Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in Chemical Engineering

Review of extremum postulates

E Veveakis[1,2] and K Regenauer-Lieb[1]

Variational principles applied to the time derivative of the second law of thermodynamics have led to significant progress of our understanding of dynamic systems. Prigogine proved that chemical species dynamically form an oscillatory pattern of minimum of entropy production, *MinEP*. The opposite *MaxEP*[3] postulate forms the foundation of continuum mechanics. The topic of which extremum is valid under what conditions is still subject of a heated debate. We posit here that the two principles emerge from a different spatial/temporal homogenisation technique. *MaxEP* derives from a macroscopic, continuum view of a non-equilibrium stationary state and *MinEP* from a microscopic discrete view of stability of a dissipative system. When both limits coincide the system can be represented by an upscaled state with reduced degrees of freedom.

Addresses
[1] University of New South Wales, School of Petroleum Engineering, CSIRO, Australia
[2] University of Western Australia, School of Mathematics and Statistics, Australia

Corresponding author: Regenauer-Lieb, K (Klaus@unsw.edu.au)

Current Opinion in Chemical Engineering 2015, **7**:40–46

This review comes from a themed issue on **Material engineering**

Edited by **Jai A Sekhar**

For a complete overview see the Issue and the Editorial

Available online 27th November 2014

http://dx.doi.org/10.1016/j.coche.2014.10.006

Introduction

For processes that happen on multiple length scales the concept of thermodynamic equilibrium becomes a multiscale illusion. When zooming out, for instance, of a process that appears at small scale to be at thermodynamic equilibrium one may find that processes at the larger scale are organised in a far from equilibrium manner. Figure 1 illustrates this multiscale illusion as a multistage transition where entropy as a definition of the direction of time looses and regains a meaning when crossing the scale [1••]. At quantum scale we deal with coupled oscillators (waveforms) that describe quantised energy levels. Prigogine points out that there is a time paradox across the scales. From a perspective of the individual oscillators there is no time arrow, but the waveforms describe time symmetric processes as evidenced by the symmetry of Schrödinger's equation. The paradox relies on the observation that at larger than quantum scale coupled oscillations introduce irreversible processes as in the treatise of Poincaré on new methods for celestial mechanics [2], where coupled multi-body oscillations lead to the breaking of the time symmetry.

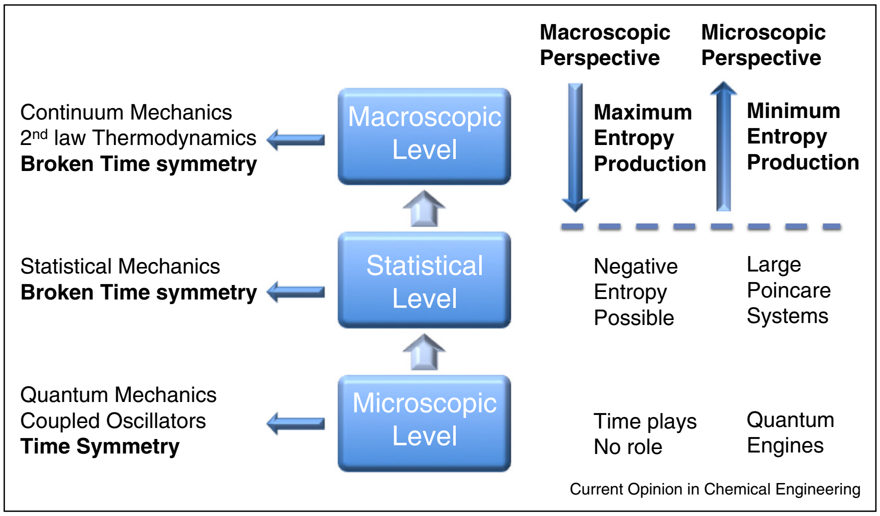
Therefore, a simple scale transition can resolve the time paradox. At microscopic level quantum engines are oscillating at discrete energy levels and time is symmetric. At larger scale energy jumps are possible which are not time symmetric (irreversible) and the system assumes a statistical configuration that Prigogine calls 'large Poincaré system' (LPS). At this level the building blocks of the fundamental microstructure are still applicable but the laws of thermodynamics are only valid at statistical level and local negative entropy becomes possible. At even larger scale the high dimension of irreducible microstates is condensed in phenomenological equations such as Fourier's, Darcy's, Stokes, Ohms, Fick's, Navier's, etc. constitutive laws of continuum material states. The diffusion equations at larger scale often incorporate implicitly those at smaller scale without explicitly considering their multiphysics. We argue that the question that lies at the heart of the debate on the validity of extremes of entropy production is from which perspective, microscopic or macroscopic, the homogenisation of micro-processes in new empirical laws originates. Is there a rigorous method that allows the identification of applicability of extremum principles?

At the continuum mechanic macroscopic level a given length scale is provided for which the continuum thermodynamic assumption applies, with the second law providing the time arrow. The rate of this fundamental law gives a representation of the evolution of the system with two possible extrema. When viewed from the macroscale, information about the irreducible microstates is not available and the system behaviour is described directly in the low dimensional form through the time evolution of the assumed state variable (usually P, V, T) defining the thermodynamic flux. The product of the flux with the associated thermodynamic force [3,4] is the entropy production and Ziegler [5] postulated that they should be orthogonal, thus obeying the *MaxEP* principle. This principle has — over the last decades — been found to be extremely useful for vastly different applications [6•,7,8•,9•].

The opposite view is that of considering the microscopic perspective which considers the known irreducible

[3] Commonly used abbreviations are also *MEPP*, *MEPR*, and *MEP*.

Figure 1



Prigogine's [1••] concept of breaking the time symmetry across scale. Continuum thermodynamic approaches only make sense above the scale of the dashed line. We discuss that this is a self similar behaviour which repeats itself through the scales over the different scales from quantum to chemical to mechanical, fluid and thermal oscillators. *MinEP* identifies the time scale for which oscillatory steady states can be identified and *MaxEP* identifies the length scale for time invariance of these states.

microstates and drops the microstates that are not correlated to the macroscopic state variables. Each of these irreducible microstates contributes to the total macroscale dissipation and one consequently looks for a solution where the system assumes stability in a macrostate such that the minimum of dissipation is achieved. We arrive at Prigogine's principle of *MinEP* [10].

These seemingly conflictive but not contradictory perspectives [11••] hence come up with two fundamentally different extrema. What is the physical meaning of *MinEP* and *MaxEP*? At what time/length scale do the two extrema coincide? We attempt to answer these questions in the current contribution.

What is the physical meaning of *MinEP* and *MaxEp*?

As an illustration for the self-organisation of the microphysical states let us consider a random assemblage of micro engines as in Figure 2. These micro-engines can be perceived as generalised irreducible microstates such as the individual thermal, electrical, biological, hydrological or chemical micro processes (engines) that contribute to the emergence of a macroscopic thermodynamic system (large circle in Figure 2). In chemistry, for instance, there are two classes of processes, classified as endothermic and exothermic engines. In a more generalised sense the endothermic micro engine requires work input and operates as a generalised heat pump, the exothermic micro engine process provides mechanical work and operates as a generalised heat engine.

Using the generalised entropy model of Figure 2 the extrema of entropy production can be understood as an uncertainty principle of internal entropy production $\tilde{s}_{irr}$ in finite time. *MaxEP* and *MinEP* thereby provide the variational bounds in finite time thermodynamics [12]. This theory grew out of the first world oil crisis in the 1970s when the realisation of a finite free energy of the planetary system Earth struck home. Two extrema for engine design then became apparent. At one extreme the engine operates to deliver as much power as possible without regard to how much fuel is wasted. At the other extreme the maximum work out of the fuel is targeted without regard to how long it takes [13•]. It appeared logical to develop a design specification where the availability A of a free energy to perform work over a finite time interval is maximised. Availability has been introduced by Gibbs [14] as a thermodynamic potential expressing the maximum extractable work of a system. For a given time increment the maximum power that can be extracted out of the system is $\dot{A}$ and given in the equation in Figure 2.

In this expression, the first term $\tilde{W}$ describes the external power input (output) into (out of) the system while the second term is the power of the Carnot engine. The third term is the Carnot refrigerator. For an observer of the macroscopic system all of these values are uniquely defined and so is the fourth term, the heat transfer (or other thermodynamic flux) through the boundaries of the macroscopic system. Uncertainty comes in through the path dependence of the irreversible entropy production