Simulation mathématique des processus agrégatifs : généralisation du modèle IdEP-IdLA

Mathematical simulation of aggregative processes: generalization of the IdEP-IdLA model

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RÉSUMÉ. Le modèle mathématique IdEP-IdLA utilisé pour étudier théoriquement la chimie des processus d'agrégation est basé sur des hypothèses spécifiques pour schématiser à la fois la description physique du matériau de départ et les méthodes de formation des composés. L'étude fait partie du processus d'abstraction sous-jacent à la construction du modèle dans le but d'introduire certaines généralisations qui augmentent la solidité de l'approche théorique dans son ensemble. En particulier, ces généralisations démontrent la résilience du modèle par rapport à un large éventail d'agrégations spatiales possibles du matériau de base. Dans un premier temps, les changements proposés sont décrits et les ajustements formels nécessaires sont apportés aux relations théoriques produites par le modèle. Par la suite, l'étude se concentre sur l'évaluation de l'impact que les générisations introduites ont sur les résultats obtenus précédemment, confirmant la validité des conclusions de principe qui en découlent.

ABSTRACT. The so-called IdEP-IdLA mathematical model, used to theoretically investigate the chemistry of aggregative processes, is based on specific hypotheses whose purpose is to schematize both the physical description of the base material and the ways in which compounds are formed. This study is part of the abstraction process underlying the construction of the model and aims to introduce a generalization that increase the solidity of the entire theoretical approach. Such a generalization demonstrates, in particular, the resilience of the model against a wide range of possible ways of spatial aggregation of the base material. After having described the proposed changes and having made the necessary formal adjustments to the theoretical relations produced by the model, the study focuses on the evaluation of the impact that the new and more general hypotheses have on the results obtained previously, confirming the validity in principle of the conclusions already reached.

MOTS-CLÉS. Entropie, Modélisation mathématique, IdLA-IdEP, Processus agrégatifs, Hasard et nécessité.
KEYWORD. Entropy, Mathematical Model, IdLA-IdEP, Aggregative Process, Randomness and Necessity.

Foreword

In previous papers [Ref.1, Ref.2, Ref.3, Ref.4] a mathematical model has been proposed for the simulation of aggregative processes of biochemical interest, both in closed systems (at equilibrium) and in open systems (more or less far from equilibrium). The purpose of the model is not to faithfully reproduce specific real aggregative phenomena, but rather to investigate, in principle, the relationship between the thermodynamic state functions that characterize a generic aggregative process. Due to the abstractions necessarily introduced in the construction of the model and taking into account its ambition to constitute a study tool as general as possible, the scientific interest of the results lies in the qualitative determination of the aforementioned relationships and not in the numerical values that the different functions assume depending on the values assigned from time to time to the parameters provided for by the theory.

One of the first problems faced in the construction of the model was to ensure the computability, objective and unambiguous, of the entropy of both the reactants and the reaction products. It was therefore necessary, from the beginning, to find a way to make the determination of the moments of inertia objective and unambiguous not only for the particles constituting the base material but mainly for the complex spatial structures that characterize the aggregates. It is evident, in fact, that any model that claims to manage a wide variety of elementary particles and an even wider variety of

compounds cannot fail to have a method for determining the inertial characteristics of each individual particle of each species. Otherwise, the possibility of assigning rotational characteristic temperatures to the different types of particles would be precluded: consequently, it would be impossible to calculate, by means of statistical mechanics formulas,[1] the specific contribution that each species brings to the absolute entropy of the entire system. It is precisely this ambition of generality that represents the characteristic of greatest theoretical interest of the model even if, at the same time, the possibility of describing specific real processes is necessarily made further away: that is, the applicability to immediately verifiable facts is sacrificed to the depth of the investigation.

With this in mind, the following concepts have therefore been adopted:

– ideal elementary particle (IdEP) which connotes all the base material

– ideal linear aggregate (IdLA) which unambiguously defines the shape and size of the generic product of aggregation of different IdEPs.

In the cited papers, specific hypotheses have been made regarding these structures in order to make the calculations possible: paragraphs 1 and 2 that follow will recall in detail the assumptions made. However, regardless of these specific hypotheses, we are led to believe that any spatial structure assigned to the IdEPs is to be considered admissible, once the calculability of the translational and rotational inertia is ensured. Equally it is believed that, in principle, any rule for the formation of the IdLAs can be accepted as long as it provides for a progressive and calculable increase of the inertial characteristics as their size increases. The morphological likelihood is therefore to be considered subordinate to the unambiguous and calculable definition of the spatial arrangements; in fact, mainly the structure hypothesized so far for the IdLAs, although constructed in a rigorous and coherent way, is significantly different from any real macromolecule. Basically, we are convinced that, once the computability is ensured, the model gives, in principle, the same answers whatever the morphological characterization of the particles.

So, we call *postulate of resilience* the acceptance that the reliability of the IdEP-IdLA model, as a tool for the qualitative investigation of aggregative processes, is generally not conditioned by the morphology of the particles, as long as it is defined in a fundamentally coherent way. The aim of this work is just to bring elements in support of the postulate of resilience. This will be done by formulating more general hypotheses such as to give rise to a wider variety of spatial arrangements of particles even if, for computational needs, they must still be considered as fundamentally linear. It will therefore be shown that such a generalization does not alter, in principle, the results already obtained and that consequently the conclusions derived from these remain confirmed.

General recalls

In order to ensure an easy reading of the following text, it is considered appropriate to recall the theoretical elements underlying the IdEP-IdLA model in a schematic form and to re-propose the relations to which explicit reference will be made in the course of the work.

a) The expression for the entropy of a homogeneous gas of linear molecules proposed by statistical mechanics is (see [8] in Ref.1 and paragraph 8.4 in Ref.5):

$$S = \frac{5}{2} nklnT + nkln\frac{V}{n} + nk\left[ln\frac{\left(\frac{2\pi k}{h^2}m\right)^{\frac{3}{2}}}{\sigma\Theta} + \frac{7}{2}\right] \qquad \text{[Joule/°K]} \qquad [1]$$

[1] See Chapter 8 in Ref.5 and Chapter 10 in Ref.6.

where:
- n is the number of particles
- k is the Boltzmann constant (=1,380649 10^{-23} Joule/°K)
- T is the absolute temperature in °K
- V is the volume in m^3
- m is the molecular mass in Kg
- h is the Plank constant (= 6,62607 10^{-34} Joule sec)
- σ is the number of symmetry (= 1 for asymmetric molecules and = 2 per symmetric molecules)
- $\Theta = \frac{h^2}{8\pi^2 Ik}$ is the rotational characteristic temperature in °K, where $I = m_r\delta^2$ is the barycentric moment of inertia in Kgm^2 (δ = length of the molecule in m e m_r= reduced mass in Kg)

b) The expression for the volume v_0 of the allocation cell for a generic linear particle is (see [9] in Ref.1):

$$v_0 = \frac{\sigma\Theta}{e^{\frac{5}{2}}\left(\frac{2\pi k}{h^2}m\right)^{\frac{3}{2}}} = 2{,}95554\ 10^{-68}\left(\frac{\sigma\Theta}{\sqrt{m^3}}\right) \qquad [m^3] \qquad [2]$$

c) The Markovian expression for the entropy of a homogeneous gas is (see [10] in Ref.1):

$$S = \frac{5}{2}nklnT + nk\left[ln\frac{V}{n} - ln\, v_0 + 1\right] \qquad [Joule/°K] \qquad [3]$$

d) The expression for the volume v^* of the allocation cell to be used in [3] in the case of a gas mixture consisting of n linear particles of different types with i ranging from 1 to N is (see [12] in Ref .1):

$$v^* = \prod_{i=1}^{N}(v_i)^{p_i} \qquad [4]$$

where:
- p_i is the probability that a generic particle is of the i-th type
- v_i is the volume of the allocation cell to be attributed to the i-th type particles in accordance with [2].

e) The exchange reaction underlying the aggregative process studied by the IdEP-IdLA model is (see [19] in Ref.1):

$$\alpha XO^* + (1-\alpha)O \leftrightarrow \sum_{\lambda=1}^{\Lambda} \nu_{O\lambda}\, O^*_{\lambda-1}O + \alpha X \qquad [5]$$

where:
- α is the molar fraction of the giver compounds
- XO^* is the generic *giver compound*, consisting of an IdEP X, called *gray particle*, and an IdEP O^* of ζ_{O^*} different colors, called *active primary particle*
- O is the generic free IdEP, called *passive primary particle*, of ζ_O different colors
- $O^*_{\lambda-1}O$ is the generic IdLA of length λ, variously composed of $(\lambda-1)$ active primary particles and a single passive primary particle at the end of the sequence
- $\nu_{O\lambda}$ is the molar fraction of the IdLAs of length λ.

f) The expressions for the entropy h_O of the population descriptor $[p_i]$ of the passive primary particles (see [25/a] in Ref.1), for the entropy h_{XO^*} of the population descriptor $[p_j]$ of the giver compounds (see [25/b] in Ref.1), for the entropy h_X of the population descriptor of gray particles (see [25/c] in Ref.1), for the entropy h_{MIX} of the IdLAs population descriptor (see [31] in Ref.1) are:

$h_O = \sum_{i=1}^{\zeta_O} p_i \, ln \frac{1}{p_i} = \gamma_O ln\zeta_O$ [6/a]

$h_{XO^*} = \sum_{j=1}^{\zeta_{O^*}} p_j \, ln \frac{1}{p_j} = \gamma_{O^*} ln\zeta_{O^*}$ [6/b]

$h_X = 0$ (as grey particles are all of the same colour) [6/c]

$h_{MIX} = (1-\eta)\left[h_O + \frac{\alpha}{1-\alpha} h_{XO^*} + \frac{1}{1-\alpha} h_\alpha\right]$ [6/d]

where

- γ_O is the *disequilibrium factor* of the descriptor $[p_i]$
- γ_{O^*} is the *disequilibrium factor* of the descriptor $[p_j]$
- η is the *coding factor*, ranging between 0 and 1
- $h_\alpha = \alpha ln \frac{1}{\alpha} + (1-\alpha) ln \frac{1}{1-\alpha}$) is the entropy of a Markov source emitting 2 signals.

g) The expressions for the entropies S_O and S_{XO^*} of the reactants, for the entropies S_X and S_{MIX} of the products and for the entropy S of the whole system as a function of the degree of reaction ξ in Joules/°Kmole (see [23] in Ref.1) are:

$S_O(\xi) = \frac{5}{2} R(1-\xi)(1-\alpha) lnT + R(1-\xi)(1-\alpha) \left[ln \frac{V}{(1-\xi)(1-\alpha)n_A} - ln(v_O) + 1 + h_O\right]$ [7/a]

$S_{XO^*}(\xi) = \frac{5}{2} R(1-\xi)\alpha lnT + R(1-\xi)\alpha \left[ln \frac{V}{(1-\xi)\alpha n_A} - ln(v_{XO^*}) + 1 + h_{XO^*}\right]$ [7/b]

$S_X(\xi) = \frac{5}{2} R\xi\alpha lnT + R\xi\alpha \left[ln \frac{V}{\xi\alpha n_A} - ln(v_X) + 1 + h_X\right]$ [7/c]

$S_{MIX}(\xi) = \frac{5}{2} R\xi(1-\alpha) lnT + R\xi(1-\alpha) \left[ln \frac{V}{\xi(1-\alpha) n_A} - ln(v_{MIX}) + 1 + h_{MIX}\right]$ [7/d]

$S(\xi) = S_O(\xi) + S_{XO^*}(\xi) + S_X(\xi) + S_{MIX}(\xi)$ [7/e]

where:

- $R = 8{,}314463$ Joule/°Kmole is the gas constant
- $n_A = 6{,}0221409\ 10^{23}$ is the number of Avogadro

h) The expression for the reaction entropy ΔS_R in Joule/°Kmole (see [32] in Ref.1) is:

$\Delta S_R = R\left[\xi_0 ln \frac{1}{\xi_0} + (1-\xi_0) ln \frac{1}{(1-\xi_0)}\right] + R\xi_0(1-\eta)h_\alpha +$
$+R\xi_0(1-\alpha)\left[\frac{9}{2}\sum_{\lambda=1}^{\Lambda} p_\lambda ln\, \lambda - \eta\gamma_O ln\zeta_O\right] - R\xi_0\alpha\left[\frac{9}{2} ln2 + \eta\gamma_{O^*} ln\zeta_{O^*}\right]$ [8]

where ξ_0 is the extent of reaction at the equilibrium.

i) The expression for the enthalpy H of the entire system as a function of the extent of reaction ξ in Joules/mole (see [35] in Ref.1) is:

$H(\xi) = \frac{7}{2} RT + \alpha\xi\Delta E$ [9]

where ΔE is the *molar energy balance*.

j) The expression for the reaction enthalpy ΔH_R (see [36] in Ref.1) is

$\Delta H_R = H(\xi_0) - H(0) = \alpha\xi_0\Delta E$ [10]

1. The original definition of IdEP

The elements that characterize the fundamental building blocks of the model are briefly recalled here. It is assumed that the ideal elementary particles (called *IdEP*) are comparable to homogeneous material segments whose mass is uniformly distributed along their length. Their inertial characteristics are therefore fully defined by only two parameters:

- the mass μ, expressed in Kg
- the length δ, expressed in m.

The model also assigns each type of particle a label called *color*. In general, different colors can be attributed to particles that also have the same inertial characteristics: therefore the color represents a sort of immaterial attribute that makes the particles qualitatively distinguishable by groups, regardless of their physical characteristics. In particular, the binding energies between IdEPs of different types depend on colors.[2] Thus described the generic IdEP, it is possible to define for each particle the *linear density* ψ_{IdEP} (in Kg/m), the *barycentric moment of inertia* I_{IdEP} (in Kgm^2) and the *rotational characteristic temperature* Θ_{IdEP} (in °K):

$$\psi_{IdEP} = \frac{\mu}{\delta} \quad [11]$$

$$I_{IdEP} = \frac{1}{12}\mu\delta^2 \quad [12]$$

$$\Theta_{IdEP} = \frac{h^2}{8\pi^2 k I_{IdEP}} \quad [13]$$

Furthermore, the volume v_{IdEP} of the allocation cell expressed by [2] and which occurs in the Markovian expression of entropy [3] takes the form

$$v_{IdEP} = 2{,}95554\ 10^{-68}\sigma\frac{12h^2}{8\pi^2 k}\left(\delta^{-2}\mu^{-\frac{5}{2}}\right) = \frac{2{,}85685\ 10^{-112}}{\rho_{IdEP}} \quad [14]$$

having set $\sigma = 2$ for the supposed symmetry of the IdEP and having introduced the allocation inertia ρ_{PEId}

$$\rho_{PEId} = \delta^2\sqrt{\mu^5} \quad [15]$$

combining mass μ and length δ in a single parameter.

2. The original definition of IdLA

The model assumes that the IdEPs can combine with each other in sequence, generating more or less long chains. It also assumes that the assembly in succession of the IdEPs gives rise to compounds that, from a morphological point of view, can be schematized as a simply aligned connection of IdEPs. Consequently, the compound formed by a number of IdEPs equal to λ has been called *ideal linear aggregate* (IdLA) of order λ. Its total mass M is equal to the sum of the masses μ of all the IdEPs that contribute to its formation and its length L is equal to the sum of all the individual lengths δ.

[2] The knowledge of the binding energies between IdEPs is crucial in calculating the reaction enthalpy, the extent of reaction at the equilibrium and the reaction entropy.

In general, the IdEPs that join to form an IdLA can belong to various types of elementary particles that differ in color. However, calculations previously carried out show that if the masses and lengths of the IdEPs present in the reagent system are not too dissimilar to each other, the individual values can be replaced by a single value μ of the mass and a single value δ of the length, equal to weighted averages of the respective individual values, without this significantly affecting the calculation of entropy.[3] Although the groups of different particles remain distinguishable by color. Consequently, even an IdLA can be considered as a homogeneous material segment and its inertial characteristics are univocally determined and easy to calculate once the inertial characteristics of the IdEPs that contribute to forming it are known, whatever their number.

For this reason, the linear density ψ^0_{IdLA} of a generic ideal linear aggregate of order λ as defined above is necessarily identical to the linear density ψ_{IdEP} of the IdEPs that compose it:

$$\psi^0_{IdLA} = \frac{M}{L} = \frac{\sum_{i=1}^{\lambda} \mu_i}{\sum_{i=1}^{\lambda} \delta_i} = \frac{\lambda\mu}{\lambda\delta} = \frac{\mu}{\delta} = \psi_{IdEP} \qquad [16]$$

where μ_i and δ_i are respectively the mass and length of the *i*-th IdEP while μ and δ represent the respective means, calculated on the λ IdEPs that form the IdLA.

3. Generalization of the definition of IdEPs and IdLAs

The IdEP described in paragraph 1 is, by its nature, materially symmetrical. However, since it gives rise to linear couplings, it is reasonable to suppose that its ends are differently set to combine in succession: they could be, for example, the seat of different electrical charges. This can reasonably lead us to introduce a first generalization of the model: the hypothesis of considering the IdEPs as asymmetrical objects.[4] In this case, the volume of the allocation cell to be attributed to the single IdEP will be:

$$v'_{IdEP} = 2{,}95554\ 10^{-68} \left(\frac{\Theta}{\sqrt{m^3}}\right) \qquad [17]$$

having set $\sigma = 1$ in [2].

As a consequence of this first generalization, the IdLAs will also be considered asymmetric.[5]

A second generalization arises from the observation that the structure of the aggregates originally taken into consideration consists of a long filament, also materially homogeneous (as well as geometrically symmetrical). Such a morphology, which derives from the serial assembly of the constituent IdEPs, also returns a structure of the aggregate that objectively differs from that of any natural polymer chain. It is therefore useful to try to formulate an alternative aggregative hypothesis which, without changing the linear nature of the aggregate (essential to be able to proceed unambiguously with its inertial characterization), mitigates the rigidity of the original hypothesis.

[3] See Fig.5 in Ref.2.

[4] Asymmetry is a larger condition than symmetry, as it implies a greater disorder. In terms of statistical mechanics it leads to double the number of possible microstates for a one-dimensional particle.

[5] In reality, already in the original model the succession of IdEPs that form an IdLA can give rise to both symmetrical and asymmetrical structures, due to color differences: however, having to attribute, for computational reasons, a single predetermined value to the coefficient σ, it was originally chosen to extend the symmetry of the IdEPs also to the IdLAs for homogeneity of approach: it is a questionable but inessential hypothesis, as will be shown later.

It is then assumed that an IdLA, while maintaining its nature as a homogeneous material segment, may have a shorter length than the sum of the lengths of the individual IdEPs and therefore a higher density than that expressed by [16]. A possible physical interpretation of this hypothesis may suggest a folding of the chain so as to give rise to a sort of matter overlapping along the axis of the aggregate. However, an IdLA will continue to be schematized as a substantially one-dimensional and homogeneous structure. It is certainly a hypothesis that implies a morphology that is still quite distant from that of many real macromolecules, but it still has some indisputable advantages:

- it is a little closer to the shape of some aggregates of biochemical interest
- it is much more general than the previous one
- it allows us to modify at will the distribution rule of the material along the axis of the aggregate and therefore makes it possible, as we have proposed, to provide a contribution to the verification of the model's resilience.

If the thickening rule mentioned above is established in mathematical terms, also in this case the inertial characteristics of this simple structure will be univocally computable as a function of μ, δ and λ. So, we assume that the length L of the generic IdLA can be expressed by a relation of the following type:

$$L = \lambda\delta\beta$$

where β is a coefficient whose value, always less than 1, produces a shortening of the IdLA: obviously, the case $\beta = 1$ would bring the IdLA back to its original non-compacted setting. Since the total mass continues to be determined by the sum of the masses of the individual IdEPs, an increase in linear density will occur. It therefore seems reasonable to assume that β should be expressed as a function of the number λ of IdEPs that form the aggregate: that is, the longer the chain, the more progressive thickening of the material along the IdLA axis is to be expected. The following relationship is then proposed:

$$\beta = \lambda^{-\frac{q}{2}}$$

where the parameter q is given the name of *thickening index*. The length L_q of the generic IdLA will therefore be:

$$L_q = \delta\lambda^{1-\frac{q}{2}} \qquad [18/a]$$

Consequently, the other characteristics of a generic IdLA can be recalculated as a function of λ and q (in addition to μ and δ): the density ψ^q_{IdLA}, the moment of inertia I^q_{IdLA}, the rotational characteristic temperature Θ^q_{IdLA} and the volume of the allocation cell v^q_{ALId}:

$$\psi^q_{IdLA} = \frac{M}{L_q} = \frac{\lambda\mu}{\delta\lambda^{1-\frac{q}{2}}} = \frac{\mu}{\delta}\lambda^{\frac{q}{2}} = \psi_{IdEP}\lambda^{\frac{q}{2}} \qquad [18/b]$$

$$I^q_{IdLA} = \frac{1}{12}ML_q{}^2 = \frac{1}{12}\lambda\mu(\delta\lambda^{1-\frac{q}{2}})^2 = \frac{1}{12}\mu\delta^2\lambda^{3-q} = I_{IdEP}\lambda^{3-q} \qquad [18/c]$$

$$\Theta^q_{IdLA} = \frac{h^2}{8\pi^2 I^q_{IdLA}k} = \frac{h^2}{8\pi^2 k}\frac{\lambda^{q-3}}{I_{PEId}} = \Theta_{PEId}\lambda^{q-3} \qquad [18/d]$$

$$v^q_{IdLA} = \frac{\sigma\Theta^q_{IdLA}}{e^{\frac{5}{2}}\left(\frac{2\pi k}{h^2}M\right)^{\frac{3}{2}}} = 2{,}95554\ 10^{-68}\left(\frac{\Theta_{PEId}\lambda^{q-3}}{(\lambda\mu)^{\frac{3}{2}}}\right) = v_{PEId}\lambda^{q-\frac{9}{2}} \qquad [18/e]$$

It is immediate to verify that the [18s], in their generality, also include the original non-compacted setting of the IdLAs. In fact, for q = 0 we obtain:

$$L_0 = \lambda\delta$$
$$\psi^0_{IdLA} = \psi^0_{IdEP}$$
$$I^0_{IdLA} = I_{IdEP}\lambda^3$$
$$\Theta^0_{IdLA} = \Theta_{IdEP}\lambda^{-3}$$
$$v^0_{IdLA} = v_{IdEP}\lambda^{-\frac{9}{2}}$$

re-proposing the way of constructing the physical characteristics of the IdLAs which have been assumed as the basis of calculations developed in Ref.1, Ref.2 and Ref.3.

In order to highlight the effect of contraction and consequent thickening of an IdLA as the index q changes, Figs.1/a and 1/b report, as a function of λ and q, the trend of the following parameters

- relative shortening $L_q/L_0 = \lambda^{-\frac{q}{2}}$
- relative thickening $\psi^q_{IdLA}/\psi^0_{IdLA} = \lambda^{\frac{q}{2}}$

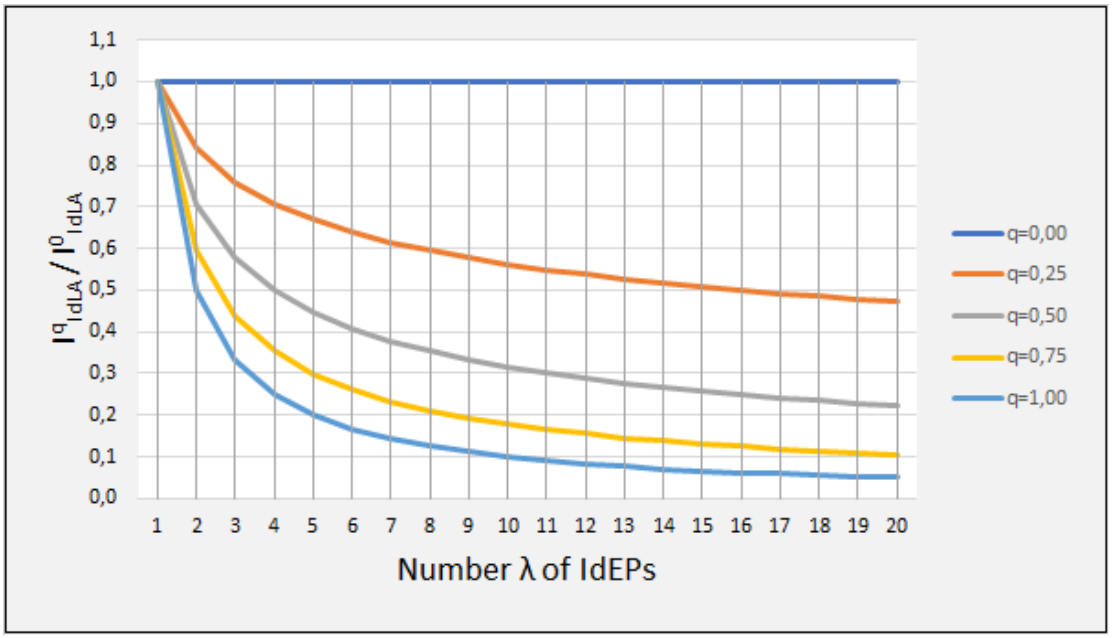

Figure 1/a. *Effect of the thickening index q on the length of an IdLA as a function of λ*

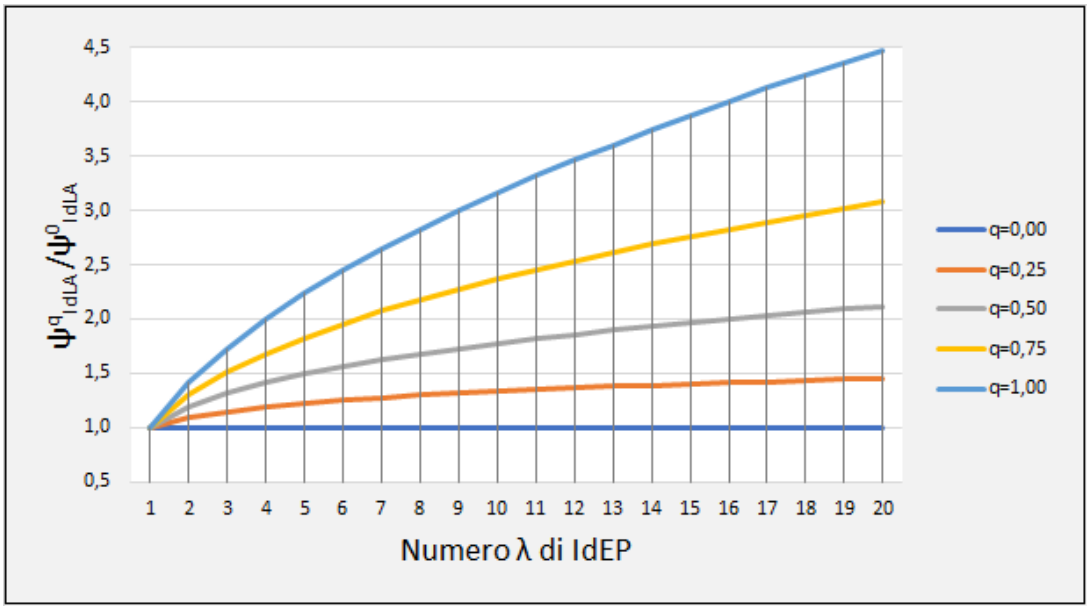

Figure 1/b. *Effect of the thickening index q on the density of an IdLA as a function of λ*

Similarly, Figs.2/a and 2/b report, again as a function of λ and q, the trend of the ratios

- between the moments of inertia $I^q_{IdLA}/I^0_{IdLA} = \lambda^{-q}$
- between the rotational characteristic temperatures $\Theta^q_{IdLA}/\Theta^0_{IdLA} = \lambda^q$

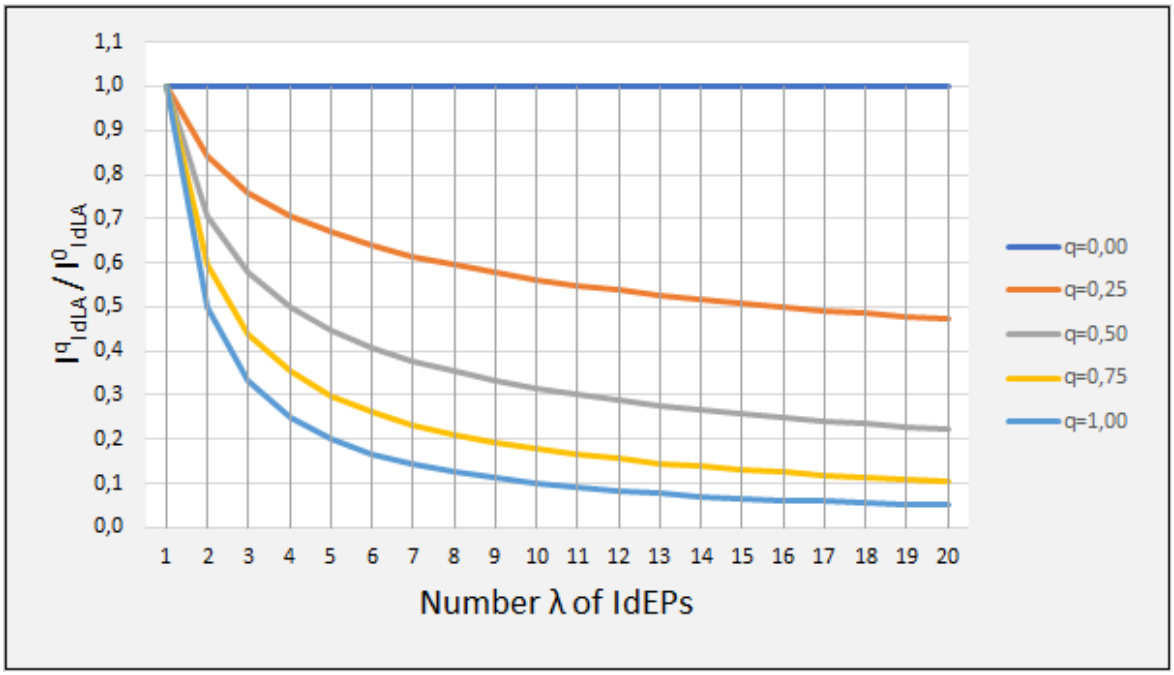

Figure 2/a. *Effect of q on the moment of inertia of an IdLA as a function of λ*

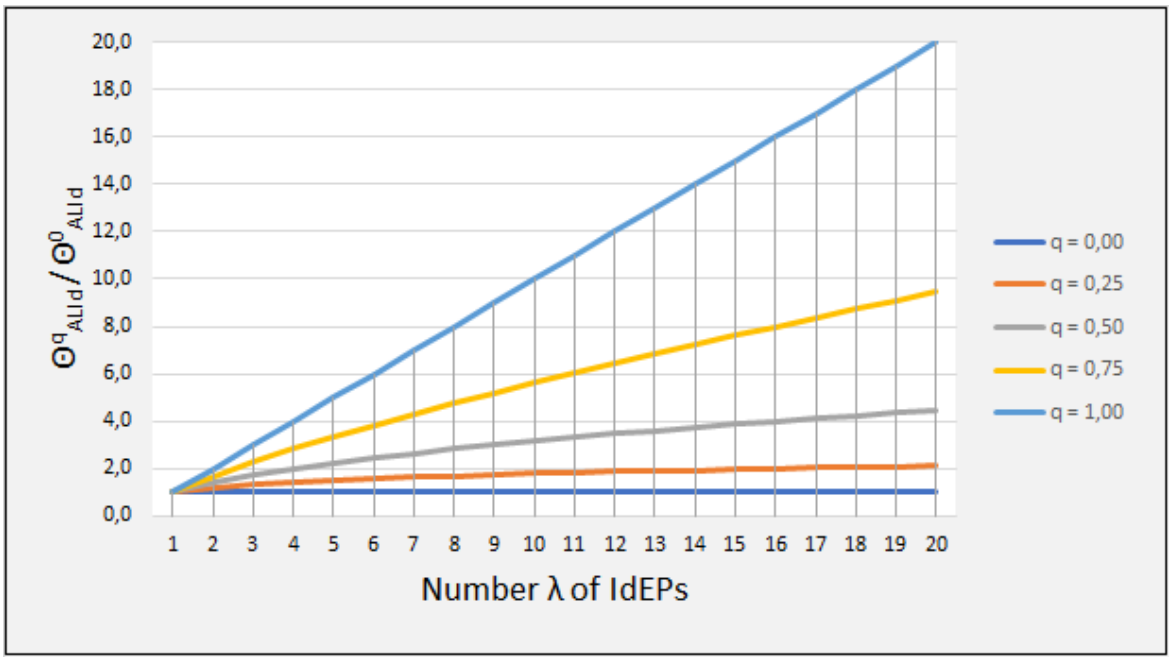

Figure 2/b. *Effect of q on the rotational characteristic temperature of an IdLA as a function of λ*

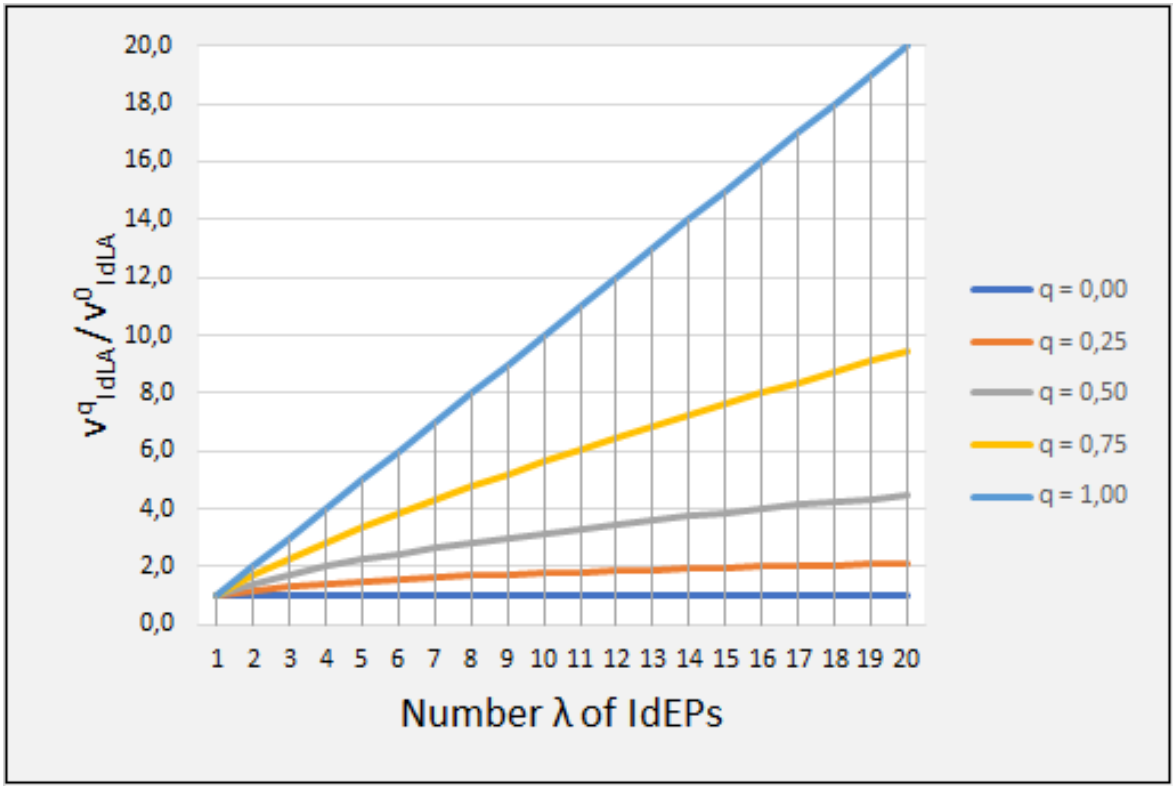

Figure 3/a. *Effect of q on the volume of the allocation cell of an IdLA as a function of λ*

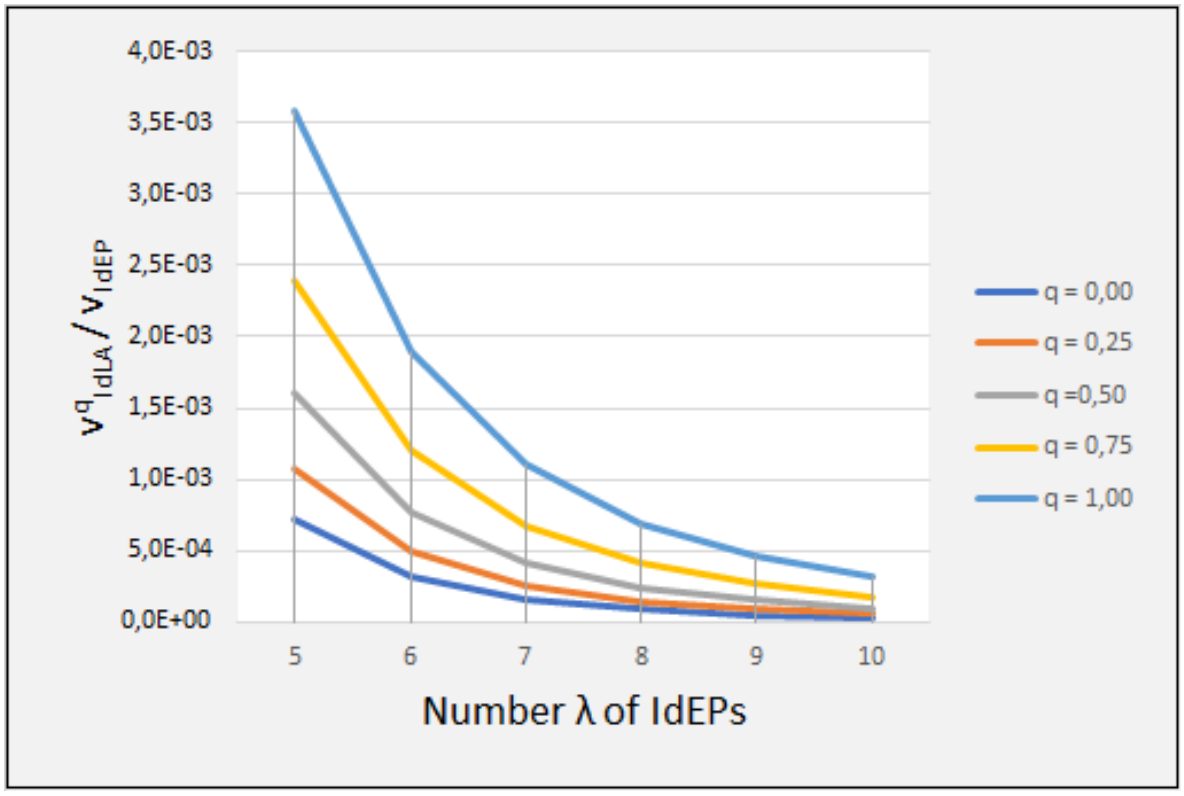

Figure 3/b. *Effect of q on the volume of the allocation cell of an IdLA compared with v_{IdEP}*

Finally, as regards the volume v^q_{IdLA} of the allocation cell expressed by [18/e], it should be noted that

- the cell volume increases as the thickening index increases, with the same mass (Fig.3/a). This means that if V is the total (constant) volume occupied by the particles of a generic aggregate, its fractionation is reduced and therefore the number of possible microstates decreases. All other conditions being equal, this implies a progressive decrease in entropy with increasing q:

this is in compliance with the statistical mechanics according to which a particle with a lower moment of inertia accesses a lower number of rotational energy levels. This is what we will actually verify below

- as the number of IdEPs (and therefore the total mass) increases, the volume of the IdLA allocation cell decreases with respect to the volume of the reference IdEP allocation cell (Fig.3/b): but the more the thickening index is great, more the relative curve assumes high values.

4. Mixture of IdLAs as a result of the aggregation process

We have already seen in Ref.2 that, in the particular case of random autopoietic aggregation[6] ($\eta = 0$), the probability p_λ of finding an IdLA of length λ (regardless of the color sequence) among the reaction products is easily calculated since the aggregate will consist of $(\lambda - 1)$ active IdEPs (with a presentation frequency equal to α) and a single passive IdEP at the end of the sequence (with a presentation frequency equal to $(1 - \alpha)$). Consequently:

$$p_\lambda = \alpha^{\lambda-1}(1-\alpha) \qquad [19]$$

Then, by means of [4], the volume v_{MIX} of the allocation cell to be attributed to the mixture of IdLAs can be calculated: in fact, by replacing the index i (which goes from 1 to N) with the index λ which goes from 1 to Λ (where Λ is the maximum significant length of the IdEP sequence), the quantity v_{MIX} and its logarithm take the following form:

$$v_{MIX} = \prod_{\lambda=1}^{\Lambda}(v_{IdLA})^{p_\lambda} = \prod_{\lambda=1}^{\Lambda}(v_{IdEP}\lambda^{q-\frac{9}{2}})^{\alpha^{\lambda-1}(1-\alpha)} \qquad [20/a]$$

$$ln v_{MIX} = ln v_{IdEP} + (q-\frac{9}{2})\Sigma_0(\alpha) \qquad [20/b]$$

having set

$$\Sigma_0(\alpha) = (1-\alpha)\sum_{\lambda=1}^{\Lambda}\alpha^{\lambda-1} ln\,\lambda \qquad [21]$$

whose value can be easily calculated as a function of α thanks to the convergence[7] of the summation $\sum_{\lambda=1}^{\Lambda}\alpha^{\lambda-1}ln$. For the model, the random autopoietic aggregation condition ($\eta = 0$) is the basis of the entire theoretical construction and therefore the starting point for the acquisition of numerical results even in variously coded conditions ($\eta > 0$).

Now, all that remains is to evaluate how the hypothesized generalization affects the results already obtained, taking into account that only the calculation of entropy is conditioned by it. In particular, it should be noted that:

[6] According to the model, the random autopoietic aggregation occurs when the binding energies that hold the giver compounds together are all equal to each other and the binding energies between the IdEPs that form the IdLAs are also equal to each other. It is a scenario whose analysis, regardless of how frequently this aggregation mode is in reality, is fundamental since, as widely explained in Ref. 2, it constitutes the reference basis for all subsequent theoretical developments.

[7] See Fig.2 in Ref.2. It should also be noted that the value of the maximum significant length Λ increases significantly with α: for $\alpha = 0{,}05$ the summation converges on stable values in the fourth significant digit already with $\Lambda = 5$ while for $\alpha = 0{,}95$ the same degree of precision is obtained with $\Lambda = 160$.

- the supposed asymmetry of both elementary particles and aggregates ($\sigma = 1$) will imply an increase in entropy since, all other conditions being equal, it doubles the number of possible microstates
- the material thickening along the aggregate axis ($q > 0$) will instead imply a reduction of entropy: the reduction of the IdLAs moments of inertia (and therefore the reduction of their rotational characteristic temperatures) will in fact reduce the number of energy levels at which the particle can access.

In comparing the results that will arise from these new hypotheses with the results obtained previously, the following notations will be used:

- STD to indicate the *standard condition*, that is those material structures already explored and discussed in Ref.1, Ref.2, Ref.3 and Ref.4 ($\sigma = 2$ and $q = 0$)
- $GEN(q)$ to indicate the *generalized condition* as previously described ($\sigma = 1$ and $q \geq 0$).

5. Effect of the $GEN(q)$ condition on random aggregations in closed systems

The aggregation process studied by the model is based on the exchange reaction [4] referred to in the introduction. In a closed system the concentration of reactants XO^* (IdLAs of order 2) and O (IdEPs) gradually reduces as the reaction progresses to give way to the reaction products $O^*_{\lambda-1}O$ (generic IdLAs of order λ) and X (IdEP). We therefore propose to evaluate, by means of [7], what impact the condition $GEN(q)$ has on the trend of the entropy $S(\xi)$ in the case of random autopoietic aggregations.

Assuming that the temperature and pressure are fixed and invariable and equal to the standard conditions,[8] the model imposes that $S(\xi)$ is determined by the following parameters

- the molar concentration of the giver compounds α
- the allocation inertia ρ of the IdEPs involved in the reaction (weighted average)
- the entropy of the population descriptor of passive primary particles h_O
- the entropy of the population descriptor of the giver compounds h_{XO^*}.

Without going into an unnecessarily detailed examination of the different possible combinations of the above parameters, it is sufficient to take into consideration the graphs of Figs.4 and 5, as substantially representative of the model's response to the two reference hypotheses STD and $GEN(q)$.[9] They refer to the conditions $\rho = 10^{-82}$ $m^2Kg^{5/2}$ and $h_O = h_{XO^*} = 1{,}5$.

The graph in Fig. 4, relating to the case in which q assumes values between 0 to 1 with $\alpha = 0{,}5$, clearly shows that the asymmetry of the particles ($GEN(0)$) implies in itself a general increase in entropy and that this increase is only partially mitigated by the increase in the q index, introducing a progressive contraction of the aggregates.

[8] T=298,15 °K, P=101.325 Pa.

[9] With regard to the detailed examination of the impact that, in the STD condition, the variations of the parameters ρ, h_O and h_{XO^*} have on $S(\xi)$, see Ref.2, paragraphs 1 and 2: in the $GEN(q)$ condition the impact is qualitatively the same.

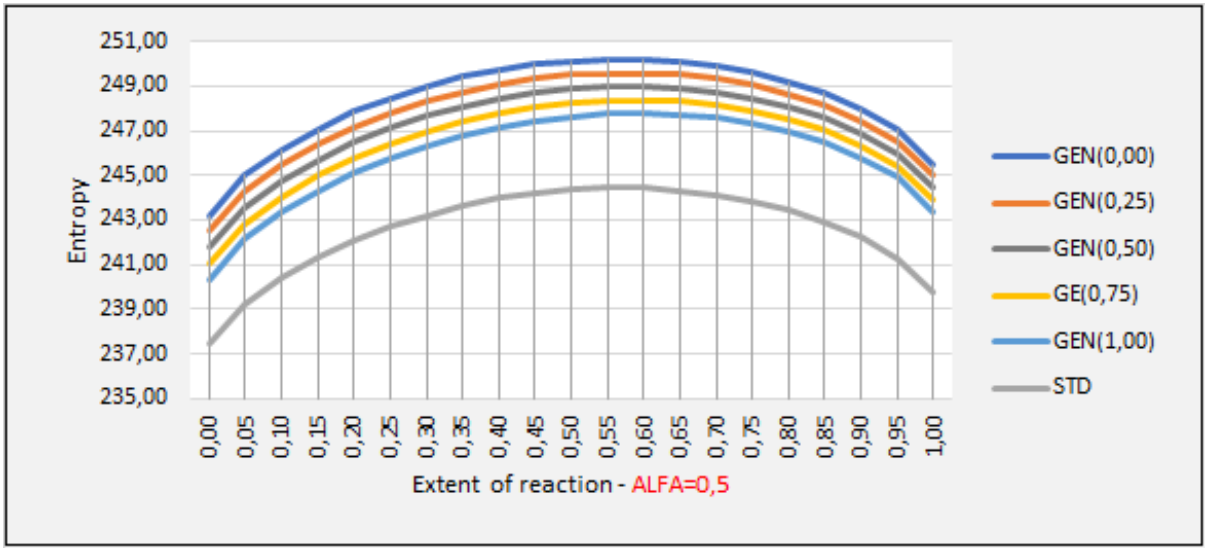

Figure 4. *Random aggregation: comparison of the effect on entropy of the STD and $GEN(q)$ conditions with $\alpha = 0{,}50$*

The graphs shown in Figs.5/a, 5/b and 5/c, which instead take into account variable values of α with $q = 1$, clearly show that in the early stages of the reaction, when the presence of giver compounds prevails over to passive primary particles (high values of α), the thickening of the giver compounds is sufficient to compensate for the asymmetry of the particles; on the contrary, for high values of ξ the difference between the conditions STD and $GEN(1)$ remains appreciable. They also show that the maximum points remain substantially unchanged for the lowest values of α (up to $\alpha = 0{,}50$ and beyond) while they tend to move slightly to the left, and therefore to anticipate the reaction, for values of α gradually higher.

As for the trend of free energy $G(\xi)$, this depends not only on entropy, but also on the enthalpy balance due to the difference between the quantity of heat gradually absorbed by the system to break the bonds that hold together the giver compounds and the amount of heat released as a consequence of the formation of the new bonds that hold the aggregates together. Consistently with the model, we assume that the quantity of thermal energy absorbed by the environment (with a positive sign) or dissipated in the environment (with a negative sign) as a consequence of the complete transformation of one mole of reactants into one mole of products is equal to ΔE.

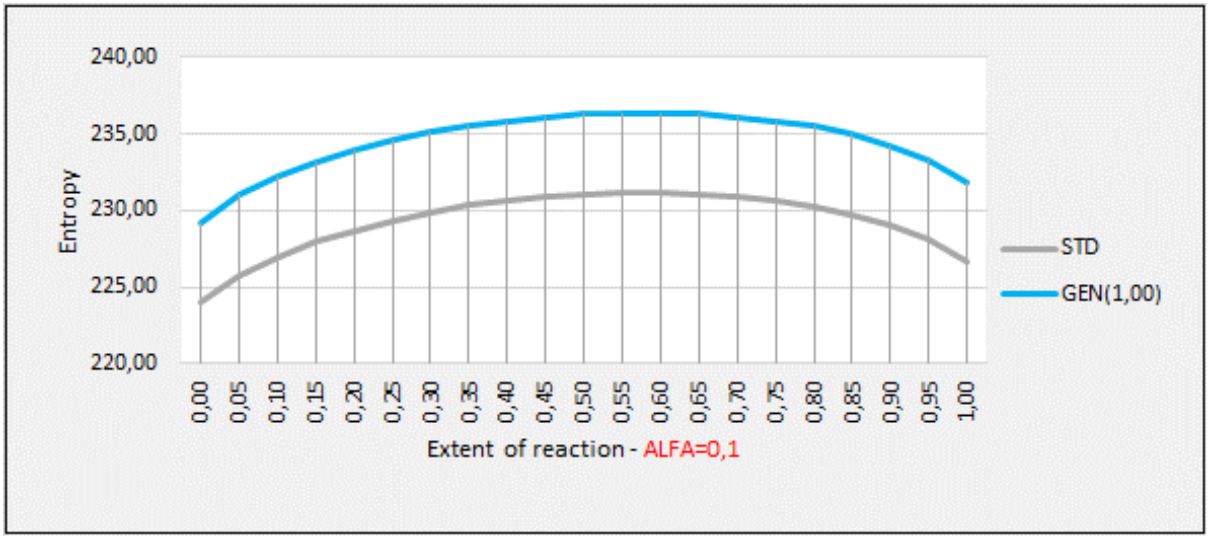

Figure 5/a. *Random aggregation: effect of the $GEN(1)$ condition on $S(\xi)$ for $\alpha = 0{,}1$*

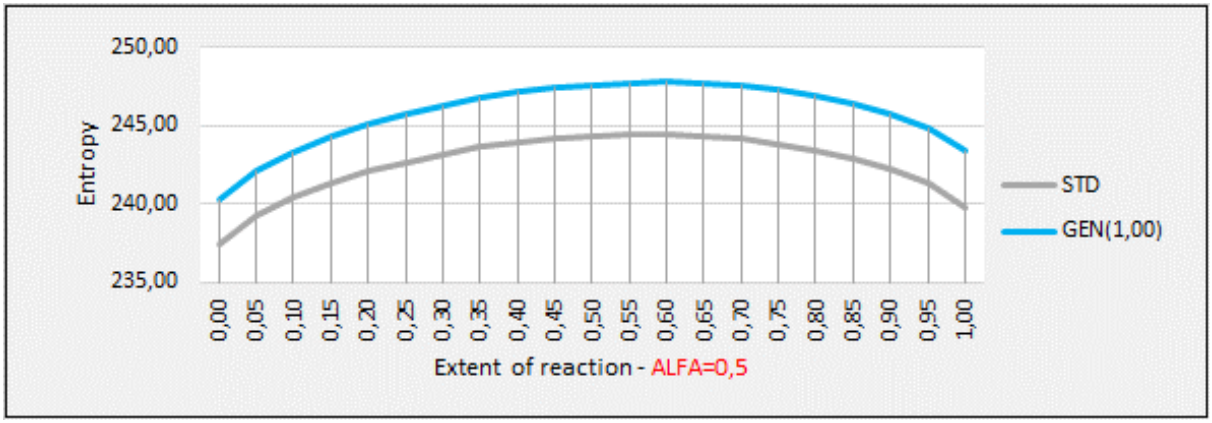

Figure 5/b. *Random aggregation: effect of the $GEN(1)$ condition on $S(\xi)$ for $\alpha = 0{,}5$*

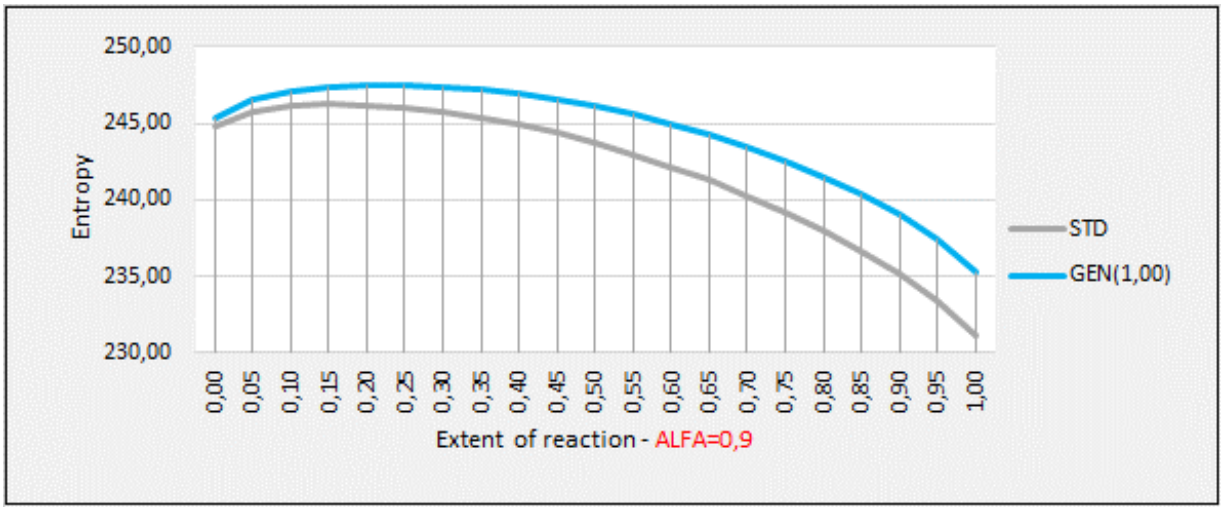

Figure 5/c. *Random aggregation: effect of the $GEN(1)$ condition on $S(\xi)$ for $\alpha = 0{,}9$*

Then, applying [9] and remembering that the Gibbs free energy in the course of the reaction is

$$G(\xi) = H(\xi) - TS(\xi)$$

calculations can be done. In particular, the graphs presented in Figs.6/a, 6/b and 6/c, representative of the model's response to the two hypotheses under comparison, show the results for the same values of ρ, h_O and h_{XO^*} assumed previously and for $\Delta E = -20$ KJoule/mole (weakly exothermic reaction).

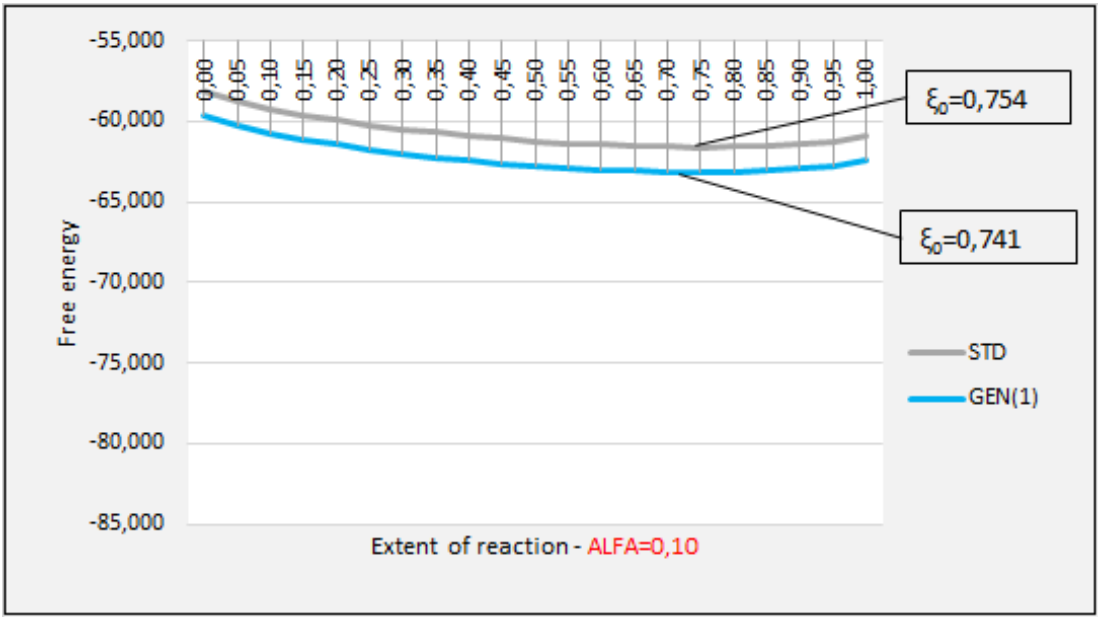

Figure 6/a. *Random aggregation: effect of $GEN(1)$ on $G(\xi)$ for $\alpha = 0{,}1$ $\Delta E = -20$ KJ/mole*

Figure 6/b. *Random aggregation: effect of $GEN(1)$ on $G(\xi)$ for $\alpha = 0{,}5$ $\Delta E = -20$ KJ/mole*

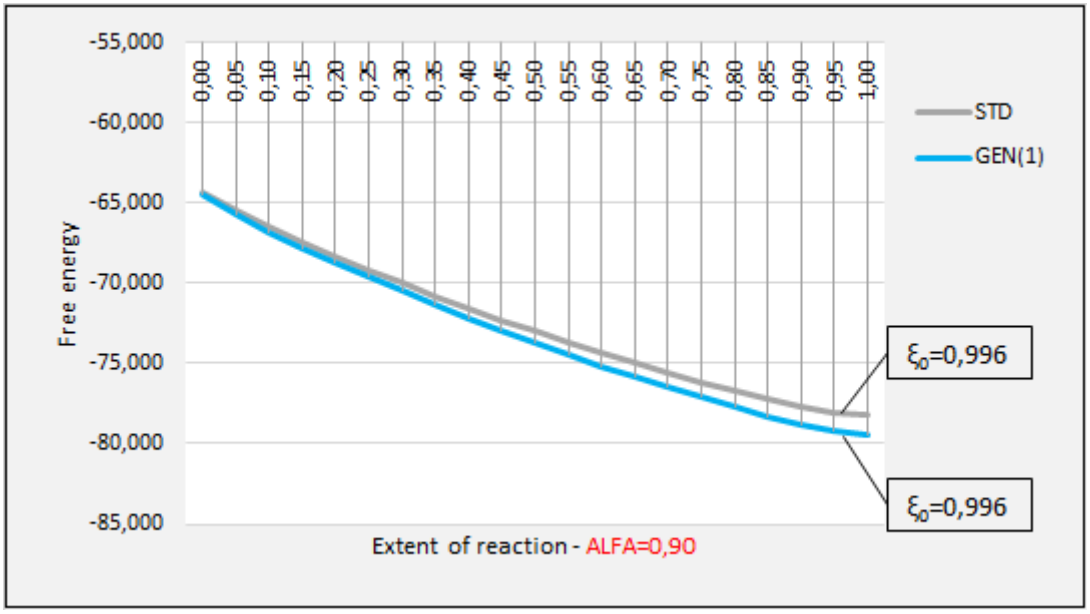

Figure 6/c. *Random aggregation: effect of $GEN(1)$ on $G(\xi)$ for $\alpha = 0{,}9$ $\Delta E = -20$ KJ/mole*

Note that the value of the energy balance ΔE chosen, in addition to being also reflected in the calculations already made in Ref.2, clearly highlights how the hypotheses affect the extent of reaction at the equilibrium ξ_0 in the case of incomplete reactions. By examining the graphs, the following information is obtained:

- the $GEN\ (1)$ condition very slightly modifies the absolute value of free energy during the reaction in comparison with the STD condition
- the differences between the two conditions tend to decrease with the increase of α: in particular, for high values of α the compared values of free energy are almost identical in the early stages of the reaction while they diverge slightly towards the end of the reaction
- the minimum points (extent of reaction at the equilibrium ξ_0)) change very little for the lowest values of α while they are substantially coincident for the highest values.

6. Effect of condition $G(q)$ on coded aggregations in closed systems

In the case of coded aggregative processes (both autopoietic and heteropoietic) the model assigns a value greater than zero to the *coding factor* η: the non-zero value of this parameter introduces elements of preferential orientation of the reactions into the system, so that the incidence of randomness[10] is progressively reduced until it disappears completely when $\eta = 1$. The factor η, in fact, impacts both on the entropy h_{MIX} of the descriptor of aggregates, and on the volume v_{MIX} of their allocation cell. With regard to the latter, the introduction of the $GEN(q)$ condition implies, consistently with the IdEP-IdLA model,[11] that [20/b] takes the form

$$lnv_{MIX} = lnv_{IdEP} + (q - \frac{9}{2})(1 - \alpha)\Sigma_{\eta}(\alpha) \qquad [22]$$

where:

[10] It should be remembered that $\eta = 0$ implies a totally random coupling mode between IdEPs while $\eta = 1$ excludes any margin of randomness in the aggregative process; in this case the reaction gives rise to products necessarily determined for quantity and quality: this is the so-called *compulsory assembly*.

[11] See paragraph 2 in Ref.2.

- $\Sigma_\eta(\alpha) = \Sigma_{min}(\alpha) + \eta[\Sigma_{max}(\alpha) - \Sigma_{min}(\alpha)]$
- $\Sigma_{min}(\alpha) = \Sigma_0(\alpha)$
- $\Sigma_{max}(\alpha) = ln\frac{1}{1-\alpha}$

Then, using [22] for the calculation of [7/d] it is possible to calculate, even in the case of the generalizations introduced, the entropy and free energy of the system during its codified transformation. As an example, Figs.7 and 8 propose the comparison between the entropy and free energy trends in the STD and $GEN(1)$ conditions for:

- the same values of ρ, h_O, h_{XO^*} and ΔE assumed previously
- $\alpha = 0{,}50$
- $\eta = 0{,}50$ and $1{,}00$

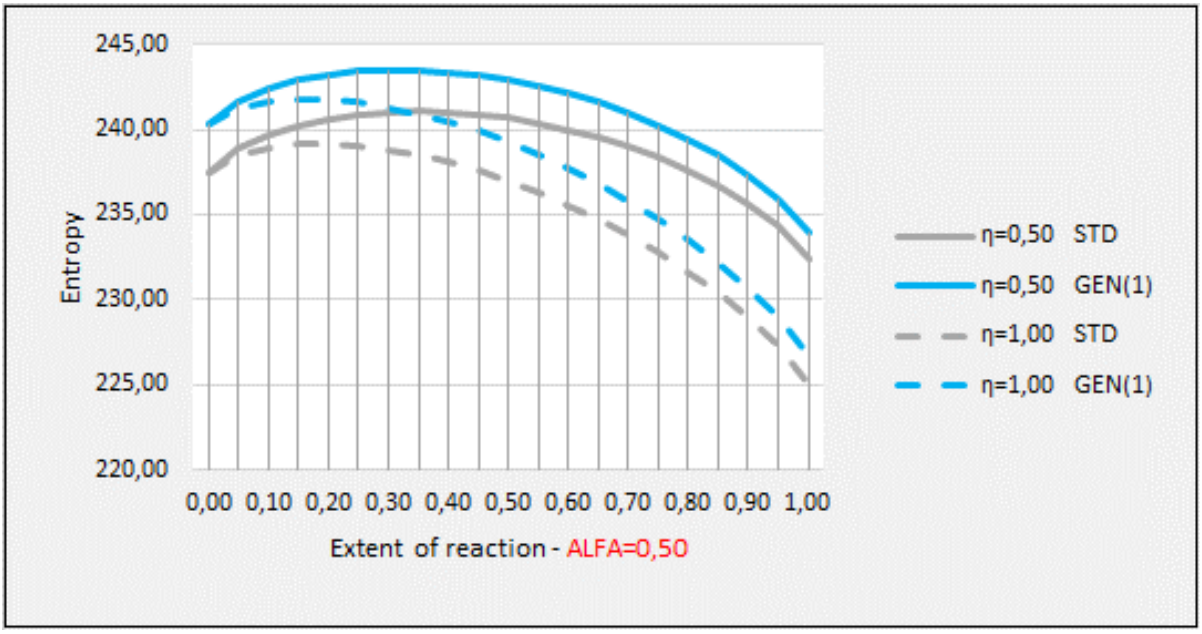

Figure 7. *Coded aggregation: effect of the $GEN(1)$ condition on $S(\xi)$ for $\alpha = 0{,}5$*

What is shown by the graphs proposed can be considered qualitatively representative of the response of the IdEP-IdLA model to the test. The examination of the results leads to the following conclusions:

- the $GEN(1)$ condition implies that the entropy always maintains slightly higher values than in the STD condition throughout the course of the reaction, even if the difference appreciably attenuates towards the end of the process; the maximum points are in advance of 0,03 for $\eta = 0{,}5$ and of 0,01 for $\eta = 0{,}9$
- the $GEN(1)$ condition implies that the internal energy maintains slightly lower values than in the STD condition during the entire course of the reaction: also in this case the difference is significantly attenuated towards the end of the process; the minimum points are in advance of 0,02 for $\eta = 0{,}5$ and of 0,04 for $\eta = 0{,}9$
- also with the generalizations introduced, what has already been highlighted in Ref.2 is confirmed; that is, as a rule, the higher the value of η the more the extent of reaction at the equilibrium is anticipated.

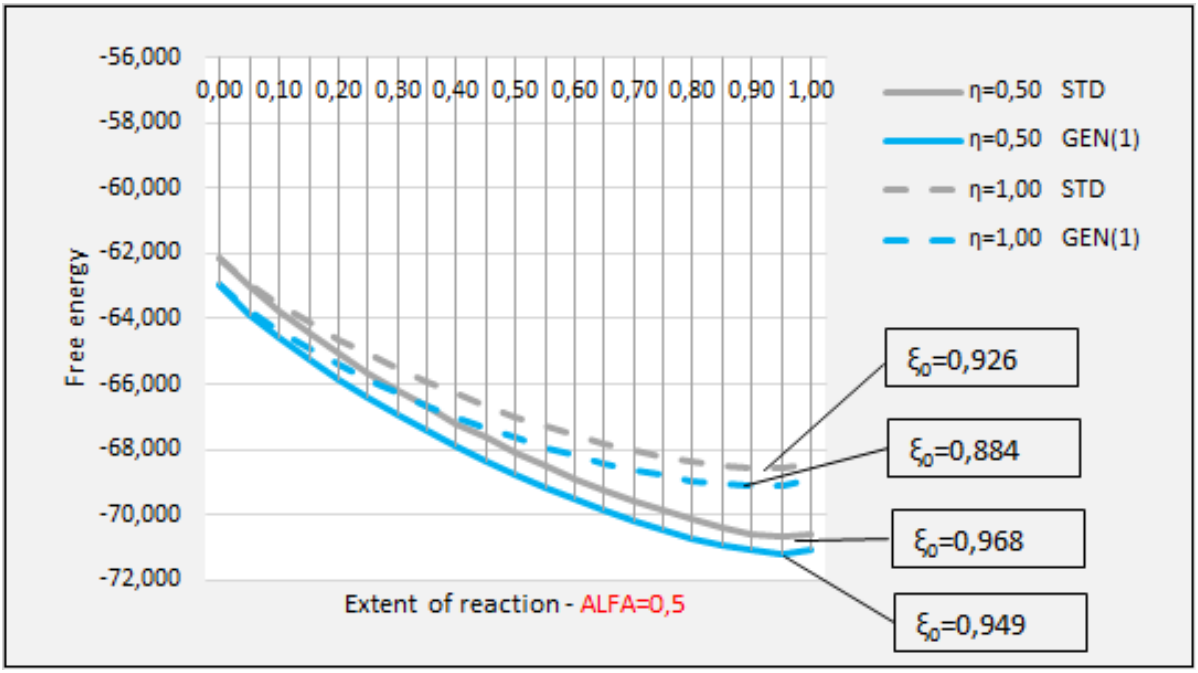

Figure 8. *Coded aggregation: effect of the $GEN(1)$ condition on $G(\xi)$ for $\alpha = 0{,}5$*

7. Reaction enthalpy, reaction entropy and reaction free energy in closed systems: effect of the condition $GEN(q)$

The determination of the extent of reaction at the equilibrium ξ_0 allows the calculation of the enthalpy variations (by means of [8]) and entropy variations (by means of [10]) which the system undergoes passing from the initial state to the state of equilibrium. The calculations show that even in the case of the generalizations introduced

- the reaction entropy ΔS_R always decreases with increasing η: the final system is more disordered than the initial one for low values of η and α while it tends to be more ordered for the higher values of these parameters
- the reaction enthalpy ΔH_R is appreciably affected by η only for low values of α: this is because when the concentration of the giver compounds is low, ξ_0 rapidly decreases with the increase of η. For the same reason, the more α approaches 1, the less ΔH_R is conditioned by η
- the reaction free energy ΔG_R decreases, in absolute value, as η increases: the coding factor pushes the system towards a final state characterized by a higher free energy value.

The table in Fig. 9 explains the results obtained under the reference conditions defined in the previous paragraph.

α	Condition	η=0				η=0,5				η=1			
		ξ_0	ΔS_R	ΔH_R	ΔG_R	ξ_0	ΔS_R	ΔH_R	ΔG_R	ξ_0	ΔS_R	ΔH_R	ΔG_R
0,10	STD	0,754	6,592	-1,508	-3,473	0,567	3,158	-1,134	-2,076	0,359	1,294	-0,718	-1,104
	GEN(1)	0,554	3,323	-1,108	-2,099	0,348	1,416	-0,696	-1,118	0,186	0,568	-0,372	-0,541
0,50	STD	0,987	2,843	-9,870	-10,718	0,968	-3,746	-9,680	-8,563	0,926	-9,352	-9,260	-6,472
	GEN(1)	0,978	1,877	-9,780	-10,340	0,949	-4,362	-9,490	-8,189	0,884	-9,166	-8,840	-6,107
0,90	STD	0,996	-13,389	-17,928	-13,936	0,992	-19,876	-17,856	-11,930	0,982	-25,954	-17,676	-9,938
	GEN(1)	0,996	-9,051	-17,928	-15,229	0,991	-15,500	-17,838	-13,217	0,980	-21,566	-17,640	-11,210

Figure 9. *Enthalpy, entropy and free energy of reaction: comparison of STD and GEN(1)* conditions for $\alpha = 0{,}5$

8. Addressing entropy in both closed and open aggregative systems

Consistent with the theory developed in Ref.2, coded aggregation can take place in two ways:

- according to an *autopoietic modality*, when the differences between the binding energies determine a preferential path of the couplings between IdEPs
- according to a *heteropoietic modality*, when the couplings between IdEPs are guided by agents external to the system, called *ordering agents*: these entities, which are not part of the reactants, are the custodians of the code that provides for the formation of the aggregates by imposing its law on the original autopoietic orientation of the system.

The heteropoietic modality, as defined above, finds confirmation in many processes of biological interest and takes place when the differences between the binding energies are very small. This would tend to leave ample room for random couplings, if the system were left free to evolve without other conditioning; but the presence of external elements, bearers of their own assembly code and capable of imposing it, forces the natural aggregative attitude of the system, producing compounds whose structure conforms to a different project.

The IdEP-IdLA model treats such a situation in the following way. We begin by hypothesizing a system characterized by an intrinsic condition (the complex of binding energies) which would spontaneously produce (in autopoietic mode) aggregates according to a process that can be characterized by a coding factor η_a (small, if not even zero). Immediately after, it is admitted that the system undergoes the external action of ordering agents that impose a more stringent coupling mode (heteropoietic mode), characterized by a coding factor $\eta_h > \eta_a$. It has been shown[12] that, with the same initial system, in the case of exothermic reactions the reaction enthalpy ΔH_R^h in heteropoietic mode can only be higher than the reaction enthalpy ΔH_R^a in autopoietic mode. That is, since the enthalpy of reaction is always negative

$$\left|\Delta H_R^h\right| < |\Delta H_R^a|$$

But, as seen in the previous paragraph, the condition $\eta_h > \eta_a$ also implies that it is

$\Delta S_R^h < \Delta S_R^a$ (the entropy of reaction being able to be both positive and negative)

$\left|\Delta G_R^h\right| < |\Delta G_R^a|$. (since the reaction free energy is always negative)

Therefore, even if the proposed generalizations are adopted the scheme of Fig. 10, already presented in Ref. 2, continues to be valid. From this it follows that the heteropoietic aggregative process can only take place if the activity of the ordering agents is accompanied by an energy dissipation that is at least a little higher than δh.[13] Indeed, only under this condition can the *addressing entropy* necessary for the entropic balance be produced.

$$\sigma = -\frac{\delta H}{T} > 0$$

[12] See paragraph 3 in Ref.2.

[13] See Fig.19 in Ref.2.

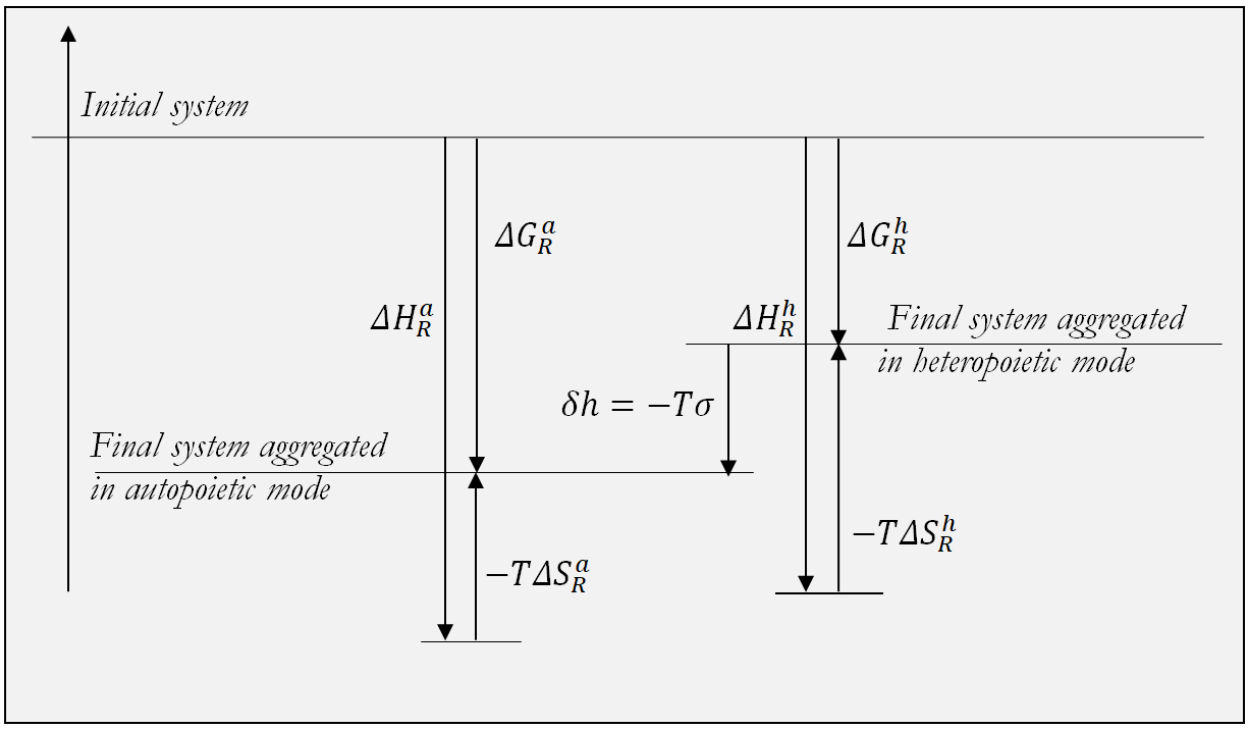

Figure 10. *Qualitative comparison between the energy development of the same system following autopoietic and heteropoietic aggregative processes.*

It must be said that this result is also to be considered valid for open systems in stationary conditions: in particular, the use of the $GEN(q)$ condition as an alternative to the already tested STD condition (Ref.3) is irrelevant as far as, close to equilibrium, the congruity of the model with the principle of the minimum entropy production is concerned. This because the condition $d_iS/dt = -d_eS/dt$ obviously disregards the logic with which the construction of the aggregates and therefore the modalities of entropy computation are defined.[14]

Not only. Since the study of the possible instability of an aggregative process far from equilibrium is managed by the model by stressing stationary systems by means of the *retro-equivalence postulate*,[15] not even the formation dynamics of the so-called dissipative structures,[16] studied in Ref. 3 in the STD condition, can in principle be considered altered by the adoption of the $GEN(q)$ condition.

Conclusions

The results presented demonstrate that the generalizations introduced do not substantially affect the conclusions reached in the context of previous studies. While remaining within the theoretical limits of a linear arrangement of particles, whatever the modalities in which the spatial structures of the aggregates are assumed to take shape, the IdEP-IdLA model provides coherent answers studies and confirms its ability to interpret correctly the thermodynamics of aggregative phenomena. The postulate of resilience is strengthened and this definitely goes in the direction of accrediting the results obtained with a very broad, if not completely general, validity. In particular, what is illustrated in Fig. 10 is validated in more general terms than in the past. Consequently, the Arianna's

[14] See [19] in Ref.3.

[15] See paragraph 3 in Ref.3.

[16] See chapter 19 in Ref.7.

conjecture discussed in Ref.4, which offers an innovative interpretation of the first emergence of life on Earth, is also corroborated

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