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Exploiting the effect of noise on a chemical system to obtain logic gates

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Abstract – Small added noise has been predicted to direct certain classes of chemical systems towards a specific enantiomeric direction, with the dependence of product asymmetry on noise levels being non-monotonic and nonlinear. Associating the product selection in such chemical reactions with different outputs, and varying noise levels to encode the inputs, we observe that the response of the system mirrors the input-output relations of different fundamental logic operations. So the complex enantioselection, under the influence of noise, allows the chemical system to effectively behave as a *logic gate*. This observation may have potential applications in the design of chemical gates, as well as provide understanding of the information processing capacity of naturally occurring chiral symmetry-breaking chemical systems, with noise acting as the logic pattern selector.

Logic gates form the basis of universal general-purpose computation [1]. So different physical principles that can yield logic outputs is of paramount interest. Very recently, there has been an attempt to use the interplay between noise and nonlinearity to obtain logic gates [2]. Here we significantly expand the scope of this new research direction by reporting the following observation: a specific chemical system can be interpreted as yielding different kinds of logic behaviour, under the influence of noise, thus effectively behaving as a *chemical logic gate*.

Consider a chemical reaction system asymmetrically perturbed by means of a very small bias in the racemization equilibrium between two enantiomers. In such systems, small additive noise amplifies the symmetry breaking, and yields biased product distributions. Our central idea here is to interpret this noise-induced product selection in this chemical system, as a *logical operation*. That is, we will show how the correspondence between enantioselection, interpreted as an *output*, and noise intensity, interpreted as *input*, mimics the input-output relations of all fundamental logic gates (see schematic in fig. 1).

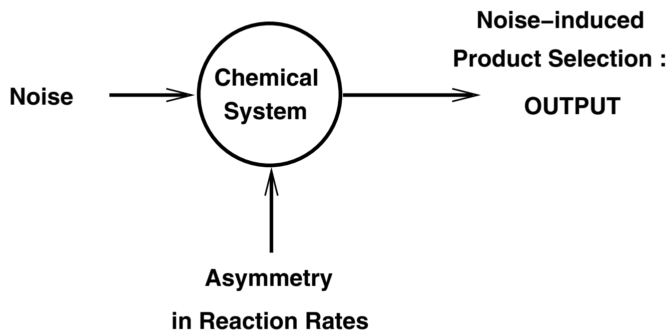

Fig. 1: Schematic diagram of a logic cell comprised of a nonlinear chemical system under small asymmetry in reaction rates, plus noise.

Now we illustrate the general concept by specific results based on theoretical studies on a kinetic network. We consider a model chemical system, where the steady-state reaction coefficient of the equilibrium is shifted slightly. It describes a prototypical chemical reaction that exhibits

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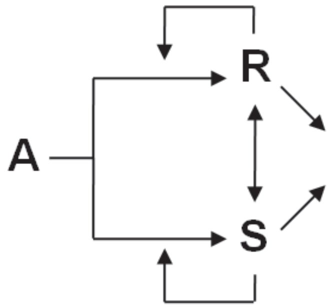

Fig. 2: Sketch of the chemical model indicating two autocatalytic feedback loops involved in the formation of the chiral products R and S from the achiral substrate A ($A+R\to 2R$, $A+S\to 2S$), the racemization of the enantiomers ($R\rightleftharpoons S$) and a cross-inhibition between them yielding an inactive product P ($R+S\to P$).

enantioselective feedback loops leading to a spontaneous amplification of any enantiomeric bias, even if provoked by random fluctuations (see fig. 2 for a schematic).

Specifically, we focus on a generic kinetic model derived from the classical scheme of chiral autocatalysis [3] in which we additionally consider the racemization between enantiomers R and S (step 6):

$$A\to R,\qquad k_0,\tag{1}$$

$$A\to S,\qquad k_0,\tag{2}$$

$$A+R\to 2R,\qquad k_1,\tag{3}$$

$$A+S\to 2S,\qquad k_1,\tag{4}$$

$$R+S\to P,\qquad k_2,\tag{5}$$

$$R\rightleftharpoons S,\qquad k_3,k_4,\tag{6}$$

A is the achiral substrate, R and S are the enantiomeric autocatalytic species, and P is an inactive product. Step 1 and 2 represents the direct formation of the product enantiomers, steps 3 and 4 gives their autocatalytic generation, and step 5 denotes enantiomeric cross-inhibition.

The key features of the above model, such as chiral autocatalysis and mutual inhibition between the enantiomers have been demonstrated to be the essential ingredients for experimental realizations of spontaneous chiral amplification and mirror symmetry breaking, such as crystallization from solution or melt, aggregation of soft condensed materials, cluster formation [4] or metal-organic synthesis under homogeneous conditions [5].

The standard operation of the above model was modified for the present work as follows:

i) Consideration of an open system at constant volume with a continuous inflow of A balanced by an outflow of the reaction mixture.

ii) Allowing a minute deviation from unity of the racemization equilibrium constant between the enantiomers, $R\rightleftharpoons S$, which is supported by physical reasoning [6].

This minute asymmetry arises by virtue of the parity-violating energy difference (PVED) that predicts an exceedingly small yet deterministic bias between the enatiometers of the same kind.

iii) Addition of noise to the differential kinetic equations This lead to the following differential equations:

$$\begin{aligned}\mathrm{d}[A]/\mathrm{d}t = &-2k_0[A]-k_1[A]([R]+[S])\\ &+k_f([A]_0-[A])+D\xi_1,\end{aligned}\tag{7}$$

$$\begin{aligned}\mathrm{d}[R]/\mathrm{d}t = &\,k_0[A]+k_1[A][R]-k_2[R][S]\\ &-k_3[R]+k_4[S]-k_f[R]+D\xi_2,\end{aligned}\tag{8}$$

$$\begin{aligned}\mathrm{d}[S]/\mathrm{d}t = &\,k_0[A]+k_1[A][S]-k_2[R][S]\\ &-k_4[S]+k_3[R]-k_f[S]+D\xi_3,\end{aligned}\tag{9}$$

$$\mathrm{d}[P]/\mathrm{d}t = k_2[R][S]-k_f[P]+D\xi_4,\tag{10}$$

where k_f denotes the flow rate constant, $[A]_0$ the inflow concentration of the achiral substrate, and ξ_i ($i=1,\ldots,4$) is a zero mean symmetrically distributed Gaussian white noise, with D being the noise amplitude. The added noise ξ_i was produced by a random number generator, using different seeds for different i (albeit with same statistical properties, characteristic of Gaussian white noise). So the numerical simulations (described in detail in [7]) were done with different uncorrelated noise sequences ξ_i superimposed on the different equations.

Numerical simulations were performed varying the asymmetric perturbation $\Delta k=k_3-k_4$, under different levels of noise. If $\Delta k=0$ the system stays entirely symmetric, and a racemic result is obtained. The condition $k_3\neq k_4$ implies that the steady-state reaction coefficients of the equilibrium $R\rightleftharpoons S$ remains shifted, favoring one enantiomer over the other. This could mimic for instance a chiral factor giving rise to an energy difference between the two enantiomers. In this work, Δk has been chosen to be positive, and so S is favored over R. Note that similar phenomena occur for the mirror image scenario as well.

When the bias in the racemization equilibrium constant has an extremely small magnitude, its effect cannot be discerned in the numerical simulations. Chiral amplification is observable only after the critical value of $|\Delta k|\approx 1.9\times 10^{-18}$ (at $k_f=0.4\,\mathrm{s}^{-1}$). Hence during deterministic simulations exceedingly small chirally asymmetric induction remains undisclosed. *However for reasonable noise levels, one observes noise-induced symmetry breaking, starting from achiral or virtually achiral initial conditions.* Hence added noise directs the chiral system into a specific enantiomeric direction while being influenced only by a sub-threshold asymmetric input [8].

While very low amplitude noise systems behaves like the deterministic case, at higher noise levels the onset of chiral symmetry breaking occurs giving rise to an entirely biased product distribution in favor of S, namely a maximum in the asymmetric distribution [9]. However, further increase in noise levels result in symmetric product distribution like in the $\Delta k=0$ case.

Table 1: Relationship between the two inputs and the output of the fundamental OR, AND, NOR, NAND, XOR and XNOR logic operations. Note that the four distinct possible input sets $(0,0)$, $(0,1)$, $(1,0)$ and $(1,1)$ reduce to three conditions as $(0,1)$ and $(1,0)$ are symmetric. Note that any logical circuit can be constructed by combining the NOR (or the NAND) gates [1].

Input set (I_1, I_2)	OR	AND	NOR	NAND	XOR	XNOR
(0, 0)	0	0	1	1	0	1
(0, 1)/(1, 0)	1	0	0	1	1	0
(1, 1)	1	1	0	0	0	1

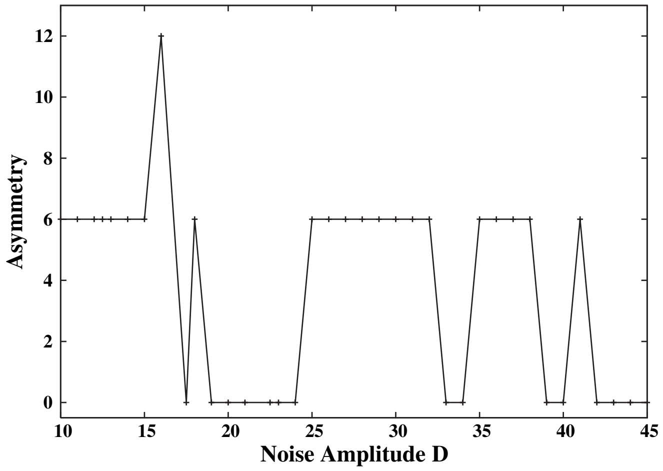

Fig. 3: Product asymmetry (see text) *vs.* noise level D (in units of $10^{-13}\,\mathrm{M\,s^{-1}}$) for the reaction rate asymmetry $\Delta k = 1.9\times10^{-18}$.

Subsequent to large time simulation, the enantiometric excess $(S-R)$ was quantified by evaluating $((S-R)/(S+R))\times S$. The entire procedure was repeated with the noise amplitude being monotonically augmented. This yielded the data points plotted in fig. 3. It is clearly evident from the figure that dependence of the product asymmetry on noise is non-monotonic and *strongly nonlinear.*

The explanation lies in the stochastic-resonance–like behaviour [8] in which for certain values of noise, the subthreshold asymmetry in the system is revealed/ enhanced in the presence of appropriate levels of noise. In other words, a small initial asymmetry which would have been lost in the deterministic evolution of the system, reveals itself in the presence of suitable levels of superimposed noise.

Chemical logic gate. – First we outline the input-output relations defining basic logic operations. Table 1 displays the truth table of all the important logic gates, with the columns giving the logic output (0 or 1) corresponding to the two inputs I_1 and I_2, for different logic functionalities that lie at the heart of all computation and information processing. Here we will demonstrate how the nonlinear dependence of the product asymmetry on noise yields different logic behaviour. Namely, we will describe how this chemical system mimics the input-output associations given in table 1 under varying noise levels.

Table 2: Encoding the input set I_1 and I_2 with noise amplitude D_{inputs} (in units of $10^{-13}\,\mathrm{M\,s^{-1}}$).

Input set (I_1, I_2)	Noise level D_{inputs}
(0, 0)	0
(0, 1)/(1, 0)	5
(1, 1)	10

Table 3: Noise levels D_{logic} yielding different logic behaviour (in units of $10^{-13}\,\mathrm{M\,s^{-1}}$).

Logic response	Noise level D_{logic}
NAND	10
NOR	14
AND	19
OR	21
XOR	24
XNOR	15

Now in order to define a logical operation, we must first define what corresponds to a logic output and what corresponds to a logic input, in the chemical system. Here we make the following association:

The *output* is encoded by the detectable biased distribution in favour of one of the enantiomers, *i.e.* $S-R$ is used to determine the logic output.

For instance, the logic response can be given as follows:

i) if $S\sim R$, *i.e.* $S-R\sim 0$, logic output is 0;

ii) if $S-R$ is reasonably large, logic output is 1.

So different product selections have a one-to-one robust correspondence to the different logic outputs, with *enhanced symmetry breaking yielding logic output 1 and no symmetry breaking corresponding to logic output 0.*

The *inputs* (I_1, I_2) are encoded by noise level D_{inputs}.

For instance, for reaction rate asymmetry $\Delta K = 1.9\times10^{-18}$, we can choose (in units of $10^{-13}\,\mathrm{M\,s^{-1}}$ (see footnote[1])):

i) $D_{inputs}\sim 0$ corresponds to input set $(0,0)$;

ii) $D_{inputs}\sim 5$ corresponds to input sets $(0,1)/(1,0)$;

iii) $D_{inputs}\sim 10$ corresponds to input set $(1,1)$.

The above yields a one-to-one correspondence between the noise amplitude and the distinct logic input sets that can occur (see tables 1, 2).

[1] As is evident from the dimensionless analysis of eqs. (7)–(10), the units of the superimposed noise should be $\mathrm{Ms^{-1}}$. By scaling the concentrations in eqs. (7)–(10) appropriately the dimension of the noise amplitude can be chosen differently if desired.

Table 4: Input-output correspondence table for different logic behaviour. The system evolves under noise level $D = D_{inputs} + D_{logic}$ (in units of $10^{-13}\,\mathrm{M\,s^{-1}}$). Refer to fig. 3 for the value of $S-R$ for different values of noise amplitude D. It is evident here that varying noise allows varying enantioselection, and consequently different logic responses.

Input set (I_1, I_2)	Noise level D_{inputs}	Logic	Noise level D_{logic}	$S-R$	Output
(0, 0)	0		10	6	1
(1, 0)/(0, 1)	5	NAND	10	6	1
(1, 1)	10		10	0	0
(0, 0)	0		14	6	1
(1, 0)/(0, 1)	5	NOR	14	0	0
(1, 1)	10		14	0	0
(0, 0)	0		19	0	0
(1, 0)/(0, 1)	5	AND	19	0	0
(1, 1)	10		19	6	1
(0, 0)	0		21	0	0
(1, 0)/(0, 1)	5	OR	21	6	1
(1, 1)	10		21	6	1
(0, 0)	0		24	0	0
(1, 0)/(0, 1)	5	XOR	24	6	1
(1, 1)	10		24	0	0
(0, 0)	0		15	6	1
(1,0)/(0,1)	5	XNOR	15	0	0
(1, 1)	10		15	6	1

Logic response control. – Now the type of logic behaviour obtained, namely AND, OR, NOR, NAND, XOR or XNOR, can also be manipulated by additive noise in a manner described below.

One can make a robust one-to-one association between the nature of logic obtained and an additional additive noise, which we label D_{logic}, where the subscript *logic* can be either AND, OR, NOR, NAND, XOR or XNOR, corresponding to the fundamental logic patterns displayed in table. 1. The total noise intensity D, under which the system evolves in eqs. (7)–(10), is then given by

$$D = D_{inputs} + D_{logic},$$

namely, the total noise intensity D, clearly and robustly encodes *both* the input sets as well as the type of logic operation.

We tabulate in table 3 representative values of D_{logic} giving rise to different logic gates in this system. When the system evolves under noise amplitude $D = D_{inputs} + D_{logic}$, one obtains different enantioselections as reflected in $S-R$ in fig. 3 and tabulated in table 4.

So it is clear that varying noise allows varying product distributions, and consequently different logic responses. By comparing table 1 and table 4 it is clear that the correspondence between the noise levels and the enantiomeric products, *exactly mirrors the input-output relations of different fundamental logic gates*. This noise-induced chemical reaction system thus behaves effectively as different logic gates. Note also that this unusual encoding is very *efficient*, in that *one* quantity is used to encode two independent entities: logic inputs and logic functionality.

For instance, if one wanted to obtain the AND logic output for two inputs $(0,0)$, one would have $D_{logic} \equiv D_{AND} = 0$ and $D_{inputs} \equiv D_{0,0} = 19$ (from tables 2, 3). So a system evolving under noise amplitude $D = D_{0,0} + D_{AND} = 0 + 19$ (in units of $10^{-13}\,\mathrm{M\,s^{-1}}$) yields product asymmetry corresponding to the output of the logic operation AND on inputs $(0,0)$. Similarly, noise intensity $D = D_{1,1} + D_{XNOR} = 10 + 15$ (in units of $10^{-13}\,\mathrm{M\,s^{-1}}$), yields the logic operation XNOR on the inputs $(1,1)$, and so on. So noise encodes the inputs. Furthermore, noise also acts as the logic selector, namely plays the role analogous to a *logic control knob*.

One then observes that the type of logic response can be changed by simply varying noise levels. This capacity of the chemical system to yield different logic functionalities, in different windows of noise, implies that the system can *dynamically switch logic operations* under different noise levels. So the system has the capacity for *reconfigurability*. Namely, this *chemical logic gate* is a flexible logic unit that can morph its response to yield either NOR, NAND, AND, OR, XOR or XNOR [10], with noise playing the role of logic selector.

Conclusions. – The interplay of noise and small asymmetry pushes a chemical system in a specific enantiomeric direction. We observe that encoding logic outputs by the entioselection and encoding logic inputs by the noise levels, yields all the different fundamental logic gate input-ouput correspondence relations. Further we can control the logic functionality by varying the noise intensity. Thus the chemical system behaves as a chemical logic gate, that can flexibly morph between different kinds of logical responses under varying noise.

Such a viewpoint then allows us to think of the chemical reaction system as a computational device. Further, this view of chemical reactions as *gates* or *valves* leading to different outputs, can allow reactions to concatenate into reaction pathways (analogous to circuits) [11].

In summary, these observations may provide conceptual understanding of the information processing capacity of various naturally occurring chemical phenomena, as well as understanding of the evolution of life with chiral preferences. It might also have potential applications in the pharmaceutical industry as means of suppressing the undesired chirality of the synthesized drugs, or in the design of chemical gates and molecular robots [12].

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