THE LADDER THEOREM

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ABSTRACT

Consider a thermodynamic system brought along a particular sequence of equilibrium states via a sequence of relaxations. This is the classic quasistatic process that, in the limit, allows the dissipation to go to zero. At each point along the process, the system relaxes to a bath that is in a state just ahead of the current state of the system. In the quasistatic limit, the baths are only infinitesimally ahead and the time of the process goes to infinity. This situation is depicted in figure 1

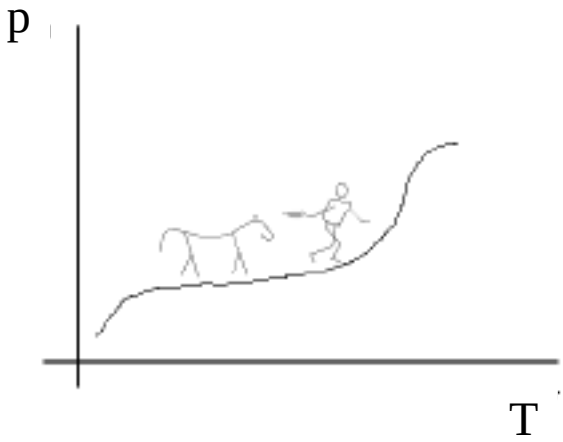

Figure 1: A horse-carrot process. The system (horse) keeps trying to relax to the position of the carrot (environment).

Consider an approximation to this process obtained by choosing K states of the system along the given process and using baths at these states for K successive relaxation processes of our system [1]. If K is large and the baths are well dispersed along the process, all of the relaxations are small. This is illustrated in Figure 2 below with the process being the heating of a cup of coffee.

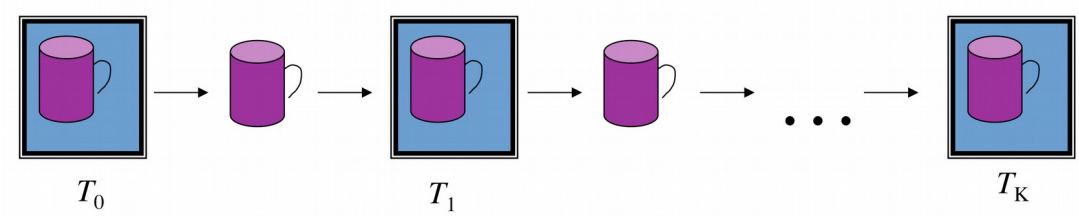

Figure 1: A cup of coffee successively relaxing to K successively hotter surroundings.

We now consider the dissipation in a small equilibration. Let $X=(x_1, x_2, \ldots, x_n)$ be a set of independent extensive variables of the system and let $Y=(y_1, y_2, \ldots, y_n)$ be the corresponding intensive variables, with

$$y_i = \frac{\partial S}{\partial x_i}$$

where S is the entropy of the system. Finally, let X_e, Y_e be the state of the system in equilibrium with the bath whose intensities are Y_e. The entropy production in the relaxation is given by

$$\Delta S_U = \int_X^{X_e} \sum_i (y_i - y_{i,e}) dx_i$$

where ΔS_U is the change in the entropy of the universe. Expanding $Y\text{-}Y_e$ to first order as a Taylor series about the state X_e gives

$$y_i - y_{i,e} = \sum_j \frac{\partial^2 S}{\partial x_i \partial x_j}(x_j - x_{jee})$$

To the same order, the second derivative matrix of S can be taken constant and the integral evaluated [1] to give

$$\Delta S_U = \frac{1}{2}\sum_{i,j}\frac{\partial^2 S}{\partial x_i \partial x_j}(x_i - x_{i,e})(x_j - x_{j,e})$$

If we take the second derivative as a metric matrix [2, 3], the set of equilibrium states of the system becomes a Riemannian manifold with distances such that

$$\Delta S_U = ||X - X_e||^2,$$

where ‖A-B‖ indicates the distance from A to B. This was for one small step. Minimizing the sum of the entropy produced in K small equilibrations gives the following optimization problem:

$$\min \sum_{k=1}^{K} ||X - X_{e_k}||^2 \qquad \text{with} \qquad \sum_{k=1}^{K} ||X - X_{e_k}|| = L = \text{constant}$$

whose solution leads to the Horse-Carrot inequality

$$\Delta S_U \geq \frac{L^2}{2K}$$

where L is the thermodynamic path length of the process and K is the number of stages in the process. This equation shows that minimizing the dissipation of a process can be accomplished by either increasing the number of stages K, or by changing the process along the way so as to shorten the thermodynamic length L between the initial and final states.

The minimum entropy production solution is achievable and has been used in the design of an energy efficient distillation column [3, 4]. The theorem is also relevant to biology. Frederiksen and Andresen [5] calculated the entropy production associated with the cytochrome chain in human mitochondria in which the chemical potential of an electron is lowered by sequential stages to extract work and produce, ultimately, ATP molecules. They demonstrated that the spacing of electron carrier molecules in actual mitochondria serves to produce close to the minimum entropy for a K-step process.

Our interest in the present manuscript is the straightforward observation that adding a (not necessarily step anywhere in a K-step process will reduce its entropy production. This follows from

$$||\Delta X_1 + \Delta X_2||^2 \geq ||\Delta X_1||^2 + ||\Delta X_2||^2,$$

which holds in a small neighbourhood provided only that ΔX_1 and ΔX_2 make an angle less than ninety degrees, i.e. that they move more or less in the same direction. We refer to this result as the **Ladder Theorem**. It is illustrated in Figure 3 below.

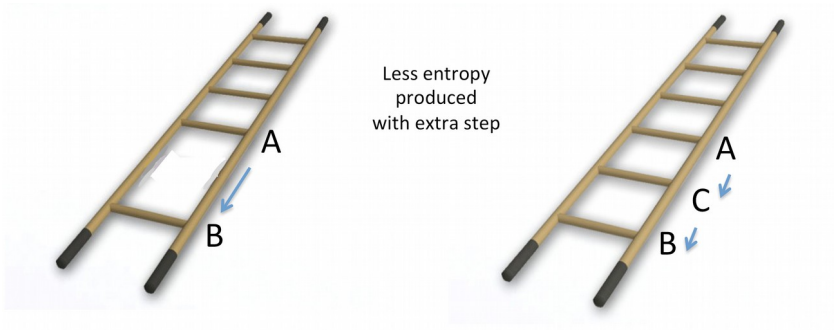

Figure 3: Inserting the step C decreases entropy production.

One illustrative biological example is again the electron transport chain (ETC) in mitochondria. The Ladder theorem assures us that if an additional molecule were to be added to the ETC, the result would be favourable in so far as it would reduce entropy production. Subsequent evolutionary processes can then select for the redox potential of the electron in the molecule to be equally spaced between two existing redox states in the ETC. Although, by utilizing this theorem, one cannot predict which new molecule will arise in the ETC, one can predict which molecule would provide the greatest fitness advantage, and thus which molecule would be the most likely to be selected for and eventually fixed within a population. This theorem might also allow for thermodynamic-based evolutionary predictions at higher biological levels, such as where new organisms might benefit most in trophic chains, or which new niche space would be the most beneficial to occupy in order to receive the greatest bioenergetic benefit.

One troubling aspect in all of this is the proviso that all the steps in the process be small. Intuitively, the small should not be needed or at least should be much larger than the restriction to constant second derivatives of the entropy might imply. In fact we believe that quite generally the only requirement is that the two subprocesses that result by adding a stage in between two stages be again in roughly the same direction. We here conjecture that this is the case and point out that Riemannian geometry provides the tools for parallel transport so there is a possibility of proving our conjecture globally, i.e. without the need for assuming the steps are small.

REFERENCES

[1] J. Nulton, P. Salamon, B. Andresen and Q. Anmin, Quasistatic processes as step equilibrations, *The Journal of Chemical Physics*, vol. *83*, pp. 334-338, 1985.
[2] G. Ruppeiner, Riemannian geometry in thermodynamic fluctuation theory, *Reviews of Modern Physics*, vol. 67, pp 605-659, 1995.
[2] P. Salamon and R. Stephen Berry. Thermodynamic length and dissipated availability, *Physical Review Letters*, vol. 51, pp. 1127-1130, 1983.
[3] P. Salamon, and J. D. Nulton, The geometry of separation processes: A horse-carrot theorem for steady flow systems, *Europhysics Letters*, vol. 42, pp. 571-576, 1998.
[4] B. Andresen and P. Salamon, Optimal distillation calculated by thermodynamic geometry, *Entropy*, vol. 36, pp. 4-10, 2000.
[5] K. B. Frederiksen and B. Andresen Mitochondrial optimization using thermodynamic geometry (unpublished), http://www.fys.ku.dk/~andresen/BAhome/ownpapers/cytochain/Nagpur-mitoopt.pdf, 2008.