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SAVINO LONGO*

The State-to-state kinetics: from a Sumerian prototype to astrobiology

Abstract – The state-to-state (STS) kinetics, in which molecules in different internal states are considered as different species in the description of chemical reactions, is one of the most productive concepts in theoretical chemistry with an endless record of successful applications. An example is the formulation of scenarios for the production of oxygen on Mars. In the STS formulation of a chemical problem, distribution functions appear, which describe the population of molecules in these different states. The problem of composition change with time can be solved only when these distributions, and their changes too, are included in the calculations. Remarkably, the basic ideas of this approach are already found, in the author's opinion, in a 40-centuries old Sumerian tablet which reports a fully theoretical cattle breeding account. This document also anticipates some basic ideas of computer science, like the execution of a program and the management of a structure of data. 40 centuries later, ideas from this prototype may help to explain the predominance of a single chiral version in biological molecules and organisms.

Introduction: the state-to-state kinetics and its importance

One of the most productive concepts of modern theoretical chemistry is the *state-to-state kinetics* (STS in the following) [1-3]. It is based on the known fact that in some chemical reactions networks, the internal state of molecules has such a strong effect on reactivity, that the molecular species must be conceived as mixtures of several components, each component of the mixture being the ensemble of molecules in a given state. According to this view the species is therefore represented as a probability distribution, the state- or energy- distribution. This concept has found

* Chemistry Department of the University of Bari and CNR, Via Orabona 4 - 70126 Bari, Italy. E-mail: savino.longo@uniba.it

wide application to the determination of chemical reaction rates in fields as different as atmospheric science, astrophysics, catalysis, energy production and many others.

A large number of very important examples can be used to illustrate the importance of the STS concept [3]. One which is gaining recently much visibility for its relevance to space technology and Mars colonization scenarios is the following: CO_2, the most important component of Mars atmosphere, may be converted to CO and atomic oxygen by a reaction where electrons in a gas are used to pump up energy into the vibrational degrees of freedom of the CO_2 molecule [4-5]. Since the most effective dissociation path is through the asymmetric stretching mode, it is necessary to distinguish the 22 vibrational levels of this mode. Electron impact processes, the so-called eV, however, can only pump energy into the lowest vibrational levels, say the first 4 or 5. Subsequently, CO_2 molecules reach the dissociation limit with the help of a different process, named VV_1, where a low excited CO_2 molecule interacts with a more excited one pushing this last to higher excitation

$$CO_2(1)+CO_2(v)\rightarrow CO_2(0)+CO_2(v+1)$$

This mechanism, which was extensively studied by Russian scientists in the 70's-80's [6], works like a «conveyor belt» where molecules are moved up the ladder until they reach dissociation, i.e.

$$CO_2(1)+CO_2(21)\rightarrow CO_2(0)+CO+O$$

Note that no dissociation occurs until the top of the internal energy ladder is reached.

A remarkable aspect of the STS reaction schemes is that the knowledge of the concentration of a given species is no more sufficient to specify its state. Knowledge of a «hidden distribution» becomes necessary, the distribution of individual molecules in individual conditions (internal state, speed, age, depending on the problem). This distribution must be computed, stored and updated in order to determine the reaction rate. The equation, or scheme, normally used to update this internal distribution is called «Master Equation». This is a classical probability expression, not to be confused with the Pauli Master Equation in spin relaxation problems. The state of the system is specified only if the distribution of molecules into this collection of states is provided.

A very early example of the role of distributions in a growth problem

Surprisingly, early studies of this idea are very old. It is claimed in the present work that they are as old as 40 centuries, and possibly more. The oldest «paper» is not even paper but a clay table: a Sumerian tablet kept in the Louvre museum (the AO5499 table). This table was found in the Puzriš-Dagan excavation, the modern

Drehem. It dates back to king Shulgi period of neo-Sumerian culture in Ur, giving to the tablet an estimated date of 2000-2100 BC. The tablet is fully written in Sumerian, on both sides. The text of AO5499 describes what is presented as a cattle breeding account, and names it the «problem of the scribe Idua». It looks at a first view as an accurate account of cows (ab_2) and bulls (gu_4) during several years (figure 1), but, as it was recognized long ago [6], the «problem of Idua» is actually the first known model of a growth process formulated on pure theoretical basis [7-8]. It introduces a distribution of cattle ages. Only adult cows ($ab_2.mah_2$) reproduce. On AO5499 the problem is solved reporting the numbers of individuals as a function of age and time (Figure 1). While a description of AO5499 and its recognition as a theoretical problem is found for example in [7], here we will adopt the modern terminology while connecting this problem to the STS kinetics.

The process involved is actually very clear and self-explanatory even after four millennia. The state of the cattle is defined by a vector N of dimension 5. This vector contains the number of cows with ages from 0 to the mature state named mah_2. In this specific example mah_2=4 which means that N is a vector of mah_2+1=5 elements, marked in the tablet as follows: calf ($ab_2.amar.ga$), 1 year old ($mu\ 1$), 2 years old, 3 years old, adult ($ab_2.mah_2$), see again figure 1.

The number of individuals of age x becomes equal to the number of individuals of age x+1 at the next «step», in this way:

$$N(0) \rightarrow N(1) \rightarrow N(2) \text{ and so on}$$

But adult cows only increase in number, with no mortality, betraying the theoretical nature of the problem

$$N(mah_2) \leftarrow N(mah_2)+N(mah_2\text{-}1)$$

The number of newborns, N(0), is calculated by a simple model: the number of newborns is equal to the number of mature cows N(mah_2), but they are distributed between males and females in alternation. This regular alternation is another, even stronger, clue of the theoretical nature of the account.

The Idua problem, from a modern perspective, anticipates many important concepts:

(1) A growth process is influenced by the distribution of different states of individuals (the STS concept);

(2) the distribution can be represented by a collection of individuals in different states (similar to a modern event-driven simulation);

(3) the evolution is essentially obtained by shifting the recorded data in a sequence (the modern «stack» concept in computer Science).

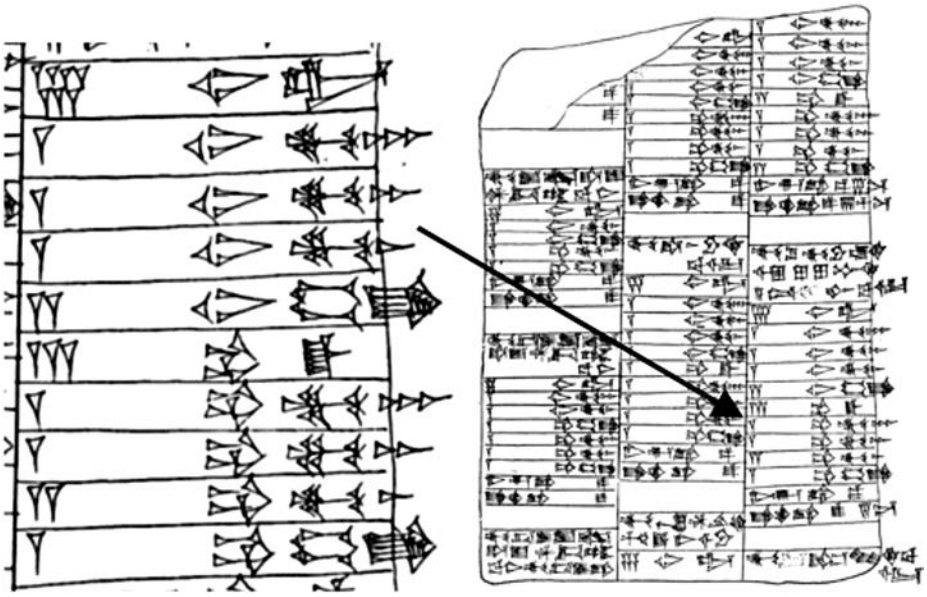

Fig. 1. The AO5499 tablet. Left: the calculated age distribution after 7 yrs. including (from above) 7 adult cows, one 3 years old, one 2 years old, one 1 year old, 2 heifer calves; 3 adult bulls, one 3 years old, one 2 years old, two 1 year old, 1 bull calf. Right: full obverse of the tablet (the simulation continues on the other side). The attribution of the problem to Idua is on the left bottom corner. Adapted from the Cuneiform Digital Library Initiative archive [7].

Idua sequences: new applications for a 40 centuries old idea

In a modern revisit of the problem of Idua, simple computer programs can be used to produce a variety of «Idua sequences», using parameter values no more limited by the original application. An example, in figure 2, extends considerably the number of states (using mah_2=20 instead of 4). The evolution of this more extended simulation displays better the structure of the sequence. The employ of these or similar deterministic sequences in chemical kinetics is suggestive, since they express in a very simple form the effect of internal distribution evolution in a multiplication process. The example in figure 2 already presents a nontrivial kinetics, due to the delays introduced by the necessity for new individuals to reach the uppermost level and contribute to the production rate. Even leaving, as here, the production rule strictly equal to those reported in the original Idua problem, the growth can be strongly influenced by different choices for the initial distribution of ages.

The study of the mathematical and numerical properties of «Idua sequences» by modern standards can be an interesting topic for new researches in theoretical chemistry and numerical analysis.

Fig. 2. Author's computer-generated «Idua sequence» with $mah_2 = 20$ and an arbitrary initial population (upper row) with only two individuals with initial state 6 and 11: time flows from top to bottom. New individuals in the 0 state appear only after 10 time-units and the internal population is continuously evolving.

It is not difficult to imagine chemical systems for which an Idua sequence could provide an insightful model: a possibility is a population of molecules which receive free energy from a substrate in successive steps and, when the stored energy is high enough to compensate for a thermodynamic or kinetic threshold, undergo *self-replication*, i.e. a reaction of the form

$$A(i) + S^* \rightarrow A(i+1) + S$$
$$A(n) + S^* \rightarrow 2A(0) + S$$

where S and S* are the energy-poor and energy-reach version of an environmental species. The self-replication step is the last one. Note the difference between self-replication and the CO_2 dissociation reaction in the previous section.

Chiral selection and prebiotic evolution

Computational models including the STS concept and self-replication, like those described by Idua sequences and in the previous section, may look artificial, but they have been actually much studied in the past and applied to some of the most fundamental problems in chemistry and biology. An example from the study on the origin of life and astrobiology is the attempt to explain the predominance of biological molecules, as well as whole organisms, which have a well-defined chirality

(L *levo* or D *destro*). This last is the geometrical property which distinguishes a left hand from a right one (thereby its name, from *χειρ*, hand). The two chiral variants, called *enantiomers*, have the same thermodynamic stability and should be present in biological systems with the same occurrence, all the opposite of what is actually found. Explanations of this predominance of a single chirality in biomolecules included many possible external causes which may have favored the formation of one species, by a process of chirality induction, or inheritance, from the environment in which the formation occurs. Among the causes considered there were the chirality of crystal surfaces on which biomolecules where first produced, polarized light, electroweak interactions, the effect of fluid vortexes [9-12].

A new concept was tested by a series of computer simulations in the group of the author a few years ago [13]. The concept is based on the breakup of the celebrated law of large numbers in statistics in a system of self-replicating individuals. The actual model proposed was very complex, involving an internal «genetic code» for any individual, but here it will be described in a simpler way to catch its essential features. The model is based on a simulation of an ensemble of individuals of two different chiral states L and D which can self-reproduce, move by drift and diffusion, and compete for «chemical energy» resources, these last are in the form of «activated cells» which appear randomly in the simulation domain.

An element of strong similarity of this computer experiment with the Idua problem is that the individuals, or «agents» in the simulation have an internal state and that this state is updated at any computational step based on the events occurring in the simulations. Only individuals reaching the uppermost level in the internal scale can reproduce themselves, with the same chirality e.g. a L individual produces another L individual and a D individual produces another D.

An essential breakthrough of this scenario is that, in the random process of replication of the two species competing for the same resources (energy, space, etc.), anomalous fluctuations, similar to critical fluctuations in thermodynamics, arise, which may push one of the alternative species to full extinction even when this last is an extremely unlike outcome according to the law of large numbers (see figure 3).

In this way a mechanism of selection between two isomers L and D initially in a racemic mixture is demonstrated. A very interesting feature of this mechanism is that it is not based on external chiral influences. The selection of a single chiral variant is, of course, random, but the selection process is immensely more effective than in a typical random process. Details of this mechanism have been discussed on ref. [13] where a quantitative explanation of the outcome is also provided based on the numerical solution of the corresponding Master Equation. It was also shown that the chiral symmetry breaking mechanism is critically dependent on the order of the destruction process, which must be pseudo-first order and not higher, e.g. second order. As an alternative to using a Master equation, accurately devised deterministic sequences could be used in the future to mimic the essential features of these prebiotic models and gain further insight into the process.

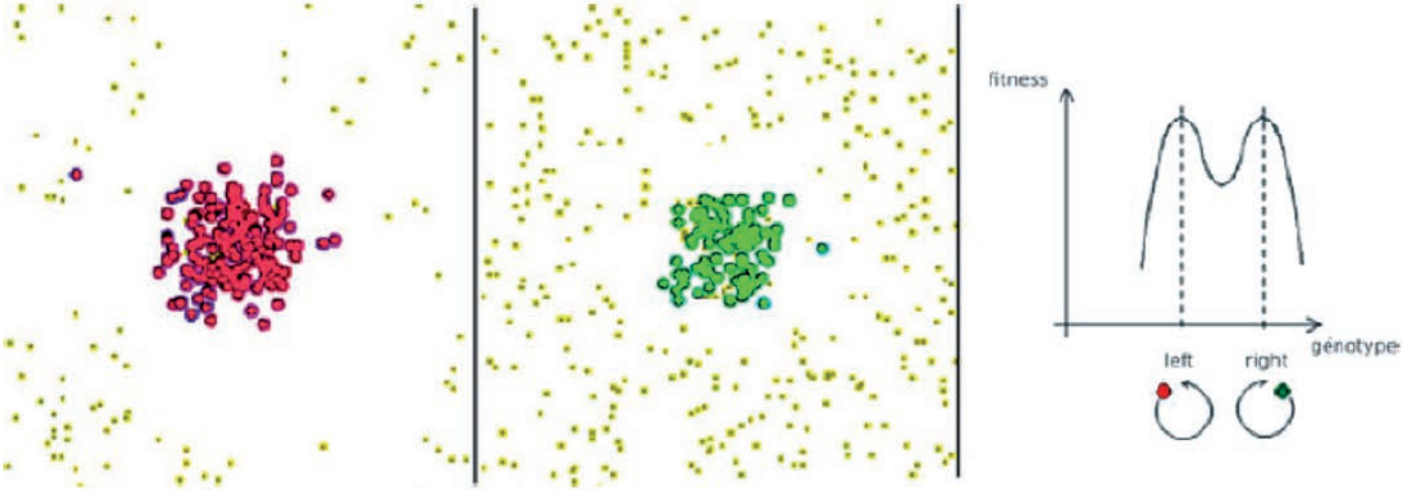

Fig. 3. In this figure, chiral species colonize a 2D space in a demonstration based on the model developed in [8]. The yellow dots are the energy reservoirs S* that bring the chiral species to a higher energy state. The chiral species are represented by circles with different colors, purple-red (L) vs. green-yellow (D). All simulations start from situations where no chirality is predominant. Left panel: simulation in which only the former chiral version remains; central panel: same situation, but opposite dominant chiral version. In the right panel, the chiral symmetry breaking exemplified by this simulation is shown. Adapted from [12].

Conclusions

The STS approach may allow us to formulate appropriate models for countless problems involving molecules which are reacting while performing transitions between their internal states. An example is the production of oxygen out of carbon dioxide on Mars. All these models assume that molecules or species climb a ladder of internal states whose uppermost step is the condition where a reaction is possible. Although this approach, so formulated, looks intrinsically tied to molecules, the inspiration behind it is much more general: an evolving distribution of individual conditions influences the global changes of the population. This idea, quite remarkably, was reported in written form, and concretely demonstrated by a test case, about four millennia ago on a clay tablet. On this tablet the formulation and solution of a problem of growth driven by a distribution of age is presented in the form of cattle accounting during several years. 40 centuries later a variant of this approach shows how a single chiral variety emerges in the course of prebiotic evolution as well as in developed organisms. This is possible since, in its very essence, the STS approach is a special case of an ancient idea of enormous versatility: is it is possible to produce a theoretical model of the changes in a system by defining a rule to calculate the next step in time and iterating the calculation process. Even more important, it is possible to get insight from the observation of the evolution of this virtual world as it evolves on the screen of the computer today, or on the tablet of the scribe in the past.

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