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The large-scale organization of chemical reaction networks in astrophysics

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Abstract. – The large-scale organization of complex networks, both natural and artificial, has shown the existence of highly heterogeneous patterns of organization. Such patterns typically involve scale-free degree distributions and small world, modular architectures. One example is provided by chemical reaction networks, such as the metabolic pathways. The chemical reactions of the Earth's atmosphere have also been shown to give rise to a scale-free network. Here we present novel data analysis on the structure of several astrophysical networks including the chemistry of the planetary atmospheres and the interstellar medium. Our work reveals that Earth's atmosphere displays a hierarchical organization, close to the one observed in cellular webs. Instead, the other astrophysical reaction networks reveal a much simpler pattern consistent with an equilibrium state. The implications for large-scale regulation of the planetary dynamics are outlined.

Introduction. – The interstellar medium (ISM) – gas and micron-sized dust particles between the stars – is the raw material for the formation of future generations of stars which may develop planetary systems like our own. Astronomical observations of interstellar and circumstellar regions have led to the identification of well over one hundred different molecules, most of them being organic in nature [1]. Motivated by these discoveries, astrochemistry – the chemistry of the interstellar gas – has developed into an active research area of astrophysics and detailed chemical models can now be constructed which reconstruct the history and role of the ISM in the evolutionary cycle of the galaxy [2]. Crucial to modeling chemical kinetics in the interstellar medium, the UMIST kinetic database [3] consists in the chemical reactions relevant to astrochemistry.

In view of the increasing data on the chemical composition of the solar system's planets from latest planetary missions, there is growing interest in the astrophysical community for modeling the weather and atmospheric chemistry of the neighboring planets. Such modeling provided extensive chemical reaction networks (CRN) [4] that expect confirmation from future

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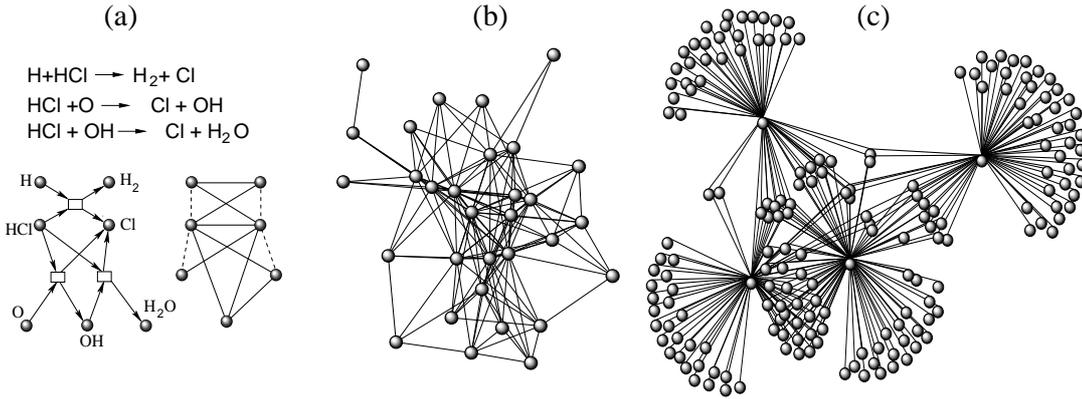


Fig. 1 – (a) Defining the reaction graph for a set of three reactions indicated in the upper part: directed bipartite graph (l.h.s) and undirected substrate graph (r.h.s), where the links between reactants and between products (dashed) may be considered or disregarded. (b) The overall reaction graph for Martian atmosphere is shown. (c) A subgraph of Earth's CRN. See text for details.

planetary missions and further modeling. Using the general approach of complex networks [5] we explore here the large-scale topology of the chemical networks associated to the interstellar medium and planetary atmospheres. As will be shown, two basic types of networks are found, being associated with the presence or absence of life.

Reaction graphs. – A CRN can be viewed as a graph where chemical species are nodes and edges represent conversion between chemicals. The most simple and typical representations of a reaction graph are shown in fig. 1a as a directed bipartite graph (l.h.s) and an undirected substrate graph (r.h.s). We have chosen to disregard the connections between the reactants, on one side, and between the products, on the other side (the dashed lines in fig. 1a). In fig. 1, we also show as examples the undirected substrate graphs associated to the chemical reactions of the Martian atmosphere (panel b) and a subgraph of the Earth network (panel c).

Two basic features common to many complex networks, from the Internet [7, 8] to cellular nets [9, 10] are their *scale-free* topology [11] and small-world structure [12, 13]. The first states that the proportion of nodes $P(k)$ having degree k decays as a power law $P(k) \sim k^{-\gamma} \phi(k/\xi)$, with $\gamma \approx 2 - 3$ for most complex networks [7, 11, 14] and with the function $\phi(k/\xi)$ introducing a cut-off at some characteristic scale ξ . The power-law distribution has no natural scale and from here networks with such distributions are called scale-free. The second refers to a web characterized by a very small diameter (average shortest path between any two vertices) along with a large clustering [12, 13]. The *average path length* $\langle L \rangle$ is the average minimum distance $d(i, j)$ between any pair (i, j) of vertices:

$$\langle L \rangle = \frac{1}{V(V-1)} \sum_{\forall i, j} d(i, j), \quad (1)$$

The *clustering coefficient* C_i associated to a node i characterizes the density of links in its neighborhood (the fraction of its neighbors that are also neighbors of each other). It is defined as $C_i = 2V_i/N_i(N_i-1)$, being the ratio between the total number of links, V_i between its nearest neighbors, N_i and the total number of all possible edges between all these nearest neighbors.

TABLE I – *Network characteristics: $V =$ vertices; $E =$ edges; $\langle K \rangle =$ mean degree; $\langle L \rangle =$ averaged shortest path; $\langle C \rangle =$ mean clustering; $r =$ assortativity. See text for more details. ISM: Interstellar medium; HC : hydrocarbon chemical network of the giant planets*

	V	E	$\langle K \rangle$	$\langle L \rangle$	$\langle L_{rand} \rangle$	$\langle C \rangle$	$\langle C_{rand} \rangle$	r	r_{rand}	Modular
Earth	248	778	6.27	2.75	3.20	0.31	0.025	-0.31	-0.006	YES
Mars	31	144	9.29	1.89	1.73	0.61	0.31	-0.10	-0.007	NO
Titan	71	396	11.16	2.08	1.98	0.55	0.16	-0.17	-0.03	NO
Venus	42	175	8.33	2.07	1.94	0.59	0.20	-0.14	-0.06	NO
HC	39	270	13.85	1.65	1.64	0.68	0.37	-0.26	-0.06	NO
ISM	400	6102	30.51	1.99	2.01	0.52	0.07	-0.24	-0.006	NO
E.coli	741	2310	6.24	3.02	3.82	0.183	0.008	-0.17	0.004	YES

The average value, $\langle C \rangle$ is the clustering coefficient of the network and may be considered as an indicator of a potential modularity [15], as discussed below. For a small world, we have $\langle L \rangle \approx \langle L_{rand} \rangle$ whereas $\langle C \rangle \ll \langle C_{rand} \rangle$, where the index *rand* refers to the random counterparts of the network under consideration [12, 13].

Astrophysical networks. – A first analysis of the CRNs of planetary atmospheres was included in [16] who considered the chemical data reported in [4] and concluded that the Earth chemical network has a scale-free degree distribution. In the quantum chemistry framework, Patra et al. [17] proposed a reaction mechanism for certain interstellar reactions using a graph-theoretical approach. The present work is a thorough exploration from the complex networks perspective of the complete data set concerning the planetary atmospheres and the astrochemical network, including the hydrocarbon chemistry of the jovian planets [4]. Among the planetary networks, the chemical reactions associated to the Titan’s atmosphere were taken from [18], involving 99 more chemical reactions than in [4].

We have determined the average characteristics of the planetary CRNs and of the astrochemical UMIST network. These measures are given in table I. A first result from this analysis (consistently with [16]) is that all networks are small worlds. The sparser of these nets is Earth, with an average degree, path length and clustering similar to those displayed by the metabolic network of *E. coli*, which has a similar size.

Column 9 gives the assortativeness [19] defined as:

$$r = \frac{E^{-1} \sum_i j_i k_i - [E^{-1} \sum_i \frac{1}{2}(j_i + k_i)]^2}{E^{-1} \sum_i \frac{1}{2}(j_i^2 + k_i^2) - [E^{-1} \sum_i \frac{1}{2}(j_i + k_i)]^2}, \quad (2)$$

where j_i, k_i refer to the degrees of the nodes at the ends of i^{th} link, with E being the total number of edges and $i = \overline{1, E}$. The assortativity coefficient quantifies the propensity of nodes to connect to nodes of similar degree. Complex networks tend to be disassortative (i. e. $r < 0$), reflecting low-degree nodes’ tendency to be connected to high-degree nodes, consistently with the patterns displayed in fig. 1c. As it results from table I, the Earth’s atmosphere network and the astrochemical network present a pronounced disassortative character, while the rest of the planetary networks show more neutral r values.

The heterogeneous character of the degree distributions is displayed in fig. 2 using the cumulative distribution for these networks. It is defined as $P_{cum}(k) = \int_k^\infty P(k') dk'$ which gives $P_{cum}(k) \sim k^{-\gamma+1}$ for scale-free nets. Both log-log and linear-log plots are shown in

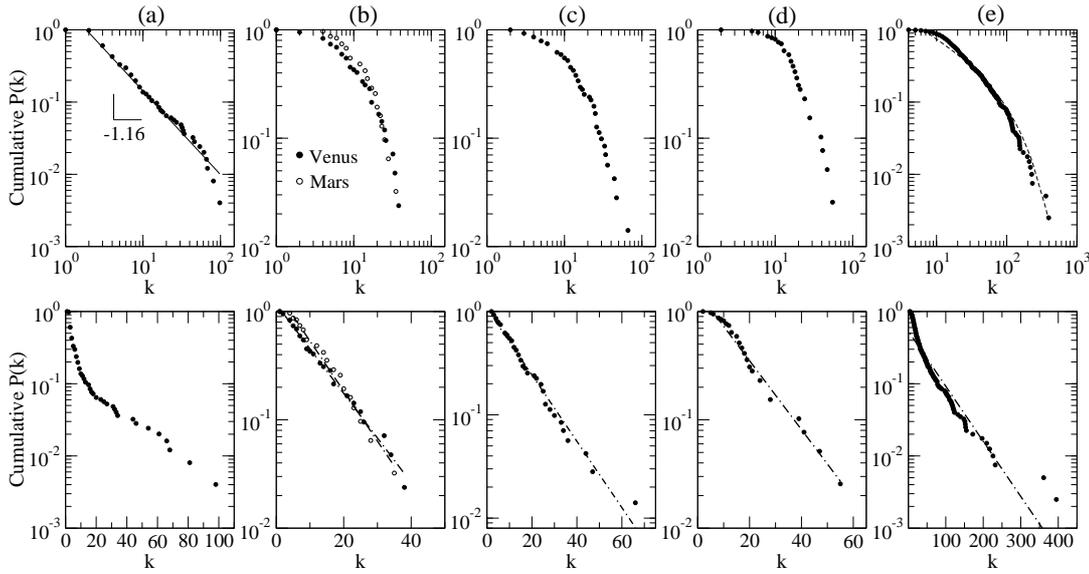


Fig. 2 – Cumulative degree distribution $P_{cum}(k)$ for the planetary atmospheres and astrochemical reaction networks represented both in log-log (*upper panels*) and linear-log (*lower panels*) scales. (a) Earth; (b) Mars and Venus; (c) Titan; (c) Hydrocarbon chemistry; (e) Interstellar medium. It reveals a scale-free distribution for the Earth network with exponent $\gamma = 2.16$ – (solid line fit); exponential distribution (dashed-dot lines) for the other networks, with the interstellar medium network falling slower in the tail than expected for an exponential decay. This CRN is better fitted by a broad-scale distribution $P_{cum}(k) \sim k^{-\gamma} \exp(-k/\xi)$ (dashed line fit).

fig. 2, as they are indicators of the type of connectivity distribution [14]. The Earth network (fig. 2a) is the only one displaying a scale-free topology. For the rest of the planetary CRNs, the good exponential fit consisting in a straight line in the linear-log plot reveals single-scale networks. From network considerations alone, the richness of the Titan’s chemistry and the poverty of Mars’ are recovered from the chemical character of the two CRNs, the former being reducing in nature while the second is oxidized. While a completely oxidized atmosphere allows no organic chemistry and therefore, no complex CRN, a reducing atmosphere such as that of the outer planets and the interstellar medium implies no limit for the complexification of carbon chains in organic chemistry. From this perspective, the richness of the interstellar medium chemistry is reflected in table I: a large highly-connected network with a broad-scale distribution (Fig. 2d). This observation discards a simple explanation for Earth’s scaling based on a high chemical diversity.

Another property that seems to be common to many complex networks is modularity [20–22]. Several methods provide valuable insight on the existence of such community structures [23]. One of them is *hierarchical clustering*, based on identifying similarities between nodes through the topological overlap matrix. The topological overlap of a pair of nodes (i, j) is defined as $O(i, j) = J(i, j) / \min\{k_i, k_j\}$, where $J(i, j)$ denotes the number of nodes to which both i and j nodes are connected. The denominator gives the smallest degree of the pair of nodes (i, j). Hierarchical clustering uses the previous matrix to identify modules based on the assumption that the larger the overlap between two nodes, the higher the probability that they belong to the same module. The algorithm repeatedly finds the highest topological

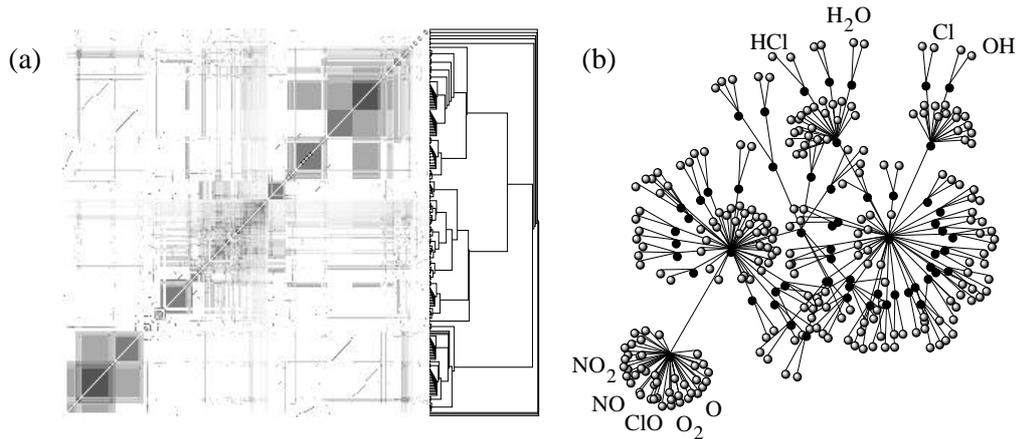


Fig. 3 – Modular structure of Earth’s atmosphere CRN. (a) Topological overlap matrix and the associated dendrogram. (b) The community tree transformed into a hierarchical community graph on the basis of the HS index: white nodes are the nodes of the original graph and the black nodes are the communities to which they belong.

overlap, grouping together the corresponding two nodes into a new aggregated node and performing a weighted average of the corresponding row and column in the overlap matrix [15], and computes the new matrix. The procedure is applied until the matrix collapses into a single value, having as final result an alternative representation of the network as a tree or dendrogram.

The result of the application of this method to the Earth’s atmosphere CRN is shown in fig. 3a, revealing certain communities of nodes characterized by higher topological overlap (dark regions). In particular, we have noticed that the main modules – the two black squares in panel (a) – include predominantly the reactants, in one module, and the products, in the other module, involved in reactions with OH (or Cl) and having as one of the products H₂O (or HCl). The community structure is a consequence of the action of the most reactive free radicals of the Earth’s atmosphere, Cl and OH, capable of reacting with almost all other elements due to their unpaired electron. Together with the rest of the atmospheric radicals, such as NO, NO₂, NO₃, ClO, they constitute the source of oxidizing power of the atmosphere, determining the lifetime and the abundance of trace species and acting as atmospheric regulators. Among all these oxidizing agents, the hydroxyl radical is by far the primary atmospheric oxidant, while O₂ and O₃, in spite of being the most abundant oxidants, are relatively unreactive. As a network measure of reactivity, the node’s out-degree recovers the reactivity hierarchy of the oxidizing agents (decreasing out-degree): OH, Cl, NO₂, O, O₂, O₃, NO, HO₂ and ClO. The Earth’s oxidizing atmosphere characterized by a great chemical disequilibrium, with both oxidizing and reducing gases in a highly reactive mixture, is the unique imprint of the terrestrial atmosphere compared to the planets of the Solar System, and these characteristics are recovered also through the analysis of its CRN.

We have also analyzed the measure of betweenness centrality (BC) [24] which counts the fraction of shortest paths going through a given edge. The edge of highest BC is likely to bridge community structures and thus by calculating and subsequently removing this edge through an iterative algorithm, one obtains a reasonably accurate unfolding of the modular structure of the graph [23]. The removal process transforms the graph into a binary tree similar to

the dendrogram from fig. 3a, but formed of bifurcation nodes representing modules and its branches, connected to submodules or individual nodes of the original graph. For the purpose of extracting the hierarchical modularization we use the Horton-Strahler (HS) [20]. From the bottom to the top of the tree, the HS index changes only when it joins a community of a similar index: the individual nodes (HS=1) join to form a group (with HS=2), which in turn join other groups to form a second level (HS=3) and so on. Thus, the communities of equal HS indexes form the same modularization level. In fig. 3b we include the associated hierarchical level-tree as it results from grouping together communities of equal HS index. The white circles represent the nodes of the CRN graph, while the black ones represent the modules to which they belong. The most relevant modules are clearly revealed in this figure. The two fans in the upper part of the figure include the products (r.h.s. fan) and the reactants, respectively (l.h.s. fan) from reactions with OH (or Cl), as discussed above. We draw the attention also on the module visible in the lower left part of the figure. It consists mainly of the highly connected core of the reactants participating in termolecular (type $A + B \xrightarrow{M} AB$) and photochemical reactions ($A + h\nu \rightarrow B + C$). It includes also the majority of the oxidant agents, some of them being depicted in fig. 3b. The neighboring module includes mainly the products of significant degree resulting from reactions.

Discussion. – Within cellular networks, metabolic pathways are one of the most relevant components of life [25]. Such networks are defined at the microscopic, cell-level scale, whereas those considered in our study deal with vast spatial scales. Moreover, cellular networks result from biological evolution, whereas the CRNs studied here are generated from mechanisms that seem to strongly depart from this scenario, although natural selection seems to be a key mechanism for the evolution of Earth’s atmosphere [26]. Other CRN’s have single-scaled or broad-scale structure.

Earth’s atmosphere is a clear exception to this rule. Our analysis shows that, together with a broad degree distribution, the CRN of our planet is also rich in correlations. This is particularly remarkable in terms of the presence of a well-defined hierarchical organization, as shown by its modular, nested architecture. What is the origin of such difference? One clear candidate is the strong, nonlinear coupling between atmosphere and biosphere. As pointed out in [27, 28], the atmosphere is the face of a planet and it tells if it is alive or dead. Its chemical composition and its departure from a near-equilibrium state are consistent with the presence of life. Our analysis gives strength to this conjecture, since the topological organization of Earth’s atmosphere displays the hierarchical patterns observed in other living structures. In this context, it is generally accepted [28] that our planet is able to self-regulate its climate and keep a chemically unstable atmosphere constant and appropriate for life ⁽¹⁾. It does so by using the incoming energy (light) to recycle the available chemicals through both positive and negative feedbacks. Well-defined cycles can be identified and regulation works over a wide range of conditions. These are all characteristics of a metabolism [29].

The dynamics and composition of the atmosphere of a given planet is a consequence of both dynamical and historical constraints. Physical factors strongly influence the final pattern at the global scale. But not less important seems the role played by historical contingencies and hysteretic processes, which can irreversibly modify a planet’s climate. Earth, Venus and Mars all had water soon after their formation 4.5 billion years ago. Venus experienced a global runaway greenhouse effect about 3 billion to 4 billion years ago. Mars followed a different path towards a runaway cooling. The common pattern of organization of both Mars and Venus CRN confirms that lack of biosphere leads to a simple, equilibrium set of reactions with a

⁽¹⁾In spite that our Sun has increased its output of heat by about 25 – 30% over the last 2500 Myr

well-defined, single-scale topology. Instead, the presence of a mechanism injecting reactive components into the reaction pool might eventually generate a complex network not unlike the ones seen in living structures at the small scale. Future work should explore the use of kinetic models to test this conjecture.

* * *

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