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Official URL : <https://doi.org/10.1016/j.cherd.2019.10.037>

To cite this version:

Gerbaud, Vincent  and Da Cunha, Sergio  and Shcherbakova, Nataliya  *A nonequilibrium thermodynamics perspective on nature-inspired chemical engineering processes.* (2019) *Chemical Engineering Research and Design*, 154. 316-330. ISSN 0263-8762

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A nonequilibrium thermodynamics perspective on nature-inspired chemical engineering processes

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Author accepted manuscript

Abstract

Nature-inspired chemical engineering (NICE) is promising many benefits in terms of energy consumption, resilience and efficiency etc. but it struggles to emerge as a leading discipline, chiefly because of the misconception that mimicking Nature is sufficient. It is not, since goals and constrained context are different. Hence, revealing context and understanding the mechanisms of nature-inspiration should be encouraged. In this contribution we revisit the classification of three published mechanisms underlying nature-inspired engineering, namely hierarchical transport network, force balancing and dynamic self-organization, by setting them in a broader framework supported by nonequilibrium thermodynamics, the constructal law and nonlinear control concepts. While the three mechanisms mapping is not complete, the NET and CL joint framework opens also new perspectives. This novel perspective goes over classical chemical engineering where equilibrium based assumptions or linear transport phenomena and control are the ruling mechanisms in process unit design and operation. At small-scale level, NICE processes should sometimes consider advanced thermodynamic concepts to account for fluctuations and boundary effects on local properties. At the process unit level, one should exploit out-of-equilibrium situations with thermodynamic coupling under various dynamical states, be it a stationary state or a self-organized state. Then, nonlinear phenomena, possibly provoked by operating larger driving force to achieve greater dissipative flows, might occur, controllable by using nonlinear control theory. At the plant level, the virtual factory approach relying on servitization and modular equipment proposes a framework for knowledge and information management that could lead to resilient and agile chemical plants, especially biorefineries.

Keywords

Nature-inspired engineering; nonequilibrium thermodynamics; nonlinear control; self-organization; virtual modular factory

1 Introduction

Chemical engineering deals with the processing of matter and energy, which requires processing with information as well. It also puts an emphasis on the development of technologies used for the large-scale chemical production and on the manufacture of products with desired properties through chemical processes. Interactions within and between processes are important, as well as dynamics. But, like a cat, chemical engineering is purring over its assets. Most of models and knowledge in use have been established decades ago. They have proven their performance to meet the XIXth and XXth century challenge of large-scale production at the lowest cost. However, within the sustainable growth challenges now everywhere in the XXIst century, priorities are renewed: less waste, renewable materials, energy efficiency, low emissions, etc, but also small-scale production distributed over a territory, close to consumers and human-aware production (workforce, inhabitants near plants, consumers). Chemical engineering must rejuvenate.

Nature also processes energy, matter and information. It is also the most realistic model of structures and processes, whose performance, efficiency and resilience can and should be envied by human-made activities.

While nature inspiration in engineering has been recognized for some time, in particular with the principle of evolution in design, so-called constructal law (Bejan, 2000), Coppens (2005, 2012) has pioneered the field of Nature-inspired chemical engineering (NICE) by enunciating three mechanisms that have different levels of engineering maturity. T1 – hierarchical transport networks – is the most advanced while T2 – force balancing – is less evidenced and T3 – dynamic self-organisation – needs even more exploration. Recently Coppens (2019) further extended this list and proposed T4 or control mechanisms in ecosystems, biological networks and modularity. For establishing bio-inspired chemical engineering, Chen (2016) has put forward a combination of microstructure – formulation – processing as the key to develop such processes.

But, nature-inspiration is far from being the norm in chemical engineering. Indeed, student's textbooks and engineer's handbooks show that chemical engineering processes are overwhelmingly designed and operated on the basis of phase equilibrium hypotheses in reaction and separation engineering, that transport phenomena are almost always described with linear phenomenological laws and that process regulation is also mostly done with linear control theory to maintain quasi-steady state operation. Most of these concepts are 50+ years old and are antipodal with Nature's way of life in a nonlinear dynamic out of equilibrium, and ever adapting state.

Nature-inspiration could then help improve performance, efficiency and resilience of chemical engineering processes. To achieve this goal, some trends have been established for biology-inspired processes, spanning both micro- and large-scale processes (Chen, 2016). For engineering as a whole, the challenge has been clearly defined in the literature (Coppens, 2005, 2012): merely copying natural structures, tools or processes or using biosourced material leads to sub-optimality because human-made objects and processes do not operate in the same context as natural processes nor with the same goals. Instead, one should decipher the hidden mechanisms and dynamics so as to develop nature-inspired engineered objects and processes.

In this paper, we pursue this same objective but from a perspective joining nonequilibrium thermodynamics (NET), constructal law (CL) and nonlinear control concepts. After presenting a roadmap for moving from classical to nature-inspired chemical engineering in section 2, we address in section 3 the mechanisms of NICE within the novel framework of NET and CL, starting from equilibrium state and ending discussing dynamical out of equilibrium states of open systems. T1, T2 and T3 are mapped in this framework and made clear under this new light when possible. While the mapping is not complete, the NET and CL joint framework opens also new perspectives that could assist NICE. Hence, section 4 outlines challenges that could inspire the chemical engineering

community at the nanoscale level, the macroscale level and in process dynamics, whose monitoring requires to implement nonlinear control.

2 From classical to nature-inspired chemical engineering

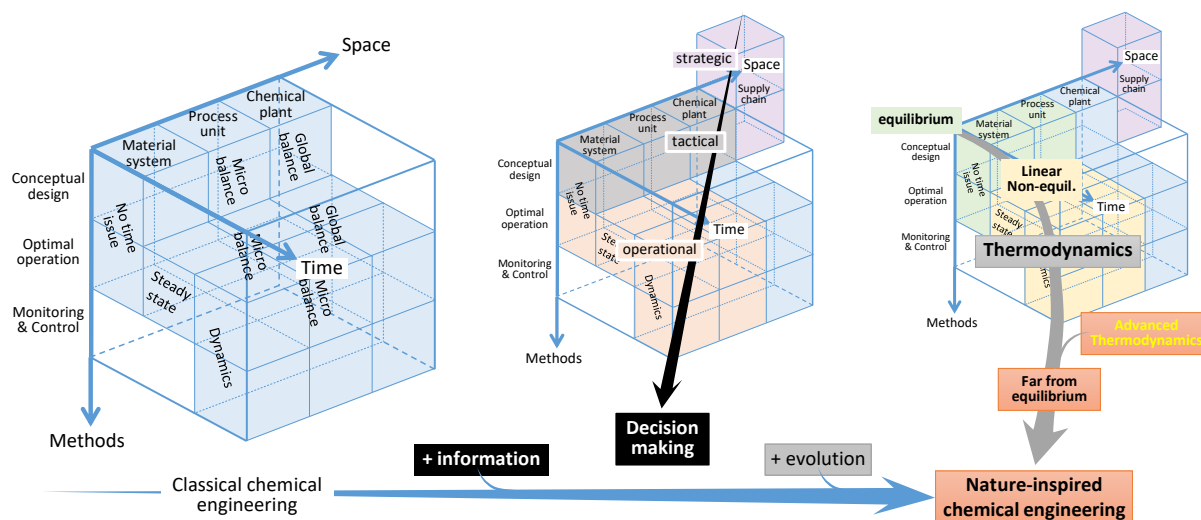


Figure 1 – From classical to nature-inspired chemical engineering: a route across information and evolution

Chen (2016) has sketched an evolution of chemical engineering to bio-inspired chemical engineering considering it as a new branch of chemical engineering due to interaction with biological sciences. But this remains a macroscopic and limited perspective. Here, we discuss more fundamental aspects and we claim that a more theoretical thermodynamic perspective is an interesting way to understand the fundamental underlying mechanisms and to shift chemical engineering toward NICE along a trajectory sketched in Figure 1, using model-driven and enterprise modelling multilevel concepts.

On the left, the $3 \times 3 \times 3$ cube displays an approximate but effective discretization of the chemical engineering domain in three directions. Here, chemical engineering systems can be split over space ($+30^\circ$ axis) into material system, process unit and chemical plant levels. This picture could be further refined by splitting each level into element, mesoscale and system scales (Li et al., 2016): a factory is composed of process unit elements where unit operations happen; and is ran within an environment when addressing the system scale. The mesoscale problem at the plant factory level concerns the process synthesis and requires dealing preliminarily with unit operations. Hence, for solving it, global steady state balances are usually considered while microscopic balances, including non-steady states balances are used to investigate unit operation of process units. In terms of methods (downward vertical axis) and time (-30° axis), a chemical engineer traditionally first carries out a time independent conceptual design stage (check thermodynamic, assess feasibility with simple models, scale-up, elaborate flowsheet, ...). He then looks for steady state operating conditions for a cost-optimal operation (refining thermodynamic modelling, simulating with rigorous models, undertaking experiments, etc.) and he goes on with monitoring and control, usually for short term dynamics (start and stop periods, process regulation with linear control theory, etc.).

The middle picture adds the issue of handling information. Already, data is information and feeds chemical engineering everywhere in the left cube representation. Here, the middle picture focuses on the decision making process that integrates information further from an enterprise viewpoint. At the strategic decision level, an extra level must be accounted for, concerning supply chain. Tactical decisions usually concern chemical plants and process unit operation during the design stage. Operational decisions are pertaining to material systems and process units during the optimal operation step as well as to monitoring and control steps.

The right picture maps some thermodynamics concepts over the chemical engineering multiscale and multilevel representation. First, one finds the common phase equilibrium assumption in material systems and process unit models; while dissipative transport phenomena in unit operation models are described with linear phenomenological laws in balance expressions.

When taking into account information, the processing of matter and energy carried out in chemical engineering covers areas similar to what Nature processes. So what is missing to promote NICE? Being inspired by Nature helps clarify the limits of today's chemical engineering and raises several questions: should we refrain our processes to run in near equilibrium conditions where linear transport law and linear control are used? Is the local equilibrium hypothesis of thermodynamics still valid in nano and microscale processes? What means efficiency for nature and for chemical engineering? Could a novel production organization be inspired by nature?

Within a NET perspective, the notion of evolution covers most of these questions that we complete later. To fulfil precise goals mostly related to survival, natural systems operate near or far from thermodynamic equilibrium, maintain a quasi-steady near-critical state, in an agile way, being adaptable to changes in their surroundings by using efficient strategies of adaptation and adaptability with nonlinear responses and synergies with other nearby systems. These issues are covered in the framework now presented.

3 Nonequilibrium thermodynamics mechanisms for nature-inspired chemical engineering processes

Chemical engineering and thermodynamics share a long history together and are inseparable. However, thermodynamics is full of misconceptions (Martyushev, 2013; Bejan, 2017, 2018) that one should be aware of especially when invoking the entropy-related notions (second law, disorder, entropy production extremum, ...). Entropy is indeed the core concept of thermodynamics. However, the connection between entropy and chemical engineering processes is nowadays overshadowed by two more pragmatic concepts, namely the thermodynamic equilibrium assumption and the use of Fick, Fourier, Newton transport phenomena laws in mass balances. The first is merely a formulation of the second law for isolated closed systems and the second refers to linearized NET equations. But, as highlighted in Figure 2, much more exists in the NET and CL framework, in particular thermodynamic coupling, stationary states, dissipative structure, spatial organization and nonlinear dynamics, that cover partially the three mechanisms T1 T2 T3 already published (Coppens, 2012).

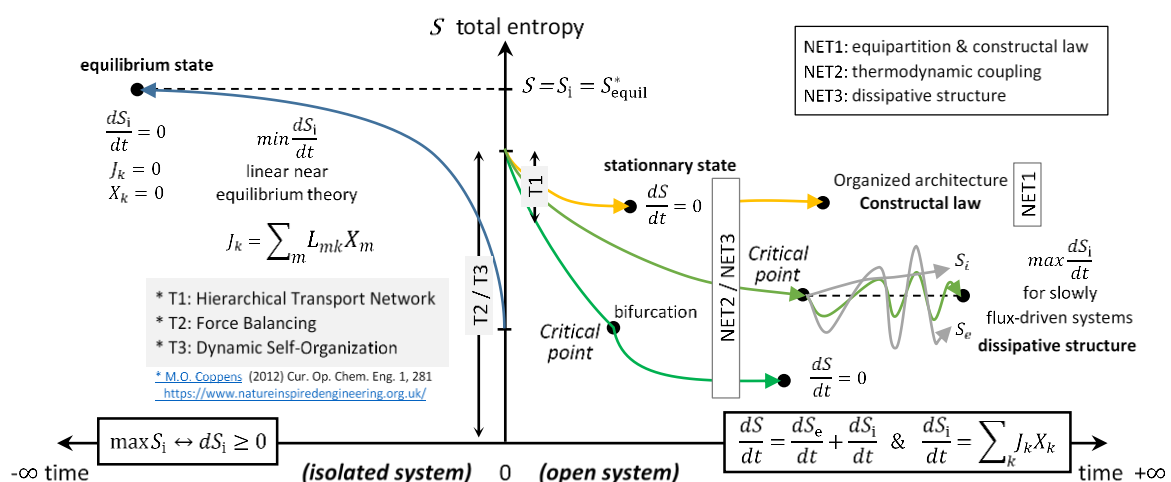


Figure 2 – Nonequilibrium thermodynamics perspective of nature-inspired mechanisms

3.1 Local thermodynamic equilibrium postulate

The spatial discretization of micro, meso and macro systems in chemical engineering (Figure 1) can be paralleled with the classical thermodynamics assumption that an elemental volume contains enough molecules for microscopic fluctuations to be negligible. This local thermodynamic equilibrium postulate establishes the familiar Boltzmann-Gibbs statistical definition of entropy S for a system of N discernible particles distributed with probability distribution $p = \{p_1, p_2, \dots, p_n\}$ among n independent microstates

$$S = -k_B \sum_{i=1}^n p_i \ln p_i \quad (1)$$

The average equation above relates the entropy to the probability of occurrence of the possible states of the system, each described by an information content $\ln(p_i)$.

Nevertheless, the local equilibrium postulate holds no longer in several systems encountered in chemical engineering, where boundaries, fluctuations, configurations and memory effects may impact the definition of local variables (Jou et al., 2010). One can recall that some of the works assigned to the ‘‘Force balancing (T2)’’ mechanisms in nature-inspired engineering evoked by Coppens (2012) discuss the impact of geometrical confinement features of the same magnitude as the molecule size: they may enhance enzymatic activity (Sang and Coppens, 2011; Sang et al., 2011) or provide opportunities for the formulation and controlled release of biological agents (Siefker et al., 2014). Such a confinement brings about local fluctuation and boundary effects that may violate the local thermodynamic equilibrium hypothesis encouraging us to use advanced thermodynamic formalism for improving modelling and understanding (see section 4.1).

3.2 The second law of thermodynamics and thermodynamic equilibrium

Consider a system described by macroscopic variables and undergoing a change along some path. The related entropy S change is the sum of an external contribution dS_e due to the interaction of a system with its surroundings and an internal contribution dS_i :

$$dS = dS_e + dS_i \quad (2)$$

The second law of thermodynamics states that the internal entropy S_i can only increase along an irreversible path or remains equal for a reversible trajectory, $dS_i \geq 0$. A consequence well-known among engineers is that heat flows from high to low temperature regions. Another one is the so-called *MaxEnt* principle, namely that the entropy of isolated systems (neither matter nor heat exchange, so $dS_e = 0$) increases until it reaches a maximum S_{equil}^* that is stable $\{\delta S = S_i - S_{\text{equil}}^* = 0 \ \& \ \delta^2 S < 0\}$. This defines the so-called macroscopic thermodynamic equilibrium.

Using the Lagrange maximisation principle under constant variables constraints over the statistical definition of entropy (equation (1)), *MaxEnt* translates readily into familiar minimum principles for Gibbs free energy G and Helmholtz free energy F at equilibrium:

$$\left\{ \max_{\text{MaxEnt}} S_i \right\} \Leftrightarrow \left\{ \begin{array}{l} \text{fixed } N, P, T \ \max \left(-\frac{G}{T} \right) \ \text{or } \min(G) \ \text{or } d(G) = -TdS_i \leq 0 \\ \text{fixed } N, P, T \ \max \left(-\frac{F}{T} \right) \ \text{or } \min(F) \ \text{or } d(F) = -TdS_i \leq 0 \end{array} \right\} \quad (3)$$

For open systems $dS_e \neq 0$ and the system evolution will not be toward an equilibrium state but toward another state, like a stationary state or a self-organized critical and dissipative state. While S_e evolution can be either positive or negative, the drivers of the positive evolution of S_i for an open system are better captured by Gibbs relation. For a multicomponent system under the local equilibrium hypothesis, it is written as

$$dS_i = \left(\frac{1}{T} \right) dU + \left(\frac{P}{T} \right) dV + \sum_j \left(\frac{-\mu_j}{T} \right) dN_j \geq 0 \quad (4)$$

3.3 Mass, energy and momentum balances

Equation (4) shows that S_i changes as a sum of irreversible contributions from transport phenomena of internal energy / heat (dU), total mass (dV), component (dN_j). To make explicit fluxes of heat and matter and reaction rates, one must use mass, energy and momentum balances for continuous system, which are more easily expressed with local microscopic specific (per unit mass) variables, for example e defined as $E = \int^V \rho e dV$ (Bird et al., 2006):

$$\begin{aligned}
 \frac{\partial(\rho_j)}{\partial t} &= -\nabla \cdot (\rho_j \mathbf{v}) - \nabla \cdot \mathbf{j}_j + M_j \sum_l v_{j,l} J_{r,l} \quad (\text{mass}) \\
 \frac{\partial(\rho \mathbf{v})}{\partial t} &= -\nabla \cdot (\rho \mathbf{v} \mathbf{v}) - \nabla P - \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{F} \quad (\text{momentum}) \\
 \frac{\partial(\rho e)}{\partial t} &= -\nabla \cdot (\rho e \mathbf{v}) - \nabla \cdot \left(\mathbf{J}_u + \sum_j e_{p,j} \mathbf{j}_j + (P \boldsymbol{\delta} + \boldsymbol{\tau}) \cdot \mathbf{v} \right) \quad (\text{total energy}) \\
 \frac{\partial(\rho u)}{\partial t} &= -\nabla \cdot (\rho u \mathbf{v}) - \nabla \cdot \mathbf{J}_u - P(\nabla \cdot \mathbf{v}) - \boldsymbol{\tau} : (\nabla \mathbf{v}) + \sum_j \mathbf{j}_j \cdot \mathbf{F}_j \quad (\text{internal energy})
 \end{aligned} \tag{5}$$

Here ρ_j and M_j are the mass density and molar mass of component j , $J_{r,l}$ is the l reaction rate, $\boldsymbol{\delta}$ is the unit tensor, P is the pressure and $\mathbf{F} = 1/\rho \sum_j \rho_j \mathbf{F}_j = -1/\rho \sum_j \rho_j \nabla e_{p,j}$ is the mass force with \mathbf{F}_j the force exerted per unit mass, derived from the component potential energy, for example due to gravitation and intermolecular interactions. $\mathbf{J}_u = \mathbf{J}_q + \sum_j u_j \mathbf{j}_j$ with \mathbf{J}_q the pure heat conduction flow and u_j the component internal energy transported by the diffusion flow. Other notations are described below. The first term on the right hand side expressed as a divergence is the convection flow while the remaining terms are conduction flows, contributions of various forces and dissipative terms. The viscous contribution associated with the shear stress tensor $\boldsymbol{\tau}$ and velocity \mathbf{v} appears in the momentum balance but also in the internal energy balance since u is obtained from the total energy balance $e = u + 1/2 \mathbf{v} \cdot \mathbf{v} + e_p$, which necessitates to compute the specific kinetic energy $1/2 \mathbf{v} \cdot \mathbf{v}$ and solve the momentum balance.

3.4 Entropy balance and entropy production equation

The entropy balance for the specific entropy s is analogous to the above expressions but is non conservative and contains an entropy source term σ :

$$\frac{\partial(\rho s)}{\partial t} = -\nabla \cdot (\rho s \mathbf{v}) - \nabla \cdot \mathbf{J}_s + \sigma \quad (\text{entropy}) \tag{6}$$

The conduction entropy flow \mathbf{J}_s has contributions from the heat conduction flow of the internal energy \mathbf{J}_u and from the specific diffusion flow \mathbf{j}_j (Bird et al., 2006). The entropy source term, or local entropy production per unit volume, σ is related to the macroscopic internal entropy by the volume integral $dS_i/dt = \int^V \sigma dV$. According to the second law $\sigma \geq 0$.

Disorganization (rather than disorder) is commonly associated with entropy. But Martyushev (2013) pointed out that the popular axiom “entropy quantity is related to order quantity” is false because it refers only to the system spatial coordinates, discarding momentum contributions and interactions within elements of the system that may also contribute significantly to organization. Equation (6) only establishes that entropy decrease, $\partial(\rho s)/\partial t < 0$, will only happen in a unit volume if the joint contribution of convection $-\nabla \cdot (\rho s \mathbf{v})$ and conduction $-\nabla \cdot \mathbf{J}_s$ entropy flows are negative and exceed σ . But as the total entropy of the system plus surroundings must increase in agreement with the second law, when the internal entropy decreases and results in more organization, the unit volume exports entropy. Freezing a liquid is a typical example as entropy decreases while the system becomes solid and heat is released to the surrounding.

The entropy source term σ is computed from equation (4) by inserting the irreversible contributions arising in the set of transport balances equations (5).

$$\sigma = \mathbf{J}_u \cdot \nabla \left(\frac{1}{T} \right) + \frac{1}{T} \sum_j \mathbf{j}_j \cdot \left[\mathbf{F}_j - T \nabla \left(\frac{\mu_j}{T} \right) \right] - \frac{1}{T} \boldsymbol{\tau} : (\nabla \mathbf{v}) + \frac{1}{T} \sum_l A_l J_{r,l} \geq 0 \quad (7)$$

$$\Phi = T\sigma = -\mathbf{J}_u \cdot \nabla (\ln T) + \sum_j \mathbf{j}_j \cdot \left[\mathbf{F}_j - T \nabla \left(\frac{\mu_j}{T} \right) \right] - \boldsymbol{\tau} : (\nabla \mathbf{v}) + \sum_l A_l J_{r,l} \geq 0 \quad (8)$$

where $A_l = -\sum_j \nu_{j,l} \mu_j$ is the affinity, $\nu_{j,l}$ is the stoichiometric coefficient of species j in reaction l . $\nu_{j,l}$ is positive for products and negative for reactants. Equation (8) is the dissipation function (Demirel and Sandler, 2004). Equation (7) collects contributions from heat transfer, mass transfer, viscous dissipation of fluid and chemical reactions. Recalling Gibbs relation, Equation (4), it shows a key concept of NET, namely that σ is a sum of the products of conjugate flows J_k of extensive variables U, V, N_j , etc and forces X_k of intensive variables, T, P, μ_j , etc :

$$\sigma = \sum_k J_k X_k \geq 0 \quad (9)$$

3.5 Linear nonequilibrium thermodynamics

Equation (9) helps identify the independent flows and thermodynamic forces to be used in the phenomenological equations. Thermodynamic forces are understood as the driving forces of transport and reaction phenomena. Near equilibrium, one can use the linear NET postulates:

1. Thermodynamic forces are not too large.
2. All flows in the system are a linear function of all the forces involved.

$$J_k = \sum_m L_{mk} X_m \quad (10)$$

3. The matrix L_{mk} is symmetric provided that J_k and X_k are identified by Equation (9).
4. In an isotropic system, the Curie-Prigogine theorem restricts coupling between flows and forces whose tensorial order differs by an even number. However, in an anisotropic medium, all couplings are possible.

The familiar phenomenological laws with positive transport coefficient for heat transfer, Fourier's law $\mathbf{J}_q = -k_e \nabla T = k_e T^2 \nabla (1/T)$, diffusion, Fick's law $\mathbf{j}_j = -D_e \nabla c_j = D_e c_j (-\partial c_j / \partial \mu_j) \nabla (-\mu_j/T)$, or momentum transfer, Newton's law $\boldsymbol{\tau} = -\mu \nabla \mathbf{v}$ obey equation (10). Introduced into each set of conjugate flow and force product of equation (7), one finds immediately that each set is proportional to the square of the thermodynamic force, respectively $\nabla (1/T)$, $\nabla (-\mu_j/T)$ and $\nabla \mathbf{v}$. Therefore, the coefficients in the form L_{ii} must be positive to ensure that the entropy production σ is positive. While Fick's, Fourier's and Newton's laws exhibit a linear dependency on a single thermodynamic driving force only, there are other cases to consider as well. For example Cahn-Hilliard or Guyer-Krumhansl's models for heat conduction exhibit nonlinear terms (Kovacs and Van, 2005, Jou et al., 2010). Furthermore, equation (10) states that all forces should be concerned when calculating any dissipative flux, which is not the case with Fick's, Fourier's and Newton's laws. This multivariable dependency is called thermodynamic coupling. Curie-Prigogine's theorem restricts coupling in isotropic media between flows and forces of the same tensorial order (like vectorial mass and heat diffusion but unlike scalar reaction phenomena and vectorial diffusion).

Nature is exploiting coupling at a grand scale. For example, electro-osmosis is responsible for epithelial fluid transport in the corneal endothelium (Fischbarg et al., 2017). Coupling is also considered as a key mechanism behind the *RNA world* hypothesis for the origin of life, because it explains the accumulation of nucleotides and DNA molecules in hydrothermal pores (Baaske et al., 2007).

Flow	Thermodynamic Force			
	Thermal	Chemical	Electrical	Hydraulic
Heat	Thermal conduction $\mathbf{J}_q = -k_e \nabla T$	Chemical osmosis $\mathbf{J}_{co} = -c_i \eta K \nabla \Pi_h$	Peltier effect $J_q = L_{qe} \frac{\Delta E}{T}$	Thermal filtration
Fluid	Thermal osmosis $\mathbf{J}_{TO} = c_i k_T \nabla T$	Dufour effect	Electrical osmosis	Advection $\mathbf{J}_{adv} = -c_i K \nabla h$
Solute	Thermal diffusion (Soret effect) $\mathbf{J}_{TD} = -D_e s c_i \nabla T$	Diffusion $\mathbf{J}_i = -D_e \nabla c_i$	Electrophoresis	Hyper filtration $\mathbf{J}_{hf} = -c_i \eta K \nabla h$
Current	Seebeck effect (Thompson effect)	Diffusion and membrane potential	Electrical conduction	Rouss effect: Thermokinetic effect

E, electric field; h, hydraulic head; K, hydraulic coefficient; k_T , thermo-osmotic permeability, $m^2/(K s)$; s, Soret coefficient; Π_h , osmotic pressure head = $\Pi_h = \Pi/\rho g$; η = coefficient of osmotic efficiency.

Table 1. Direct and coupled transport phenomena (Demirel and Gerbaud, 2019, reprinted with permission from Elsevier)

Some couplings are summarized in Table 1. While they have been identified experimentally more than a century ago, only a few chemical engineering processes fully consider them, like in membrane transport when osmotic pressure due to concentration gradient counterbalances hydrostatic pressure (Hwang, 2004); or like in thermodiffusion when ordinary diffusion ($-D_e \nabla c$) counterbalances thermal diffusion flow ($-c D_T \nabla T$) affecting the volatile composition distribution in oil reservoirs (Faissat et al., 1994). For polystyrene fractionation, the Soret coefficient $soret = D_T/D_e$ for dilute solutions of polystyrene in tetrahydrofuran is around 0.6/K, despite small value of the thermodiffusion coefficient, $D_T = 1 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1} \cdot \text{K}^{-1}$. This indicates that the change of polystyrene concentration per degree is 60% (Schimpf and Giddings, 1989). The thermal gradient drives solute molecules with larger Soret coefficients from the solutes with smaller Soret coefficients. The degree of coupling $q = L_{km}/(L_{kk}L_{mm})^{1/2}$ is a useful dimensionless parameter as well as the energy conversion efficiency $\eta = \text{output}/\text{input}$ for analysing coupled processes (Demirel and Sandler, 2002a).

This balancing of phenomena brings the opportunity to mention “Force balancing (T2)”, the second theme in nature-inspired engineering evoked by Coppens (2012). However, T2 seems different and rather invokes balance between confinement and physical forces (CfNIE, 2019). Out of the twelve T2-related works available at CFNIE website, only one of them (Liu et al., 2009) actually mentions *force balance*, when referring to the Maxwell-Stefan approach to model self-diffusion on zeolites, but does so in a simple way. It states that Fick’s law invoked in the Maxwell-Stefan model is the balance between the driving force for diffusion (i.e., the gradient of chemical potential) and the forces resulting from friction with other species as they interdiffuse.

There are likely some opportunities in exploiting more systematically thermodynamic coupling in chemical engineering, both in steady state and in dynamic operation. In this way, reaction-mass transport coupling between the chemical reactions and the transport of substances in bioenergetics are exemplary as they enable facilitated and active transport of substrates and products across cells membranes (Demirel and Sandler, 2002b).

3.6 Thermodynamic efficiency

At the unit operation scale, thermodynamic efficiency can help define design and operating parameters that minimize irreversibility – entropy production. Whereas infinitely slow reversible operation is not desirable, minimizing irreversibility can be sought (Andresen, 2011). For example, in distillation under optimal operating conditions agreeing with cost and energy optimum (Gerbaud et al., 2019), the column temperature profile is usually increasing smoothly from top to bottom without sharp bend. This agrees with two criteria derived from linear NET when all thermodynamic forces are monitored,

either the principle of equal thermodynamic distance (Sauar, et al., 2001), or the principle of equipartition of forces which minimizes the entropy production (Tondeur and Kvaalen, 1987, Kjelstrup et al., 1998). Both indicate that optimal operation is achieved by distributing thermodynamic force gradients, $y_i \nabla \mu_i / T$ for distillation columns, evenly across the apparatus, which results in small temperature steps from tray to tray (Sauar, et al., 2001). Similarly, one should have a uniform Gibbs energy of reaction $\Delta_r G / T$ for chemical reactors (Sauar et al., 1997) and a uniform $\nabla T / T$ for heat exchangers, which happens more readily in countercurrent than in concurrent heat exchangers (Tondeur, 1990). When some forces are not controlled, “the EoEP, but also EoF are good approximations to the state of minimum entropy production in the parts of an optimally controlled system that have sufficient freedom” and is not too far from equilibrium (Johannessen and Kjelstrup, 2005).

The equipartition principle has been used in one of the cases illustrative of the T1 mechanism – hierarchical transport network (Coppens, 2012) by Kjelstrup et al. (2010) for designing a new fractal gas supply system for a polymer electrolyte membrane (PEM) fuel cell inspired from human lung. The gas supply system in a PEM fuel cell works as follows: (a) a single gas stream is distributed to the entire surface of the cell, and (b) the transport mechanisms changes from convection (inside the flow plates) to diffusion (inside the porous transport layer). Both these features are also observed in human lungs. The novel fractal distributor allows the oxygen to be homogeneously distributed along the cell’s surface. The earlier nanoporous catalytic layer is now replaced by a macroporous/nanoporous layer, and macroporosity distribution is constrained to ensure uniform entropy production and minimize total entropy production. One should then expect that it will be optimal in some economic sense (Tondeur and Kvaalen, 1987). Indeed, it showed a reduction of 75% in the amount of catalyst required, whilst increasing the energy efficiency by 10-20% (Kjelstrup et al., 2010). In membrane separation, the design of a composite membrane with layers of nanostructured films enables to achieve remarkable solvent permeance and high retention of dissolved solutes (Karan et al., 2015).

Nevertheless, this discussion about thermodynamic efficiency is limited to unit operations within a given design process unit architecture. It does not address the time evolution of the design or of the operation that we now discuss.

3.7 Steady state evolution

Once the full expressions of the dissipative fluxes are explicated in terms of all forces according equation (10), they are inserted into the partial differential balances (equation (5)) which are solved along with boundary conditions to obtain all state variables time and space evolution. Indeed, chemical processes are time dependent and it is worthy to decipher what evolution means in thermodynamics. For a macroscopic isolated closed system, the second law states that it evolves toward thermodynamic equilibrium (left side of Figure 2). Done in a reversible way, it requires an infinite time, which implies that power, as the ratio of work over time, is null. So irreversibility must be assumed in processes to do some work, hammering the shortcut thinking that process improvement, in particular regarding energy consumption, must go through a thermodynamically reversible operation.

For open systems, evolution will not achieve thermodynamic equilibrium but could well reach a stationary state (right side of Figure 2) which obeys the following relation:

$$\left\{ \frac{dS}{dt} = \frac{dS_e}{dt} + \frac{dS_i}{dt} = 0 \right\} \Leftrightarrow \left\{ \frac{dS_e}{dt} < 0 \text{ since } \frac{dS_i}{dt} > 0 \right\} \quad (11)$$

As internal entropy must increase, reaching a stationary state requires that the system is not isolated and entropy exchanged with the surrounding is negative, implying a balancing between external (e.g. heat) and internal (equation (7)) entropy contributions to the total entropy. One could take advantage of thermodynamic coupling (section 3.5): in the Soret effect, a temperature gradient imposed from outside may counterbalance the diffusion flux inside the system.

3.8 Dynamic evolution

The third and last theme for nature-inspired engineering proposed by Coppens (2012) is T3 – Dynamic Self-Organization. Continuous manufactories are generally designed for steady-state operation, and fluctuations are seen as anomalies that need to be “controlled”. However, this “stationary” way of thinking, common in process engineering, has deprived engineers from fully exploring the time dimension in the design of unit operations and processes, which Coppens’ proposal with T3 mechanism encourages somehow. More specifically, theme T3 draws inspiration from organized, natural structures that appear as a result of intermittent stimuli from their surroundings. The classical example is that of sand waves. Sand waves (the organized structure) are formed through oscillatory wind tides (the intermittent stimulus). Inspired by this phenomenon, Coppens and van Ommen (2003) proposed the use of oscillating gas flow in fluidized beds. They found that oscillating the gas inlet flowrate (the intermittent stimulus) creates a regular bubble pattern (the organized structure) at the lower part of the bed. This helps increasing control over the otherwise chaotic hydrodynamics of the bed. Furthermore, it prevents channelling and clumping, improving processes such as combustion and drying (Coppens, 2012). Another example is related to mixing operation. Compared to the stirred tank reactor, the soft elastic reactor inspired by the animal upper digestion track improves mixing, inducing it by periodic wall deformations triggered by a peristaltic movement (Liu et al., 2018).

3.8.1 Fluctuation theorems, irreversibility and second law

Introduced by Evans and Searles, fluctuation theorems (FT) are numerous (transient FT, integral FT, detailed FT, ...) (Mittag et al., 2007). Here, they help clarify the notion of reversibility and the second law statement. Consider an evolution trajectory between two states and its entropy production quantity, with a time distribution and a time-average value over interval $\tau > 0$, $\bar{\sigma}_\tau$. A fluctuation relation examines the symmetry of $\bar{\sigma}_\tau$ around its value $a = 0$, and compares the probability of the forward path $p_F(\bar{\sigma}_\tau = +a)$ with that of the reverse path $p_R(\bar{\sigma}_\tau = -a)$. Among FT, Crooks’ relation states for systems in which the relaxed initial and final states have the same free energy, that

$$\frac{p_F(\bar{\sigma}_\tau = +a)}{p_R(\bar{\sigma}_\tau = -a)} = e^{a\tau} \quad (12)$$

Two remarks are worth mentioning. First, both extensive entropy production and path time interval τ are small for a microscopic system, so the exponential limit goes to unity, exemplifying microscopic time reversibility as $p_F = p_R$. Equation (12) hints that the same ratio p_F/p_R can be obtained when $a\tau$ is constant. But for a reversible path ($\bar{\sigma}_\tau = 0$) reaching the final state requires an infinite time. So, for large system, irreversible evolution is unavoidable and welcome. It will make the probability ratio in equation (12) greater than unity, thus enabling the system to effectively reach the final state. Secondly, analyzing the average $\langle \dots \rangle$ over many paths along the evolution trajectory, equation (12) is analogous to $\langle \bar{\sigma}_\tau \rangle \geq 0$ (Demirel and Gerbaud, 2019). This is a statement of the second law, demonstrating that the second law is *valid on average*. This implies that there can exist *some* paths with *negative* internal entropy production, while on average the entropy production is positive.

3.8.2 Constructal law

Whereas thermodynamics deciphers the phenomenological mechanisms, the CL is a principle of design, resulting in how will evolve the organization, architecture and structure for living and nonliving systems in nature (Bejan and Lorente, 2013; Bejan, 2017). CL is about survival by increasing efficiency, territory and compactness (Bejan and Lorente, 2004). Considering a global flow resistance (opposite of performance) R, the global internal size V, and global external size (covered territory) L, survival is achieved depending on what is fixed:

$$\begin{aligned} R \text{ minimum at constant L and V} &\Leftrightarrow \text{easiest flow access} \\ V \text{ minimum at constant R and L} &\Leftrightarrow \text{compactness or more free space} \\ L \text{ maximum at constant V and R} &\Leftrightarrow \text{maximal spreading} \end{aligned} \quad (13)$$

Equation (13) shows the importance of the CL to engineers. Indeed, the three features at the right-side of the arrows (*easiest flow access, compactness or more free space, maximal spreading*) are the drivers for the conception of transport networks. When designing the pipe network for a chemical plant, engineers want to minimize the pressure drop (i.e., the resistance to the flow) in order to lower the cost of pumping. However, transport of corrosive fluids requires expensive materials, such as titanium or zirconium alloys. In those cases, engineers may prefer to minimize the capital cost of construction (i.e., minimize the material used for transport) by accepting a fixed maximum pressure drop. This is similar to the second principle listed in equation (13). Finally, road networks are conceived to connect the different parts of a city. The optimal configuration in this case is the one covering the maximum territory available, following the third principle in equation (13).

The fractal gas supply distributor in the PEM cell (Kjelstrup et al., 2010) evoked earlier in Section 3.6 is one of the illustrative cases of T1 mechanisms Hierarchical transport network (Coppens, 2012). It displays some fractal-like geometrical features alike those derived from the CL (Bejan and Tondeur, 1998). Performance of such hierarchical fuel cells are greatly improved in terms of increased current density, maximum power density, lower pressure drop (Trogadas et al., 2018). Fractal tree structures emerge from CL, when it is necessary to connect one point with an infinite number of points covering a surface/volume. Fractal structure also facilitates scale-up. Two examples are the vascular and the respiratory networks in the human body. Tree-shaped networks are also found to dissipate energy uniformly (West et al., 1997) and to operate near optimality in terms of momentum and heat flow resistance (Bejan and Tondeur, 1998, Coppens, 2012). This feature illustrates some connection of both the CL and T1 mechanism with the principle of equipartition of entropy production that was already evidenced by Coppens (2012). Along its evolution, Nature has promoted such transport network which favors its survival and minimizes irreversibilities. It should be a source of inspiration for engineers.

3.8.3 Minimum and maximum entropy production

Taking a broader perspective of a system evolution, the NET community has debated about two principles: minimisation of entropy production (*minEP*) and maximisation of entropy production (*maxEP*) which are encompassed by Ziegler's maximisation entropy production principle (Martyushev, 2013).

Historically, *minEP* was derived by Prigogine for systems near equilibrium where linear phenomenological equation (10) applies and some forces are kept constant (Moroz, 2011, Kondeputi and Prigogine, 2014). Then, the entropy production is a quadratic definite expression: $dS_i/dt = \int^V \sigma dV = \int^V \sum_{m,k} L_{mk} X_m X_k dV$. Prigogine established that if a system has n independent forces (X_1, X_2, \dots, X_n), and j of them are held constant ($X_1, X_2, \dots, X_j = \text{constant}$), then the other flows $J_{j+1}, J_{j+2}, \dots, J_n = 0$ at the stationary state with minimum entropy production represented by

$$\left\{ (X_k \text{ fixed } (k = 1, \dots, j)) \quad \text{minEP} = \min_{X_{j+1}, \dots, X_n} (dS_i/dt) \right\} \quad (14)$$

The so-called maximum entropy production principle (*maxEP*) proposed by Ziegler has a broader reach, including far from equilibrium where linear phenomenological laws may no longer be valid (Martyushev and Seleznev, 2006). This principle states that for given forces, the system sets the fluxes in order to maximize entropy production. Despite being generally well-accepted in academia, there is still a debate on its application beyond linear regime for some systems in particular for compound systems with independent parts (Poletini, 2013; Martyushev and Seleznev, 2014).

$$\left\{ (X_k \text{ given } (k = 1, \dots, n)) \quad \text{maxEP} = \max_j (dS_i/dt) \right\} \quad (15)$$

In a unifying perspective, *minEP* principle is also shown to be related to Ziegler's *maxEP* principle (Moroz, 2011). Quoting Martyushev (2013), physical and biological system evolutions comply with both principles: “*for small times, the system maximizes the entropy production with the fixed forces and, as a result, the linear relations between the fluxes and forces become valid; for a large-scale of*

time, the system varies the free thermodynamic forces in order to reduce the entropy production". Moroz (2008) interpretation is similar as over time entropy production is minimal but it proceeds as fast as possible by maximizing the energy dissipation rate. Li et al. (2016) pictured this temporal sequence as a compromise between mechanisms that may dominate under different operating regimes and could be formulated as a multiobjective variational problem (Li et al., 2018).

maxEP has also led Prigogine to introduce the concept of dissipative structure often associated with self-organized criticality (SOC). The SOC concept is a strong driver for nature-inspired processes because evidences exist that many natural systems lie in a SOC state (Bak, 1996). Dissipative structures are far from equilibrium and energy-sustained states which existence can be justified as states that enable (often in a nonlinear way) a faster dissipation (maxEP) than would linear mechanisms occurring near equilibrium. For open-system they may last as long as energy flows in while for closed system they last for a limited time along the path toward thermodynamic equilibrium (Moroz, 2008). Submitted to external changes in their surroundings, they will evolve in an unpredictable manner, either shifting to another SOC state with different organization, undergoing cyclic evolution around the critical SOC state following so-called punctuated equilibrium evolution, or something else. Properties of SOC are debated but one agrees that an initial fluctuation becomes amplified until criticality is reached and that some phenomena follow a power law distribution: size vs frequency, duration and amplitude of punctuated equilibria, etc, which leads to scaling (Pruessner, 2012).

Many phenomena considered as SOC have been described with the help of thermodynamics principles minEP and maxEP depending on which constraints are holding (Dewar et al., 2014). Out of the linear region, there exists a generalization of the maxEP principle (Martyushev and Seleznev, 2006). In particular, for slowly-driven flux systems, maxEP principle has been proposed as the thermodynamic driver for the emergence of SOC (Dewar et al., 2014, Dewar and Maritan, 2014). Benard cells are an example of SOC not far from equilibrium: convection cells appear in a heated liquid over some critical threshold of external heating. Compared to heat conduction, convection is then more efficient for dissipating in the fastest way the heat provided, and entropy production is maximal.

$$\{(\text{slowly-driven flux } J_k) \quad \text{maxEP} = \max(dS_i/dt)\} \quad (16)$$

While discussing T1 mechanism (hierarchical transport network), Coppens (2012) has mentioned that diffusion-dominant transport networks are usually uniform and non-scaling. As convection becomes dominant, scaling like fractal structure may occur, which is also a feature attributed to SOC as discussed above. Li et al. (2018) further added reaction as a mechanism leading to clustering. This recognized feature has been used to design hierarchically structured catalyst where nanoporous grains not limited locally by diffusion are dispersed into a macropore network of optimized uniform porosity (Trogadas et al., 2016a, 2016b, Hartmann and Schwieger, 2016). The emergence of dynamic heterogeneity in several chemical engineering applications has been postulated to be caused by a compromise in competition between mechanisms that are driven either by minEP or maxEP principles (Li et al., 2018).

SOC are discussed in many scientific domains: engineering, biology, climatology, economics, social sciences. One aspect of SOC lies in their presupposed adaptability to changes in their environment. Some have recognized that their evolution is unpredictable but follows irregular cyclic successions of so-called punctuated equilibria, alternation of fast and slow response to external stimuli. The theory was proposed in evolutionary biology (Gould and Eldredge, 1977, Bak, 1996).

Appealing as it seems in terms of robust operation for chemical processes needing to cope with increasingly variable inputs or outputs nowadays, the SOC state evolution likely requires appropriate controls far from equilibrium.

3.8.4 Nonlinearity vs. controllability

Even if the dissipative fluxes (equation (10)) are linear with respect to the thermodynamic forces, the partial differential balance equations (5) for the state variables may exhibit nonlinearities (e.g. due to convection terms). By integrating over the entire system, nonlinearity might also emerge. In chemical engineering, control systems are used to ensure the stability of the prescribed process regime, typically, a steady-state regime. For this purpose, a linear approximation of the nonlinear process in terms of deviations from the targeted regime is sufficient to model the process behaviour. However, far from the equilibrium or from a stationary state of the system, the linear approximation of the nonlinear macroscopic balances may no longer be valid. This makes impossible the analysis of the dynamics and controllability of the thermodynamic system with classical linear control methods. On the other hand, criteria of controllability, observability and optimality of nonlinear dynamical systems, originally introduced for the purpose of control of artificial automated systems, can be successfully applied to the analysis of natural systems like minimal time control problem for fed-batch bioreactors (Bayen and Mairet, 2013) or finding optimal intervention strategy to epidemics (Sharomi and Malik, 2017), or other systems exploiting nonlinear phenomena.

In this section, we assume that the behaviour of a thermodynamic system can be described by a system of ordinary differential equations of the general form

$$\frac{dx}{dt} = \mathbf{f}(\mathbf{x}, \mathbf{w}) \quad (17)$$

where $\mathbf{x} \in M$ is a vector of state variables of the systems belonging to the state space manifold M and $\mathbf{w} \in \Omega \subset \mathbb{R}^m$, $m \leq \dim M$, denotes the vector of control parameters. The vector function $\mathbf{f}(\mathbf{x}, \mathbf{w}) \in \Omega$ describes the set of generalized flows of the systems. We further assume that it is sufficiently smooth to verify all the theoretical results discussed below. In the case of distributed systems, the state vector \mathbf{x} contains the momenta associated to the distributed variables via their convolution with the density distribution function, for instance, in the case of hydrodynamics, density, momentum density and entropy density (Grmela, 2015).

The system (17) is said to be controllable if any given pair of initial and final states \mathbf{x}_0 and \mathbf{x}_f can be steered by its trajectory by an appropriate choice of control $\mathbf{w}(t)$. Near equilibrium, the behaviour of the nonlinear systems is well approximated by the linear system of the form $d\mathbf{x}/dt = \mathbf{A}\mathbf{x} + \mathbf{B}\mathbf{w}$ and the famous Kalman controllability criterion provides the necessary and sufficient condition of controllability of a linear system:

$$\text{rank}[B: AB: \dots A^{n-1}B] = n \quad (18)$$

Without loss of generality, we may rewrite general equation (17) as an affine control system of the form:

$$\frac{dx}{dt} = \mathbf{f}_0(\mathbf{x}) + \sum_{k=1}^m w_k \mathbf{f}_k(\mathbf{x}) \quad (19)$$

with piece-wise constant controls. Equation (19) can always be obtained by an appropriate choice of state variables and control parameters. The drift term $\mathbf{f}_0(\mathbf{x})$ describes the natural evolution of the system in absence of control, while the vector fields $\mathbf{f}_k(\mathbf{x})$ describe the influence of the control parameter w_k on the global dynamics of the systems. Then, the controllability analysis of a nonlinear system (19) relies on the computation of the iterated Lie brackets of the control and drift vector fields¹.

The Lie bracket $\text{Lie}\{\mathbf{f}, \mathbf{g}\}$ is the Lie derivative of \mathbf{g} along the flow generated by \mathbf{f} . It measures the commutativity of the flows generated by the vector fields in the state space. In fact, a pair of flows generated by a pair of vector fields commute if and only if their Lie bracket is zero. The Lie algebra of

¹ The Lie bracket of pair of the vector fields \mathbf{f} and \mathbf{g} is a vector field $[\mathbf{f}, \mathbf{g}] = \mathbf{f} \circ \mathbf{g} - \mathbf{g} \circ \mathbf{f}$ whose components can be computed as follows: $[\mathbf{f}, \mathbf{g}]_k(\mathbf{x}) = \sum_{j=1}^n f_j(\mathbf{x}) \frac{\partial g_k}{\partial x_j}(\mathbf{x}) - g_j(\mathbf{x}) \frac{\partial f_k}{\partial x_j}(\mathbf{x})$, $k = 1, \dots, n$

control system (19) is the vector space generated by the vector fields $\mathbf{f}_0, \dots, \mathbf{f}_m$ together with their iterated Lie brackets:

$$\text{Lie}\{\mathbf{f}_0, \dots, \mathbf{f}_m\} = \text{span}\{\mathbf{f}_0, \dots, \mathbf{f}_m, \dots, [\mathbf{f}_{i_1}, [\dots, [\mathbf{f}_{i_{k-1}}, \mathbf{f}_{i_k}]]], i_k \in \{0, \dots, m\}, k \geq 1\} \quad (20)$$

The control system (19) is said to verify the Lie Algebra Rank Condition (LARC) if every direction in the state space M can be realized by a vector field $\mathbf{g} \in \text{Lie}\{\mathbf{f}_0, \dots, \mathbf{f}_m\}$, i.e.

$$\text{Lie}\{\mathbf{f}_0, \dots, \mathbf{f}_m\}(\mathbf{x}) = T_{\mathbf{x}}M \text{ for all } \mathbf{x} \in M \quad (21)$$

where $T_{\mathbf{x}}M$ is the tangent space to the state space manifold M at point \mathbf{x} . The following criteria provide the controllability conditions (Jurjevic, 1997).

1. In absence of restrictions on the controls, i.e. if $\Omega = \mathbb{R}^m$, LARC condition (21) is sufficient for the controllability of nonlinear affine control system (19).
2. If the set of controls is bounded, the driftless system $d\mathbf{x}/dt = \sum_{k=1}^m w_k \mathbf{f}_k(\mathbf{x})$ verifying the LARC condition (21) is controllable provided that 0 belongs to the interior part of the control set $\Omega \subset \mathbb{R}^m$.
3. Control system with (19) verifying (21) is controllable if the drift vector field is recurrent, i.e. for all initial conditions and in absence of controls, $d\mathbf{x}/dt = \mathbf{f}_0(\mathbf{x})$ returns arbitrarily close to its initial state at some time.

LARC's condition (21) generalizes Kalman's linear system condition (18) for nonlinear systems, but it is much stronger. Indeed, a linear approximation of a controllable nonlinear system is controllable in the sense of criterion (18), but the opposite is not true. In particular, a nonlinear system evolving far from equilibrium under the influence of large control functions can be controllable even if its linear approximation close to an equilibrium is not.

The typical obstacle to the controllability is the existence of the dynamical invariants of the system, called first integrals. The application of the LARC allows recognizing the existence of such hidden invariants. The following example of a fed-batch bioreactor illustrates this concept. The dynamical model of a bio-reactor with single species is given by the following system of equations (Bayen and Mairet, 2013):

$$\frac{dz}{dt} = -\mu(z)b + w \frac{z_{\text{in}} - z}{V}, \quad \frac{db}{dt} = \mu(z)b - w \frac{b}{V}, \quad \frac{dV}{dt} = w \quad (22)$$

where b, z are concentrations of biomass and substrate, $V \in [0, V^{\text{max}}]$ is the volume of the tank, $w \in [0, w^{\text{max}}]$ is the controlled input flow rate, z_{in} is the substrate concentration in the input flow and $\mu(z) > 0$ is the growth rate function of the bacteria. This system can be written in the affine form $\frac{d\mathbf{x}}{dt} = \mathbf{f}_0(\mathbf{x}) + w \mathbf{f}_1(\mathbf{x})$, with \mathbf{x} of dimension 3 where

$$\mathbf{f}_0 = (-\mu(z)b, \mu(z)b, 0)^T, \mathbf{f}_1 = \left(\frac{z_{\text{in}} - z}{V}, -\frac{b}{V}, 1 \right)^T, \mathbf{x} = (z, b, V) \in \mathbb{R}^+ \times \mathbb{R}^+ \times [0, V^{\text{max}}]. \quad (23)$$

Starting the iterative Lie bracket computation to find an extra third direction in addition to the already independent directions \mathbf{f}_0 and \mathbf{f}_1 , we get for the first bracket

$$[\mathbf{f}_0, \mathbf{f}_1] = \left(\frac{(z_{\text{in}} - z) b \mu'(z)}{V}, -\frac{(z_{\text{in}} - z) b \mu'(z)}{V}, 0 \right)^T = -\frac{(z_{\text{in}} - z) \mu'(z)}{V \mu(z)} \mathbf{f}_0 \quad (24)$$

In fact, going further with the Lie bracket computation one will always get the drift direction \mathbf{f}_0 , so LARC condition (21) is never fulfilled since we cannot get a third direction necessary to span the tangent space $T_{\mathbf{x}}M$. Indeed, the following quantity $K = V(b + z - z_{\text{in}})$ is constant and thus invariant for the evolution of the system (22). This means that the system is not controllable in the original state space whatever is the grow rate function $\mu(z)$. By introducing the constant K , the original problem (22) is reduced to the following one:

$$\frac{dz}{dt} = -\mu(z) \left(\frac{K}{V} - z + z_{\text{in}} \right) + w \frac{z_{\text{in}} - z}{V}, \quad \frac{dV}{dt} = w \quad (25)$$

with $\widetilde{\mathbf{f}}_0 = (-\mu(z) \left(\frac{K}{V} - z + z_{\text{in}}\right), 0)^T$, $\widetilde{\mathbf{f}}_1 = \left(\frac{z_{\text{in}} - z}{V}, 1\right)^T$, when written in the affine form shown in (19). The LARC condition is trivial and satisfied (condition 2 above). Then, since $b > 0$, the reduced system is controllable provided that the growth rate $\mu(z)$ verifies certain properties making the vector field $\widetilde{\mathbf{f}}_0$ recurrent (condition 3 above).

4 Challenges for nature-inspired chemical engineering

Bearing in mind Coppens' mechanisms and the NET mechanisms that we have attempted to elucidate, engineers may be able to innovate by questioning the hypothesis behind the models they use, instead of taking them for granted. For instance, we have suggested examining the relevance of classical models for novel systems, to think of thermodynamic coupling, to consider larger flows in the nonlinear regime that would be still safe to operate with appropriate non-linear regulation, and to envision a novel resilient production organization. These are the challenges that we explore in this section.

4.1 Change in the system: examining the local equilibrium hypothesis

The local thermodynamic equilibrium assumption remains valid at remarkable small scales, for example down to 8-18 particles subjected to large temperature gradients (10^{12} K/m) and mass fluxes (13 kmol/m²s) in homogeneous systems and slightly larger but still small values in porous or interfacial system (Kjelstrup et al, 2008, Schweizer et al., 2016, Kjelstrup et al., 2018). Indeed, a criterion based on the magnitude of local relative fluctuation of state variable has been devised for testing the validity of the local equilibrium hypothesis (Kjelstrup et al. 2008) and if that is true classical NET can be used. But the local thermodynamic equilibrium may be violated in many aspects in some rheological, thermal, polymer applications (systems with non-negligible relaxation times), chemical reactions or non-newtonian fluids (nonlinear phenomenological equations), configuration-dependent systems, micro and mesoscopic-fluctuation-dependent systems, nanoscale systems, systems with wavelength-dependent phenomenological diffusion, systems with long-range interactions or long-range microscopic memory, Observed state variables are then very different from the bulk one predicted by classical thermodynamics, like the melting point depression for nanoparticles (Letellier et al., 2007), or a time lag of the propagation of heat flow where Fourier linear phenomenological equation predicts that the heat flow is felt instantaneous and everywhere in the system (Lebon and Jou, 2014).

In such cases, new variables related to configuration, fluxes or gradients can be introduced in the thermodynamic equations in addition to classical state variables to account for memory and boundary effects. Many approaches coexist (Demirel and Gerbaud, 2019). One can define a nonequilibrium temperature starting from the equilibrium bulk temperature but dependent on heat flux within the ENET formalism (Jou et al., 2010); incorporate time evolution of mesoscopic dynamics in the GENERIC formalism to analyse dynamic evolution (Öttinger, 2005); take into account local fluctuations with mesoscopic thermodynamics (Rubi, 2008) or re-examine the extensive character of several variables like entropy from either a statistical viewpoint revisiting Boltzmann-Gibbs statistics (Tsallis, 1988, Tsallis et al., 1998) or from a phenomenological approach more suited to chemical reactions (Turmine et al., 2004; Letellier et al., 2015). In these latter works, the effect of confinement is handled by considering geometric boundaries as a fuzzy interface, introducing a non-extensive contribution of the interfacial energy in the internal energy. Internal energy and entropy then become non-extensive de facto. It would be interesting to use such advanced thermodynamics formalism for studying nanoscale confinement effects as in works referred to the Force balancing T2-mechanism (Sang and Coppens, 2011, Sieker, et al., 2014).

4.2 Change in the environment: resilience and efficiency

The variability of raw materials is well managed through chemical engineering activities based on fossil fuels. However, there is a concern about the adaptability of processes to the variability and intermittence of renewable material and energy. As chemical engineers become ever more involved in the design and operation of such processes, they face two challenges that resonate with Nature's remarkable capabilities: efficiency and resilience. Resilience is the ability of a system to overcome changes in its surroundings so as to maintain operation. Efficiency is a master goal in industrial operations. Efficiency is related to resource usage, in particular energy.

In nature, biochemical reaction processes are complex cyclic processes archetypal of processes that must keep functioning, whatever the changes in nutrients, in demand and in environment. Whereas kinetic equations and statistical models can describe such processes satisfactorily, the NET theory can help describe energy pathways and coupling in a quantitative manner and formulate the efficiency of energy conversion in bioenergetics. For example, mitochondria in biological cells respond to the cell energy demand through the production of adenosine triphosphate (ATP) further used in metabolic activities, like synthesizing protein molecules, transporting ions and substrates or producing mechanical work. Thanks to the monitoring of the coupling between ATP production (J_p) and oxygen consumption (J_o), mitochondria maintain a quasi-steady state robust to external and internal changes in the cell energy demand (Stucki, 1991). ATP-utilizing reactions act as a load as well as thermodynamic buffers that regulates the process efficiency. This regulatory mechanism based on monitoring the degree of coupling $q = L_{PO} / (L_{PP}L_{OO})^{1/2}$ allows oxidative phosphorylation to operate with an optimal use of the exergy contained in the nutrients for achieving various objectives: maximize ATP production at optimal efficiency $(J_p)_{opt}$ at $q = 0.786$, maximize power output at optimal efficiency $(J_p X_p)_{opt}$ at $q = 0.91$, minimize energy cost for a net ATP production $(J_p \eta)_{opt}$ at $q = 0.953$, or minimize energy cost for net output power $(J_p X_p \eta)_{opt}$ at $q = 0.972$ (Stucki, 1980; Demirel, 2004).

It is tempting to make a parallel with challenges met at a macroscale level as suggested by Chen (2016) when he compares the biofuel production circular production to a cellular biochemical cycle and calls for improving operational efficiency, scalability and robustness. In a biorefinery, renewable raw material processing requires usually to spend a lot of energy to remove the water in large excess before manufacturing any commodity. In terms of resilience, biorefinery plants must comply with a strong variability of raw material flowrate and compositions and with a market induced variability of output demand as well, while maintaining an efficient operation. In this case, efficiently maximizing production or output power and/or minimizing energy costs are routine objectives. Reasoning at the plant scale may help identify flux and forces whose coupling regulation would help to increase the resilience of the process.

4.3 Distributed production and the management of information

Going a step further, the self-organization critical state embraced by many natural systems advocates for a possible novel organization of chemicals production that would be robust to changes. It is superfluous to claim reaching a SOC state for a plant, but one can think to design a self-organized plant.

Roughly speaking, SOC system adapts to changes by mobilizing fast and strong response when the change is sudden and milder response when it is slow. The way different responses are occurring can be paralleled with the solicitation of alternative mechanisms triggered by thermodynamic coupling in cells in response to cell energy demand changes (Stucki, 1991). In a self-organized plant that would suggest to get access to several mechanisms, by designing several production lines with alternative

processes. For obtaining a chemical product, several production pathways may be available. Different pathways will employ different feedstocks, reactions, catalysts, temperatures, pressures, etc. Conversion rates and efficiency will also differ depending on the pathway.

Multiplying the production routes is a way to robustness, but will likely be costly. To improve economic viability, Budzianowski and Postawa (2016) have proposed the total integration of biorefinery systems by combining platforms using different biomass feedstock and by considering environmental and social issues as well. In the same spirit, the optimization of eco-industrial parks should encourage industrial symbiosis. Chen (2016) has envisioned the large-scale biofuel production from microalgae as a circular production route similar to a biochemical cellular cycle. But, this is so far restricted to material and energy network, lacking a proper formulation of social objectives (Boix et al., 2015).

These biorefinery and eco-industrial proposals call for a tight spatial integration that may fail to provide enough flexibility. A way out is to envision a modular chemical plant, as proposed by the F3 factory modular equipment project (Buchholtz, 2014) that demonstrated how a flexible scalable continuous technology, like standardized process equipment containers, can, for low- and medium-scale productions, achieve reductions in start-up, building and operating costs, in energy consumption, in waste, etc. Material and energy exchange interface should be standardized as well, in the spirit of a physical internet network (Montreuil et al., 2013).

The aforementioned flexibility should also concern automation as well as logistics and supply chain (Weber, 2016). More generally, the self-organized plant should qualify as agile, where agility is defined as encompassing detection, adaptation, responsiveness and efficiency (Barthe-Delanoe et al., 2014). To meet the challenge of handling information in a modular multipurpose multiple feedstocks factory, the next step is the shift from a physical factory integration perspective to a virtual factory perspective. Using a model-driven engineering approach, a metamodel for knowledge management and collaborative process design has been conceived in the case of biorefineries of a novel kind. They are seen as a virtual assembly of data and information, operated with a mediation information system and relevant to stakeholders who provide ‘services’ to meet the flexible demand described as ‘collaborative objectives’ within a ‘context’ about location, weather forecast, consumer, biomass physical property information (Houngbe et al., 2018). This virtual factory approach refers to what is called servitization, already in use regarding business models (Baines et al., 2017), and that must now expand to the chemical plant level: context and demand help generate an ad-hoc production pathway that is materialized as an assembly of blocks providing services. Underlying ontologies help managing the process and information workflow and its governance through the multiple scale hierarchy from the process unit to the industrial plant (Benaben et al., 2016; Zhou et al., 2018). In practice, the mediation information system assesses new collaborative objectives (e.g. change in demand) and context changes (e.g. impure feedstock) to design a novel production line built through the reuse of existing devices (unit operations, energy suppliers, logistical units). A case study is presented in Houngbe et al. (2019).

But how to reach and maintain a self-organized state far from equilibrium, like a SOC system? There is evidently a necessity to refer to what Coppens’ recently called the mechanism T4 (control mechanisms in ecosystems, biological networks and modularity). In our case, this is where nonlinear control comes into picture.

4.4 Nonlinear control

4.4.1 Dynamic state equation far from equilibrium

What if we accept to run a process with large driving forces and fluxes? This might prompt potentially unstable or erratic behaviour leading to failure of the process. In this case, risk monitoring cannot be handled only with linear control theory as the evolution of the system is governed by a full nonlinear

model (17) and nonlinear control has to be used. Though it is a common practice in chemical engineering to express a system of n balance equations of irreversible nonequilibrium process in terms of $(2n + 1)$ extensive (\mathbf{x}) and intensive (\mathbf{y}) variables and a thermodynamic potential, forming the complete thermodynamic phase space, the real system depends only on n state variables, for instance, extensive variables \mathbf{x} . The general formulation (19) written for a controlled thermodynamic system in the affine control form becomes

$$\frac{d\mathbf{x}}{dt} = \mathbf{f}_0(\mathbf{x}, \nabla_x \Psi) + \sum_{k=1}^m w_k \mathbf{f}_k(\mathbf{x}, \nabla_x \Psi) \quad (26)$$

where $\Psi(\mathbf{x})$ is the chosen thermodynamic potential, for instance, internal energy, and $\nabla_x \Psi$ is its gradient in the space of variables \mathbf{x} . Though the best choice of the state variables is a matter of scientific discussion (Maschke, 2016), equation (26) is an affine control system and the LARC condition can be used in the design of control strategies. Another way leading to the equations of form (17), (19) or (26) is the GENERIC approach identifying conservative and dissipative contributions to the dynamics (Ottinger, 2005, Grmela, 2018)

4.4.2 Optimal control and entropy-related principles

The nonlinear control theory framework can be applied to any nonlinear dynamical system depending on a set of parameters varying in time. In particular, it may provide an effective tool to construct an appropriate control action respecting *MaxEnt* or *minEP* and *maxEP* principles, as suggested by Moroz and Wimpenny (2011), in the context of bio-inspired processes with the use of the variational principle. Along with the classical Lagrangian approach used by many authors (Martyushev and Seleznev, 2006), this can also be done using the Pontryagin maximum principle (PMP) (Pontryagin et al., 1962, Moroz, 2008). The PMP framework provides the necessary conditions of optimality and the associated optimal control strategy. The subsequent geometric analysis enables the selection of the final optimal path and related control actions for achieving a given objective. It will also inform the engineer about the bifurcation points corresponding to an alternative mechanism solicited in response to changes affecting the systems. For that to happen, the mechanisms must be known beforehand and be included in the optimal control equations.

Assume that the system described by general equation (17) is controllable and consider all possible trajectories of the system starting at $\mathbf{x}(0) = \mathbf{x}_0$ and arriving at $\mathbf{x}(t_f) = \mathbf{x}_f$ at fixed final time $t = t_f$. Let $\mathbf{w}(t)$ be the control function realizing the minimum of a cost functional $C(\mathbf{w})$

$$C(\mathbf{w}) = \int_0^{t_f} \varphi(\mathbf{x}(t), \mathbf{w}(t)) dt \quad (27)$$

Then there exists a continuous curve $\mathbf{p}(t): [0, t_f]$ and a real number $p^0 \leq 0$ such that the following condition holds true:

$$\text{a) the pair } (\mathbf{p}(t), p^0) \neq (0, 0) \text{ for all } t \in [0, t_f] \quad (28)$$

supplemented with two conditions for almost all $t \in [0, t_f]$

$$\text{b) } \frac{d\mathbf{p}}{dt} = \frac{\partial H}{\partial \mathbf{x}}(\mathbf{x}(t), \mathbf{p}(t), p^0, \mathbf{w}(t)), \quad \frac{d\mathbf{x}}{dt} = -\frac{\partial H}{\partial \mathbf{p}}(\mathbf{x}(t), \mathbf{p}(t), p^0, \mathbf{w}(t)) \quad (29)$$

$$\text{c) } H(\mathbf{x}(t), \mathbf{p}(t), p^0, \mathbf{w}(t)) = \max_{\mathbf{v} \in U} H(\mathbf{x}(t), \mathbf{p}(t), p^0, \mathbf{v}) \quad (30)$$

Here H is the pseudo Hamiltonian function associated to the control system (17):

$$H(\mathbf{x}(t), \mathbf{p}(t), p^0, \mathbf{w}(t)) = \mathbf{p} \cdot \mathbf{f}(\mathbf{x}(t)) + p^0 \varphi(\mathbf{x}(t), \mathbf{w}(t)) \quad (31)$$

The constant p^0 , analog to the Lagrange multiplier in the classical calculus of variation, is defined up to a positive constant. In practical computations, $p^0 = -1$ for achieving the minimum of $C(\mathbf{w})$. Similarly, trajectories of system (17) $\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, \mathbf{w})$ maximizing $C(\mathbf{w})$ (equation (27)) must verify conditions (28) – (30) with $p^0 = +1$. A special class of optimal trajectories verifying conditions (28) – (30) with $p^0 = 0$ are called abnormal trajectories and are intrinsically related to the structure of the dynamical system itself, whatever the type of the imposed optimality criterion.

If the final time t_f is not fixed (free final time problem) the following additional condition holds:

$$d) H(\mathbf{x}(t), \mathbf{p}(t), p^0, \mathbf{w}(t)) = 0 \quad \text{for all } t \quad (32)$$

In that case, one may further look for the fastest trajectory connecting the states \mathbf{x}_0 and \mathbf{x}_f . Then, $\varphi(\mathbf{x}(t), \mathbf{w}(t)) = 1$ for all t and conditions (29) and (30) hold for the shorten Hamiltonian function $H^0(\mathbf{x}(t), \mathbf{p}(t), \mathbf{w}(t)) = \mathbf{p} \cdot \mathbf{f}(\mathbf{x}(t))$, while conditions (28) and (32) become

$$a') \mathbf{p}(t) \neq 0 \text{ for all } t \in [0, t_f] \quad (33)$$

$$d') H^0(\mathbf{x}(t), \mathbf{p}(t), \mathbf{w}(t)) \geq 0 \quad (34)$$

The PMP framework is much less known in the chemical engineering community than the classical Lagrangian approach. It opens an new perspective to explore the *MaxEnt*, *minEP* and *maxEP* principles on nature-inspired systems.

For example, application of optimal control for various chemical kinetics (linear, exponential, Michaelis-Menten kinetics) can be found in Moroz and Wimpenny (2011). They used the following cost functional $\mathcal{C}(\mathbf{w})$ for a free final time t_f where the equilibrium state is reached

$$\int_0^{t_f} (\Phi(\mathbf{x}(t), \mathbf{w}(t)) + \Psi(\mathbf{x}(t))) dt \rightarrow \min \quad (35)$$

Ψ is again the thermodynamic potential (for example Gibbs free energy) and Φ is the dissipative function related to entropy production as in equation (8). Ψ can be interpreted as the penalty for being in nonequilibrium state (Moroz, 2008). Equation (35) can also be interpreted as the fastest dissipation or maximum energy dissipation rate. It leads to an optimal trajectory for reaching a stationary state, starting from a nonequilibrium state. This corresponds in Figure (2) either to the left side for an isolated system, for reaching the thermodynamic equilibrium where entropy is maximum (*MaxEnt*) (or Gibbs free energy or Helmholtz free energy is minimal), or to the right side for an open system reaching a steady-state in the fastest dissipation way, both along a path minimizing the entropy production *minEP*.

The operation of a distributed production plant evoked in section 4.3 necessitates to apply a trajectory that could be deduced from such an optimal control formulation. In response to external changes, control switches along the optimal path would then be triggered. For example, this operational monitoring of information within the virtual factory management information system could lead to select a novel production line arrangement, in compliance with the selected cost criterion. In brief, the modular multipurpose virtual factory is essentially a self-organized factory. The operation of such factory embraces the nonlinearity of the macroscopic balance equations describing the different processes. This operation should then be monitored along trajectories deduced from optimal control, approached and implemented with nonlinear control.

5 Conclusion

We have contributed to put into the light mechanisms underlying some natural processes in order to develop innovative, efficient and resilient chemical engineering processes and factories. The three pioneering nature – inspired mechanisms by Coppens (2012) have been examined in the framework of NET, CL and nonlinear control theory. The Hierarchical transport network – T1 mechanism has been related to three topics, thermodynamic efficiency, CL and scaling in fractal structure that may emerge in self-organized critical system as well. The current definition of Force balancing – T2 mechanism does not provide clear guidelines on the aspects of the nature one should get inspiration from. It appears to be a broader concept that can be split among counterbalancing of thermodynamics driving force to reach a stationary state, thermodynamic coupling, efficiency and the study of confinement effects with the help of advanced thermodynamics concepts. The theme T3 – Dynamic self-organization draws inspiration from organized, natural structures that appear because of intermittent

stimuli from their surroundings and refers to self-organization and entropy production extremum principles. Evidently, the T1-T3 mapping is not complete because NET and CL frameworks have no pretention to be universal. Nevertheless, the NET and CL joint framework opens also new perspectives and both sets coexist and are valuable.

Coppens' 2012 assessment of the maturity of these mechanisms remains valid: T1 is mature and underlies most NICE works, leading to possible industrial implementations in porous materials (Hartmann and Schwieger, 2016), encouraged by the development of 3D-printing (Parra-Cabrera et al., 2018), while T2 and T3 need more attention. Nevertheless, despite significant performance increase, T1-based achievements remain a timid foray into NICE and restricted mostly to steady-state process units. Hence, the proposed NET and CL framework has hinted at several other perspectives. At the unit operation level and below, pertaining for many natural systems, the local impacts of confinement, fluctuations, configuration must be firstly properly described with advanced thermodynamics concepts to start thinking of innovative NICE processes. At the process unit level, a theoretical framework already exists. For example, thermodynamic coupling should be exploited along with dynamic states far from equilibrium that would be monitored with the help of nonlinear control schemes. At the plant level, many-body natural systems are the inspiration. From them, a novel distributed production is foreseen, implementing a robust self-organisation along a trajectory that would be compliant with entropy production extremum principles and resilient to external changes. An optimal control formulation of entropy production in which the Hamiltonian would include for example alternative production pathways, might give the proper trajectory.

6 Acknowledgments

The authors thank Anne Marie Barthe Delanoë and Michelle Hougbe for their fruitful discussion on virtual factory.

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