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Formal descriptions for formulation

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Abstract

Two formalisms used to describe the physical microstructure and the organization of formulated products are given. The first, called "complex disperse systems formalism" (CDS formalism) is useful for the description of the physical nature of disperse matter. The second, called "non periodical organizational space formalism" (NPOS formalism) has the same operators as the CDS formalism, but different elements; it is useful to describe the arrangement of any objects in space. Both formalisms can be viewed as the same, applied to different orders of magnitude for spatial size.

Keywords: Molecular gastronomy; Formalisms; Food; Disperse systems

1. Introduction

Food, drugs, cosmetics and other formulated products are generally complex chemical and physical systems (Dickinson, 2006; Cotte, 1992; Teisseire, 1991). They are generally composed of many parts, each made of different phases aqueous solution, gas, fats . . .), and their organoleptic (for food) or bioactive (for drugs) properties result from the spatial distribution of their molecules (Belitz and Grosch, 1999). Here we shall consider two formalisms used (1) for the description of the "matter" of their various parts, and (2) for the description of the organization of these parts in the full products. We shall see how these two formalisms can be mixed for a comprehensive description at any scale.

2. Matter description

Disperse systems (Hunter, 1986; Everett, 1988; Lyklema, 1991; Hiemnez, 1986; De Gennes, 1997; Jones, 2002) are frequent in food and drugs. For example, emulsions are known with this name since 1560, when the French surgeon Ambroise Paré (1509–1590) understood that white liquids like milk or cream were often composed of water and fat; he created the name "emulsion" after the Latin word *emulgere*, to draw milk (Trésor, 2006). The gel state was characterized in 1861 by Thomas Graham, who proposed a classification of different substances according to their "diffusive power" (Djabourov, 1988; Lehn, 1999). Famous physicists such as Michael Faraday or Albert Einstein contributed to the study of disperse systems (Everett, 1988; Atkins, 1998; De Gennes et al., 2002).

When more complex systems are considered (for example, multiple emulsions), physics generally focus on the interface, i.e. local descriptions of macroscopic systems, or on some thermodynamic properties (Israelachvili, 1992; Dickinson, 1994). However, this way of doing has two main disadvantages. First the global description of the systems is then lost. Then, in more complex – but familiar – systems, such as potato tissues or ice creams, the denomination are rather complicated. Potatoes, for example, are suspensions dispersed in gels, as amyloplasts (solid starch granules of size less 20 μm) (Bowes, 1998; Alvarez et al., 2002) are dispersed into the cytoplasm of cells (water or gel, depending on the description level), this phase being dispersed into the network of cell walls responsible for the "solid" behaviour of the whole potato (Fig. 1). Ice cream is another example of food complex system that should be called "multiple suspension/foam/emulsion", as gas (air) bubbles, ice crystals,

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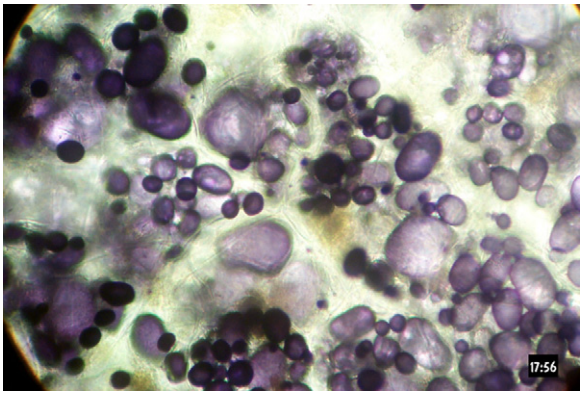

Fig. 1. Potato cells observed using optical microscopy. The starch granules were stained in blue using iodine (the size of the biggest is about 20 μm). (Potato micrography). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

proteins aggregates, sucrose crystals, fat (either crystals or liquid droplets), etc. (depending on the "recipes" and of the processes used) are dispersed in an aqueous solution (Sztehlo, 1994). On the other hand, the names "potato" or "ice cream" are probably not admissible names in physics textbook because they are imprecise and restricted to food.

This is why the same idea as the one put forward by the French chemist Antoine Laurent de Lavoisier (Paris, 1743 – id., 1794) was proposed at the 2002 *European Congress on Interface Science* (This, 2003). Lavoisier introduced the now classical formula in chemistry because he wanted to facilitate the description of molecules and chemical processes: "In order to better show the state of affairs, and to give directly, in one sight, the result of what goes on in metal dissolutions, I have constructed a special kind of formulas that look like algebra but that do not have the same purpose and that to not derive from the same principles: we are far away the time when chemistry will have the precision of mathematics, and I invite to consider that these formulas are notations whose object is to ease the operations of the mind" (Lavoisier, 1782).

2.1. CDS formalism

The same usefulness applies to this new formalism for complex disperse systems (CDS formalism), but the physical nature rather than the chemical composition is considered here. For food, where liquids are mostly water and mixtures of triacylglycerols, symbols G, O, W, S respectively stand for "gas", "oil", "water", "solid". As usual in soft matter science, "oil" is any lipophilic liquid, and "water" is any aqueous solution; of course, a symbol E (for ethanol) could be added if necessary (and in other fields than food, other symbols could be introduced).

The arrangement of the various phases can be geometrically or topologically described. As recommended by the IUPAC, @ symbol describes inclusion (topology): e.g. O@W applies to some oil phase included into a water phase. But physical chemistry also uses traditionally another symbol, "/", to describe the random dispersion of a large number of structures of one phase into another phase, such as in W/O (emulsion) (Hunter, 1986). And as many phases can be dispersed into another, the "+" symbol is needed to describe this, such as in (G + O)/W for an aerated emulsion, where water W is the continuous phase where gas G and oil O are dispersed. As for symbols, other connectors could be added if necessary to fully describe complex disperse systems, but up to now no addition was needed.

Some rules give more coherence to the formalism.

- The first one is to write the various components of a sum (+ symbol) in alphabetical order. For example, custard, with oil droplets (from milk), air bubbles (introduced during initial whipping of sugar and egg yolks) and small solid particles (due to egg coagulation during thermal processing) are to be described as (G + O + S)/W. This rule is the key to uniqueness of formulas associated to physical systems.
- Repetitions can be described by exponents. For example, egg yolks are made of concentric layers called light and deep yolk (Anton, 1998) deposited respectively during the day and the night; their number is about 9, as shown on ultrasound scan pictures (This, 2003). In such a case, as each layer is composed of granules (S) dispersed into a plasma (W), the full yolk could be described as $(S/W)^{@9}$.
- Another precision is to give the quantity of each phase as a subscript. For example, O_{200}/W_5 would describe oil into water emulsion with 200 g of oil and 5 g of water. Using such subscripts, conservation laws can be used and equations can be written, expressing these laws during transformations.
- As the size of structures is important, they can be indicated into brackets, such as in the emulsion O_{200} $[10^{-6}–10^{-5}]/W_5$, where the powers of ten indicates the minimum and maximum radii of dispersed oil droplets.
- At the end of formula, if necessary, the smallest structures considered can be given, as a "frequency cut-off", in brackets: the last brackets in a mayonnaise formula such as O $[10^{-5}, 10^{-4}]$/W $[d > 10^{-5}]$ show that the structures considered are larger than 10^{-5} m, i.e. that granules of egg yolk are not taken into account as their size is between 0.3 and 2 μm (Causeret et al., 1991). This particularity of the CDS formalism is a way to take into account with different formula the various scales in systems.
- Some simplifications can be done. For example, G/G or W/W are respectively equal to G or W.

Up to now, all food systems considered could be described using this formalism. But the reverse question can be asked: do all formula corresponds to possible systems? The question is difficult because many disperse systems are only metastable and not thermodynamically stable. In emulsions or in suspensions, for example, creaming and sedimentation rates depend on the size of structures or on the nature of surfactants (Atkins, 1990), but these systems are not stable. It is therefore a question of smartness to make these systems, or of kinetics, not of thermodynamics. Also the CDS formalism should be compared to the classic one used for phase diagrams in alloys (Prince, 1978; Lagrasso, 1996; Ferro and Saccone, 2004). It has the advantage to show clearly the physical structure of matter described, but primarily to limit

the description to a pertinent order of magnitude for sizes, due to the frequency cut-offs.

Indeed, many interesting systems based on the CDS formalism can be produced using a pump-driven microfluidic desk-top apparatus for automated continuous making of blends, emulsions, foams, and, where necessary, suspensions, at the example of simplified model systems in the context of low-viscosity food processing. After a principle that we proposed in 2002 (the arrangement in line and in parallel of many microreactors), such a device called a "pianocktail" (the name being given after a novel by the French writer Boris Vian) (Vian, 1947) was realized by Volker Hessel and his colleagues of the *Institut fur Mikrotechnik Mainz*. Using an 11-inlets system, more than 100 millions different systems can be achieved (Fig. 2) (Hessel et al., 2005).

2.2. Using formula

As in chemistry, describing objects is not the primary purpose of the CDS formalism; the main point is describing transformations (here physical transformations). For example, milk cream is primarily made of a fatty phase and a water phase (Burckheim and Djemek, 1990). It is sometimes described as "oil-in-water emulsion resulting from the concentration of milk", but this is not true, as part of the fat is solid at room temperature (Michalski et al., 2004); hence a formula such as (O + S)/W should be preferred to O/W, and the production of whipped cream could be described by the equation:

$$(O + S)/W + G \rightarrow G/[(O + S)/W] \quad (1)$$

Using CDS formula is one important key for innovation: in 1995 a new dish named "Chocolate Chantilly" was based on Eq. (1) (This, 1996). In practice, the making of such product is easy: first make a chocolate emulsion O/W by heating chocolate into a water phase (the proportion of chocolate and water has to be chosen so that the final fat/water ratio is about the same as the ratio in ordinary cream). Then whip (+G) at room temperature while the emulsion is cooling: after some time (some minutes, depending on the efficiency of the cooling), a "chocolate mousse" G/[(O + S)/W] is obtained. This mousse contains no eggs, contrary to traditional chocolate mousse (Larousse gastronomique, 1996) and the texture can be the same as in whipped cream. As whipped cream is called "Chantilly cream" when sugar is present, the name "chocolate Chantilly" was given to the new dish. Of course, the same equation holds when chocolate is replaced by cheese or foie gras, or even butter, leading to "cheese Chantilly", "foie gras Chantilly", or "butter Chantilly" (This, 2002).

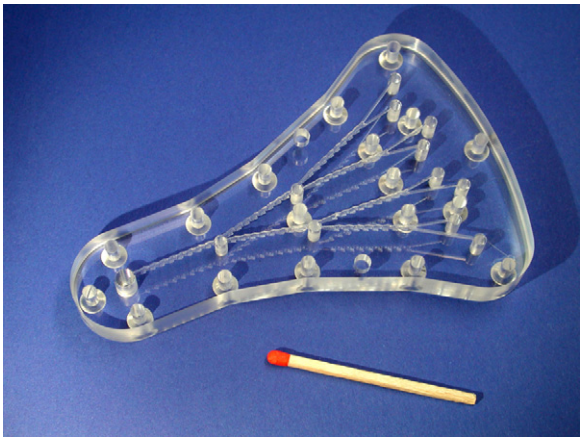

Fig. 2. The microreactor array at the core of the pianocktail: 11 inlets can be supplied with gas, liquid, granular solid phase. (Microreactor array for the pianocktail).

Another example shows how the uses of these formulas lead to new systems with both scientific and culinary interest. The formula O/W can be made with oil dispersed into water using surfactants. For example, if oil is whipped into egg white, the egg proteins can make a "mayonnaise without egg yolk", which is an emulsion oil-into-water (O/W). If, instead of egg white, oil (about 200 ml) is added to a solution of gelatine (5 ml water plus 0.5 g of gelatine), an O/W system is also obtained. In this second case, there is some slow limited coalescence (the mechanism of which remains to be studied) until the gel is set. Finally a jellified emulsion is made:

$$O/W \rightarrow (O/W)/S \quad (2)$$

The jellified emulsion that is made from water, gelatine and oil is a physical gel, i.e. a reversible system. Would it be possible to make a chemical gel trapping an emulsion? If an emulsion made from egg white and oil is heated (1 min, kitchen microwave oven, full power) so that some swelling of the emulsion is obtained, the temperature (100 °C) is above 61 °C where egg coagulation occurs (Vadehra and Nath, 1973), and a chemically jellified emulsion is obtained.

2.3. A wealth of new dishes

The easy invention of new complex disperse systems using the CDS formalism leads to new scientific questions. Let us consider any formula, with letters A, B, C ... K and symbols chosen as described above in the set {/, @, + ...}. For example: $((G + O + S_1)/W)/S_2$. Such a formula can lead to a new dish (but perhaps also a new drug system). Let us assume that the dish should have the taste of lobster. The cook could: (1) prepare a lobster flavoured oil by heating lobster shells in oil: O; (2) prepare a lobster purée by grinding lobster meat: S1; (3) prepare a lobster soup by cooking shells with onions, carrots, thyme, laurel, tomatoes ...: W; (4) disperse the purée S_1 and the oil O into the soup W with gelatine as a surfactant $(S_1 + O \rightarrow (S_1 + O)/W)$; (5) introduce some gas into the emulsion $((S_1 + O)/W) + G \rightarrow (S_1 + O + G)/W)$; (6) wait until the gelatine makes the gel $(((S_1 + O + G)/W \rightarrow (S_1 + O + G)/W)/S_2)$. A name was given to this particular new dish in 2002: it is "faraday of lobster", in honour of Michael Faraday (This, 2001). Of course, as the formula applies to many different products, "faradays" are a general class of dishes.

The number of possibilities is innumerable. It can be easily calculated that, using four phases and four connectors, the

number of formulas is 114,688, and more than 10^6 with six phases: there is plenty of room for innovation!

2.4. Application to sauces

As a demonstration of its usefulness in molecular gastronomy (This, 2002), this formalism was applied to French classical sauces as compiled from classic or official culinary books (Gringoire et al., 1901; Carême, 1847; Escoffier, 1901). This study was based on some observations using optical microscopy (frequency cut-off $d > 10^{-5}$) such as: (1) thermally treated plant samples dissociate so that cell aggregates (W/S) can be formed as well as individual cells (W@S); (2) culinary filtration does not dissociate small cell aggregates; (3) grinding animal or plant tissues disintegrate cells; (4) depending on the processing time, different results can be obtained when starch granules are heated in water, such as fully gelatinized granules (W/S), or partially gelatinized granules with a solid core (S@(W/S)).

Finally, 23 categories were found; in order of complexity, these categories were W, O, W/S, O/W, S/W, (O + S)/W, (W/S)/W, O + (W/S), (G + O)/W, (G + O + S)/W, (O + (W/S))/W, (S + (W/S))/W, ((W + S)/O)/S, (O + S + (W/S))/W, ((W/S) + (W@S))/W, (O + (W/S)/W)/S, ((O + (W/S))/W)/S, (O/W) + ((G + O)/W), (O + (W/S) + (W@S))/W,(S + (W/S) + (W@S))/W, (((W/S) + (W@S))/W)/S, (O + S + (W/S) + (W@S))/W, (O + S + ((G + O)/W))/W.

Some simple types are surprisingly missing. In particular, "foamed veloutés" ((G + (W/S))/W) are not difficult to produce practically, and it is a question of why such sauces were not "invented" by cooks of the past. This last question led to a separate study of the number of kinds of sauces in function of time. For this study, traditional French culinary books were used (Menon, 1755; Marin, 2001). The increasing number of types of sauces shows that culinary empiricism had probably not enough time to develop all kind of sauces (Fig. 3).

3. Describing the non-periodical organization of space

Whereas the CDS formalism describes the matter of which food and drugs (and more generally formulated products) are composed, these formulated products are frequently highly organized systems, made of many parts. Moreover, this organisation is frequently very important for flavour or bioactivity (Relkin et al., 2004). In order to get a full description of systems, another formalism seemed to be needed. As crystallographic descriptions apply only for periodical organization (Kettle, 1999), they cannot be used for the description of man made systems, which are often non-periodic in space or even irregular.

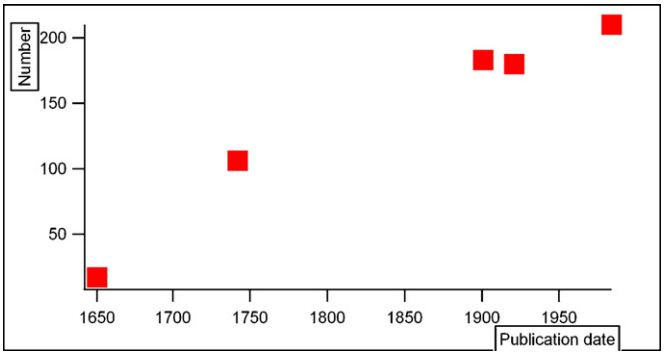

Fig. 3. The number of French sauces types in history. (Curve number of sauces types with time in history).

In order to give a full formal description of formulated products, the same idea as above (using "objects" and "connectors") was proposed. However, in the "non periodical space organization" formalism (NPSO), it was found useful to describe parts as objects of particular dimension: D_0, D_1, D_2, and D_3. D_0 stands for zero dimensional objects ("dots"), i.e. objects whose size in the three directions of space is more than one order of magnitude lower than the "reference size" (see below). D_1 stands for "lines" (with only one macroscopic dimension), D_2 for surfaces (with two macroscopic dimensions), D_3 for volumes. If necessary, D_x objects could be considered, x being non integer, and these objects being then fractals (Mandelbrot, 1982). Reference size has to be defined more precisely: for food systems, it would be the size of the plate, but more generally, reference size, being the scale where the full object is considered, can be added in brackets, when needed. For example, $D_1[10^{-5}]$ would indicate a linear structure whose length is of the order of magnitude of 10^{-5} m (and, accordingly, whose radius is more than one order of magnitude lower). The direction of sheets and fibres is sometimes usefully added, using the Cartesian equation in the same bracket.

Again the various objects D_k are included in formula using connectors: here again the connector @ represents inclusion; geometrical connectors such as σ_x, σ_y, σ_z represent respectively superposition in the direction x, y and z (but any particular direction could be given by the Cartesian coordinates of a vector, such as in (u, v, w), or even other coordinates systems such as $\{r, \theta, \varphi\}$ for spherical organisation). However, in many systems, some disorder has to be described, and this is why new connectors should be used instead. In particular, the/connector is again useful for the description the disordered accumulation of objects in space. Other connectors could be added when needed.

Using this new formalism, only topology is considered, and the geometrical shape of formulated products is not described: a square has the same "formula" as a disk.

4. Questions about using formalisms

As the two previous formalisms use the same operators, they can be mixed easily, in order to get a more precise description of formulated systems (the name "CDS/NPSO formalism" is proposed). For example, meat, being formed of aligned muscular fibres full of a jellified solution (Kopp, 1986) could be described as $D_{1,x}$(W)/D_3(S), if x represent one arbitrary direction. And an oil-into-water emulsion could be described by D_0(O)/D_3(W).

How helpful are these formalisms if they are applied to real biological structures, with a high level of complexity? First, the frequency cut-off property is a way to bring some order in the complexity of real systems, as it was shown with the "number of kinds of sauces" question. Then even when a complex object such as a living cell is considered, the fact that some

particular structures are detected with various observing tools demonstrates that the CDS/NPSO formalism applies. Of course, the description can be sometimes cumbersome, such as for the Golgi apparatus, for example, but the use of "random distribution operators" such as/is a way to get a description of such complex systems. Moreover, the number of connectors could be increased when new particulars cases are met (up to now, even in such complex fields as sauces, only the four connectors given above were useful).

Whatever will be the answer to this question, the "Graal" of all this field remains the prediction of the physical/biological/chemical/organoleptic properties of systems after their formula. This structure/activity question remains after years of study in the field of drug design, and there is certainly no easy solution. However, restricting the question to the first CDS formalism, some ideas can be proposed. First it would be helpful to get a variability of properties depending on some formula. For example, the viscosity of emulsions could be followed when the oil content or the droplet size distribution is changed. This could lead to a map in the multidimensional space of systems with regions describing systems of the same kind, regarding to this particular property.

Then the pianocktail could be used for this study in an automated way: if it is programmed in order to produce particular systems at regular time intervals, a conveying belt could bring these systems in an automated measurement device, in order to get rapidly a large data bank where relationship between formula and properties could be explored.

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