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FINITE-TIME THERMODYNAMICS TOOLS TO ANALYZE DISSIPATIVE PROCESSES

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I. INTRODUCTION

“Staging free energy” is a term introduced to describe the necessary investment of free energy into a thermodynamic system to allow certain near equilibrium processes to proceed in a desired direction and in finite time (Chapter 4). Such processes may seem—if viewed detached from their surroundings—to be truly reversible. However, if one views them together with the changes occurring in their environment, it becomes clear that they are not completely reversible. This is the assumption formalized in Chapter 4 which asserts that truly reversible processes proceeding in finite time do not exist.

Thus it was suggested in Chapter 4 to dub such processes invertible instead. Nonetheless, the seemingly reversible processes proceeding in finite time point to the problem that to localize the necessary dissipation is a nontrivial problem,

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especially in biological systems, where many processes occur simultaneously on a molecular level.

While it is certainly not easy to find ways to quantify the dissipation occurring in conjunction with those invertible processes, there are already a number of methods established successfully in a more macroscopic setting. These methods evolved in the field of finite-time thermodynamics, which was started in 1975 in Steve Berry's group [1]. The field started with investigations of thermodynamic processes that proceed in finite time. For such processes, losses make the associated efficiencies lower than expected from reversible limits. The field of finite-time thermodynamics considers the following four questions:

- Does dissipation necessarily occur if a thermodynamic process takes place in finite time?
- If so, what is the dissipation for a given process taking place in a given time?
- What is the minimum dissipation necessary for a given net change and a given time?
- What are the processes that achieve that minimal dissipation?

The first question is answered by the finite-time impossibility principle, which can be put in the form of a non-existence theorem of perpetual motion machines of the third kind (Chapter 4). A number of different approaches have been developed to answer the second question [2–4]. The last two questions are typically treated by optimization and control methods [5, 6]. Such methods were originally used on simple heat engines [7–10] and later on a large variety of systems where the following references are only a selection [11–22]. A typical problem for process optimization is, for instance, the piston path in a heat engine [14, 23, 24]. While we here concentrate on the dissipation of free energy, in other circumstances the analysis of finite-time processes puts its focus on other measures like the maximization of power [25, 26]. In this note, we want to present four concepts which highlight the basic features of finite-time thermodynamics and shed some light on the staging free energy problem. These concepts are also promising candidates for further development and application in biological systems.

II. TRICYCLES

Conceptually the interpretation of the fluxes entering and leaving a thermodynamic system is nicely illustrated by the so-called tricycle formalism [27]. This formalism splits the fluxes into a part connected to the reversible operation of the process under investigation and a fully dissipative part. A further separation of the fully dissipative part into the unavoidable irreversibilities associated with the type of process chosen and the excess irreversibilities associated with suboptimal operation was later introduced [28].

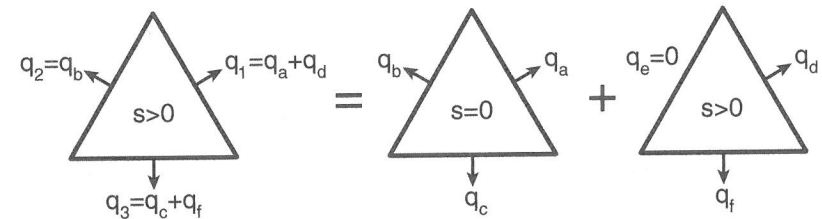


Figure 1. Tricycle decomposition of a thermal process into a reversible component and a totally irreversible component. The quantities q_1 , q_2 , and q_3 are the heat flows into the reservoirs with temperatures T_1 , T_2 , and T_3 , and s is the entropy production. Adapted from [27].

The tricycle formalism is based on conservation equations for the process in question. A heat exchange system is represented pictorially in Figure 1 by a triangle with heat flow rates q_1 , q_2 , and q_3 into reservoirs with temperatures T_1 , T_2 , and T_3 . A conventional heat engine or refrigerator is a special case with one of the temperatures, for example T_1 , infinite, such that no entropy flow is associated with this energy flow, and q_1 is identifiable as power. Any such process can then be divided into a reversible part with zero rate of entropy production, $s = 0$, and a totally irreversible component.

The idea behind the tricycle is that it represents either a cyclic or a continuously operating energy conversion system. Energy conservation in a thermal system requires

$$q_1 + q_2 + q_3 = 0. \quad (1)$$

For a cyclically operating system, the q_s are cycle averages. The corresponding rate of entropy production s is given by

$$s = \frac{q_1}{T_1} + \frac{q_2}{T_2} + \frac{q_3}{T_3} \geq 0. \quad (2)$$

It is now possible to decompose the three flows q_1 , q_2 , q_3 into a triple q_a , q_b , q_c for which the total entropy flow $s = 0$, the reversible part, and the remainder, q_d , q_e , q_f , which carries all the irreversibility. This decomposition is not unique unless a further restriction is imposed. We choose $q_e = 0$.

Nothing new, of course, is learned from such a decomposition *per se*, but by putting in specific loss mechanisms like heat resistance, friction, and heat leak, the rate dependencies of such irreversibilities can be deduced. It may seem that these three loss mechanisms should be treated individually, but they are in fact interdependent and can be solved simultaneously. The decomposition provides the advantage of giving the costs or losses for suboptimal operation.

The tricycle formalism (see also References 29 and 30) with the reversible contributions separated off enables one to focus on the losses and calculate which are the most serious ones. Certain processes, like ordinary distillation, have unavoidable irreversibilities built into them. It will then be convenient to divide the loss-tricycle, q_d , q_e , q_f , further into one for the unavoidable losses and one for the excess losses. Comparing different (e.g. separation) processes, the latter tells how much room there is for improvement of this particular process, and the former how much energy can be saved by developing an entirely new, more nearly reversible process.

Such a decomposition would be very interesting for processes of biochemical interest. How much of the staging investment and dissipation are unavoidable and thereby intrinsic to the mechanism and how much to suboptimal operation is of biological interest. We would expect that optimality regarding the operation would be selected for on a much shorter time scale than improvements in the unavoidable costs.

III. THERMODYNAMIC LENGTH

Another very interesting concept to quantify and bound the dissipation in a thermodynamic process is 'thermodynamic length.' This length is calculated with a metric in the space of thermodynamic equilibrium states. The metric matrix is the matrix of second derivatives $U_{ij} = \partial^2 U / \partial X_i \partial X_j$ of the energy with respect to the extensive variables X_i and X_j (entropy, volume, mole number, etc.). The U_{ij} play an important role in the calculation of the change in the internal energy of a system if its extensive variables are varied by small amounts:

$$U - U^e = \frac{1}{2} \sum_{ij} U_{ij} (X_i - X_i^e) (X_j - X_j^e). \quad (3)$$

Here $U - U^e$ represents the availability of a system that relaxes from its state \underline{X} to \underline{X}^e , its state of equilibrium with its environment.

The first and second law of thermodynamics endow the U_{ij} with the positivity needed for a semi-metric on the surface of thermodynamic equilibrium states. In fact U_{ij} has the positivity to be a metric everywhere except along changes in the amounts of coexisting equilibrium subsystems [31]. For example, if we heat a coexisting mixture of (say) ice and water, the system moves along a degree of freedom with $U = U_0 + \Delta H_{\text{melt}} \cdot (\text{amount of ice melted})$. Along this degree of freedom, U is linear and thus its second derivative vanishes along such directions [3, 32]. Such modes also play an important role in distillation processes [33–35].

Based on this metric, one can define a length L for a path P between two thermodynamic equilibrium states of a system

$$L = \int_P \left(\sum_{ij} U_{ij} dX_i dX_j \right)^{\frac{1}{2}}. \quad (4)$$

Note that here L is independent of the way in which the path is parametrized.

Salamon and Berry [3] named this length 'thermodynamic length' and constructed a bound for the entropy production by establishing a connection between the thermodynamic length of a process and the availability dissipated in that process. In particular, they considered an endoreversible system which exchanges fluxes dX_k of extensive variables with an environment. Each of those fluxes flows over a 'potential' difference, that is, a difference between the respective conjugate variable Y_k of the system and Y_k^e of the environment.

Then one can show that for processes which proceed endoreversibly along equilibrium states, the availability loss

$$-\Delta A^u = \int \sum_k (Y_k^e - Y_k) dX_k \quad (5)$$

is bounded by

$$-\Delta A^u \geq L^2 \frac{\epsilon}{\tau}, \quad (6)$$

where L is the length of the path from the initial state i to the final state f , τ is the duration of the process and ϵ is a mean relaxation time for the system.

The singularity of this metric along coexisting equilibria results in $L = 0$ for movement along such degrees of freedom. As commented on in Chapter 4, a number of such degrees of freedom are used in biological systems. These degrees of freedom enable the associated processes to proceed forward or backward with very small input of free energy and can achieve near perpetual motion machine performance.

As concerns the bound (6), a recent generalization [36] has pushed through a derivation based on any control variables. The prospect of basing optimal control of molecular manipulation protocols using the associated geometry appears promising.

IV. WORK DEFICIENCY

As pointed out above, the bound (6) obtained for the loss of availability [37] rests on the assumption that all the dissipated energy $\int \sum_k (Y_k^e - Y_k) dX_k$ ends up at the temperature of the environment without doing any additional work en route. This is

not the only possibility. If the process takes place at a temperature different from the environment, this dissipated work carries with it some residual availability equalling what remains to be extracted by a (reversible!) heat engine that carries this heat to the environment temperature¹. It turns out that for such systems, the connection to thermodynamic length is not via the loss of availability but via a new quantity called “work deficiency”.

Let $d\underline{X}_{mn}$ be the flux of extensities \underline{X} from subsystem m to n and let \underline{Y}_m and \underline{Y}_n be the vectors of the corresponding intensities of subsystems m and n , respectively. Then the work deficiency dW^d is defined as

$$dW^d = \frac{1}{2} \sum_{mn} (\underline{Y}_n - \underline{Y}_m) d\underline{X}_{mn}. \quad (7)$$

It equals the work which one could have extracted from the process performed reversibly. For further work see References 38–41.

A thorough investigation shows that the bound provided by the thermodynamic length is in general one for the work deficiency

$$W^d \geq L^2 \frac{\epsilon}{\tau}. \quad (8)$$

The loss of availability is on the other hand always connected to the entropy production

$$-\Delta A^u = T_0 \Delta S^u. \quad (9)$$

This entropy production is in turn bounded by a similar length-squared inequality, but using another length defined by the second derivative matrix of the entropy [3].

The generalization of the original Berry/Salamon result [3] presented in Inequality (8) highlights an important point in connection with the Holliday junction paradox: it is crucial to analyze the pathways along which the free energy in a biological system is degraded. Even though this free energy ends finally up as heat in the environment, the dissipation can take place via a cascade of processes, which can store and later make use of the remnant availability. In particular, availability freed by a conformational change in a molecule might—before becoming thermalized to vibrational modes—power another reaction. This is exactly what needs to be carefully accounted for to find accurate values of the staging free energy.

¹ This issue of whether or not to count the residual availability in a heat stream was also at the core of the controversy regarding the equivalence of minimum entropy production and maximum power as criteria of merit for finite time processes [13, 25].

V. ACCOUNTING FOR STAGING FREE ENERGY WITH NETWORK THERMODYNAMICS

As already pointed out in the Introduction, processes without dissipation do not occur in nature if performed in finite time. The real goal then for such processes is to account for their dissipation, that is, the entropy production going on. This—in general—is a nearly impossible task, especially if the process in question is related to many different constituents of the overall system. For instance, in biological systems, it is unclear where one can sensibly draw a border for what one considers “the system”.

However, there are thermodynamic tools available that guide in such situations. The emergence of network approaches like endoreversible thermodynamics [17, 42] provides the means to organize the analysis of complex thermodynamic processes such that the ongoing loss in staging free energy can be attributed to the different dissipation mechanisms at work. This analysis allows us to localize and quantify this dissipation. This approach has proven very helpful in a variety of processes, including those occurring in heat engines operating in finite time [5, 6]. Even for complex systems, it was shown that a coarse description gives quite good results [43].

To achieve this, endoreversible thermodynamics makes one particular assumption, namely that all dissipation occurs in the transport between reversible subsystems. This might seem to be a strong requirement, however, in many cases, the description can be quite coarse; one can get a long way by catching the major dissipative processes.

The transport between the subsystems always consists of at least two interdependent fluxes: energy and another thermodynamic extensity, for instance entropy (for heat transport), a particle flux or a charge flux. The accounting then proceeds via the corresponding intensive thermodynamic quantities. In the cases above, these quantities are the temperature, the chemical potential or the electric potential.

It is important to note that these intensive thermodynamic quantities will in general depend on *all* the extensities present in the system, that is, the change in the charge content or the volume will have impact not only on the electric potential or the pressure, but also on the chemical potential or the temperature of the system. With respect to the initial Holiday junction paradox, this means that one has to perform a very subtle analysis of these cross dependencies.

In Figure 2, we show how such a thermodynamic network might look for the protein folding case. The two configurations of the protein—folded and unfolded—constitute two subsystems of a wider network which encompasses also a reservoir for what we here call control reagent A, a chemical whose concentration controls the configuration of the protein. The transport between the two configurations (i.e. flux between the two compartments) is controlled via the chemical potential for control reagent A. The flux between any two compartments, however, will be dissipative, as a flux only occurs for a finite difference in the chemical potential of the transported quantity.

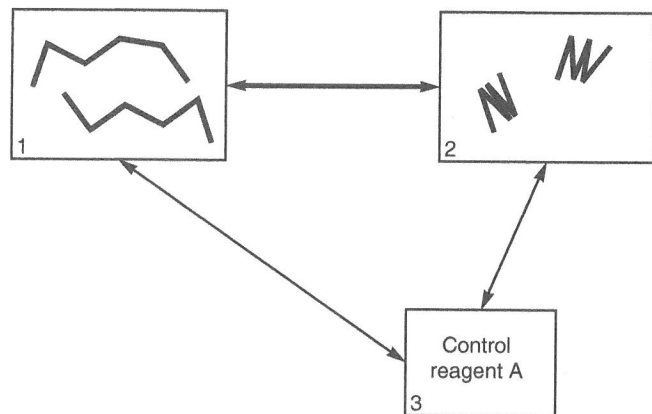


Figure 2. The figure shows a part of a thermodynamic network of endoreversible subsystems. Here, two of the subsystems (1 and 2) represent the folded and unfolded states of a protein. Subsystem 3 is a reservoir for a control reagent A. When the concentration of A in the first two subsystems changes due to an influx (black arrows) from reservoir 3, this change influences the chemical potentials for the folded and unfolded protein, thereby creating a flux (thick black arrow) of the protein between the folded and the unfolded states.

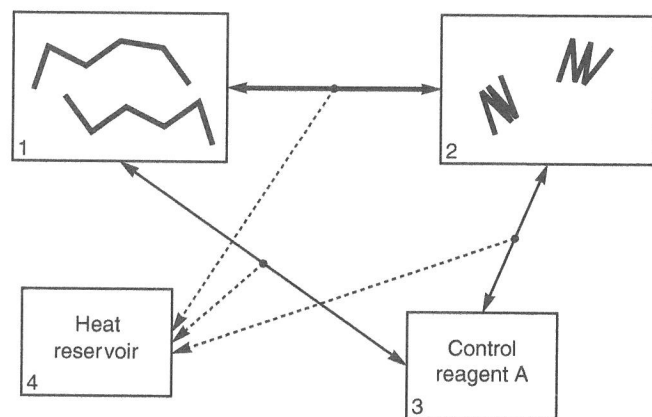


Figure 3. The figure shows the same three subsystems of a thermodynamic network as Figure 2. Now a fourth subsystem, a heat reservoir, is added which takes up the free energy dissipated in the processes described in Figure 2. The dissipated free energy flows are depicted by dashed arrows. Note that the irreversibilities in this endoreversible approach only occur in conjunction with the fluxes between the reversible subsystems.

The dissipated energy shows up as heat input into the subsystems of the network; in Figure 3, for display reasons, they all end up in one heat reservoir. In reality the heat (i.e. the dissipated energy along with the produced entropy) is of course distributed into the different subsystems present.

Beyond the descriptive power of the endoreversible approach it opens new questions: Can we—from the network structure (and some transport properties)—obtain bounds on the entropy production?

This could also shed light on the biological systems where apparently reversible processes might not take all the changes in the system into account, which make the process feasible. A network approach might then show, where the staging entropy production did occur.

VI. CONCLUSION

In this chapter, we presented four concepts: the tricycle, thermodynamic length, work deficiency, and network thermodynamics. They reflect in part the development which was started by Steve Berry and coworkers in a field called finite-time thermodynamics. These concepts show the evolution of conceptual approaches as well as the arrival of applicable thermodynamic tools. These methods developed in a variety of directions. While tricycles by definition have systems with three heat reservoirs in mind, finite-time thermodynamics methods have also been extended to systems with more heat reservoirs [44]. Beyond the realm of macroscopic systems, these concepts have been extended during the past years also to the realm of quantum systems [45, 46]. While network thermodynamics has proven its usefulness in macroscopic applications like the analysis of internal combustion engines, the complexity of biological systems remains a challenge. But again, a basic goal of finite-time thermodynamics might help: address the major dissipative processes and determine their entropy production. In that sense, the challenge for the Holiday junction paradox is to localize where the staging free energy is needed and what its dissipative pathways are (Chapter 4).

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