Disequilibria and Escapements

The engines that bring matter to life

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1 Introduction

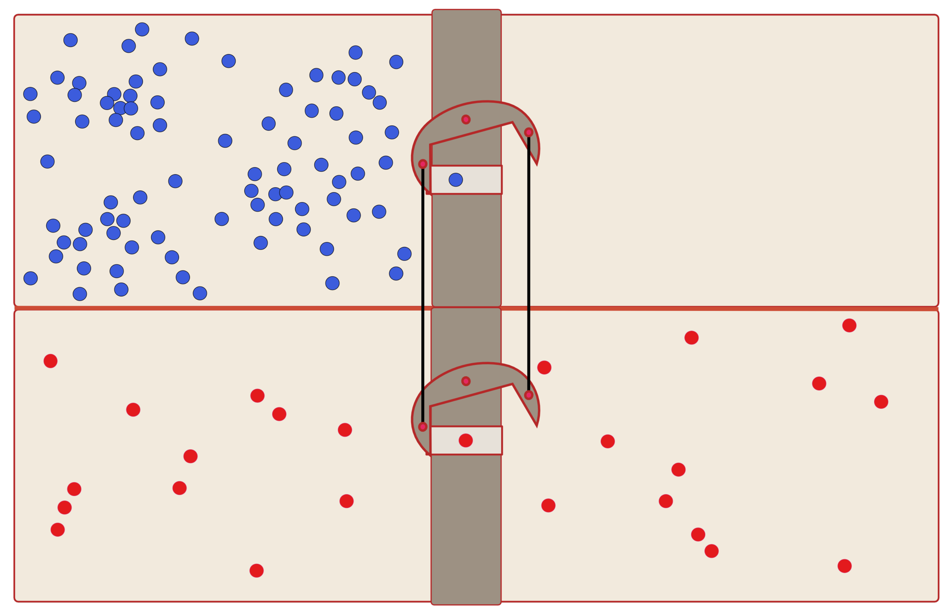
- Living systems, as their most characteristic and distinguishing property, are frantic, thousand-ring circuses of extreme and dynamic disequilibria; wrought in both structure and process; requiring incessant regeneration.
- They must therefore, by the 2nd law, be powered by the enslaved dissipation of external disequilibria via a clockwork cascade of disequilibria conversions; each created disequilibrium the daughter of a dissipating (and greater) disequilibrium to which it is coupled. Life is NOT powered by the consumption of energy; but then neither is anything else.[1]
- Bioenergetics is entirely a hierarchical cascade of disequilibria conversions (not of energy conservation, or energy transfer; at all).
- The emergence of life is indivisible, as a categorical absolute (we contend), from the emergence of bioenergetics, understood in these terms.[2][3]
- Disequilibria conversions of the kind needed are far from automatic, are not just chemistry, and can only be carried out by molecular engines that are by no means just enzymes.
- These conversion engines act as Brownian ratchet escapements, forcing the incremental relaxation of the driving disequilibrium to be conditional on (gated by), and thereby trapping, completed instances of the driven reaction - which are themselves caused by thermal fluctuations from the bath.

2 Disequilibria in real life

- The ATP disequilibria, life's main power bus: the ratio $[ATP]/[ADP][Pi]$, is maintained at $10^9 - 10^{11}$ above its equilibrium value! Note that ATP at equilibrium w.r.t. its hydrolysis products carries zero "free energy" no matter what its concentration ($\Delta G^{\text{reaction}} = 0$). Each ATP is consumed in $\approx 1-2$ min.; half or more body weight in ATP turnover per day.
- That disequilibrium is mainly produced via ATPsynthase acting as a disequilibrium converter driven (on a $\approx$ 4 for 1 basis) by the dissipation of a transmembrane proton concentration disequilibrium which itself is pumped to a voltage gradient of $\approx$ 30 Million V/m roughly 10 fold the breakdown voltage of dry air!
- The proton gradient disequilibrium is in turn (typically) generated by a cascade of disequilibria conversions coupling the dissipation of redox disequilibria to the pumping of protons "up hill" across the relevant membrane; etc. In general the flux through this conversion cascade is the rate limiting factor for life.
- But how do disequilibria conversions actually work? And how might the essential ones have arisen abiotically to ignite the emergence of life?

3 How (all) disequilibria are created

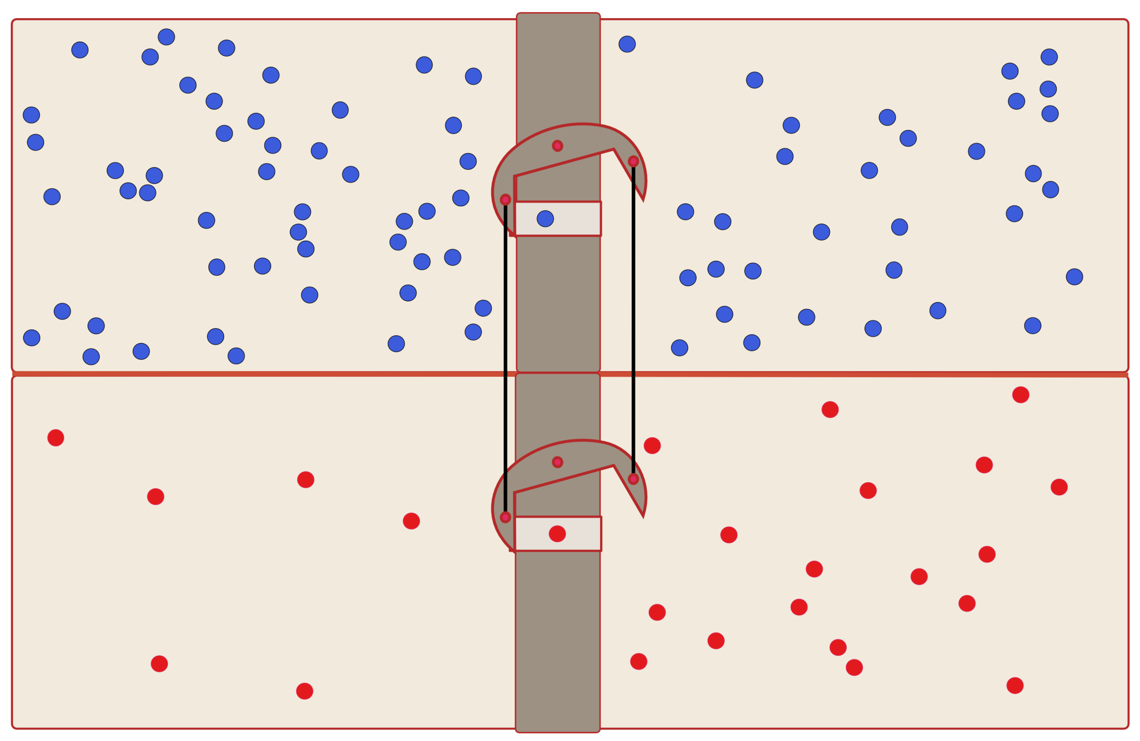
- By mechanistically coupling statistically opposed processes, via Brownian ratchet escapement mechanisms.
- Simple example: two coupled diffusion processes.



- Starting state: full disequilibrium in blue; approximated equilibrium in red. Particles and escapement motions driven by thermal fluctuations.
- Rule: Escapement can flip direction only if both slots are in the same state (loaded or empty) (though typically it is allosterically biased left if both are open, biased right if both are loaded). It is a type of Brownian ratchet.

4 How (all) disequilibria are created

- The partial disequilibrium (in red) is created at the expense of the partial relaxation of blue's disequilibrium.



- Final, steady state; neither process is in its own equilibrium configuration.
- However, the entropy of the system, $S_{tot} = S_{blue} + S_{red}$, is maximum, in stationary conditions.

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5 A dynamical model

- Can we write a dynamical model to obtain quantitative predictions about how disequilibria engines work?
- Say that we have N_B blue particles and N_R red particles. We call β the ratio of the gas sizes, i.e., $\beta = N_B/N_R$.
- Let α be the probability per unit of time that *both* particles arrive to the two slits.
- If we know the initial condition (e.g. the starting system of slide 3), the system has one degree of freedom, e.g, the concentration of blue particles in the top left chamber, x.
- We can then write down a simple system of ODEs which describes the system:

$$\dot{x} = \alpha(1-x)\left(\beta + \frac{1}{2} - \beta x\right) - \alpha x\left(-\beta + \beta x + \frac{1}{2}\right)$$

- The equation provides two predictions:
  - The concentration in the top-left chamber when the engine reaches stationarity is $\frac{2\beta+1}{2\beta+2}$.
  - The timescale to reach stationary conditions is $\alpha^{-1}(\beta+1)^{-1}$.

6 Conclusions

- Life is inherently an incredibly far-from-equilibrium activity comprising, and driven by, a myriad of disequilibria-creating (endergonic) processes each of which must of necessity (2nd law) be generated by being mechanistically coupled to the (exergonic) dissipation of a greater disequilibrium (life is not powered by energy consumption).
- The required driver-driven disequilibria couplings work by means of escapement mechanisms which:
  - "Rectify" thermal fluctuations impacting the "driven" reaction by blocking their effect except for those that happen to produce a completed instance of that reaction (by "exciting" it sufficiently, "up-hill", "counter entropically").
  - Then, triggered by that completion, trap the event by allowing the exergonic (quasi-irreversible) driving process to complete. This escapement logic creates one disequilibrium at the expense of dissipating another, larger one. There is no transfer of energy from the driving to the driven reaction.
- The mathematical analysis in slide 5 can be refined, using a more elaborate model which takes stochastic fluctuations into account. In this way, we can compute the stationary distribution around the steady state of the engine, the entropies in the four chambers and the rate of entropy production which drives the system to stationarity (work in progress).

References: **[1]** see: Schrodinger. *What Is Life?* Cambridge Univ Press, 1967 and also the Forward in that edition by Roger Penrose; Boltzmann. 1886, in: Theoretical Physics and Philosophical Problems; Selected Writings (Vienna Circle Collection), chapter: *The Second Law of Thermodynamics*, pages 13–32. Kluwer (D. Reidel Publishing Co., Dordrecht, Holland; 1974).
[2] Branscomb E. and Russell M., (2013) BBA, 1827, 62-78. **[3]** Russell M.J., et al., (2013) PTRS-B, 368: 20120254.