described by Gilles (1998); Farschman et al. (1998), and Hangos et al. (1999).[56,5,57] Jillson and Ydstie (2005)[51] recently developed a process systems analog of Tellegen's theorem which allows for the very efficient analysis of complex thermodynamic networks. In such systems a very natural decomposition ensues which allows one to develop distributed process control and optimization methods using strong stability and optimality results that have been developed for the analysis of electrical circuits (Peusner, 1986; Ydstie, 2005).[60,58]

Inventory control is most useful for when the term *p* is absent since the modeling requirements are minimal. This is case for conserved properties like total mass, energy and components that do not undergo chemical transformation. Farschman et al. (1998)[5] demonstrated that we get a unique solution to the inventory control problem and stability provided the equation

$$\hat{\phi}(m, z, d) + \hat{p}(z, d) = 0$$

has a unique inverse with respect to the manipulated variable *m*. Farschman et al. (1998)[5] refers to this property as $\varepsilon -$ controllability. This condition fails close to maximum conversion point for component *B* in reaction scheme A → B → C. A further discussion is provided by Ruszkowski at al (2005).[27]

There are many examples of control that at are strictly input passive.

Result R5: The PID control

$$\hat{\phi}(m, d) + \hat{p}(m, d) + \frac{dv^*}{dt} = -K_c\left(e + \frac{1}{\tau_I}\int_0^t edt + \tau_D\frac{de}{dt}\right)$$

is strictly input passive for any choice of $K_c > 0$ and τ_I, $\tau_D \geq 0$. The dissipation rate is given by $\beta_C = K_c$.

Proof: First define the variables

$$\dot{s} = e$$
$$V = \frac{K_c}{2\tau_T}s^2 + \frac{K_c\tau_D}{2}e^2$$

where dot denotes time derivative. We now define

$$u = -K_c\left(e + \frac{1}{\tau_I}s + \tau_D\dot{e}\right)$$

Hence, by multiplying through with *e*

$$eu = -K_c\left(e^2 + \frac{1}{\tau_I}es + \tau_D e\dot{e}\right)$$

Hence

$$eu + K_c e^2 = -\frac{K_c}{\tau_I}es - K_c\tau_D e\dot{e} \tag{27}$$

We now differentiate the storage function to give

$$\dot{V} = \frac{K_c}{\tau_T}s\dot{s} + K_c\tau_D e\dot{e} \tag{28}$$

By using the fact that $e = \dot{s}$, and combining Eq. 27 and Eq. 28 we get

$$\dot{V} = -eu - K_c e^2$$

It follows from Definition D1 that the PID controller is input strictly passive with dissipation rate $\beta_C = K_c$.

If τ_I and τ_D are equal to zero, then the closed-loop response is given by the first-order equation

$$e(t) = \exp(-K_c t)e(0)$$

Thus, the closed loop time-constant is given by $\tau_{\mathrm{CL}} = 1/K_c$. Setting K_c very large gives fast response whereas setting K_c small gives slow response.

The method is not limited to PID control. For example, it is often possible to write

$$\phi(m, z, d, t) + p(m, z, d, t) = \mu(m, z, d, t)^T\theta \tag{29}$$

where $\mu(m,z,d,t)$ is a vector which depends on observable quantities, and θ is a vector of unknown parameters.

Result R6: The parameter adaptive controller

$$u = \mu(m, z, d, t)^T\hat{\theta} + \frac{dv^*}{dt} = -\mathbf{C}(e)$$
$$\frac{d\hat{\theta}}{dt} = -g\mu(m, z, d, t)e$$

is strictly input passive for any choice of adaptive gain $g > 0$ provided the feedback controller **C** is strictly input passive.

Proof: We first note that from Eq. 29, and the definition of *u,* we can write

$$u = \mu^T\hat{\theta}(t) + \mu^T(\theta - \hat{\theta}(t)) + \dot{v}^*$$

We, therefore, have by multiplying through with e

$$eu = e\mu^T\hat{\theta}(t) + e\mu^T(\theta - \hat{\theta}(t)) + e\dot{v}^*$$

This we re-arrange to give

$$\mu^T(\theta - \hat{\theta}(t))e = eu - e\mu^T\hat{\theta}(t) - e\dot{v}^* \tag{30}$$

We now define the storage function

$$V = \frac{1}{2g}(\theta - \hat{\theta}(t))^T(\theta - \hat{\theta}(t))$$

By differentiating V we get

$$\dot{V} = g^{-1}(\theta - \hat{\theta}(t))^T(-\dot{\hat{\theta}}(t))$$

By using the adaptive update law for $\hat{\theta}(t)$ we have

$$\dot{V} = (\theta - \hat{\theta}(t))^T\mu(m, z, d, t)e$$

Using Eq. 30 we get

$$\dot{V} = eu - e\mu^T\hat{\theta}(t) - e\dot{v}^*$$

From the control expression we have $\mu(m, z, d, t)^T\hat{\theta}(t) = -\dot{v}^* - \mathbf{C}(e)$. It follows that we may write

$$\dot{V} = eu + e\mathbf{C}(e)$$

The input strict passivity property follows from Definition 1 since **C** is input strictly passive.

We can use nonlinear feedback. Sliding mode inventory control is described by Wang and Ydstie (2004).[61] As noted by Shinskey (1967)[3] it is often advantageous to use a nonlinear feedback gain so that the controller takes the form

$$\phi(m, z, t) + p(m, z, t) + \frac{dv^*}{dt} = -K_c|v - v^*|(v - v^*)$$

This gives the high gain for large errors and small gain for small errors. Strict input passivity is easy to establish. Finally, we can implement any kind of gain scheduling (hybrid) controller

$$\phi(m, z, t) + p(m, z, t) + \frac{dv^*}{dt} = -\mathbf{C}_i(e), \quad i = 1, \ldots, N.$$

where C_i I = 1,2,3,. . ...denotes a sequence of dynamic operators so that $\Pi_{i=1}^{k}\mathbf{C}_i$ is passive for all k. A recent exposition of passivity theory, and its connections with nonlinear and $H\infty$ robust control is given by van der Schaft (1996).[32]

Invariant Sets and Stabilizability

In this section, we are interested in establishing the existence of invariant sets when we apply inventory control to process systems. A process system was defined by Ydstie and Alonso (1997)[36] to be system of conservation laws with a concave extension which satisfies the laws of thermodynamics. In our context this means that we can apply Assumptions A1 and A2 to the system of conservation laws (Eq. 14).

We have seen that application of ISP inventory control to a process system guarantees according to the passivity theorem that the inventories converge to their setpoints. We are now interested in seeing what happens to the remainder of the variables. We are in particular interested in seeing what happens if we control the total mass and energy of the system to constant setpoints E^* and M^*. We then get

$$\lim_{t\to 0}(M - M^*) = 0 \quad \text{and} \quad \lim_{t\to 0}(E - U^*) = 0$$

The total mass and energy are defined so that

$$M = \sum_{i=1}^{n} M_i \quad \text{and} \quad E = U + K + P$$

All these variables are bounded from below (by zero, with exception of U which can be defined relative to an arbitrary reference point). It follows that there exist invariant sets $\mathbf{Z} \subset \mathbf{\Sigma}$ so that $\lim_{t\to\infty} Z \in \mathbf{Z}$. By continuity and concavity we conclude that similar invariant sets are defined for the intensive variables. The sets are especially simple for the total mass and energy since they are determined by the setpoints. It is well known that the invariant sets corresponding to the remaining variables may be quite complex, especially for the case of chemical reactions.

We now have the following results

Lemma L3: The process system with input and output pair defined so that

$$u = (\tilde{f}(0) - \tilde{f}(L)) + \int_0^L \tilde{\sigma}dx + \frac{dv^*}{dt}$$
$$y = (M - M^*)$$

is strictly state passive on the set Σ^* if there exist, and $\beta_0 > 0$ so that

$$\int_0^L \tilde{f}^T\tilde{X} - \tilde{w}^T\tilde{\sigma}dx + \tilde{f}^T\tilde{w}\big|_0^L \geq \beta_0\tilde{w}^T\tilde{w}$$

Proof: First define the storage function

$$Y = W + V$$

where W is defined by Eq. 21 and V by Eq. 25. We get, using Corollary C1 and Result R4

$$\frac{dY}{dt} = \tilde{f}^T\tilde{w}\big|_0^L - \int_0^L (\tilde{f}^T\tilde{X} + \tilde{w}^T\tilde{\sigma})dx + (v - v^*)^T\left(\phi + p + \frac{dv^*}{dt}\right)$$

The result follows.

Lemma L3 gives sufficient conditions for strict state passivity on the set Σ^* for a process system with nonlinear reaction and transport rates. In the limit this allows us to use the classical contraction type analysis which is used in variational calculus to establish tight bounds for stability using first-order conditions. This approach for stability analysis of nonlinear systems can give tight bounds for nonlinear stability as long as the trajectories are noncritical.[51]

Result R7: Suppose that we have following properties satisfied

1. $\int_0^L \tilde{f}^T\tilde{X} - \tilde{w}^T\tilde{\sigma}dx + \tilde{f}^T\tilde{w}|_0^L \geq \beta_0\tilde{w}^T\tilde{w}$ for some $\beta_0 > 0$.
2. The total mass and energy is controlled using ISP inventory control.

Then there exist constants c_0 and c_1 so that we have

$$\int_0^t\int_0^L \tilde{w}^T\tilde{w}dt \leq c_0 < \infty \quad \text{and} \quad \int_0^\infty e^T e dt \leq c_1 < \infty$$

If in addition w_i and y are uniformly continuous then it follows that $\lim_{t\to\infty}\|\tilde{w}\| = 0$ and $\lim_{t\to\infty}\|y\| = 0$.

Proof: Follows directly from Lemma 3.

If set points and boundary conditions are constant and the solutions to the steady-state equations

$$\frac{\partial f_i}{\partial x} = \sigma_i \quad i = 1, \ldots, n$$

are continuous then we can conclude that

$$\lim_{t\to\infty}\|w(x)^* - w(x, t)\| = 0 \quad \text{and for all} \quad x \in [0, L]$$

w^* denotes the solution to the steady-state problem, hence, we get

$$\lim_{t\to\infty}(T_1 - T^*) = 0 \quad \lim_{t\to\infty}(P_1 - P^*) = 0 \quad \lim_{t\to\infty}(\mu_{i1} - \mu_i^*) = 0$$

In this case the invariant set is very simple and corresponds to a point in the space of intensive variables.

To summarize, the results in this section establish that chemical process systems are strictly passive and, hence, stabilizable if the reaction rates are Lipshitz continuous $\boldsymbol{L} > 0$ and the dimension of the system (L) is not too large. The stability condition can be expressed in terms of a Dahmkohler type number and all intensive variables converge to stationary points under inventory control. The theory can be extended to study stability more complex and time-varying invariant sets due to the introduction of the storage function R.

Application to 1D TRPs

In this section we illustrate the application of inventory control to a TRP described by the equation

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} + \sigma$$

with $t \in [0, \infty)$ and $x \in (0, L)$, Hulburt boundary conditions

$$c(0, t) = c_0(t)$$
$$\frac{\partial c(L, t)}{\partial x} = 0$$

and undergoing a first-order reaction of the form A → B with reaction rate

$$\sigma = -kc$$

where k is constant and c is the local concentration of chemical specie A. In this example there is only one state variable. Ydstie and Jiao (2004)[26] and Ruszkowski et al. (2004)[27] apply the inventory control method to more complex examples.

Result R8: The transport-reaction system (Eq. 22) with input and output defined so that

$$u = (\tilde{f}(0) - \tilde{f}(L)) + \int_0^L \tilde{\sigma}dx$$
$$e = (M - M^*) \tag{31}$$

is strictly passive if

$$\beta = \left(\frac{D\pi^2}{L^2} + k\right) \geq 0$$

Proof: Follows by application of Lemma L1 and Corollary C2. Full developments are given by Ruszkowski (2003).[27]

We see that the system is stable since k is positive. The main objective of the section is to look at a range of feedback control structures that can be used to control the inventory.

In light of the motivation behind passivity theory for control design, we now consider developing stable control structures with passive input and output pairs as shown in Eq. 31. A proportional feedback controller is the simplest type of controller which is strictly input passive. We get

$$(\tilde{f}(0) - \tilde{f}(L)) + \int_0^L \tilde{\sigma}dx = -K_c(M - M^*) + \frac{dv^*}{dt}, \quad K_c \geq 0 \tag{32}$$

The control law is quite general in the sense that we are free to choose manipulated variables including flow rate, inlet composition or the total reaction rate. In our particular case the inlet flux $f(0)$ admits the decomposition

$$\tilde{f}(0) = vc(0) - v^*c^*(0)$$

We can choose to manipulate the transport velocity *(v)* or the inlet concentration (*c(0)*). Regardless of the choice, for the control law (Eq. 32) to be solvable, specific criteria must be satisfied. The requirements are as follows:

1. The righthand side of control law (Eq. 32) must be well defined and invertible with respect to the manipulated variable so that the control action can be implemented.

2. The geometry of the system must be chosen so that the system is strictly dissipative. This can always be achieved by choosing L small.

The first point ensures that a control action can actually be calculated; this may set some limitations on selection of the manipulated variables as we discuss a companion article (Ruszkowski et al., 2004).[27] The second point ensures that all states (controlled and uncontrolled) reach a stable stationary point.

In the following examples we do not include the term dv^*/dt in the control laws.

Example 1. In this example, we perform a servo control study. A step change is induced to the inventory set point, and the transport velocity (v) is chosen as the manipulated variable. The control law (Eq. 32) takes the form

$$((vc(0) - v^*c^*(0)) - (vc(L) - v^*c^*(L)) + \int_0^L (\sigma - \sigma^*)dx = -K_c(M - M^*)$$

Solving for velocity (v) we obtain ratio control

$$v = \frac{1}{c(0) - c(L)}\left(-K_c(M - M^*) - \int_0^L \tilde{\sigma}dx + b^*\right)$$

where the constant b^* is defined so that

$$b^* = v^*c^*(0) - v^*c^*(L) - \int_0^L \sigma^*dx$$

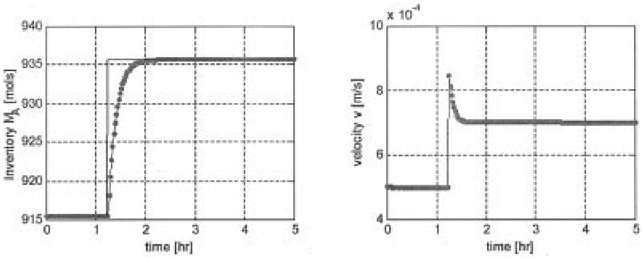

Figure 10. Servo control simulation results under proportional feedback and nonlinear feedforward control for Example 1.

The graph on the left shows the controlled output (Inventory $y = M_A$). The graph on the right shows the manipulated input (Velocity $u = v$).

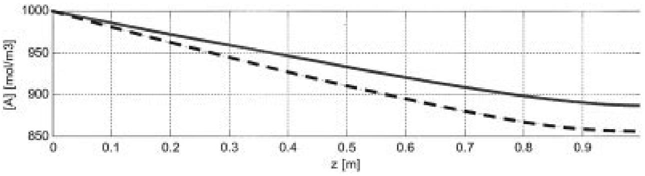

Figure 11. Initial (dashed) and final (solid) concentration profiles for Example 1.

The control consists of proportional feedback (P-FB) term, a feedforward (FF) signal from offset in the reaction rate and a constant. This control law is well defined as long as *c(0)* is not equal to *c(L)*, which is the case if the reaction is present. If there is no reaction present then the controllability is lost and it is not possible to control the concentration of A using this or any other method.

The response of the inventory will be given the first-order relationship

$$M(t) = M^* + e^{-K_c t}M(0)$$

Thus, $1/K_c$ gives the time constant of the closed-loop system. Figure 10 shows the system's response to an inventory set point change. The transport velocity converges to a stationary value as the inventory (*M*) converges to its set point. The inlet boundary condition is unchanged, but nonetheless a new concentration profile is achieved due to a change in space-time velocity, as shown in Figure 11.

One disadvantage of the proportional control approach is the necessity for *a priori* knowledge of steady-state offsets. One way of overcoming this inconvenience is to drop the steady state terms and use integral action. In this case, the new proportional and integral action feedback-feedforward (PI-FB/FF) control law becomes

$$v = \frac{1}{c(0) - c(L)}\left(-K_c\left((M - M^*) + \frac{1}{\tau_I}\int_0^t (M - M^*)dt\right) - \int_0^L \tilde{\sigma}dx\right)$$

The PI and PID controllers also represents a strictly passive systems so the interconnection will be stable. The simulation is now repeated without any a prior knowledge of the steady state related terms. The response is comparable to previous results as shown in Figure 12.

We now consider approximations that can be made while maintaining passivity.

1. The term *1/(c(0)−c(L))* is positive and can be ignored. The response will be nonlinear instead of linear, but asymptotic stability is maintained.

2. The term $\int_0^L \tilde{\sigma}dx$ can be omitted from the control law if it is bounded. We can now use high-gain feedback like sliding

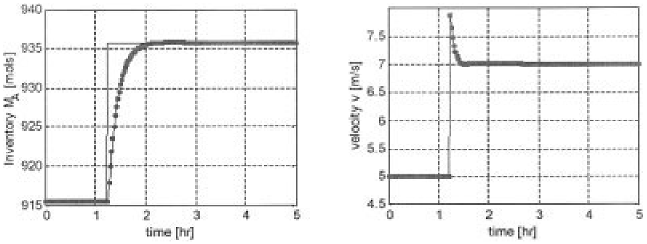

Figure 12. Servo control simulation results under proportional integral feedback and nonlinear control for Example 1.

mode control. Passivity ensures that we converge to a sliding surface characterized by zero error (Wang and Ydstie, 2004).[61]

In other words, the infinite dimensional system is stabilized PID type inventory control, and no knowledge of the process model.

Example 2: We now manipulate the inlet boundary condition (*c(0)*) instead of the transport velocity. Solving for this quantity, the control law now becomes

$$c(0) = c(L) + \frac{1}{v}\left(-K_c(M - M^*) - \int_0^L \tilde{\sigma} dx + b^*\right)$$

where b^* is constant as defined earlier. In this case we loose controllability as the velocity decreases toward zero. This is expected since we cannot control the concentration when there is no flow. Figure 13 shows the response of the system under this control strategy. The inlet concentration converges to a stationary value as the mass inventory M exponentially converges to its set point.

In the examples we achieved the desired inventory levels employing two different control approaches. Therefore, it is possible and advantageous to choose the manipulated variable that facilitates greatest controllability and stability. In practice, however, the choice of a control strategy may be limited by the availability of control variables and other equipment constraints.

Example 3: We perform a regulatory control study were the transport velocity acts as a step disturbance. To maintain a constant inventory set point, the inlet concentration (*c(0)*) is manipulated. For this experiment, a proportional feedback/feed-forward controller was tested. Figure 14 shows the results. The concentration profiles are shown in Figure 15. The profile is "tilted" counterclockwise with respect to allow a velocity change while maintaining the holdup of component A constant. This figure shows that different internal conditions can give the same macroscopic holdup.

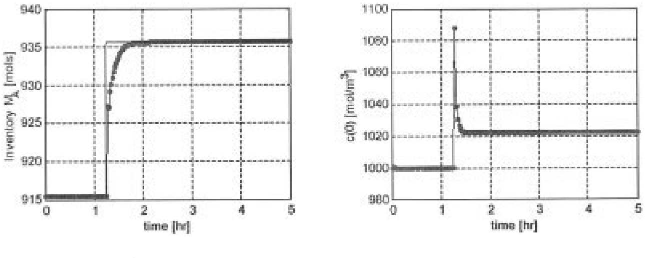

Figure 13. Servo control simulation results under proportional feedback and nonlinear feedforward control for Example 2.

The graph on the left shows the controlled output (Inventory $y = M_A$). The graph on the right shows the manipulated input (Inlet concentration $u = c(0)$).

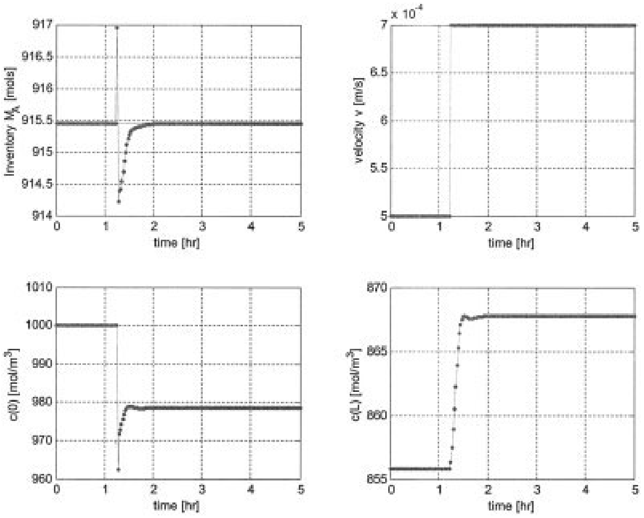

Figure 14. Disturbance rejection simulation results under proportional feedback and nonlinear feedforward control for Example 3.

The graph on the top left shows the controlled output (Inventory $y = M_A$). The graph on the top right shows the disturbance input (velocity $d = v$). The graph on the bottom left shows the manipulated input (inlet concentration $u = c(0)$). The graph on the bottom right shows the outlet concentration *c(L)*.

In all three examples, whether the system was influenced by a proportional controller or a proportional integral controller, it was able to converge to a stable stationary point.

Conclusions

In this article we have proposed a method to integrate physics and process control by developing a thermodynamic based approach to passivity based control of transport-reaction systems. The class of systems we consider is quite broad and encompasses a wide range of classical processes in chemical, biochemical and metallurgical process engineering, as well as control of small-scale systems, as long as the Boltzman principle holds and coarse graining can be applied. We provided a review of the notion of passivity and related this to the second law of thermodynamics. Using a local storage function con-

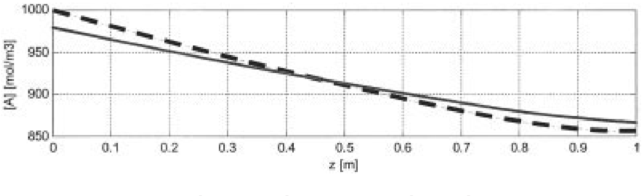

Figure 15. Initial (dashed) and final (solid) concentration profiles for Example 3.

Note that the concentration profile adjusts so that molar holdup of component A is kept constant.

sisting of microscopic and macroscopic elements, we derived sufficient conditions for strict passivity and stability properties by relating the storage function to thermodynamics using Gibb's tangent plane method. This result also delineated general control structures for controlling convection-diffusion-reaction systems. An array of feedback/feedforward control structures were reviewed including PID, adaptive, nonlinear and gain scheduling control. The theoretical results were illustrated with a numerical simulation of a 1-D convection-diffusion-reaction model. We showed the response for setpoint changes for two types of control configuration. In one case we controlled the inventory using flow rate as manipulated variable, in the other case we used the inlet concentration. In the final simulation we investigated the disturbance rejection property of the control system.

Acknowledgments

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In an interesting discussion in the poster session at the 2003 AIChE meeting in Indianapolis, Professor Mike Doherty of UMass/UCSB pointed out that stability conditions developed from the storage function A introduced by Alonso and Ydstie (1997[36]), are going to be equivalent to those using the Gibbs tangent plane condition.

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Appendix: Review of Classical Irreversible Thermodynamics and Symmetry of the Linear Laws

In this appendix we revisit two classical problems in linear irreversible thermodynamics (LIT). The first problem concerns the issue of stability. The second problem concerns the question of whether or not steady-state thermodynamics can be formulated via a variational principle. Note that while the constitutive laws for heat and mass transport, as well as chemical reaction are assumed to be linear, this does not imply linearity since we still allow for nonlinear phase behavior as given by for example by the Peng-Robinson equation of state.

Onsager and Prigogine were both awarded Nobel prizes for contributing to LIT: Onsager for having established symmetry of the conductance parameters using microscopic reversibility; Prigogine for having established the principle of minimum entropy production using Onsager symmetry as his point of departure. The ideas are closely related to the principles of le Chatelier-Braun and Maxwell's theorem of minimum heat dissipation. A very readable account of these ideas can be found in the book by Kondepudi and Prigogine (1995).[63]

The entropy density is defined so that for any nonempty volume V

$$S = \int_V \rho s dV$$

We can now use HLE write

$$\frac{\partial \rho s}{\partial t} = \frac{\partial \rho s}{\partial \rho z}\frac{\partial \rho z}{\partial t} = w^T \frac{\partial \rho z}{\partial t}$$

By using the transport Eq. 14 we get

$$\frac{\partial \rho s}{\partial t} = w^T\left(-\frac{\partial f}{\partial x} + \sigma\right)$$

From which we get the conservation law for the entropy

$$\frac{\partial \rho s}{\partial t} + \underbrace{\frac{\partial (w^T f)}{\partial x}}_{\text{Entropy Flux}} = \underbrace{f^T \frac{\partial w}{\partial x} + w^T \sigma}_{\text{Entropy Generation}} \tag{A1}$$

The second law of thermodynamics stated in the local form is easily derived from Eq. A1. It states that the rate of entropy generation is positive so that

$$\sigma_S = f^T X + w^T \sigma \geq 0 \tag{A2}$$

where the thermodynamic forces X are defined in Eq 18. By combining Eq. A1 and inequality (Eq. A2), and integrating we obtain the celebrated Clausius-Planck inequality which was used as the starting point for the stability theory by Ydstie and Alonso (1997).[36]

By using the flow decomposition (Eq. 15) we have from Assumption A2

$$\sigma_S = f_{\text{conv}}^T X + f_{\text{diff}}^T X + w^T \sigma \geq 0$$

Using the definition of the forces in Eq. 18 we have

$$f_{\text{conv}}^T X = u\rho \begin{pmatrix} \hat{U} \\ \hat{V} \\ \hat{M}_1 \\ \hat{M}_2 \end{pmatrix}^T \frac{d}{dx} \begin{pmatrix} 1/T \\ P/T \\ -\mu_1/T \\ -\mu_2/T \end{pmatrix}$$

By writing this expression out term by term and using the fact that $u\rho = \dot{M}$ we get

$$f_{\text{conv}}^T X = \dot{m}\left(\hat{U}\frac{d}{dx}\left(\frac{1}{T}\right) + \hat{V}\frac{d}{dx}\left(\frac{P}{T}\right) - \hat{M}_1 \frac{d}{dx}\left(\frac{\mu_1}{T}\right) - \hat{M}_2 \frac{d}{dx}\left(\frac{\mu_2}{T}\right)\right)$$

Using the Gibbs-Duhem Eq. 3 we conclude that

$$f_{\text{conv}}^T X = 0$$

Inequality (Eq. A2) can, therefore, be written

$$\sigma_S = f_{\text{diff}}(X)^T X + w^T \sigma \geq 0 \tag{A3}$$

By using the expression Eq. 16 we have

$$w^T \sigma = -\frac{1}{T} P \frac{\partial u}{\partial x} + \frac{1}{T} P \frac{\partial u}{\partial x} - \sum_{i=1}^{nr} \frac{\mu_i}{T} \sigma_i + 2\mu \frac{1}{T} \left(\frac{\partial u}{\partial x} \right)^2$$

The first two terms represent reversible work and they cancel. From Eq. A3 we, therefore, get

$$\sigma_S = f_{\text{diff}}(X)^T X - \sum_{i=1}^{nr} \frac{\mu_i}{T} \sigma_i + 2\mu \frac{1}{T} \left(\frac{\partial u}{\partial x} \right)^2 \geq 0$$

We can, therefore, write the local form of the second law so that

$$\sigma_S = f_{\text{diff}}(X)^T X + \sigma_R^T \mathbf{m} + 2\mu \frac{1}{T} \left(\frac{\partial u}{\partial x} \right)^2 \geq 0 \tag{A4}$$

where

$$\mathbf{m} = \left(-\frac{\mu_1}{T}, \ldots, -\frac{\mu_{nr}}{T} \right)$$

The first term in expression (Eq. A4) represents entropy generation due to heat conduction and diffusion. The second term represents entropy generation due to chemical reaction, and the third term represents entropy generation due to viscous dissipation.

LIT assumes that the constitutive equations for diffusive flow and chemical reaction are linear. This gives

$$f_{\text{diff}} = \mathbf{L} X \tag{A5}$$

and for the reactive terms we get

$$\sigma_R = \mathbf{K} \mathbf{m} \tag{A6}$$

where **L** and **K** are constant matrices. From expression (Eq. A4) we can, therefore, write the entropy production as a quadratic form

$$\sigma_S = X^T \mathbf{L} X + \mathbf{m}^T \mathbf{K} \mathbf{m} + 2\mu \frac{1}{T} \left(\frac{\partial u}{\partial x} \right)^2 \geq 0 \tag{A7}$$

In order to satisfy the second law for all possible variations in forces and intensive variables it is, therefore, necessary and sufficient that $\mu \geq 0$ and that the eigenvalues of **L** and **K** are nonnegative since T is positive[7].

Result A1: Suppose that **L** has eigenvalues $\lambda_i \geq \alpha_0 > 0$. The stationary state of a process system with linear laws (Eqs. A5 and A6) and constant boundary conditions is stable.

Proof: This follows immediately from Result R3 since Assumption A3 is satisfied.

Strict positivity of **L** implies that the resistance matrix $\mathbf{R} = \mathbf{L}^{-1}$ is bounded which it means that the medium has some conductivity. Superconducting materials have the best stability as might be expected, since gradients cannot be sustained at all. We note that while the dissipation due to fluid flow has been included, the result does not say anything about fluid flow stability since the Lyaponov function(al) does not include the momentum.

We now want to address the issue of Onsager reciprocity (symmetry of **L**) and see how symmetry is related to Prigogine's "principle of minimum entropy production". de Donder (Kreuzer, 1981, Kondepudi and Prigogine, 1995)[48,63] showed that chemical reactions (not necessarily equilibrium reactions) can be modeled using affinities. We review this theory very briefly here. Consider a system with n species and r chemical reactions. We then have

$$\sum_{i=1}^{n} v_{ji} s_i = 0, \quad j = 1, \ldots, r \tag{A8}$$

where ν_{ij} is the stochiometric coefficient of species s_i as it enters in reaction j. For example if we have $n = 3$ and $r = 1$, and reaction

$$2\mathbf{A} + \mathbf{B} \leftrightarrow \mathbf{C}$$

then we have $\nu_1 = -{}_2$, $\nu_1 = -{}_2$ and $\nu 3 = 1$.

The affinity of reaction j is defined so that

$$A_j = \sum_{i=1}^{n} v_{ij} \frac{\mu_i}{T} \quad j = 1, \ldots, r \tag{A9}$$

The affinity is equal to zero if reaction j is at equilibrium (Sandler, 1996).[45] de Donder, therefore, proposed to set the reaction rate proportional to the affinity so that for reaction $r_j = k_j A_j$. We can then combine Eqs. A8 and A9, and write the expression for the reaction rate for component k so that

$$\sigma_k = \sum_{j=1}^{nr} v_{kj} k_j A_j = \sum_{j=1}^{nr} v_{kj} k_j \sum v_{ij} \frac{\mu_i}{T}$$

This we can write on the vector matrix form

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[7] Any square matrix, say **B**, can be decomposed into a symmetric matrix **S** and an antisymmetric matrix **A** where **A** has zeros on the diagonal. We write this decomposition so that $\mathbf{B} = \mathbf{A} + \mathbf{S}$. We therefore have $x^T \mathbf{B} x = x^T \mathbf{S} x$ for any vector x. It follows that inequality (A7) doesn't imply symmetry.

$$\sigma_k = \sum_{j=1}^{nr} k_j \mathbf{v}_j \mathbf{v}_j^T \mathbf{m} \tag{A10}$$

where $\mathbf{v}_j = (v_{1j}, \ldots, v_{nj})^T$. We can now write

$$\mathbf{K} = \sum_{j=1}^{nr} k_j \mathbf{v}_j \mathbf{v}_j^T \tag{A11}$$

Equation A10 now has the form given in Eq. A6. It follows that **K** automatically is symmetric.

Lars Onsager (Onsager and Machlup, 1953),[64] however, argued that in LIT **L** must also be symmetric due to microscopic time reversibility (Kreuzer, 1984).[48] This property prompted Prigogine to propose the principle of minimum entropy production at steady state. He was able prove the generality of the principle using example problems. Later, we generalize the results due to Onsager and Prigogine, by showing that in the linear case minimum entropy production and symmetry are equivalent.

Result A2: Consider an LIT system. The functional $\Phi = \int_0^L \sigma_S(w, X, x, t)dx \geq 0$ is minimized at steady state if and only if $\mathbf{KL}^{-1}(\mathbf{L} - \mathbf{L}^T) = 0$.

Proof: We have shown above that the rate of entropy production is independent of the center of mass velocity since the Gibbs-Duhem orthogonality allows us to write $X^T \rho v z = 0$. Without losing generality, we set $u = 0$. At steady state we then have

$$\frac{d(\mathbf{L}X)}{dx} = \mathbf{K}w \tag{A12}$$

By differentiating (A7) with respect to X we have

$$\frac{\partial \sigma_S}{\partial X} = X^T\mathbf{L} + (\mathbf{L}X)^T$$

hence

$$\frac{d}{dx}\left(\frac{\partial \sigma_S}{\partial X}\right) = \frac{d(X^T\mathbf{L} + (\mathbf{L}X)^T)}{dx} \tag{A13}$$

Likewise

$$\frac{\partial \sigma_S}{\partial w} = w^T\mathbf{K} + (\mathbf{K}w)^T \tag{A14}$$

Using the steady-state equation A12 with A13 and A14, we get

$$\frac{d}{dx}\left(\frac{\partial \sigma_S}{\partial X}\right) - \frac{\partial \sigma_S}{\partial w} = \frac{dX^T\mathbf{L}}{dx} - w^T\mathbf{K}$$

Using the symmetry of **K** and the steady-state Eq. A12 we get

$$\frac{d}{dx}\left(\frac{\partial \sigma_S}{\partial X}\right) - \frac{\partial \sigma_S}{\partial w} = w^T\mathbf{KL}^{-1}(\mathbf{L} - \mathbf{L}^T) \tag{A15}$$

Using the assumption $\mathbf{KL}^{-1}(\mathbf{L} - \mathbf{L}^T) = 0$, we get

$$\frac{d}{dx}\left(\frac{\partial \sigma_S}{\partial X}\right) - \frac{\partial \sigma_S}{\partial w} = 0$$

However, these are the Euler-Lagrange equations for the functional Φ and it follows that Φ is at an extremum. Suppose now that $\mathbf{KL}^{-1}(\mathbf{L} - \mathbf{L}^T) \neq 0$. Then there exists w so that the right hand side of Eq. A15 is not equal to zero. The E – L gives the necessary and sufficient conditions for an extremum for this problem (Gelfand and Fomin, 1963),[65] and it follows, therefore, that the functional Φ is not minimized for general w.

That the extremum indeed is a minimum follows from the fact that the entropy production with linear laws is convex according to constraint (Eq. A7).

We see that the condition of Result A2 is satisfied if **L** is symmetric. It is also satisfied for nonreacting systems since we then have $\mathbf{K} = 0$. Minimum entropy production, therefore, is a more general principle than symmetry.

Prigogine developed a local stability result by using the second-order variation of the entropy as a Lyapunov function and looked at small deviations from equilibrium steady states (Glansdorff and Prigogine, 1970; Kreuzer, 1981; Kondepudi and Prigogine, 1998).[66,48,63] This theory was quite successful for diffusion, heat conduction and many other phenomena that can be modeled using linear rate expressions.

The linear theory was not successful for the analysis of systems far from equilibrium. The use of linear reaction is especially troublesome and LIT, therefore, has limited scope for practical application (Wei, 1966).[67] Another important problem with LIT is that it does not address input-output behavior. In order to make use of the formalism for control it is necessary, therefore, to develop theory that can (1) deal with instabilities that arise due to nonlinear phenomena, and (2) address the input output behavior as we have done is the main body of this article.

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