Electronic supplementary information

In Command of Non-Equilibrium

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Criterion for spontaneously occurring processes

Equation (3), stating the criterion for process to occur spontaneously as $dS^{universe} = \delta Q/T > 0$ (and $dS^{universe} = 0$ for reversible processes) is the general definition of the Second Law of Thermodynamics, but it is impractical to use. When the system is in thermal equilibrium with its surrounding (*i.e.* $T^{system} = T^{surrounding}$) it is more convenient to split the entropy change of the universe into a contribution from the system and one from the surrounding:

$$dS^{universe} = dS^{system} + \delta Q^{surrounding}/T^{surrounding} = dS^{system} + \delta Q^{surrounding}/T^{system}. \qquad \text{(Eqn. S1)}$$

Since the uptake of heat by the surrounding equals the heat transferred from the system, $\delta Q^{surrounding} = -\delta Q^{system}$, eqn. (S1) translates into

$$dS^{universe} = dS^{system} - \delta Q^{system}/T^{system} \qquad \text{(Eqn. S2)}$$

According to the Second Law, $dS^{universe}$ is > 0 for all spontaneous and zero for reversible processes (*i.e.* at equilibrium). We therefore rewrite eqn. (3) as:

$$dS^{system} - \delta Q^{system}/T^{system} \geq 0, \qquad \text{(Eqn. S3)}$$

an expression that no longer depends solely on the system and no longer on the entire universe. We can therefore drop the superscript. Moreover, for an isobaric process $\delta Q = dH$, so that

$$dS - dH/T \geq 0, \qquad \text{(Eqn. S4)}$$

and using the Gibbs Helmholtz relation, $dG = dH - TdS$,

$$dG \leq 0, \qquad \text{(Eqn. S5)}$$

which is exact and identical to eqn. (3) for isothermal processes at constant pressure and thus a very good approximation for may processes of living systems or in the laboratory. For isothermal processes at constant volume the corresponding expression, $dF \leq 0$, where F is the Helmholtz Free Energy, can be derived in an analogous way.[1]

The kinetic control of processes

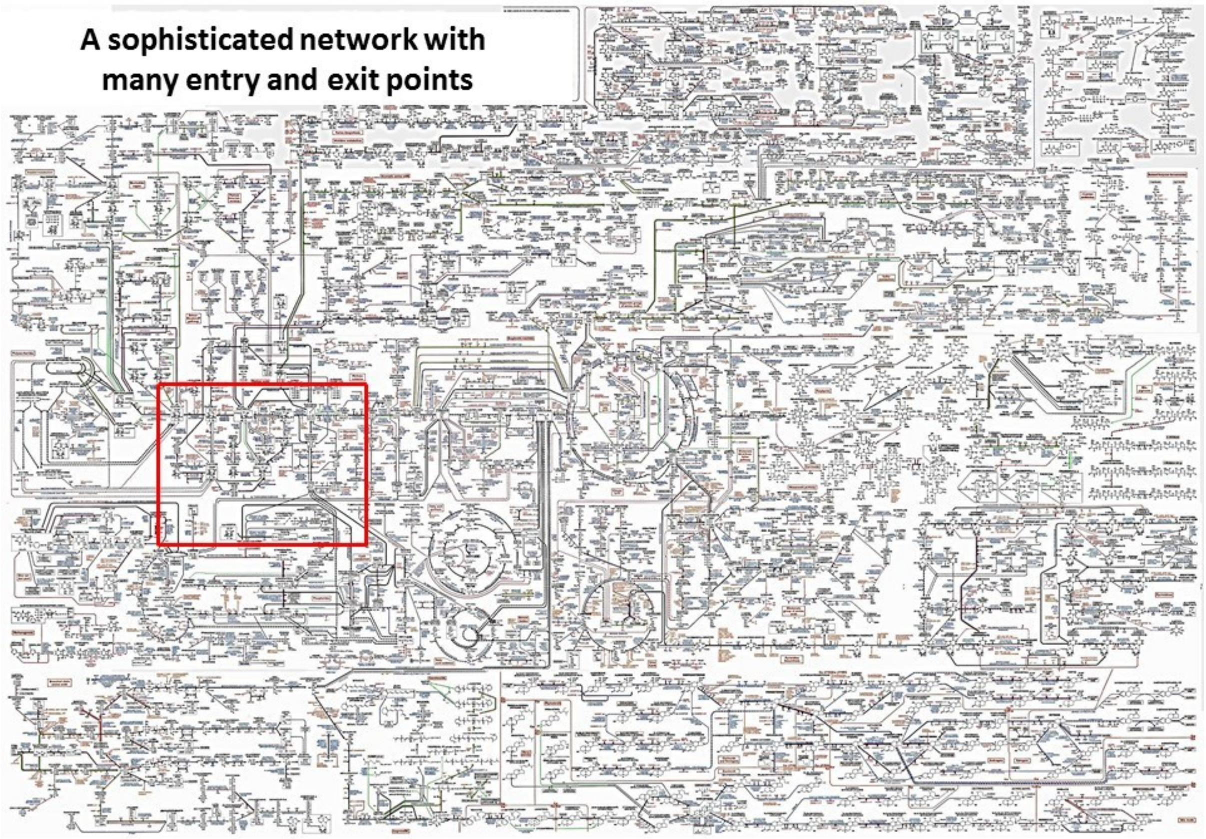

Figure S1: ROCHE Biochemical pathways in the human metabolism developed by Gerhard Michal [2] (This figure is not intended to be read; it should only provide an impression of the complexity of the human metabolism).

Boltzmann's statistical definition of entropy

The number of ways W how a number of k black fields can be arranged over $n \geq k$ fields at single occupancy of a field is calculated as follows. For the first field (A) there are n free options, for the second one (B) there are n-1 options, then n-3 (C) and so on, until (n-k+1) for the last one:

$$W = n\,(n-1)(n-2)(n-3)\ldots(n-k+1)$$

$$= \frac{n\,(n-1)(n-2)\ldots(n-k+1).(n-k)(n-k-1)\ldots1}{(n-k)(n-k-1)\ldots.1} = \frac{n!}{(n-k)!}$$

(Eqn. S6)

This is the case when the fields (A,B,C...) are distinguishable, because they are marked in some way. For the example with n = 9 and k = 3 we have W = 9·8·7 = 504, 6 of them are displayed in Figure S2. If we remove the mark on the fields, these 6 options become indistinguishable. The number of distinguishable ways gets reduced by the number of permutations of the k fields, which is $k\ (k-1)\ (k-2)\ldots\ 1 = k!$ so that for the case of indistinguishable black (and indistinguishable white) fields we have:

$$W = \frac{n!}{k!(n-k)!} = \binom{n}{k} = \binom{n}{(n-k)}$$

(Eqn. S7)

This is a binomial distribution. It is symmetric and has a maximum for $k = n\text{-}k$, as seen in the plot of *ln W* as a function of k (Figure S3). The curve reminds of the behaviour of the entropy of mixing of two ideal gases as a function of mole fraction. In fact, what we have here is just the mixing of black and white fields.

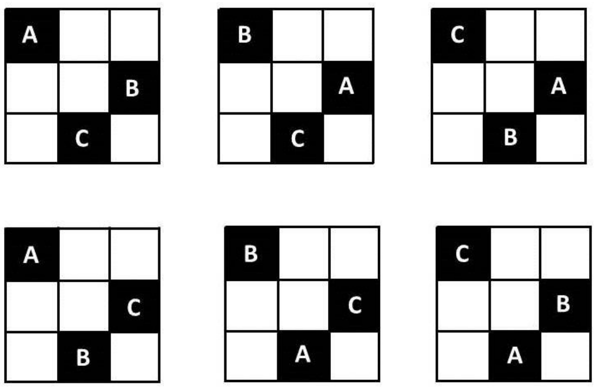

Figure S2: Selected arrangements of three black fields marked A,B,C over 9 fields. They are distinguishable as long as the black fields are distinguishable by virtue of the lettering but indistinguishable when the fields are not marked, as in Figure 5 (a) and (b) of the article.

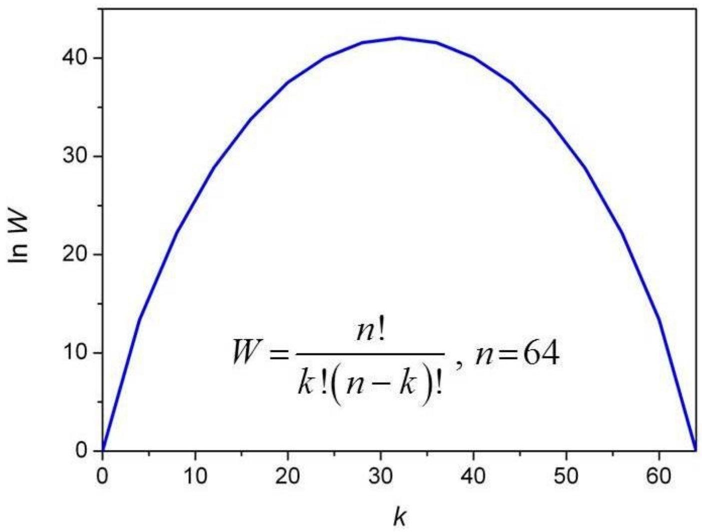

Figure S3: Logarithmic plot of the number of possible arrangements of a number of *k* black fields over the 64 fields of a checker board. The maximum occurs for $k = n/2 = 32$. There are $W = 1.833\times10^{18}$ possible arrangements of 32 black fields over 64 fields. They all have the same probability, *i.e.* there is no difference in entropy between more ordered or disordered arrangements of these 32 fields.

References

1) P. W. Atkins, Physical Chemistry, Oxford University Press, Oxford, 1978.
2) G. Michal, D. Schomburg, Eds., *Biochemical Pathways: An Atlas of Biochemistry and Molecular Biology*, 2nd. Ed, John Wiley Sons, Hoboken, USA (2012).