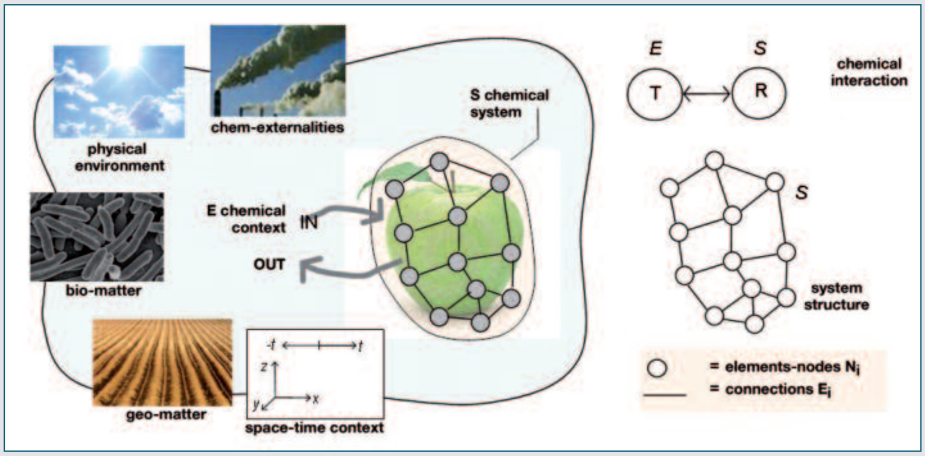

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CAN FORMALISED SYSTEMS HELP TO SIMULATE APPLIED CHEMICAL PROBLEMS?

Such abstractions as graphs can simplify, conceptualize and simulate "communication" problems in, between or among chemical systems. I.e. concerning matter, energy or information transports in real contexts: materials or bio-matrices as well as techno-, geo- or eco-scenarios and situations.

Graph Theory deals with relations between "objects" from a given "collection" [1-2], i.e. elements from a given system. Graph Theory was extensively applied to chemical combinations problems, e.g. numbers of the possible structural isomers of a given compound [3-5], topology of molecules [6-9] and kinetics [10-11]. A common approach is to consider molecules as molecular graphs: formal networks of nodes connected by edges representing atoms and bonds. In this paper we now approach the problem to represent as formal graphs "chemical problems in their contexts". I.e. how chemism or matter transport problems can be mapped by means of theoretical nets. The nodes now identify with such structure elements as molecules, phases or compartments of virtual "boxes" where chemical systems are subjected to interaction with a given matter context in the form of surrounding, physical systems and subsystems involved in matter or energy exchanges. Edges identify with these transports or with information abstract relations connecting these nodes.

Examples and discussion

This work integrates two previous papers focussed on a *Systems-Theory* approach to materials properties based on IN/OUT relations [12, 13]. Chemical systems can be sets of atoms organised in molecules, as well as sets of molecular species jointed by a network of

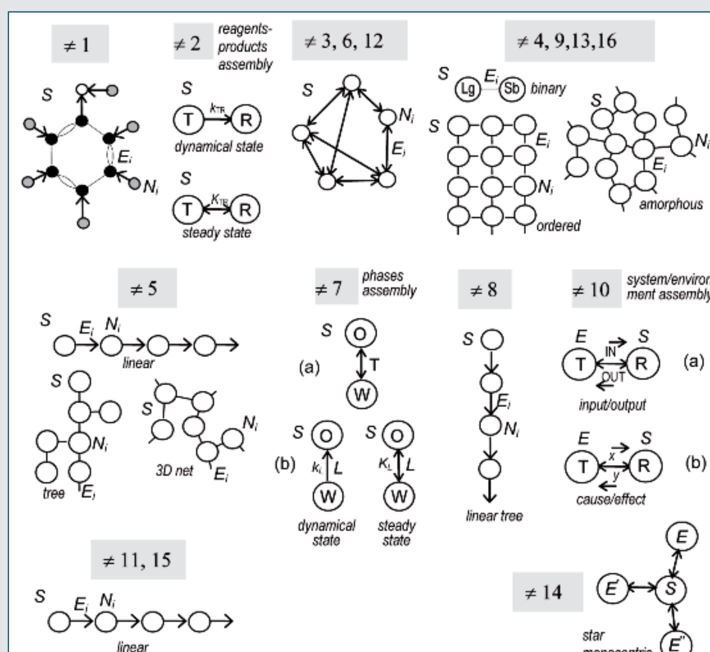

Fig. 1 - Graphs topologies related to the Tab. 1 systems. S = system, N_i = nodes, E_i = edges. T = transmitter, R = receiver. In ≠ 4, Lg = ligand, Sb = substrate. In ≠ 7, O = oil phase, T = tensioactiv component, W = water phase, L = lipophilic component. In ≠ 10, E = environment, IN, x = inputs (from T to R), OUT, y = outputs (from R to T). In ≠ 14, E, E′, E″ = environmental phases.

Tab. 1 - Mixed approach of Systems Theory (elements, interactions) and Graph Theory (nodes, edges, edge orientation and weight) to chemical systems. Interactions/edges specified as transports. Size scale, between subnano- and mega-, increasing from ≠ 1 to 16. Number signs explicated in the text list.

≠	System	elements / graph nodes	interactions / graph edges, connections	edges orientation	transport
1	- molecules - polyions	atoms coupled ions	shared electrons (covalent bonds)[a] exchanged electrons (ionic bonds)[a]	Y/N[b]	matter/energy
2	chemical transformation	reagents, products	- tranformation arrow[b] - pathway arrow	Y Y	matter/energy information[d]
3	- chemism (non-living/abiotic context) - biochemism (living context)	molecules	- tranformation arrow[c,e] - pathway arrow	Y Y	matter/energy information[d]
4	- aggregation structures (phases) - supermolecular assemblies (clusters) - ligand-substrate binary complexes	- molecules - ions (in crystals), macroions, monomers (in polymers)	- secondary forces (secondary bonds) - electrostatic forces (ionic bonds) - shared electrons (covalent bonds)	Y/N[b]	energy (electric fields)
5	cells, microorganisms	- monomers (in polymers) - molecules (in aggregates)	- shared electrons (covalent bonds) - affinity forces (secondary bonds)	Y/N[b]	matter/energy
6	colloids (nano-, meso-structures)	subcellular components (organelles)	- functional relations[f] - exchanged fluxes[g]	N Y	information[d] matter/energy
7	physico-chemical assembled structures (multi-phases, multi-components)	phases/components	interphases bonds[h] phases interfaces (linkage action)[h]	Y	matter/energy
8	materials, *bio*-matter, *geo*-matter	organization/morphology levels scale levels (from macro- to nano-)	hierarchical inclusion relationships hierarchical succession, order, link	Y	information[d]
9	materials in mechanical contexts	rheological units (atoms, molecules, colloids, micro-particles)	inter-units bonds (primary, secondary) forces transmissions/fluxes	Y/N[b] Y	matter[i]/energy[l] information[d]
10	materials in *tech* or *lab* contexts	material and process (system and environment)	- unit operations fluxes[g] - "I/O" cause/effect relations[m]	Y Y	matter/energy information[d]
11	manufacture or process plant	steps flowchart (=chemical conversions and unit operations	transformation arrows[e], fluxes[g] pathway arrows	Y Y	matter/energy information[d]
12	manufactured artifacts macroorganisms ("living artifacts)	components, different assembled parts (organs in "living artifacts)	- joints, gears, links, adhesion films - functional relations[f]	N N	energy (adhesion) information[d]
13	discretized artifacts discretized macroorganisms	space geometrical points (meshes domains, nodes grids)	proximities, distances	N	none (formal, space connections)
14	organisms and artifacts in *env* contexts: natural growing resources, raw-materials, final artifacts, wastes in their contexts[o]	morphological parts, artifact parts[n], environment (=context[o]) parts[n]	exchanged fluxes[g]	Y	matter/energy
15	the same as ≠ 14, now connected in a sequential chain[o]	the same as ≠ 14	- exchanged fluxes[g,p] - pathway arrows	Y Y	information[d]
16	discretized terrestrial environments	the same as ≠ 13	the same as ≠ 13	N	the same as ≠ 13

[a]Bonds energies ΔH as edge weights.
[b]Yes (Y) or not (N) according to electronegativity differences (ionic, polar vs. homopolar covalent bonds).
[c]Kinetic and equilibrium constants k (direct k_{TR} and inverse k_{RT}) and K (global ratio) as edge weights.
[d]Select, order, sequence, locate or place in a 2-3D space context (≠ 2, 3, 8, 9, 11, 15); assign, attribute, couple (≠ 6, 12); identify, set up, lay out cause/effect links (≠ 10).
[e]Chemical reactivity or conversion routes in a given context, abstract (undefined location, undimensioned space and time) or mapped on a real matter surface or space (2-3D heterogeneous topochemism) that again can be: unanimated (mineral, geochemical, abiotic) or animated (cells, microorganisms, living macroorganisms, living communities connected by chemical signals) or tech (production plant).
[f]Function attributes are assigned to any component of the system (object, organism).
[g]IN/ACC/OUT balance amounts and transport constants (molecular diffusion D, heat conduction h, mass transfer k_m) as edge weights.
[h]Formed by an amphiphile component T. Lipophilic L components (or hidrophilic H) do not form interphase bonds but distribute between the system immiscible phases according to the reciprocal solubilities: kinetic extraction constant k_L and equilibrium partition coefficient k_L as edge weights.
[i]Kinematic elastic deformation or plastic flow.
[l]Conservative stretching of bonds or dissipative viscous flow (bonds breaking and reformation); momentum flux.
[m]Physical laws constants κ as edge weights (system constants, in the general forms $y = f(\kappa, x)$).
[n]Physical or conceptual/functional compartmentalization or splitting into neat compartments enveloped by physical boundaries.
[o]Context = growing, farming environment (morphogenesis), physical environment (air and water as turbulent fluids, gravity, pressure etc.), mining, harvesting, slaughtering environment (isolation, separation from the context), tech environment (processing), testing environment (laboratory apparatus), "shelf" environment (storage, maintenance), exercise/use environment (e.g. human body of the consumer, proximate or contact phases as atmosphere, rain, supporting, striking or containment solid surfaces), disposal environment, eco-system environment.
[p]System-environment interactions along the product life-cycle chain.

reactions or by environmental "super-systems" or "systems of systems" among whose they share (Tab. 1, Fig. 1 and the following explicative list of number signs).

Now virtual *communication networks* can model and simulate exchanges and relations in and among these systems. I.e. *graphs* as "systemic layouts" of chained relations meaning actions (→, causality), interactions (↔or ⇆, circular causality, feedback) or generic links (—, connection).

≠ 1. *Molecule* as topological unit with polar, non-polar or ionic bonds. 2D (formulas) or 3D (molecular models) networks. Oriented edges due to electrons shifts, standing for polarized bonds due to electronegativity differences. Tab. 1 example: C_6H_5OH phenol molecule, electronegativity scale O > C > H. Reactions mechanisms are really topological rearragements of two of such colliding units as # 1 is (or one unit, autorearranged), involving intermolecular and intramolecular movements of connections or electrons among atomic nodes indicated by pathway-arrows.

≠ 2. *Chemical reaction* as formal, abstract transmission from a transmitting source T to a receiving one R, meaning matter (and energy) flow; i.e. engineering viewpoint of the chemical mass transport *from* the reagents T *to* the products R (oriented graph vs. equilibrium bi-oriented graph, or bi-oriented flux of the communication system). Minimal graph structure, or T — R simple binary graph.

≠ 3. *Chemism* as network of the reactions involved in a certain context: 1) abstract 2D map of multiple equilibria in an *homogeneous* medium (e.g. vine or meat colour that depends on the equilibrium system of the antocians in aqueous solution or of the hemoglobins in blood as influenced by pH or oxygen uptake); 2) map of multiple equilibria superimposed on a real morphological 2D/3D map of the context as a virtual chemical-process layout spreading in an *heterogeneous* medium (e.g. map of the biochemical pathways superimposed on a morphology map or sketch-plan of the organism or microorganism where occur, giving specific locations; ex.: photosynthesis cycle in plants chloroplasts, biogeochemical cycles, chemical reactions at electrodes and electrolyte parts of a fuel cell or of an air-oxydized material). Topochemical models as series-parallel, side, dendritic and loops combination circuits (connections/net topology); some critical chemicals as "pools" or highly connected "network-hubs".

≠ 4. Molecules and polymers *space conformations* and isomers, binary ligand-substrate or molecule-receptor complexes in heterogeneous systems (catalysis, pharmacodynamics, chemisorption, sensorial perception/communication etc.), crystallographic unit cells, crystal defects structures, lattices, solutions/liquids structures, clusters, polyhedral or nanotubes fullerene-based structures, random walks in a confined space, lattice or square grid (diffusional molecular or colloidal motion) etc. Graphs of the spatial components or nodes located in a space equipped with a metric (spatial networks, nodes topology).

≠ 5. Aggregation and macromolecular *colloids*, as more or less ordered assemblies of monomers units in 1-3D (juxtaposed, sequenced, dendritic, randomised etc.): nano-crystals, nano-filaments, nano-films, nano-vacuols, nano-drops, polymers crystallites, liquid crystalline assemblies, fractal gels/aggregates etc (nodes topology).

≠ 6. Nano- and micro-biological *living systems*, whose compartmented sub-systems are organelles of specific chemical and functional activities, strongly interconnected in order to assure the ultimate whole-system chemism and function. See graph analogy with system ≠ 3.

≠ 7. Physico-chemical *multi-phase/multi-component systems* of a minimum of two immiscible components (components ≥ 2, phases ≥ 2) stabilized by an interfacial, amphiphilic, third component of linkage (a); ex. oil/tensioactiv/water or O/T/W systems, stabilised colloidal systems as emulsions, sols, foams. If the third component is lipophilic or hidrophilic rather than amphiphilic (b), simply distributes between the two oil/water phases (preferential extraction, partition).

≠ 8. *Materials* in the wide sense of organized *tech*- and *bio*-matter (living) or unorganized *geo*-matter (soil), thinked as morphological systems ordered on structure-levels as in a virtual chinese box or matryoshka doll (*nested*- or *inclusion*- or *containment* hierarchy, hierarchical relations among sub-structures as nested sets: composite or macro-parts, fibers or grains, microphases, microfibers, microlaminae or microcells sub-structures, nano-components, molecules or polyions, atoms, subatomic particles. An ordered set can be represented by an acyclic graph. I.e. a graph of sequenced levels that is an embryonic form of organizational chart or tree-graph; a node represents any level of populations of sub-structures of a same class (rank); edges are hierarchical, vertical links connecting any superior node to the corresponding subordinate one. The hierarch or top level is the whole external shaped material.

≠ 9. Elastic or viscous "*mechanical bodies*" with a continuous interconnected network of chemical and/or physical bonds, subjected to a manufacturing or service external stress and an internal order/disorder lattice reorganization.

≠ 10. Raw and intermediate *matter processed* by reactors and plant machines or subjected to test apparatus (process environments). System/environment interaction viewed as a transmission/reception T/R communication: a) the transmitted inputs *to* the system are given back *to* the environment as outputs (matter/energy balance physical viewpoint: IN + GEN = ACC + OUT; b) stimulus/answer abstract viewpoint: $y = f(x)$ cause/effect or *x/y* undependent/dependent variables relations). Physical connections as IN/OUT exchanges (multi-components partitions between or among the internal system multi-phases and the external ones at the contact). Cause/effect connections as "I/O" relations in the form of common "*x/y*" phenomenological laws.

≠ 11. Qualitative and quantitative flowchart of the *process*, step by step, including not only materials, primary and side products but also labour and utilities as well. Process as abstract network of the single steps or superimposed network on a real plant map (process layout). Physical connections as IN/OUT quantitative exchanges. See graph analogy with system ≠ 3 but mainly in linear order.

≠ 12. *Manufactured products* as sets of different assembled parts, whose internal functions contribute to whole artifact functions (functions deployment, *Function Analysis Techniques FAST*). Biunivocal code of the binary correspondences between parts and corresponding function attributes. Formal analogy with macroorganisms, as insects or farm-raised foods.

≠ 13. Continuous space domain of a given *artifact* or *macroorganism*, e.g. a fresh fruit or frozen fish, discretized into a set of discrete finite triangular subregions like the frame elements of the *Finite Element Analysis* (FEA) or CAD design: triangulation cells and gridpoints. Object space discretized into a 2D or 3D grid of uniform cells (topological space) to allocate a distribution map of molecular concentrations. Lattice analogy with system ≠ 4 (space map here broken into geometrical units, where gridpoints = net nodes or uncontinuous, "isolated" points).

≠ 14. A *manufactured product* exposed to a given environment in the course of its entire life cycle: growing raw matter (e.g. a plant in the soil and atmosphere, an animal in the farming), processed raw matter (see ≠ 10), tested product (laboratory tests), manufactured good in exercise (e.g. a shoe or a textile in body contact, or subjected to laundry or mechanical friction, exposed to rain, air and radiation, an ingested food subjected to physical and chemical breakdown on the inside of specialized organs etc.), disposed good in the environment. I.e. a multi-compartmented system (artifact as set of multi-parts or multi-components) gone in contact with multi-phase environments (see heading Figure). Connections frame as in system ≠ 10.

≠ 15. Qualitative and quantitative flowchart of the product *life cycle*: product virtual pathway crossing the various ≠ 14 environment scenarios of its life (virtual environment compartments as physical phases, boxes or containers). Sequential connections as in system ≠ 11, IN/OUT balances (ecobalance, *Life Cycle Analysis* or LCA). See graph analogy with systems ≠ 3 and 11.

≠ 16. The same of ≠ 13 but now referred to an environment part such as a *terrestrial area* or site.

Edges topology (transports layout). Topological analysis focussed on the connections (Tab. 1), shows groups of families ranging from the steady attractive forces (real bonds, ≠ 1, 4, 5 and 7) to numerical flows (real vectors, ≠ 6, 10a, 11, 14 and 15), to syntax relations as signs sequences (space or time ordering-pathways signifying space or/and temporal successions or locations, ≠ 2, 3, 11 and 15 as well as 13 and 16) to communication, hierarchical or conceptual links conveying some information form (≠ 2, 3, 6, 8, 10b, 11, 12 and 15).

Wedge weights. Can be equilibrium and rate constants K_e and k_r of chemical reactions or partitions, transport constants D, h, k_m, matter and energy fluxes Φ_m and Φ_E, bond energies ΔH, lattice, grid or discretized space distances d specifying lengths information etc.

Nodes topology. Attention focussed on the observed spatial networks (Fig. 1), allows to emphasize that the nets topologies cover the ring, binary, mesh, grid, dendritic, tree (hierarchical), linear and star graph-families [1-2]. Tech artifacts and macroorganisms, i.e. un-living and living matter organized as compartmented systems subjected to internal and external transports, can be modelized by graphs conceptually isomorphic.

Behaviours. Connection networks as those of populations of molecules (ex. ≠ 2, 3, 4 and 9), that are characterised by bi-directional edges (direct and inverse directions, initial and feedback, or ⇆), are really oscillating networks subjected to complex dynamical behaviour. Conversely steady, fixed or abstract networks (ex. ≠ 1 and 7) show static behaviour. More precisely, graphs with uni-oriented connections (→) simulate transports states and so circuits having dynamical behaviour; un-oriended graphs (—) model stationary/morphological states and so maps of parts having static configurations.

Conclusions

System Theory and *Graph Theory* deal respectively with the IN/OUT interactions and the connections topology *in* the systems and *between* interacting systems or *between* a system and its surrounding. The superimposition of the basic principles of both, allow us to represent in formal models the structure and interactions involved in the real aspects and real situations where chemical transformations are involved. Interaction mechanisms, i.e. system transformation mechanisms, are thus sketched in the both aspects of structure (nodes topology rearrangements) and energy/matter changes (edges topology, edges weighted by fluxes).

Graphs models, due to their singular property of scale invariance, can thus be utilised to represent sub-nano-, nano-, micro-, macro- and mega-scale systems in terms of concise iconic models, according to the Tab. 1 numbering. Further stage of the suggested approach is to develop quantitative graphs models from both the usual IN-OUT and graph-matrices mathematical viewpoints.

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RIASSUNTO

Sistemi formalizzati per la soluzione di problemi chimici applicativi

Dispositivi schematici come i grafi, accoppiati alle risoluzioni dell'analisi input/output di sistema, consentono di rappresentare in modo pratico l'essenziale natura dei "problemi chimici di contesto". Dove cioè l'aspetto chimico deve concretamente collocarsi in matrici, situazioni e scenari sede di trasporti combinati di materia, energia o informazione, di varia scala e natura: bio-, tecno-, geo- o eco-logica.