On the Motive Power of Chemical Transformations in Open Systems

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Abstract The classical basic concepts of cyclic processes and the efficiency of heat engines are used here to conjecture about the laws of thermodynamics for open systems that can exchange matter with a surrounding environment. An ideal chemomechanical elastic bar is envisioned that changes its stiffness while undergoing a chemical transformation which is, in turn, influenced by the axial strain of the bar. Stable equilibrium states are identified as minimizers of the total energy, which is assumed to be nonconvex in type. If the bar is loaded and then alternatively placed in environments at chemical potentials either $\mu_1$ or $\mu_2 > \mu_1$, a reversible cycle analogous to the classical Carnot cycle may be traced. In this case, the environmental “chemical potential” plays the role of the temperature and the “chemical work” the role of heat. For the system, the main form of interaction with the exterior, other than mechanical work, is the exchange of mass of a component at different environmental chemical potentials. It is then possible to obtain an elementary theory of chemical engines in which efficiency estimates (in terms of environmental chemical potentials) and related pertinent issues can be discussed. This model may serve as a basis for analyzing coupled chemo-mechanical processes occurring in materials such as ionized gels for possible applications as actuators, and to interpret complex phenomena in biological systems, such as the chemical kinetics of smooth muscles.

Keywords Chemical transformation · Phase transition · Chemomechanics · Chemomechanical engine · Efficiency · Non-convex minimization · Muscles

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Dedicated to the memory of Donald Carlson, a friend and special colleague.

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1 Introduction

The concept of a cyclic process has played a central role in the origins of thermodynamics, especially in the formulation of its fundamental laws as restriction on what an engine working in a cycle can or cannot do. In classical work, reference is made to the Gedankenexperiment of a cylinder containing an ideal gas with a movable piston at one of its ends. The piston is alternatively placed in contact with an insulator or heat reservoirs at two different temperatures $T_{\text{min}}$ and $T_{\text{max}} > T_{\text{min}}$, and the gas is allowed to expand and contract “reversibly”, either adiabatically or isothermally, following the Carnot cycle. From the principles of thermodynamics, the maximum efficiency obtainable from any heat engine working between the two temperatures $T_{\text{min}}$ and $T_{\text{max}}$ is well-known to be equal to $1 - T_{\text{min}}/T_{\text{max}}$. The result is universal: no other device employing thermal energy and heat reservoirs at temperatures lying between $T_{\text{min}}$ and $T_{\text{max}}$ could ever do better, because of the second law for cyclic processes.

Here, we use the idea of cycles to discuss and make some conjectures about the laws of thermodynamics for open systems, i.e., systems that can exchange matter with the surrounding environment. No formal theory as a modification or alternative to the classical theories is presented: we limit ourselves mostly to conjecture on what the concepts needed for a possible extension of the fundamental principles of thermodynamics to open system might be. As a Gedankenexperiment, we draw upon our work in [1] and consider an elastic bar which undergoes a chemical transformation due to the mass transport of some substance $S_1$ from a surrounding environment. The substance $S_1$ reacts with the substance $S_0$ of which the bar is made. The reaction is supposed to follow a prescribed stoichiometric relationship and the system is “ideal”, in the sense that the chemical transformation is reversible. The volume of the bar, as well as its elastic modulus, varies with the degree of chemical reaction and if the bar is loaded axially, this load will affect not only the strain in the bar, but also its chemical affinity and, consequently, the degree of reaction.

In nature there are materials for which the ideal chemomechanical system described above represents a fair approximation. An example is given by filaments of an ionic gel [16] that are bathed in an acid solution: the gel can swell or contract due to variations of the chemical composition of the surrounding environment. Moreover, the kinetics of biological systems such as muscles is also chemically driven by receptors and changes in ion concentration. Understanding the maximum efficiency obtainable by a chemomechanical open system may serve as a criterion to conceive optimal artificial actuators and, possibly, to understand the underlying processes in biological systems such as muscles, for the optimization of an athletic performance.

The plan of the paper is as follows. In Sect. 2, ionized gels are briefly reviewed as paradigmatic examples of chemomechanical materials. In Sect. 3 a model is proposed based upon the minimization of a non-convex energy, conceived to be a function of the strain and a chemical state-variable. In Sect. 4 the counterpart of the Carnot cycle for a chemomechanical open system is discussed, deriving an upper threshold for its efficiency. Conclusions about possible abstract formulations of the second law of thermodynamics for isothermal chemomechanical cycles are discussed in the last Sect. 5.

2 Chemomechanical Materials

The aim of this section is to present examples of chemomechanical materials to which the model hereafter presented may apply. To this respect, one of the most interesting class of