

Bioorganic Materials from the “Unit Structures” Viewpoint

by Gianni Grasso

Bioorganic materials are physical bodies structured on several levels of organization, whose understanding is fundamental in biochemical, agrotechnological, biotechnological, pharmaceutical and environmental research. These materials show complex characteristics that can be simplified in terms of their so called “unit structures”. By transferring from the processes a concept wholly similar to the one of unit operations, we can thus describe the properties and classify the structure of the different materials independently of their specific chemical or physical composition. This can be practically obtained introducing the “unit structures” concept as idealized category of given material structure-elements. “Unit structures” approach, in the concise form of axiomatic model, seems thus an effective tool in order to approach and to resolve in a 360°-oriented global view, technological problems of structure-properties correlations in complex materials such as the bioorganic ones are. Thus between micro- and macro- structures, the entire spectrum of nanostructures finds its systematic allocation.

The *unit operation* idea is already currently utilized to classify and formalize the technological transformations of the chemical processes. By transferring from the processes to materials a concept entirely similar to the one of unit operations, we can describe the properties and classify the structure of the different materials independently of their specific chemical or physical composition. This can be practically obtained introducing the concept of “*unit structure*” as idealized category of given material *structure-elements*; i.e. as model or fundamental structure of any sub-system of the real body.

Physical bodies are structured on several levels of organization, the understanding of which is fundamental in technological, biochemical, pharmaceutical and environmental research. New trends in supermolecular, biological, medicinal, bioinorganic and food chemistry [1-5] overlap organic chemistry, biology and biophysics, showing how structures determine functions and activities. These interdisciplinary applications demonstrate the necessity to apply chemistry in a physical body context [6], whose increasing importance is for example showed by the subsections and paper topics covered by the journals on Materials Science founded on chemical aspects [7].

Generally inorganic materials have a relatively simple structure, usually set up on crystal grains coming from crystalliza-

tion nuclei grown until they mutually adhere. Preconstituted organic materials as wood, leather, vegetables, foods, textiles or coal show, with respect to the inorganic ones, typical complexity and organization characteristics coming from their biological structural hierarchy [8, 9]. Maybe this is the reason why for these materials the typical, unifying and systematic approach of the Materials Science based on kinetics and thermodynamics, is lacking. Complexity can be firstly analyzed in terms of systems structure conditioning their behaviour (system identification). Complexity can be thereafter simplified considering bioorganic materials in terms of their unit structures defining all their chemical, physical and biological levels of organization as well as dynamical behaviour.

The need to bridge the gap between organic and inorganic materials is strongly felt, also due to the emerging projectual philosophy of the “tailor-made” functional [10] or biotechnological products, as well as of the “soft” materials [11].

Bioorganic materials complexity picture

Simplest structures coexisting in organic materials are the ordinary gas, liquid and solid phases. Gases are always molecular systems. Liquids of pure substances or solutions are dynamic structured clusters, but again homogeneous molecular systems. Conversely liquid dispersions, with respect to molecular liquids, are both molecular (dispersing medium) and particle (dispersed phase) sets. Particles of intermediate dimensions (suspensoids) confer to ordinary phases the typical structures of the colloidal or generally of the “soft”-matter systems. Gases and liquids are micro- and macro-dispersed, re-

G. Grasso, Ministero dell’Industria - Stazione Sperimentale per l’Industria delle Materie Concianti - Via Nuova Poggioreale, 39 - 80143 Napoli and Dipartimento di Biologia (Tecnologie Alimentari) - Facoltà di Agraria - Università della Basilicata - Via Anzio, 10 - 85100 Potenza. ssip@iol.it

Table 1 - Conceptual meaning of the derived relations

- (1) 1st equivalence hypothesis or "system analogy"
- (1') 2nd equivalence (complexity, totality) hypothesis or "whole-structure analogy"
- (2) organization or hierarchy criterion
- (3) In-Out algebraic relation
- (4) 3rd equivalence (reductionism, partiality) hypothesis or "dominant-structure analogy"
- (5) independence hypothesis
- (6) surrounding medium-system (thermodynamic) interaction
- (7) 4th equivalence hypothesis or "thermodynamics analogy" (= "physico-chemical system")
- (7') "physical system"
- (7'') "chemical (homogeneous) system"
- (8) 5th equivalence hypothesis or "continuum analogy" (= "continuum system")
- (9) "nano- system"
- (10) "microbiological system"
- (11) "biochemical system"
- (12) "biological system"
- (13) "composite system"

spectively as pores and capillaries.

Solids have to be better considered. Amorphous solids can be considered like very viscous liquids, i.e. non-structured. Other solids are always structured; also those simple polycrystalline are sets of particles ("grains") each being in turn a set of molecules arranged in monocrystal lattices. Their properties are therefore depending on both these coexistent structures. Organic solids, due to their greater molecular weight, are divided in two classes: i) the molecular ones, as the simpler carbohydrates or fats; ii) the polymeric ones, as cellulosic, starchy or collagenic polymers, that are typically semicrystalline i.e. with both crystalline (micelles, spherulites) and amorphous domains and so both the typical solids and concentrated-liquids properties.

Finally, organic natural bodies are also composite solids; i.e. diphasic systems in which both the coexisting phases (matrix and fibres or particles) are solid or where a solid network of cellular walls entraps a viscous, gel-like phase.

Organic materials are really a mix of such simpler structures and many other ones. Therefore, in order to make these models applicative to polystructured systems too, as the organic materials are, an analytical and simplifying approach concerning their whole structure has to be firstly considered. By formalizing the system complexity in terms of Sets-Theory symbolism, the equations derived in our treatment can assume a conceptual meaning of precise hypotheses, criteria or sets basic relations (Table 1).

Syncretic approach: holism and reductionism

We start from the general approach coming from Systems Theory [12], that can be applied to analyze in an integrated way complex systems and allows us to consider materials as systems of sub-structures. Any material body M is a "cybernetic macroobject" with several levels of structuration k and system nature. In other words, it is formally identifiable with a set M (=structure model of M) hierarchically structured by sub-sets or component parts M_k progressively constituted by

populations of smaller and smaller elements, contained in greater elements. Such populations of elements can be sets of atoms, sets of molecules, sets of macromolecules, sets of colloidal particles with the nature of sets of microphases, sets of microorganisms, sets of corpuscular or fibrous histological elements, sets of micro- and macrodispersed phases with domains visible at microscope scale or to the naked eye, and finally sets of formal, geometric elements such as the shape and dimensions of the whole body.

The *real* structure of the whole M is all these M_k physical component parts but together with I_k relations (=interactions, i.e. bonds) among them

$$M \equiv M \text{ where } M = \{ \dots M_{k\dots} \} + \{ \dots I_{k\dots} \} \quad (1)$$

Eq. (1) contains both the structure and energy terms, I_k being the so called "unit energies" or classes of bonds (e.g. covalent, ionic, van der Waals, capillary forces etc).

From the structural viewpoint, these M_k components will be nevertheless understood for sake of simplicity in the following. That is we can formalize the several structure-levels being recognizable in the real bodies M in terms of structure-elements categories; i.e. in terms of "unit structures" [13, 14] or structure-models M_k of which they are composed, classified according to their order of magnitude (Table 2)

$$M \equiv \{ \dots M_{k\dots} \} \quad (1')$$

or more exactly

$$M \equiv \{ \dots M_{k\dots} \} + \{ \dots I_{k\dots} \} \quad (1'')$$

These sets of structures are all mutually organized by means of inclusion relations (\subset) that formalize their reciprocal interactions (Figure 1)

$$M_{k-1} \subset M_k \subset M_{k+1} \quad \forall \text{ level of structure } k \quad (2)$$

Thus any sub-system M_k is a model sub-set of the whole structure M and materials are considered as populations of simple structure-elements having definite M_k structures and so well-known $\{ \dots y_j \dots \}_{k=\dots} \{ \dots y_{jk} \dots \}$ sets of associated properties (y_{jk} =value of the property j related to the k sub-structure); i.e. the M_k unit structures have simple, formalizable structures

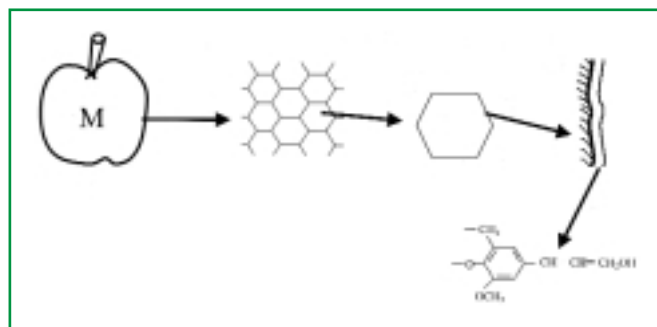


Figure 1 - Pictorial view of the inclusion relation acting among the unit-structures, showed by the honeycomb cell-network of a vegetal body, the single cell, the cell wall, the wall ultrastructure, the interior, surface and adsorbed molecules. Related concepts range from composite-science to biology and biochemistry, physical chemistry and chemistry

Table 2 - Iconic models M_k of meso-, micro- and macrostructures

(classification of the fundamental unit structures: g=gas, l=liquid, s=solid)

Homogeneous

Pure substances (Å or cm scale, i.e. subnano- or macro-)

Single components in a macroscopical chemical viewpoint (moles) or microscopical one (molecules)

g (kinetic model); l (hole model); s: ionic, molecular, crystalline, amorphous (glasses), real (defects, hole model)

Solutions (Å or cm scale)

Multi-components in a macroscopical chemical viewpoint (moles ratios) or microscopical one (molecular ratios)

g gaseous mixtures; l liquid solutions; s solid solutions (glasses)

Phases (cm scale): pure substances or solutions in a macroscopical physical viewpoint

Heterogeneous

Colloids (\approx nm- μ scale, i.e. meso- or from nano- to micro-)

l/g¹ fog, spray

s/g aerosol, powders (granular matter), smokes

g/l foams (liquid); g/l interfaces

l/l colloidal emulsions (microemulsions) type O/W or W/O, latex, liposomes, vesicles
interfaces l/l between immiscible liquids

s/l particulate sol (microcrystals, fillers, spores)

supermolecular sol of associations (pigments, crystallites in partly amorphous polymers, micelles, liquid crystals)

macromolecular sol, hydrophilic colloids (polymeric monofilaments), broths

fibrillar sol (microfibrils), cells organelles (e.g. membranes)

lamellar sol (film, mono- and plurimolecular membranes, surface mono- and plurilayers, epilamina)

concentrated sol (pastes, mushes)

interfaces s/l, double electric layers (Stern); films on liquids (Gibbs adsorption), films of surfactants

g/s solid foams (microporous solids, molecular sieves), solid aerogel

interfaces g/s; films on solids (Langmuir or BET adsorption)

l/s solid emulsions (butters, creams, "microencapsulated" solids)

gel (continuous solid matrix with morphology of: filaments, lattice, network, "castle of cards", jellies)

gel-polyelectrolytes (acid/base or ionic exchange resins)

microgels or amorphous domains in partly crystalline polymers

s/s alloys (crystalline grains, spherulites), solid sol (granular compact solids, crystallites, particulates), xerogel

supermolecular AB complexes (e.g. host-guest inclusions, antigen-antibody associations, polymer-molecule² conjugates)

nanocomposites; interfaces s/s (of specific adhesion)

Suspensoids (\approx μ -mm scale, i.e. from micro- to supramicro-)

l/g droplets, rains

s/g composites (solid phase dispersed with morphology of knitted-fabric network: textiles), fluidized beds, air microorganisms

g/l³ foams

l/l rough emulsions

s/l rough dispersions, supermolecular associations nucleated and grown (flocs, coagula, sludges, muds), water microorganisms
cells organelles and cells suspensions

s/l-g pellicles, limit stagnant layers at interfaces s/fluid or interphases

g/s solid foams (voids); local continuum-discontinuities (pores, cracks, fractures) subject to nucleation and propagation

l/s "encapsulated" solids

s/s composites (solid phase dispersed with morphology of: globules, inclusions, filaments, fibres, tubules, flakes, laminae, textiles, cells grouped in compartments); microorganisms associations or colonies; pellicles (of mechanical adhesion), s_A/s_B microcomposites: s_A entrapped in gel matrix, encapsulated in gel coat, adsorbed on active particle (biofilm) or into a porous matrix (membrane); s_A =cell, enzyme (biocatalyst), s_B =gel (e.g. Ca-alginate), active polymer or silicate

Idealised structures

Material point and continuous body (continuum) of Mechanics and Transport Theory: stressed, migrated, permeated body⁴

Elemental length-, angle-, surface- or volume-elements of differential or integral calculus: dx, dr, d θ , dS, dV etc; fractals

¹Colloid dispersed/ dispersing continuous medium (or matrix). ²E.g. PEG-active molecule specialty. ³Suspensoid dispersed/dispersing medium (or matrix). ⁴Solid, fluid subjected to σ - τ , v, T, c fields (=stress, velocity, temperature, concentration): mechanically stressed body (structure-elements, composite-elements or defects system) and fluidynamically stressed body (viscous or vortices system), migrated body (dynamical transient-state), permeated body (dynamical steady-state).

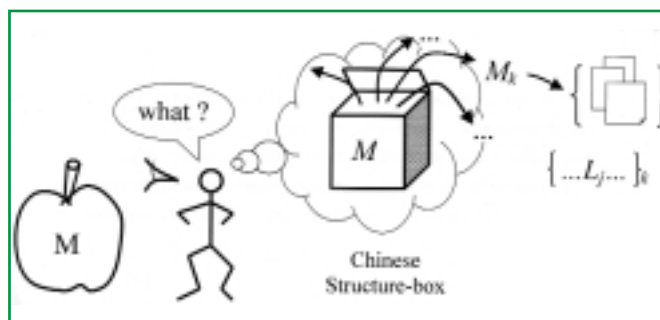


Figure 2 - Conceptual model clarifying how the unit-structure concept ($\dots M_k \dots$) fills gap between real body ($=M$) and scientific knowledge of the single disciplines. Key: "eye"=a view of, \mathcal{A} provided by, $\{\dots L_j \dots\}_k$ set of intellectual concepts signified by the scientific laws referred to each k unit-structure

and thus a series of well-defined and characteristic y_{jk} unit properties correlated to their specific ϕ_{jk} structural parameters by means of specific L_{jk} structural laws

$$L_{jk}: \phi_{jk} \rightarrow y_{jk} \text{ namely } y_{jk} = y_{jk}(\phi_{jk}) \text{ or } y_{jk} = \kappa_{jk} \phi_{jk}^n \quad (3)$$

where $n=1$ for linear and $n \neq 1$ for non-linear stimulus-answer or ϕ_{jk} - y_{jk} cybernetic behaviour (e.g. Newton and Bingham viscosity laws, respectively $\tau=\eta\dot{\gamma}$ and $\tau=\eta\dot{\gamma}^n$). These structural laws are coming from the physical sciences heritage concerning the individual M_k unit structures, e.g. chemistry for molecules populations, microbiology for microorganisms populations, composites-science for matrix and inclusions elements, chemical thermodynamics for phases and component-moles populations etc.

M_k unit structures are ubiquitarily distributed among all kinds of materials and have general properties (structural laws) of formal set-up independent of specific materials-compositions, where the unique impact of materials structure and composition is on the κ_{jk} materials constants (e.g. viscosity coefficient in the Newton and Bingham laws).

The problems on materials processing start with soft or unstructured problems concerning "which"-type of questions, focussed on the systems structure; i.e. they examine the problem (see Figure 2 where we actualise Eqs. (1') and (3)). The implementation process will further request the conversion of "which" to "how".

If some high characterizing "dominant-structure" can be recognized, strictly correlated to some specific material properties, we can speak of a "dominant-structure analogy" being significant for these properties

$$M \equiv M_k \quad (4)$$

or more exactly

$$M \equiv \{M_k, I_k\} \quad (4')$$

where M_k =structure-model k and $M_k \in \{\dots M_k \dots\}$; i.e. we can speak in terms of a critical unit structure to which the whole body in some cases can be formally reduced. This clearly appears taking into consideration that some individual, single elements can be ideally considered as enucleated; as if they were taken out from the specific context (=interactions and so influence) of the hierarchical organization in which they are en-

veloped in the material. I. e. as if the remaining part of the material, or the complementary system ($M-M_k$), was not influent

$$M_k \not\subset M_{k+1} \text{ or simpler } M_k \not\subset M \quad (5)$$

Knowledge on materials is relatively good at the level of: i) particles governed by quantum laws (*submicroscale*: electrons, atoms and molecules); ii) bulk materials approximated by continuum models (*macroscale*). But intermediate matter, at *mesoscale* and *microscale* level, shows *sui generis* properties where quantum and continuum models overlap or exclude each other. Chemical systems at mole level behave as continuous macrosystems, at molecular level as quantum mechanical submicrosystems.

The problems on materials processing conclude with hard or structured problems concerning "how"-type of questions, focussed on the systems behaviour; i.e. they examine the specific problem situation (see Figure 3 where we actualise Eq. (4) and introduce the surrounding/system interaction as well as the system-state concept).

Macrostructures

Sub-structures such as phases and components represent the system *macrostructure* in thermodynamical sense, conditioning its behaviour. They allow to approach organic materials and their transformation properties (both equilibrium and kinetic) in the view of the Materials Science. In this perspective, bodies and materials were firstly considered as systems being interfaced with the surroundings, whose thermodynamic state Ψ_i is characterized by the $(T, P, \dots n_p \dots)$ state-variables

$$\Psi_i = \Psi_i(T, P, \dots n_p \dots) \quad (6)$$

Thus at equilibrium any physical system is describable in terms of its m component phases $\{\dots \phi_m \dots\}_{T,P,n}$, from which all its physical properties y_i having technological interest are arising. Any chemical system is instead characterizable in terms of molar (=molecular) n_p quantities and so concentrations $\{\dots c_p \dots\}_{T,P}$ of its components p

$$M \equiv (\{\dots \phi_m \dots\}, \{\dots n_p \dots\})_{T,P} \quad (7)$$

Eq. (7) considers materials as both physical and chemical (=physico-chemical) systems, involved in distribution of components between phases $[p_\alpha \rightarrow p_\beta \forall p]$ as well as in chemical heterogeneous transformations $[\Sigma(v_p p_\alpha)_R \rightarrow \Sigma(v_p p_\beta)_P]$; α and β schematically indicate two system phases and v_p indicates stoichiometric coefficients. In particular, simpler cases are the physical or "phase" transformations in multicomponent systems of fixed composition $[\{\dots p_\alpha \dots\}_\alpha \rightarrow \{\dots p_\beta \dots\}_\beta; n_p = \text{const} \forall p]$ and the chemical homogeneous ones, i.e. gaseous or solution $[\Sigma(v_p p)_R \rightarrow \Sigma(v_p p)_P]$ "components" transformations

$$M \equiv \{\dots \phi_m \dots\} \text{ at } T, P, \dots n_p \dots = \text{const} \quad (7')$$

$$M \equiv \{\dots n_p \dots\} \text{ at } T, P = \text{const} \quad (7'')$$

Descriptions of engineering sciences, such as those mechanical (statics) and involving transport phenomena describable in terms of scalar, vectorial or tensorial fields (heat, matter, momentum), are otherwise based on the "continuum" viewpoint;

i.e. bodies are thought as sets of "material points" $P=P(x, y, z)$ mutually adherent and positioned with respect to an external coordinate system

$$M \equiv \{ \dots P(x, y, z) \dots \} \text{ at } T, P, \dots n_p \dots = \text{const} \quad (8)$$

Continuous body is thus another macroscopic unit structure, likewise composed of virtual microscopic unit-structures. Aside their "system-structure" meaning, Eqs. (7) and (8) join thus chemical and chemical engineering-type notions concerning dynamic (kinetic) properties of the system.

Mesostructures

Beside these sub-structures, a lot of *meso*- and *micro*structure have to be considered. Real structures can thus be classified according to the scheme of Table 2. For this purpose we have mixed the systematics of classification of homogeneous and heterogeneous systems with the one of molecular systems; i.e. pure substances and solutions, colloids, suspensions and composites. In this context both real and virtual structures recognizable in the materials are presented as, for example, the thin layers and interfaces due to their impact on transport properties, adhesion etc. Unfortunately, also defects are structural elements being typical of solids. Thus Table 2 summarizes over sixty unit structures more or less frequent in materials, and thus always potentially present.

Mesoscopic structures represent an intermediate state of matter between continuous materials and single molecules, with unique physical/chemical and often self-assembling properties and again governed by " (T, P, n_p) "

$$M \equiv \{ \dots M_k \dots \}_{\text{nano}} \text{ at } T, P, \dots n_p \dots = \text{const} \quad (9)$$

They are representative of the typical colloids: liquid crystals, fluid membranes, fractals, giant micelles, supramolecular assemblies, nanofilms undergoing wetting or spreading phenomena, nanocomposites where matrix includes nanoparticles etc. Nanoscience is the growing interdisciplinary "soft" matter science covering mesoscopic aspects of the matter.

Microstructures

Typical sub-structures of organic bodies are the microorganisms, whose N_s populations (=plate counts of the microbial species) depend on the environmental chemical compositions of Eq. (7"), being p =critical bioactive components such as H^+ , H_2O , O_2 , nutrients, biocides etc.

$$M \equiv \{ \dots N_s \dots \} \text{ at } T, P, \dots n_p \dots = \text{const} \quad (10)$$

In presence of microorganisms, chemical systems represented in Eq. (7") complicate dramatically due to the presence of the metabolic intermediates and final products of cellular biochemistry

$$M \equiv \{ \dots n_p \dots \}_{\text{bio}} \text{ at } T, P, \dots N_s(n_p) \dots = \text{const} \quad (11)$$

If the organic body of our technological interest is a "living object" of $\{ \dots M_k \dots \}_{\text{bio}}$ component parts such as ordered cells organelles, cells and complexes of cells (tissues), we can consider it from a morphological viewpoint too

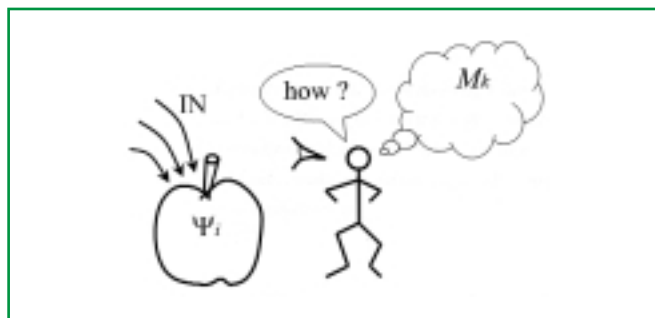


Figure 3 - Conceptual model clarifying the technological action on the body and hypothesis on the dominant unit-structure involved (M_k). Key: IN =surrounding-variables striking the system (thermal T , mechanical P or material at interface n), Ψ_i =specific system-state, "eye"=a view of

$$M \equiv \{ \dots M_k \dots \}_{\text{bio}} \text{ at } T, P, \dots N_s(n_p) \dots = \text{const} \quad (12)$$

Obviously, the physical composite systems of the suspensions and their matrices showed in Table 2 are also included among microstructures (mc subscript=microcomposite)

$$M \equiv \{ \dots M_k \dots \}_{\text{mc}} \text{ at } T, P, \dots n_p \dots = \text{const} \quad (13)$$

So in accordance with Eq. (1'), organic materials M are actually polystructured systems, obeying an organization criterion. In them we can contemporaneously identify several fundamental structures M_k mutually related in order to achieve their functional integration and so functional cumulative properties.

Models of properties: from collective to singular properties

The structure of biological organic materials reveals a system nature, i.e. an organized complexity based on intelligence and autorganization criteria strictly connected to their functionality. Therefore it is common that some property (effect) is related to a complex of interacting structures (causes), according to the "several-one" relation concept. In this event a global approach would be required, starting from understanding and describing the system considered as the wholeness of its structures and interconnections. That is the whole system behaviour is *more* than that one of the sum of its single parts and holds Eq. (1) or (1'). This is the case of *complexity* and we can speak of *collective* behaviour related to *constitutive* material properties, such as elastic modulus and viscosity coefficient, where κ_{jk} material constants in Eq. (3) should be properly represented as κ_{jM} or simply κ_j .

Nevertheless, less complicated situations are often occurring, where we can refer the explanation of the system properties to the knowledge of structure and characteristics (interconnections, interactions mechanism) of some of its specific, "emerging" elements, according to the "one-one" relation concept. This is the case of *reductionism* and holds the general Eq. (4). Anyhow, it is only the experimental observation that confirms the supposed mechanisms, a *posteriori* indicating the "dominant" sub-structures involved in any given property appearance or phenomenology.

Thus it is possible to introduce some "method simplification" that is interpretative of some aspects of complexity. For example this is the case of thermodynamics, that considers only

a particular set, the macroscopic one, of the body unit-structures [Eq. (7)]. The same applies for the physical, chemical or continuum properties [Eqs. (7'), (7'') and (8) respectively]. In these situations we can speak of emerging *singular* behaviour (or properties) and we can recognize the pragmatical and simplifying meaning of any reductive, technological approach. The validity of such approximation is subject to a correctness of two hypotheses, such as those ones of complexity and reductionism: i) the formal decomposition in some structure-models $\{...M_k...\}=M$ of a wholeness M that in effect is not decomposable, and in which the whole or real system is not properly the simple sum or set of the parts ($M=complete$ model); ii) the identification of the wholeness in some its sub-set, that is of the real system M in some its dominant structure-model M_k ($=partial$ model).

Thus syncretic approach based on Eqs. (1-1') or (4) is anyway relevant, giving respectively a broad integrated picture (whole) and a specialized one (parts) of the investigated system.

Conclusion

The problem of the description of the whole-material properties is a problem of the description of its "unit structures", whose properties are in itself well-known and described by the single sciences: physics (7'), chemistry (7''), thermodynamics (7), mechanics and transport-phenomena of the engineering sciences (8), colloids science (9), microbiology (10), biochemistry (11), biology (12) and others. After we have formally reduced the real system M to a proper system-model M , or to a series $\{...M_k...\}$ of structure-models (=parts), we can start to extrapolate its technological behaviour; i.e. its properties. Table 2 therefore is proposed as a propaedeutical lecture-key of the complexity of whatever material. Obviously, besides these M_k structural elements, their I_k mutual interactions have to be jointly considered, i.e. their energy aspects as Eqs. (1'') and (4'). Eqs. resumed in Table 1 and whose symbols and operators are properly explained into words (see also their text description), form the series of propositions or *axiomatic* model of our "unit structures theory".

"Unit structures" approach seems thus a deployment tool in order to approach and resolve in a 360°-oriented, global view, technological problems of structure-properties correlations in complex materials such as the bioorganic ones.

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