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Non-Equilibrium Structures: How can they be maintained?

A hypothesis

The work we have done over the past 10 years concerns systems that are out of global equilibrium [1]. These systems can be found everywhere, in nature and in industry. Nature has evolved over billions of years and, according to Darwin, only the fittest have survived. It is therefore likely that the systems that have survived are efficient in some sense. Can the understanding of natural structures be helpful for man-made designs of energy-efficient systems? Our hypothesis is that they can be, in a wide sense, for our survival. But what does efficiency mean in this context? And what is meant by a non-equilibrium system or a structure out of equilibrium? How can we obtain, measure and maintain non-equilibrium structures? Let us answer these questions by examining some examples, and then look at the consequences.

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An equilibrium structure

The most well-known examples of structures in equilibrium are minerals and crystals. A crystal possesses a particular order, and this order does not change over time, at least not on a time scale that we can observe. A rock crystal is composed of silicon and oxygen atoms arranged in a tetrahedron. Table salt (NaCl) has a cubic structure, see Picture 1.

A measuring scale was established already in 1860 to measure order. The measure is called entropy, with the symbol S. Perfect order has $S = 0$. In a collection of many particles, the entropy is very large. It grows if there are more and different particles. Negative entropies do not exist.

Picture 1.
The crystal structure of table salt
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A non-equilibrium structure

In a non-equilibrium structure, the components are moving in a measurable way. There are many examples that components move in an orderly

Picture 2. A dynamic structure: flying geese
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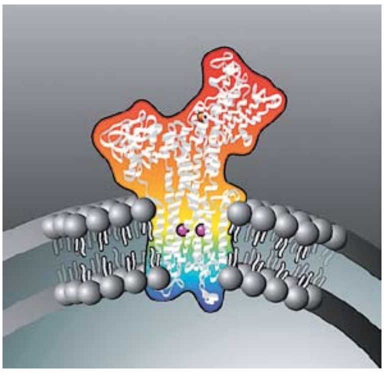
fashion. Take, for instance, a flying flock of geese (Picture 2). The group of birds fly in a V-shape. We know that this conserves energy for the group as a whole. It is the same in professional teams of bicyclists. Supporting team members take turns leading at the beginning of a race in order to conserve the energy of a potential winner. How can geese or bicyclists maintain their structure? By eating or by obtaining energy from the outside, of course! *A non-equilibrium structure is maintained by a supply of energy from the outside.*

Picture 3. Giant's causeway in Ireland. Is this a frozen dynamic structure?
(Private photo)

A non-equilibrium structure collapses if the energy source is removed. However, we can observe structures that have been dynamic, but are now locked or fixed in position. Take, for example, the "Giant's causeway" in Ireland, see Picture 3. Hexagonal or pentagonal cells seem to be frozen in an enormously large collection of cells. In some geological past time, each cell may have been a unit in a larger system with an overall order; an order that was maintained by a large geothermal gradient. But we need not go to Ireland to see a former dynamic structure. We can do experiments in the kitchen. Cook rice with a high influx of heat to the pot, and observe a pattern of regular gas pockets in the rice when the water has evaporated. Do the same with



Picture 4. The Ca-ATPase. An enzyme that pumps calcium ions uphill towards higher concentrations and more order, by means of chemical energy

spaghetti in an abundance of water, and see the regular pattern in which the long soft threads arrange themselves when the water disappears. The experiment has already been done by Adrian Bejan, so you might want to compare your results with his by looking into his book [2]. The molecular pump that we study [3] creates order by storing calcium ions in a closed vesicle (a small pocket) at a high concentration. Picture 4 gives a cartoon. Chemical energy is used to accomplish this.

The earth as a non-equilibrium system

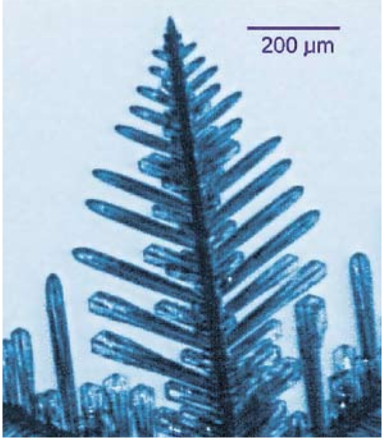
The method that we use to study dynamic structures can be applied to the earth. The earth contains numerous dynamic structures. All living beings can be seen as such. More living beings therefore mean lower entropy on the earth. Order is maintained by a *net* flux of entropy away from the earth. The entropy influx from the sun leads to order decrease or positive entropy, while the entropy outflux from the earth, J_s^{out}, leads to a decrease in entropy. A balance equation links the contributions:

$$\frac{ds}{dt} = J_S^{in} - J_S^{out} + \sigma = \frac{J_{energy}^{in}}{T^{sun}} - \frac{J_{energy}^{out}}{T^{earth}} \qquad (1)$$

This balance is the second law of thermodynamics. It governs all conversions involving energy. On the left hand side is the internal (negative) entropy change per unit of time and volume, *ds/dt*. After the first equality, we have the net flux of entropy into the earth, $(J_s^{in} - J_s^{out})$ plus the entropy that is produced in the process of creation and maintenance of structures, σ. This quantity represents the friction that has to be overcome in a dynamic structure (remember the efforts of the team of bicyclists) and is always positive. The entropy flux is defined by the energy flux divided by the appropriate temperature. If the energy flux from the sun is not accumulated on earth over time, it is equal to the energy flux out, according to the first law of thermodynamics. This gives $J_{energy}^{in} = J_{energy}^{out}$. The entropy flux difference is therefore negative, because the temperature of the sun is 5000 K, while that of the earth is around 300 K. This is what we want. But a positive entropy production may, at least in principle, threaten that situation.

Are there limits to growth caused by the production of entropy?

Can we change a non-equilibrium structure? The answer is yes. We do so by changing the rate of energy input into the system or by altering the stress on the system. Take the formation of ice crystals, for example. When the air is rather humid and the temperature is close to zero degrees centigrade, ice tends to form needle-like crystals like those in Picture 5. When the temperature is well below zero, ice grows in largely different forms, for example, in flat hexagonal crystals, or so-called depth hoar crystals. The structure can be seen as an adaption to the external stress.

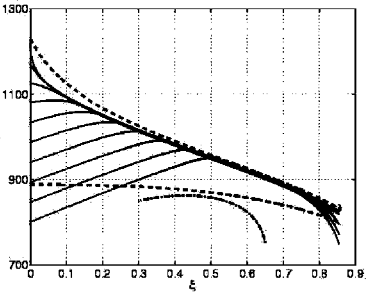


Picture 5. Ice needles
http://www.scienceclarified.com/images/

Considering the earth as a system once again, we know that the stress on our resources increases as the population grows. More entropy will be produced for this reason. A solution may be the creation of new structures. Changes are necessary for many reasons. And changes come with entropy costs. There is always a positive entropy production to pay for maintenance and construction. In this manner, there may be a limit to growth if the entropy production becomes too high. One might say that humanity *is facing an entropy challenge*. Entropy production cannot be too large as the earth must be able to sustain it. It is very difficult to calculate these quantities for the earth as a whole, but a systematic approach has now started.

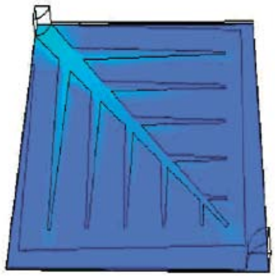
Energy efficient designs are needed

What can we do to counteract the increased entropy production in the world? Clearly, we can become more efficient in our use of resources. We destroy order when we use fossil fuels. For this and many other reasons, it is important to look for possibilities for more energy efficient design. By studying the natural lung system, Gheorghiu *et al.* [4] found that the entropy production was *constant* in the bronchial as well as in the alveolar regime of the human lung! This finding was also a property of the energy efficient apparatuses studied by Kjelstrup and co-workers, see ref. [5] for further references. For instance, Johannessen and Kjelstrup [6] found that chemical reactors with *minimum* entropy production (a minimum waste of energy) had *constant* entropy production. The reactors operated along a so-called highway, illustrated in Picture 6. The highway picture was adopted because the highway is often used for driving that is beneficial for fuel use. We know that it is better for a car engine to avoid sudden acceleration and braking. It is this experience that has now been generalised, by us [4-6] and others [2], to design many processes that involve energy conversion. They should be constructed after determining the dynamic structure of the process that leads to minimum entropy production.



Picture 6. The highway in state space for chemical reactors defined by temperature and composition along the black band. Reprinted with permission of *Chem. Eng. Sci.*

The sum total of such activities will reduce the strain on the systems of the earth. We are now working to find structures, e.g. fuel cells that are beneficial according to these views. Does the structure in Picture 7 have these properties? This is just one example. A series of similar studies should be undertaken to meet the entropy challenge.



Picture 7. A new design of oxygen supply system to fuel cells? From Morgan Fuel Cells, 2003.

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