

Systemic Thermodynamics of Soil Water

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ABSTRACT

We show how the systemic approach to represent and model the internal and external organizations of the soil, which is an innovative way in pedology, could have led us to the definition of nested and hierarchical thermodynamic systems and subsystems. Specifically, we review systemic theory of the natural environment, in our case – the representative pedon (the smallest spatial unit in soil science) and its internal organization – namely: the soil horizons, their pedostructure with their two aqueous phases at thermodynamic equilibrium and, finally, the gas and the solid phases. Thereafter, we show how to further deepen the study of the soil hydrostructural properties – by adding two levels of the water molecule organization: both intramolecular – in relation to its atoms – and intermolecular – in relation to other water molecules of the aqueous phase under study. In thermodynamics of soil water, we show how the corrected Gibbs-Duhem equation explains not only results obtained solely by using the systemic approach – considering the Gibbs free energy constancy for each phase related to the solid phase – but also provides an explanation of why in such a case no external energy input or energy exchange should be necessary to ensure the chemical potential variation as a function of water content for each phase in soil. Specifically, we might explain the entropy production without energy exchange, which might be attributable to changes in the atomic vibration amplitudes compensated by the concomitant increases in their vibrational frequencies. Thus, the basic laws of thermodynamics do become apparently visualizable when the soil water evaporates in contact with the surrounding air – just up to the achievement of the pertinent thermodynamic equilibrium.

Key words: Systemic approach of soils, Hydrostructural pedology, Thermodynamics laws, Molecular and atomic organizational levels, Gibbs-Duhem equation, Systemic thermodynamic variables, Soil water pressure, chemical potential of soil water.

1. INTRODUCTION

1.1. An ancient subject put in the form of a thermodynamic equation

The primary natural elements known and viewed as such since ancient times are: *Fire, Earth, Air, Ether* and *Water*. The mixture of these five elements ought to form material bodies in their three aggregate states (Solid, Liquid, and Gas), which are existing at different *temperature* states (between cold and hot states) and different *humidity* states (between dry and wet states).

Noteworthy, in his book entitled "*The thermodynamics on the soil solutions*", Garrison Sposito, a renowned thermodynamicist, has used solely four out of the actual five primary elements (*Fire, Earth, Air, Water*) for establishing the successful expression of the fundamental Gibbs free energy equation under the conditions of temperature, pressure and humidity:

$$dG = -SdT + VdP + \mu_s dm_s + \mu_w dm_w + \mu_a dm_a \quad (1)$$

Apparently, physicochemical thermodynamicists followed the Great Revolution in Natural Science taken place between the end of the XIX-th and the beginning of the XX-th centuries. Remarkably, one of the brightest philosophic/methodological markers of this fruitful and seminal revolution is getting rid of the unintelligible Ether concept. In the French literature, e.g., Louis de Broglie could have highlighted this interesting drive by his stating: "*Any particle, ever isolated, has to be imagined as in continuous 'energetic contact' with a hidden medium*"^{*)}). Moreover, de Broglie had also pointed out that this '*medium*' "*could not serve as a universal reference medium, as this would be contrary to relativity theory*"^{*)}.

Philosophically, Einstein was interpreting the Hermann Minkowski's relativity theory just as a skillful approach to deal with the '*hidden medium*' deciphering the ancient Ether concept. Indeed, the skillfulness of Einstein's approach consists in implicit dealing with this unintelligible Ether concept: Specifically, if we do theoretically solve equations of motion for a huge number of microparticles, we may arrive at a number of particle trajectories to be largely non-interpretable within the framework of our presupposed theory. It is then OK to skip (or, *hide*) such mathematical solutions by declaring them 'physically relative'. Furthermore, Minkowski's theory might be useful in treating such parasitic (at the first glance!!!) solutions separately from the main theoretical frameworks, by formulating the pertinent 'relativistic' branches, suggests Einstein. This is just what Einstein has learned from Planck's bold suggestion to theoretically treat the unintelligible Entropy *S* in terms of a Probability *W*, in using the famous Boltzmann's formula $S = k \cdot \ln(W)$. If we may guarantee that the latter formula is correct, it is possible to treat the Entropy concept IMPLICITLY, without but any bother as for the actual physical sense of both the Entropy and the Probability. Planck's seminal result was to prove the full validity of the Boltzmann's formula by theoretically treating thermal irradiation of any material body within the framework of the "Energy Quantum" hypothesis.

The well-recognized over-all success of the above-sketched methodology does not prove that any other methodology would be sheer impossible. The actual depth of thermodynamics expressible by its basic Energy Conservation and Transformation Law was truly interesting for a lot of colleagues all over the world.

To stay reading French literature of that revolutionary time, we encounter a noticeable book by Gustave Marqfoy, *Loi des équivalents et théorie nouvelle de la chimie*, 1897. Nowadays, no one is knowing Gustave Marqfoy, 1831-1899, an educated engineer occupying a position of a provincial tax commissioner in Gironde. In his time of spare, Marqfoy was interested in the Basic Thermodynamic Law and its significance for the Natural Science as a whole, but in

^{*)} Annales de la Fondation Louis de Broglie, Volume 12, no. 4, 1987.

^{**)} Nicola Cufaro Petroni, Jean Pierre Vigier, *Dirac's Aether in Relativistic Quantum Mechanics, Foundations of Physics*, v. 13, pp. 253-286, 1983.

particular for Chemistry. Here, we would like to present our English translation of the relevant part of the concluding remark to his 1897 book:

PART XVII – SUMMARY

Below I summarize the conclusions of the work at hand:

I. – There has been Creation.

II. – Matter exists in Creation. It was created with pre-matter and pre-energy that preexisted.

III. – Pre-matter, or raw material of matter, is what we denote as ether.

The ether is an Essence, which ought to be manifestable by the mass existing in the state of maximum diffusion. Ether is capable of filling every void in space.

The pre-existing source of energy I would denote pre-energy, which here I am not talking about.

IV. – Using pre-matter and pre-energy, the Creator could have formed the Atom. Matter is therefore a sum of atoms.

Matter, likewise Essence, is unique, homogeneous, and identical to itself.

It is not infinitely divisible.

It is an agglomeration of atoms.

The divisibility of Matter ought to stop at the atomic level.

Therefore, the atom is the ultimately last limit of the smallness, beyond which Matter can no longer exist.

V. – The atom is composable of a massive nucleus formed by a concentration of ether, and of a kind of plasma surrounding this nucleus, which constitutes an energy storage.

Its shape might be likened to that of the plant or animal cell.

Taken itself, it is representable as a kind of mineral cell.

The atom, when it is armed with energy, does potentially contain the entire physical world.

The number of atoms ought to be indefinite.

The atom ought to be representable as bathing and/or moving in the ether.

The atom is impenetrable to the ether, whereas the ether ought to fill out the porous void of the atom. Such a representation ought to deserve further discussions. ...'

Would we now try translating the above utterances into the language of the modern physical chemistry, we do come to the following conclusion, which might irritate the adepts of de Broglie and his comrades-in-arms – without but losing its intrinsic eligibility:

Whereas the revolutionary stepping-down to microscopic atomic/molecular levels of the Matter does require principally novel physical theories, it is never wise to reject the Mathematical Physics in favor of the Physical Mathematics, because, mathematically seen, many-body problems ought to be intrinsically fuzzy owing to the Sorites Paradox. Surely, it is throughout OK to skillfully treat any concept, which is not immediately intelligible, in IMPLICIT way – and in such cases, we do need truly specific mathematical tools, we do need even to re-consider the very logical framework... The activities of such a kind do belong to the Physical Mathematics, whereas Mathematical Physics would then be looking for the proper mathematical tools to try solving physical problems with the help of EXPLICITLY representing all the physical concepts necessary for the solution.

Consequently, the above-mentioned sheer difference in treating the ancient Ether concept is reflecting the actual oppositeness in the methodological approaches. The systemic approach

we wish to discuss here is an attempt to tackle complicated problems in their EXPLICIT representation.

To discuss our approach, Eq. 1 is recast according to the theory of the time to obtain the thermodynamic potential $\Phi(T, P, m_s, \mu_w, \mu_a)$, which is more practical for interpreting physico-chemical experiments on soil water:

$$d\Phi = -SdT + VdP + \mu_s dm_s - m_w d\mu_w - m_a d\mu_a \quad (2)$$

The controlled variables of the derivative are: Temperature, Pressure, mass of solid, chemical potential of soil water, and chemical potential of air, respectively. "The potential F may be employed to describe thermodynamic processes in soil systems that contact thermal, volume, water, and air reservoirs" (Sposito, 1981, p.189) (1).

With the above methodological introduction in mind, we recognize that this equation, likewise other similar ones in thermodynamics, does allow neither accessing the expression for the matrix potential of soil water μ_w , nor revealing the exact relationship between μ_w and the soil water pressure h_w . Something is still missing in our understanding of natural phenomena, and we want to show here that it is the systems approach applied to the organization of the natural environment, including the soil at depth, which is the way to explicitly understand the thermodynamics of soil water. We show here that it is pedology, the science of the natural organization of soils, which has the possibility of solving the soil and water couple thermodynamics.

We remember the Sacred Text which tells us: "... *You see the inert and lifeless earth and, as soon as we bring down the water on it, it rises, it increases in volume and it germinates all kinds of couples of dazzling beauty*". (Koran, Surat 22, verse 5; trans. Dr. Salah Eddine Kechrid 1984).

1.2. The physics of water in the natural environment from the 1980s

The soil water thermodynamics ought to be the first entry to fundamental research about water in the natural environment. Big names in chemical thermodynamics were following one another until the 1980s, when the theory had seemingly become well-established and no-longer-evolvable.

Howbeit, the existing theory could still not properly explain certain experimental facts stressed by, e.g., such a physical chemist as P. Low (2-4), and certain questions remained unanswered. It was impossible to theoretically understand the difference between the osmotic pressure and the matrix potential, and we tended to confuse thermodynamic potentials with energy by mass. Furthermore, the dimensional products of such principal thermodynamic variables as temperature and entropy are still unknown, which prohibits any development of any discipline other than mathematics.

Then, from the 1990s on, colleagues performing fundamental research into the physics of soil water have abandoned the water thermodynamics in favor of hydrodynamics "in continuous porous media" assumed to be inert in regard to water and rigid. Thermodynamicists were no longer imposing the framework for modeling water in the soil, so that hydrologists or agro-pedologists were putting forward standpoints free from thermodynamics laws. They had introduced the concept of "Elementary Representative Volume" (REV) as a work hypothesis yet

contrary to the notion of soil organization in pedology. In fact, removing the role of the soil's solid-phase hierarchical structure from the soil-water modeling problem amounts to simultaneously excluding the pedology and thermodynamics from the physical modelling of natural processes (interaction of water with clay particles internal and external to the aggregates) (5). In addition, the naturalistic scientific discipline "pedology", which should have been most capable of pursuing fundamental research in modeling the soil-water interaction, was more and more beholden to oblivion – in striving after the ultimate arrival at its novel name of *Soil Science*.

It is against this principal opposition between soil scientists and hydrologists in regard to soil water modeling that Braudeau and Mohtar (6) have shown the need for a paradigm shift in the choice and definition of variables to describe the internal soil organization and its water behavior. The paradigm shift they have advocated consists in substituting the hydrologists' principle of REV by the (pedological) principle of SREV (Structural Representative Elementary Volume) to decisively orientate the soil water modelling toward the systemic approach taking into account the actual levels of soil's hydro-functional organization pedologists observe. It is the systemic approach that could have made it possible to reasonably combine both horizontal (soil mapping) and vertical description of the natural environmental organization at the scale of the *soil pedon*, with the latter representing a soil mapping unit. This is just a completely novel approach to studying the natural organization – valid not only in pedology but in the general systemology (systems science) as well – and giving rise to a new discipline in the Earth science, *Hydrostructural Pedology*, that has (systemic) links to all the available aspects of the hydro-agricultural environment (6, 7, 8).

Thanks to this conceptually new approach, the soil water thermodynamics might now be approachable from a different physical basics. We have established the thermodynamic equation for the soil water suction curve characteristic of the soil pedostructure. Recently, this could have led us to developing the physical model (9) for describing vibrational motion of the water molecules in the liquid and gaseous phases of the pedostructure at thermodynamic equilibrium state, by pursuing the works of thermodynamicists who follow Gibbs – but correcting some elements of their theory.

1.3. The basic problem facing the soil and water sciences: how to model the soil water interaction and dynamics?

In 1988, we have suggested a novel experimental approach in the Soil Science: the continuous measurement of the shrinkage curve (soil volume versus the water content) for soils deemed to be non-swelling, namely tropical ferruginous soils and ferralitic soils (10). Such curves are obtainable after the development of a continuous and very precise measuring apparatus for the shrinkage of a small soil sample (around 100 cm³) subjected to drying, in going from its saturated state to its dry state. The precision of the measurement does allow physical modeling of this curve apart from anything known nowadays and any current research project. These shrinkage curves do reveal two types of soil water occupying two poral spaces of very different hydrostructural behaviors, which renders it possible to distinguish and quantify them as belonging to the water in the '*inter-aggregate porosity*' state (we dub it *macro*) – and to the '*internal porosity*' water state within primary aggregates (we dub it *micro*) (11).

For the scientific community concerned, i.e., soil scientists, hydrologists and agronomists, the problem is to enrich the existing thermodynamic and hydrodynamic theories of the soil with these two types of soil water being different from each other by their position in the soil structure (5). However, previous theories (soil hydrodynamics, soil thermodynamics) could not forecast such a case. Only a single phase of liquid water was conceivable in modelling the water retention by the soil, with this phenomenon to be dependent on the pore radii and on the chemical content of dissolved ions (osmotic pressure). Rare were the thermodynamicists like P. Low (4) who questioned such concepts when trying to explain water suction by the soil.

Braudeau et al. (12) have kept “alive” this problem of the ‘*two types of water*’ by adapting Le Moigne’s systems modeling theory for description and modeling of soil organization both at the soil surface and deeply inside the soil. This way to associate two aspects in the same theory (the systemic approach) is completely new. This is how we may simultaneously treat the flat pedological cartography (cartography of soil units) and the pedological depth by describing and physically modeling the pedon^{+) with its nested sub-organizations (horizons, pedostructure, primary peds, sands, silts, clay). Among other benefits, this does help properly highlight the operational reality of the soil pedostructure and its two water types for mapping and modeling agronomic systems (8).}

The development of soil-water models reveals two competing methodological approaches that are incompatible: *the one* embodying the principle of REV (Representative Elementary Volume), which brings us to mono-scale modeling approaches of “black-box” type – and *the other* respecting the hydrostructural and hierarchical organization scales of the soil by employing the SREV concept instead, which enables our practicing systemic multi-scale physical modeling, thus seamlessly combining the local and the global modeling (6,7). Here, we quote the abstract of a groundbreaking article (7) fiercely contested by hydrologists^{§) – to outline principles and methodology adopted for characterization and systemic modeling of the soil mapping units described by their *representative pedons* – as well as by their *hydrostructural properties* (Figure 1).}

^{+) The pédon is the smallest spatial unit in soil science.}

^{§) Abstract of the work “A multi-scale “soil water structure” model based on the pedostructure concept”. February 2009, Hydrology and Earth System Sciences Discussions 6(1). DOI: 10.5194/hessd-6-1111-2009:}

“Current soil water models do not take into account the internal organization of the soil medium and, consequently, ignore the physical interaction between the water film at the surface of solids making the soil structure, and this structure. In that sense they empirically deal with the physical soil properties that are all generated from this soil water – structure interaction. As a result, the thermodynamic state of the soil water medium, which constitutes the local physical conditions, namely the pedo-climate, for biological and geo-chemical processes in soil, is not defined in these models. The omission of soil structure from soil characterization and modeling does not allow for coupling disciplinary models for these processes with soil water models. The objective of the article is to present a soil water structure model, Kamel®, which should be liable to open the deadlocks above-mentioned.

This computer model was developed based on a new paradigm in soil physics where the hierarchical soil structure is taken into account allowing for defining its thermodynamic properties. After a review of soil physics principles which forms the basis of the paradigm, we describe the basic relationships and functionality of the model. Kamel® runs with a set of 15 soil input parameters, the pedo-hydrate parameters, which are parameters of the physically-based equations of four soil characteristic curves that can be measured in the laboratory. For cases where some of these parameters are not available, we show how to estimate these parameters from commonly available soil information using published pedotransfer functions. A published field experimental study on the dynamics of the soil moisture profile following a pounding infiltration rainfall event was used as an example to demonstrate soil characterization and Kamel® simulations”.

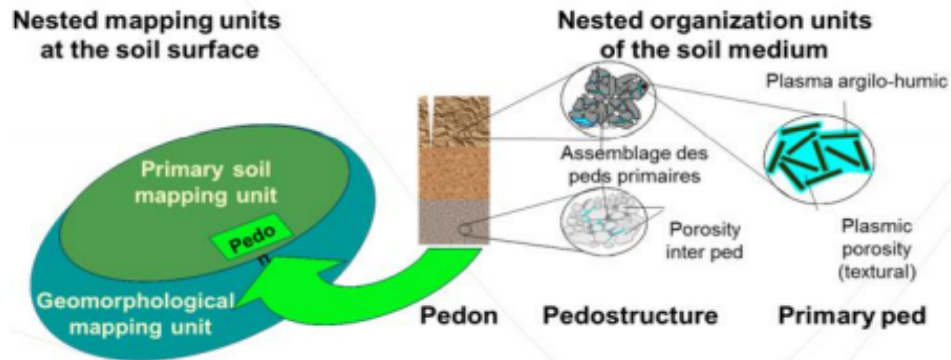


Figure 1: Schematic representation of the internal and external hydro-functional levels of the soil generally described qualitatively by the pedologist (taken from Braudeau & Mohtar, 2009).

The article (7), despite its openness toward trans-disciplinarity allowable by systemic approach in regard to soil and water sciences, has not been acceptable for publication in the hydrological journal affiliated to the discussion forum; this does clearly demonstrate the actual methodological break between the two disciplines. Nowadays, this break is still persisting while each discipline does have its well-defined niche in the field of physical systemic modelling the natural environment as shown in Figure (2).

2. GOING FROM THE SYSTEMIC PICTURE OF ENVIRONMENTAL MEDIUM TO THE WATER THERMODYNAMICS IN NATURAL SYSTEMS

2.1. Recognition of organizational scales and organized systems in pedology

2.1.1. Applying the General System Model (Le Moigne 1994) to Pedology

From the year 1999 on, we may start speaking about the characterization of the soil structure, and the new pedology field 'Hydrostructural Characterization' emerges – as a result of inventing the novel device for continuous measurements of the soil shrinkage curve – and formulating the physical model for the latter (13,14). Thus, the gradual paradigm shift toward the systemic approach begins. In 2001 the pioneering work "A pedological information system, the SIRS -Soils on the irrigated perimeter of Cébala-Borj-Touil (Lower Valley of the Majerda)" is published in a special issue of the Bulletin "Sols de Tunisie" of the "Direction des Sols" in Tunis. The book (12) defines and exposes the first concepts displayed in this novel paradigm, namely: *pedostructure*, *hydrostructural properties*, *systemic mapping of soils according to their hydrostructural properties*, *Soil-SRIS*¹. It is in the form of figures, that we do present below some basic theoretical principles of the "systemic approach" applied to the Pedology, as we could have defined it from the Le Moigne's "Model of the General System"(1994) (15); later on, we have theorized this "systemic approach applied to pedology" – just to create the fundamental methodological reference for the new discipline of earth sciences, "hydrostructural pedology" (16).

¹ SRIS-Soils : spatially referenced information system of soils, translation of SIRS-Sols : Système d'Information à Référence Spatiale sur les Sols.

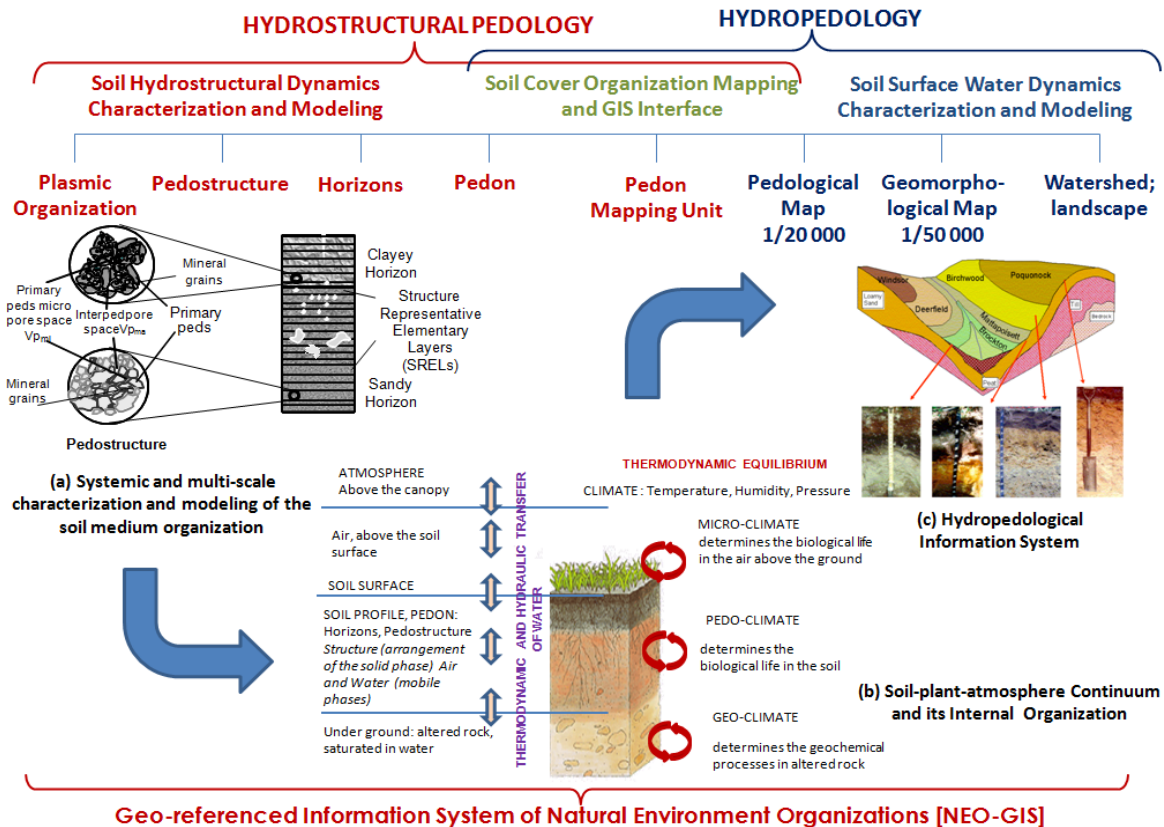


Figure 2: Hydrostructural pedology and Hydropedology, two “new” disciplines of earth sciences appearing in 2008-2009 (From EJAS Braudeau et al. 2018).

“The General System theory is the theory of modeling objects of any kind (natural, artificial, complex) using an artificial object gradually shaped by the human thought that L. von Bertalanffy does suggest dubbing ‘General System’. ... The General System theory is just the exposition of the modeling theory: the exposition of the General System’s coherent properties – i.e., a modeling tool”. (Le Moigne, 1994, p. 60).

Le Moigne (1994) has methodically described the General System – exhaustively defined as an active, stable object evolving in an environment and in relation to a finality – in the 3D reference frame, which is universal in the sense of systemic analysis: functional, ontological and genetic (cf. Fig. 3^s) for the relevant illustration of such an approach).

^s) Fig. 3 has been taken as is from the report of the Tunisian Soil Directorate, and this is why it is in French.

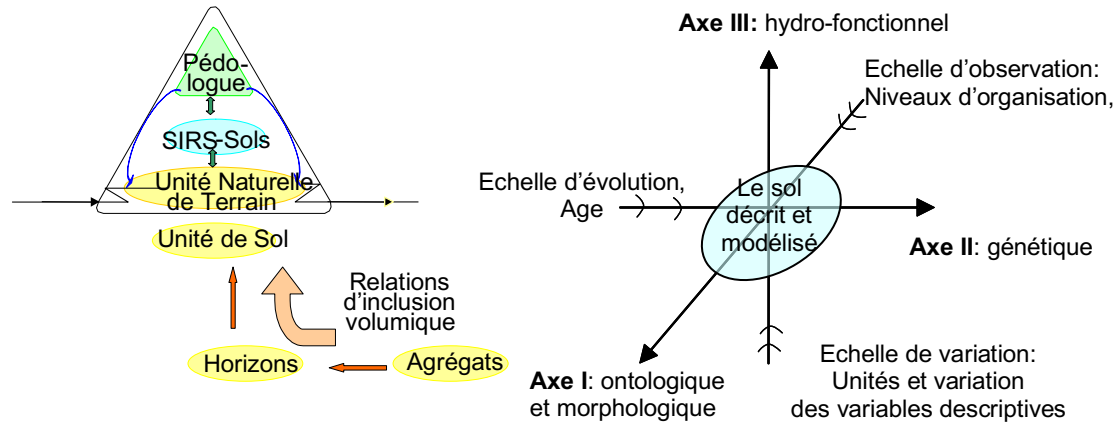


Figure 3: Description of the modeled object in a three-axis universal reference frame.

Important changes we have introduced into the Le Moigne's theory consist in the following:

- 1) the graduation of the three coordinate axes – just to recognize the organization levels on the morphological axis – the evolution stages on the evolution/genesis axis – as well as the parameters of the hydro-functional state variables.
- 2) the volume delimitation assignments to the *General System*, as well as to the three subsystems including the *Operating System (SO)*, the *Information System (SI)* and the *Piloting System (PS)*.

In fact, we cannot speak of any system without mentioning the delimitation of the nested systems and subsystems becoming recognizable after implementing the concept of SREV (Structural Representative Elementary Volume). There ought to be an obvious link with the notion of a large-scale thermodynamic system, but before arriving at these scale levels (pedostructure – plus its aqueous and solid phases) we would like to describe below the way to establish the “systemic” link between the anthropomorphous environment, that is, that arrangeable by humans – and the natural environment under the observation by pedologists.

The adequacy between the two environments, anthropomorphous and natural, is a problem debatable for a long time during studies of complex and multidisciplinary object-systems. It is this same question that interests us here but our reference to the General System model urges our limiting ourselves to the cases of anthropomorphous soil environments placed under a progressive spatialized management and covering several levels of scale: likewise, a regional, communal, etc. hydro-agricultural environment. This is just how we arrive at the case Fig. 4 depicts, where two environments are distinguishable from the outset – first, by their operating system organizations – and also as a result of their respective IS (Information Systems). Hence, the following two points might be observable:

- The transversal relationship (in the same medium) of a system operating from one level to another one (and therefore also from one SRIS to another) is a relationship of the strict spatial inclusion: that is, the knowledge of whether some level's intrinsic characteristics be applicable at the higher levels – plus the knowledge of how such characteristics be distributable at the latter levels.

- The information crossing between the two parallel information systems, that of the pedologist and that of the manager (Fig. 4), is achievable by crossing the basic units of the two systems: the soil unit for the former – and the plot for the latter.

This above observation is important because, in fact, we aim at carrying out our agronomic modelling on the basis of the SRIS information available and we address our attention exactly to the unit resulting from this cross-point {soil unit <-> plot}, i.e., to the unit qualifiable now as *agronomic*. Second, thanks to the *SRIS* at higher management levels (see Fig. 4^{s)} for schematic illustration), the modelling of agronomic units is easily integrated (exhaustive summation of areas) into simulations at the levels of higher scale to provide the desired estimates of production, accumulation and evolution of the management units georeferenced at these higher level scales. The reliability of the simulation results is therefore based upon the quality of the agronomic modeling the agronomic unit (soil unit <-> plot) depending on the quality of the hydrostructural modeling of the soil module (the soil unit) – and therefore on its proper delimitation and characterization (7).

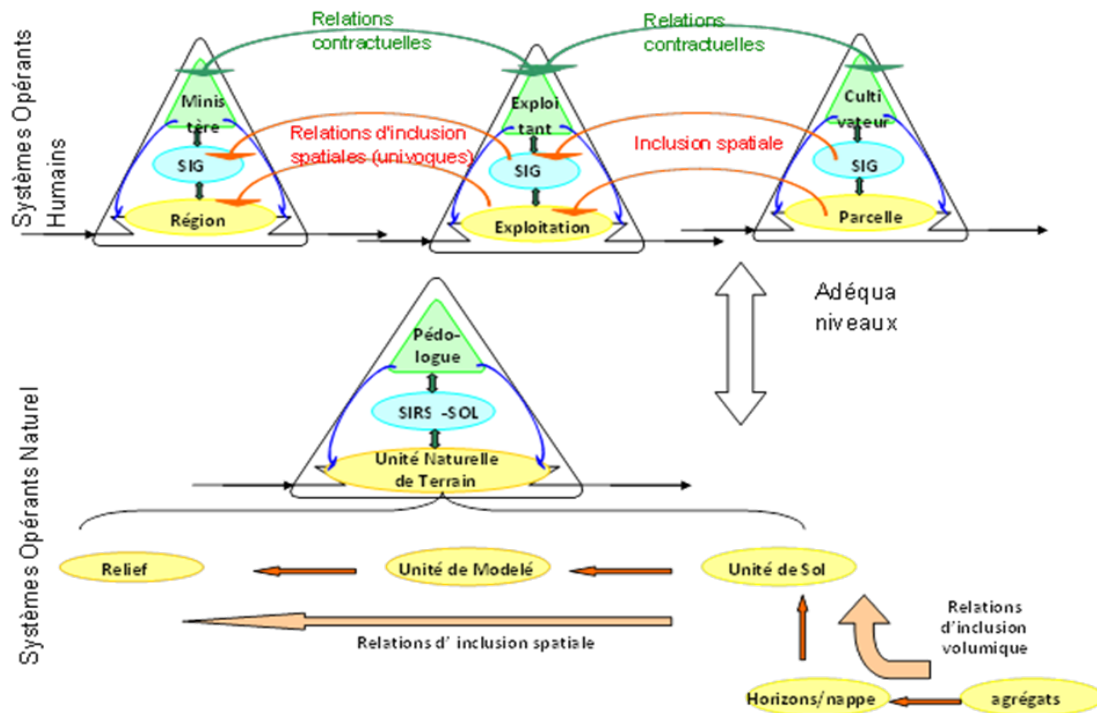


Figure 4: Operating systems of the natural and human environments; giving rise to, respectively, the Soil-SRIS and the GIS. The match between the different General Systems (scientific disciplines, managing systems ...) is between their respective Information Systems (Braudeau et al. 2001)

The above analysis reveals the qualities GIS (Geographic Information System) must possess for better discerning its usage as the medium for modeling information and decision support (simulations). To sum up, GIS must consist of the following features:

- GISs at the integrated management levels of the agricultural area.
- Soil-SRIS depicting nested levels of natural organization.

^{s)} Fig. 4 has been taken as is from the report of the Tunisian Soil Directorate, and this is why it is in French.

- a physical characterization of soil units, in regard to the internal levels of their organization and their hydrostructural properties.

2.1.2. The concept of "Structural Representative Elementary Volume" (SREV) necessary for the systemic description of the pedon

In fact, the SREV (6, 7) boils down a volume of the soil cutout representing the soil sample whose internal structure has been preserved (for the study). Thus, we cut out the integral structure, and the resulting mass should remain constant within the volume of thus cut-out. On the other hand, the liquid and air phases are not disturbed by this fictitious cutting – and they should continue to flow freely through it. As a result, we get a thermodynamic (since delimited) system closed in regard to its structure and freely open to the flow of water and gas. Consequently, we may consider an undisturbed sample taken from the soil horizon as a sample of this horizon's pedostructure, i.e., a tri-phasic medium made-up of an assembly of primary aggregates and possibly coarse particles (coarse sands, nodules, gravels, etc.) in variable quantities.

The particular properties of such a structural representative elementary volume (SREV) are as follows:

1°) Its delimitation is unambiguous: Once traced during the discretization of the medium, it would always envelop the same constant mass of solids making up the structure. Unlike REV, this envelope is therefore impermeable to the solid phase – while it is remaining permeable to the mobile liquid and gaseous phases available in such a structure.

2°) All the variables defined on a SREV are no longer related to the variable volume of the SREV but to the mass of the structural solid phase circumscribed in this volume. Unlike those of a REV, such variables are therefore physically defined in relation to the internal and hierarchical organization of the "ground environment". Thus, a SREV exemplifies a soil sample of the soil horizon's matrix medium.

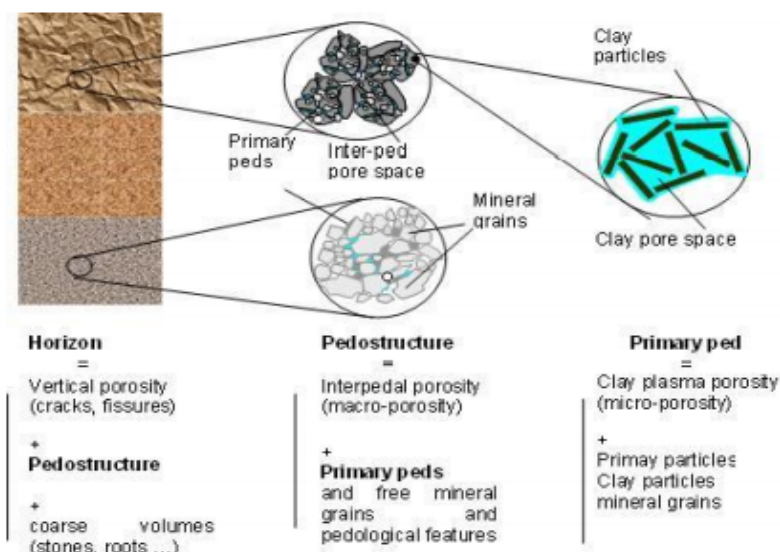


Figure 5: Schematic representation of the hydro-functional levels of a *pédon* generally described qualitatively by the pedologist (taken from Braudeau & Mohtar, 2009).

Such a possibility of transforming the medium-soil organization into a system thanks to the SREV concept ought to have a major consequence in soil physics, namely that the notions of structure and hierarchical organization of the “medium-soil” should henceforth be employable and explicable in the physical and thermodynamic equations of the soil-water models.

2.1.3. The internal organization of the pedon

Thanks to these two SREV notions and systemic description reference frame, pedon's hydrostructural functioning may now be describable and properly modelled in the ‘*three-description-axes*’ systemic paradigm (Fig. 3) – and, moreover, at the different organizational scales of the latter (7, 17).

The different levels of hydro-functional organization inside the soil and on its surface would be properly recognizable and definable on the axes I and III in their connection to each other. Therefore, pedological mapping for the recognition and characterization of soil units in the landscape should be expressible (see Figs 1,2) in connection with the internal organization and hydrostructural functioning of the representative pedon (cf. Fig. 5).

Generally speaking, the pedon modeled by the Kamel® computer model (7, 17) is the soil volume of 1 m² in area and 1m20 in depth, which is considered representative of the soil unit it belongs to. A visual observation on the terrain (soil pit) defines the horizons of the pedon distinguishable mainly by their structural morphology (type of structure, color, porosity, etc.). Using the SREV concept to define the systemic variables for the detailed description of pedon and its internal organization allows us to physically (non-empirically) model pedon's hydrostructural functioning at different levels of its nested organization observable in Fig. 5 (pedon, horizon, pedomorphology, primary aggregates). It is this hydrostructural modeling of the soil that Kamel® has performed and described in detail. Below we present the table of variables employable in such models:

Table 1: Systemic descriptive variables of the pedomorphology used in the Kamel model

Functional levels linked to the pedomorphology	Specific volume (dm ³ /kg)	Specific pore volume (dm ³ /kg)	Specific water content (kg/kg)	Soil water retention (kPa)	Hydraulic Conductivity (dm/s)	Non saturating water (kg/kg)	Saturating water (kg/kg)
Horizon SREV		$\overline{Vp}_{fiss}$	W_{fiss}	h_{fiss}	k_{fiss}		
Pedomorphology SREV	$\overline{V}_{ps}$		W_{ps}	h	k_{ps}		
Interpedal pore space		$\overline{Vp}_{ma}$	W_{ma}	h_{ma}	k_{ma}	w_{st}	w_{ip}
Primary peds		$\overline{Vp}_{mi}$	W_{mi}	h_{mi}	k_{mi}	w_{re}	w_{hs}
Primary particles	$\overline{V}_s$						

The Kamel® model equations have nothing to do with the mathematical statistics, whereas formatting their variables is systemic and physically definable. The model equations have practically gotten their current theoretical basis already in 2009 (7). Finally, slight corrections to them and their experimental confirmation using the specific device ‘Typosoil’² – have appeared in 2014. ‘Typosoil’ is unique on the market, because it is capable of simultaneously measuring both shrinkage curve and the suction curve for one and the same soil sample.

² Typosoil user manual for soil hydrostructural characterization. (pdf) *ResearchGate* doi: 10.13140/2.1.2605.3920

At the same time, the above activities could confirm applicability of theoretical systemic approach to tackling natural-environmental posers by pedologists – who could recognize the hierarchy of different hydro-functional organizational scales – both laterally in the landscape – and vertically in the soil (16).

Only one thing is remaining unresolved, which we could have theoretically solved in our most recent article (18) – namely, the water conductivity of the soil. The colleagues have long been studying theoretically this soil property, but they have always tended to describe it using empirical equations, whose parameter values become available via pedotransfer functions having unclear physical sense. We could have found the very exact form of the theoretical water conductivity equation; however, to access it, we had to redefine the relevant descriptive variables in the systemic way, while introducing two phenomenological scale levels for the water – the molecular and atomic one. In fact, this is just the organizational scale level, where *hydrodynamics* (molecular flow definition) and *thermodynamics* (dimensional definition of the analogous chemical potential at a squared speed) ought to seminally encounter each other.

Herewith, we would like to present the thermodynamic theory of soil water just as it emerges from both of our most recent review articles (9, 18).

2.2. Taking into account the levels of molecular and atomic organizations in the thermodynamic theory of soil water

2.2.1. The conceptual model of the energy distribution in a thermodynamic fluid phase

In 2020, we could have introduced the conceptual model establishing both molecular and atomic organizational levels for the two aqueous phases available in the pedostructure (9). This way, we may view all the conventional thermodynamic variables through their dimensional identities (dimensional products of space, time, mass and electric charge). As a result, we do get rid of the space fundamental ambiguity inherent in such principal thermodynamic variables as Temperature, Entropy, Pressure and Chemical Potential (to correctly decide whether these are extensive or intensive).

The basic premise is straightforward; there are two energy types distributed in the Euclidean: that of the atoms experiencing vibrations within molecules – and that of the molecules moving freely through their occupational space within the respective phases.

Therefore, a molecule, in any of the fluid phases, does basically carry two types of energy (Fig. 6):

- The *internal kinetic energy of the molecule “i”* in the *pedostructural fluid phase α* is the sum of the atomic vibrational energies, for which the expression and the dimensional product are, respectively:

$$E_{mi} = \frac{1}{2} M_w \omega^{-2} \lambda^2 \equiv ML^2 T^{-2} \quad (3)$$

with ω being a period and λ – an amplitude of an atomic vibration.

• The **external kinetic energy of a molecule “i” in the fluid phase α** is the molecular kinetic energy achievable in the intermolecular space of the fluid phase (via Brownian motion); hence, its expression and dimensional product are, respectively:

$$E_{mvi} = \frac{1}{2} M_w v^2 \equiv ML^2 T^{-2} \quad (4)$$

with v being the molecular velocity.

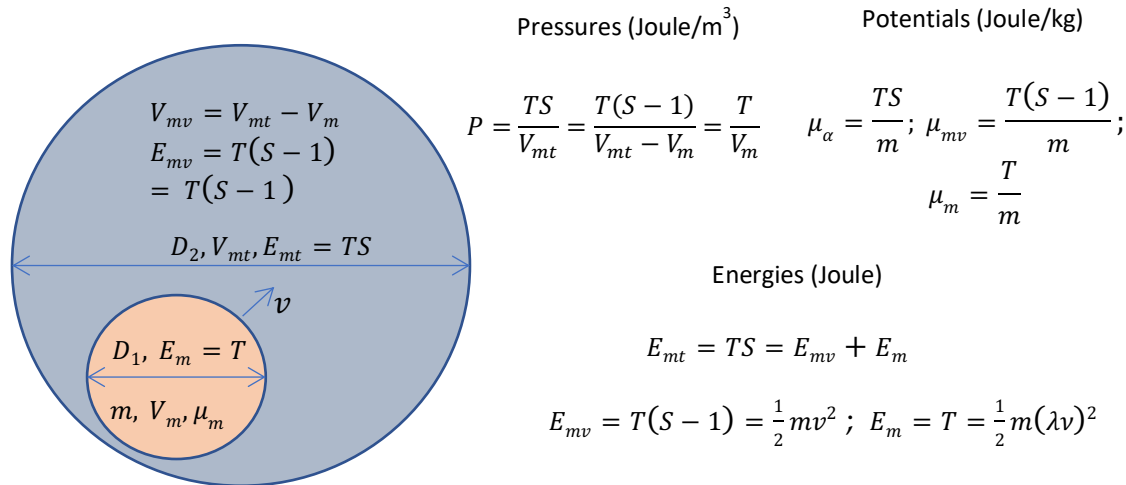


Figure 6: This depicts conceptual model of the thermodynamic equilibrium at the molecular scale, where v stands for the molecular velocity. Here, we see a molecule (in red), which has its own volume V_m . We do represent this molecule together with its immediate environment by a sphere of diameter D_2 (red + blue), which defines the occupational volume V_{mt} for our molecule in the phase. The external volume of the molecule (in blue) is $V_{mv} = V_{mt} - V_m$, the volume of its external energy. (Systems: Braudeau and Mohtar, 2020)

This is the first time to work with the molecular model for the organization of a natural thermodynamic fluid phase (the water apart of – or within the – soil). Hence, each point in the phase is correspondent to a molecule “i” having its primary characteristics: its internal energy $E_{mi} = T_i$, with T_i defining the pertinent temperature, its mass M_i , its internal energy volume V_{mi} , its total (internal and external) energy volume V_{ti} , and its entropy S_i . To sum up, each point in the fluid water medium should define the relevant values of:

The *water chemical potential*, at the atomic (or intramolecular) level:

$$\mu_{mw} = T_w/M_w - \text{and at the phase level: } \mu_\alpha = T_w S_w/M_w \quad (5)$$

The *water pressure*, at the atomic (or intramolecular) level:

$$P_{mw} = T_w/V_{mw} - \text{and at the phase level: } P_\alpha = T_w S_w/V_{tw} \quad (6)$$

Because P_{mw} and P_α should be equal everywhere within the phase at equilibrium, the *water pressure of the phase* reads:

$$P_w = T_w/V_{mw} = T_w S_w/V_{tw} = T_w(S_w - 1)/(V_{tw} - V_{mw}) \quad (7)$$

The *water density*, at intramolecular – and at the phase – levels:

$$\rho_{mw} = M_w/V_{mw} - \text{and } \rho_w = M_w/V_{tw} \quad (8)$$

2.2.2. The extensive, intensive, and pseudo-intensive nature of thermodynamic variables

Braudeau (2020) has shown that the intensive or extensive quality of thermodynamic variables might only be correctly definable at the *molecular* and *atomic* organizational levels of fluid phases. It is by considering *these two levels* of organization – the molecular level representable with some point “i” within the phase – and the over-all phase level formed by $\sum_i N_i$ constituent molecules – that we may properly grasp the difference between the intensive or extensive qualities of thermodynamic variables.

It is then straightforward to establish the actual relationship between the descriptive variables of one molecule representing one point of the phase – and the relevant molecular characteristics. Indeed, the intensive variable does keep the same value at any of the two scale levels (of the molecule and of the phase), whereas to characterize the entire phase, we must multiply the relevant extensive variable by the number of molecules of same species available within the phase.

Any intensive variable can only be a fractional number that follows the simple law of equal fractions: $\frac{a}{b} = \frac{c}{d} = \frac{a+c}{b+d}$. The mean of an extensive variable does have a physical meaning – whereas the mean of an intensive variable does not. This does explain why Gibbs' equations for thermodynamic potentials, where temperature is taken as an intensive variable, could not be suitable for hydrodynamicists, as we shall see later on.

We have shown (9) that variables such as *entropy* S_α , *pressure* P_α , *chemical potentials* μ_m and $\mu_{w\alpha}$ are truly **intensive**, so they have the same values at several organizational scales, whereas variables such as *temperature* $\bar{N}_i T_i$, *volumes* $\bar{N}_i V_{m_i}$ or $\bar{N}_i V_{t_i}$ and *mass* $\bar{N}_i M_i$ of the molecule “i” within the phase are **extensive***), where $\bar{N}_i$ is the *molar concentration* of the chemical species “i” in the phase, representing the value of $\bar{N}_i \mathcal{N}_a$ molecules ($\mathcal{N}_a$ stands for the Avogadro number).

The third case is that of **pseudo-intensive** variables: these are the molecular variables (or molar, but multiplied by the Avogadro's number), which we consider at their molecular level for the entire phase. At thermodynamical equilibrium state, such molecular descriptive variables as mass, volume, energy content, do have the same values for the same molecules (water, e.g.) within the entire phase.

*) Please note: Every conventional book on thermodynamics introduces Entropy as a ‘function of the state’ for a thermodynamic system, and considers it *extensive* – likewise, e.g., the system's volume. Entropy is then said to have corresponding intensive (*size-independent*) properties for pure materials only – and therefore – the corresponding intensive property should be *specific entropy*, which is the entropy per mass of the substance involved. But it is, in fact, a much more serious problem – to properly decide whether Entropy be intensive or extensive as it is... To sum up, if you treat Entropy IMPLICITLY – via the Boltzmann-Planck formula $S = k \cdot \ln(W)$, the above-sketched story is then fully correct. But EXPLICITLY seen, Entropy is just a sum of *Counteractions* in regard to *Actions* due to the relevant Driving/Livening Force (*Vis Viva*). But, in such a representation, Entropy should then surely be size-independent, i.e., intensive, likewise Time, which would be *size-dependent* solely within the conceptual frame of the so-called ‘*spatial-temporal continuum*’, which is but nothing more than a theoretically motivated ‘metaphysics’ having no immediately recognizable relationship to our Actual World... Howbeit, both *Pressure* and *Temperature* are conventionally representable as *intensive* variables.

For example, we have shown that μ_m , the molecular chemical potential of any molecule in the system, is intensive and should have the same value at any point of any fluid phase available in the system at equilibrium, regardless of the relevant molecular mass, i.e., whatever the type of the molecule – in whichever available phase – would be. We think that it is just this true intensive property of μ_m that may mistakenly be attributable to temperature, whereas we consider the latter to be *extensive* at the over-all phase level – but pseudo-intensive – if we do associate it with a molecule of any type at the corresponding molecular level of some phase under study.

This property makes it possible to take the *water temperature* as the reference temperature, because the water's molecular temperature has the same value everywhere in the system – according to:

$$T_w = \mu_m M_w \quad (9)$$

Thus, the variable T_w , the temperature of one mole of water taken at an equilibrium state, we should treat as a pseudo-intensive variable, if we consider it at the molecular scale of the phase, likewise the molar mass of water M_w as well as both the intra- and inter-molecular molar volumes, V_{mw} and V_{mvw} .

2.2.3. The three equivalent expressions for the Energy notion

The three types of molecular energy – *internal*, *external* and *total* – should necessarily stay in some relation among each other, which the intramolecular vibrations and the “shocks” or encounters with the surrounding molecules ought to ensure. The Brownian motion of molecules defines an average volume of the space occupied by each molecule according its mass. Entropy being the ratio of the occupational volume (total volume) of a molecule to its internal volume in the thermodynamic fluid phase, should then also be the ratio of the total molecular energy within the phase to its internal molecular energy.

Further, we could have shown that the total energy of the molecule is the product $T_w S_\alpha$ – where S_α is the entropy of the entire phase, which is equal to $S_w = \frac{V_{tw}}{V_{mw}} = \frac{V_{ti}}{V_{mi}}$. Therefore, at thermodynamic equilibrium, we have the equalities:

$$T_w S_w = T_w \frac{V_{wt}}{V_{wm}} = T_w \frac{V_{wt}}{V_{wm}} \frac{V_{wt}}{V_{wt}} = P_{wm} V_{wt} = P_{w\alpha} V_{wt} \quad (10)$$

knowing that $P_{wm} = \frac{T_w}{V_{wm}}$ and $P_{w\alpha} = \frac{T_w S_w}{V_{wt}}$

Dividing all the terms by the molecular mass of water we arrive at the following expression for the chemical potentials:

$$\frac{T_w S_w}{M_w} = \frac{P_{w\alpha} V_{wt}}{M_w} = \mu_{wm} S_w = \mu_{w\alpha} = \frac{P_{w\alpha}}{\rho_w} \quad (11)$$

Thus, at the molecular and atomic scale, we may cast the energy of the pedostructural aqueous phases under three different forms:

$$T_w S_w = P_{w\alpha} V_{wt} = \mu_{w\alpha} M_w \quad (12)$$

Therefore, the main result of our approach is the study of the pedostructural aqueous phases organization at the molecular level. Each term is formed by a couple of variables, the one of which is extensive, the next one associated with the number of molecules in consideration, and the final one is intensive, i.e., having the same value at any point of the phase – and hence for each molecule.

Multiplying each term of the equality (12) by $\bar{N}_{w\alpha}$, the molar number for the aqueous content's phase " α " in the soil system, we finally obtain:

$$\bar{N}_{w\alpha} T_w S_{w\alpha} = \bar{N}_{w\alpha} P_{w\alpha} V_{wt} = \bar{N}_{w\alpha} \mu_{w\alpha} M_w \quad (13)$$

whereas the following should then be true as well:

$$\bar{S}_{w\alpha} T_w = \bar{V}_{w\alpha} P_{w\alpha} = \bar{M}_{w\alpha} \mu_{w\alpha}$$

2.3. Corrections to and the use of Gibbs-Duhem equation for the potential determination of Gibbs free energy

2.3.1. Adopting the systemic approach to definition of thermodynamic natural systems, their subsystems and pertinently nested descriptive variables

Based on the above, we should still introduce some relevant corrections to the Gibbs' theory of thermodynamic potentials.

This consists in the way we understand the notion of thermodynamic system to properly employ the latter within the frame of systemic approach to hydrostructural pedology (Braudeau et al. 2016) – and the SREV principle – to model the soil water. Braudeau et al. 2009 and Braudeau et al. 2014 do introduce the methodology. It is a question of adopting the reality of the pedostructure and its systemic description, likewise that of the soil horizon and that of the pedon in pedology.

This renders it possible, firstly, to view the scale of the pedostructure as a hydro-functional organizational subsystem of the soil horizon, secondly, to consider the two aqueous phases in this subsystem with their internal systemic description variables valid for all the soil types – and, finally, to introduce the newly studied molecular and atomic levels.

Now, it is possible to apply the Euler equation for the Gibbs free energy to each of the two phases $\alpha \equiv$ (micro or macro) within the pedostructure, as Braudeau et al. (2014) have done to show that the free energies of the two phases are different and, remarkably, do not vary with the water content:

$$\bar{E}_{tw\alpha} = \mu_{w\alpha} W_\alpha = cte - \text{and } \mu_{w\alpha} = \frac{\bar{E}_{tw\alpha}}{W_\alpha} \quad (14)$$

for each phase available in the pedostructure.

We may introduce the notion of *soil water retention pressure* to describe the internal pressure of the aqueous phase within the soil, which does maintain the thermodynamic equilibrium between the two aqueous phases of the pedostructure, when the water content is changing. Such a notion is in effect directly expressible by the Gibbs-Duhem equation – just as Braudeau (2020) could have shown (9), and this fact we will recall hereafter. Meanwhile, since the notion of *internal pressure of the liquid phase* does not exist explicitly in the Gibbs theory of

thermodynamic potentials, and its 'system' notion is also different, the Gibbs-Duhem equation must be corrected as follows, according to our definitions and terminology:

$$\bar{S}_{w\alpha}dT_w + \bar{V}_{mt_{w\alpha}}dP_{w\alpha} - W_{\alpha}d\mu_{w\alpha} = 0 \quad (15)$$

where $\bar{S}_{w\alpha} = \bar{N}_{w\alpha}S_{\alpha} = \frac{\bar{V}_{mt}}{V_m}$ - holds, remarkably, under the condition that V_{mt_w} depends on T_w only.

2.3.2. Using the Gibbs-Duhem equation for the physical modeling of the water in soil

Using the Eulerian form of the Gibbs free energy : $\bar{G}_{w\alpha} = \mu_{w\alpha}W_{\alpha}$, we obtain directly from (15) the exact total differential of $\bar{G}_{w\alpha}$:

$$d\bar{G}_{w\alpha} = \bar{S}_{w\alpha}dT_w + \bar{V}_{mt_{w\alpha}}dP_{w\alpha} + \mu_{w\alpha}dW_{\alpha} \quad (16)$$

From equation (15) we deduce the relation between the soil water pressure $P_{w\alpha}$ and the soil water chemical potential $\mu_{w\alpha}$, at constant temperature T_w , for which $\rho_w = cte$:

$$dP_{w\alpha} = \rho_w d\mu_{w\alpha} \quad (17)$$

After integrating (16) between the aqueous states W_{α} and $W_{\alpha Sat}$, we arrive at the expression for the soil water retention pressure h

$$h = P_{w\alpha} - P_{w\alpha Sat} = \rho_w(\mu_{w\alpha} - \mu_{w\alpha Sat}) \quad (18)$$

This soil water retention pressure h must be equal in the two phases of the pedostructure ($\alpha \equiv macro$ or $micro$), so that Braudeau et al. (2014) have obtained the following expression (19):

$$h = h_{ma} = h_{mi} = P_{w\alpha} - P_{w\alpha Sat} = \rho_w(\mu_{w\alpha} - \mu_{w\alpha Sat}) \quad (19)$$

and, according to equation (14), we arrive at the exact thermodynamic relationship between the water content for this or that of both aqueous phases within the pedostructure - and the water retention pressure reads as follows:

$$h = h_{ma} = h_{mi} = \rho_w \bar{E}_{ma} \left(\frac{1}{W_{ma}} - \frac{1}{W_{ma Sat}} \right) = \rho_w \bar{E}_{mi} \left(\frac{1}{W_{mi}} - \frac{1}{W_{mi Sat}} \right) \quad (20)$$

Finally, Eq. 20 allows us to calculate the two water contents W_{ma} and W_{mi} as a function of the total water content W by solving the quadratic equation (19).

This result owes nothing to statistics, since we obtain three absolutely identical $h_{ma}(W_{ma})$, $h_{mi}(W_{mi})$ and $h(W)$ curves reproducing the experimental curve measured continuously at more than 99% of accuracy. The link with thermodynamics would never have been understandable without applying the systemic approach as a framework for interpreting the relevant physical data.

Let us now look at the impact of this result upon the significance of Eq. 14 at the molecular level.

2.3.3. Meaning of the equation $\bar{E}_{tw\alpha} = \mu_{w\alpha}W_{\alpha} = cte$ at the molecular level

The systemic approach we use to define the variables makes it easy to move from one scale level onto another, with all the relevant hydro-functional scale levels being defined and representable down to the atomic scale. This allows us to interpret the results even much more precisely:

The only variables changing at some constant T are:

- $\bar{N}_{w\alpha}$ and, consequently, the extensive variables of the phase: $\bar{V}_{w\alpha}$, and $\bar{M}_{w\alpha} = W_\alpha$
- V_m – the only pseudo-intensive variable – and the intensive variables depending upon it:

$$P_\alpha = \frac{T}{V_m}, S_\alpha = \frac{V_{mt}}{V_m} \text{ – and – } \mu_{w\alpha} = \frac{T_w}{M_w} \frac{V_{mt}}{V_m} = \frac{P_{w\alpha}}{\rho_w} \quad (21)$$

Finally, we may draw the conclusion that what we dub ‘pressure’, ‘soil suction’ etc., should be a variation of the energy density concentration attributable to a single water molecule – as compared to the saturated state. Such a volume concentration variation is not due to any increase or decrease in the energy itself, as we would normally interpret this, but to decreases or increases in the volume enveloping this energy portion, i.e., in fact, in the molecular volume. The interpretation we give to the increase in $h_\alpha = P_{w\alpha} - P_{w\alpha^\circ} = \rho_w(\mu_{w\alpha} - \mu_{w\alpha^\circ})$ – just as the water content decreases – ought to be as follows:

In 2014, Braudeau et al. (19) have observed experimentally that $\bar{G}_{w\alpha} = \bar{E}_{w\alpha} = \mu_{w\alpha}W_\alpha = \text{cte}$ at constant temperature (except for the sign)

- 1) The explanation given at that time has been that the surface charges of the clay particles, which constitute the organized structure of the solid phase, retain their relative positions during any variation in the water content of the phase: the energies the water molecules gain by interacting to these surface charges do remain constant and well differentiated – both inside the primary peds: E_{wmi} – and outside them: E_{wma} .
- 2) When there is a decrease in the water content (W_α), the water suction increases – and so does its chemical potential. Howbeit, this volume (or mass) concentration of the phase energy ($P_{w\alpha}$ or $\mu_{w\alpha}$) increases – if the water molecule’s volume (V_m) decreases at some constant over-all volume (V_{mt}).

This variation in molecular volume as a function of decrease in the water layer above the clay plates, while the temperature remains constant, has only one possible explanation: the energy of the intramolecular vibrations should have two parameters: *the frequency* ν and *the amplitude* λ . Now, we recall that the molecular volume is equal to the sum of the relevant atomic volumes – as the molecular temperature should be the sum of the relevant atomic internal energies. But what atoms and the parent molecule do have in common ought to be the chemical potential $\mu_m = \frac{T_j}{M_j} = \frac{T_i}{M_i}$, which might thus deliver the very realistic criterion of thermodynamic equilibrium in the system. An increase in the suction pressure $P_{w\alpha}$ at constant temperature T_i would indicate a decrease in the molecular volume V_m , which should then result in the amplitude (λ) decrease accompanied by an increase in the molecular vibrational frequency (ν), so that the internal energy ($T_i = \sum T_j$) remains constant. The thinner the water layer gets at the surface of the clays – and the more water molecules approach the fixed surface charges of the clays – the more the molecular volume decreases owing to atomic vibrations, whereas the corresponding vibrational frequency increases. Contrariwise, the external molecular volume of the same molecule $V_{mv} = V_{mt} - V_m$ should still increase by the same amount, just as V_m decreases, which results in the increase of the volume V_{mv} **and a decrease in the shocks’ frequency – along with the maintenance of the velocity ν – and of the relevant kinetic energy.**

3. HOW WE SHOULD UNDERSTAND THE HEAT NATURE – AND THE NOTIONS OF REVERSIBLE AND IRREVERSIBLE PROCESSES.

3.1. Explicit formulation of the two thermodynamics laws

The molecular Brownian motion defines the average volume in the space occupied by the molecule, and we dub it V_t . In accordance with the first principle of thermodynamics, the two forms of energy, i) the atomic energy within the molecular volume and ii) the kinetic energy of the molecular Brownian motion are equivalent. According to the 1st principle of thermodynamics we may then state that the global energy of the molecule E_{mt_i} ought to be the product TS , where S is entropy, which should here be equal to $S_\alpha = \frac{V_{mt_i}}{V_{m_i}}$ at the molecular level

– and we do arrive at the following relation:

$$E_{mt_i} = T_i S_i = T_i \frac{V_{mt_i}}{V_{m_i}}. \quad (22)$$

Therefore, at the molecular level, we have, $d(TS) = TdS$ at constant T ($SdT = 0$), which is the heat “irreversibly exchanged” – just as the founders of thermodynamics dictate:

$$\delta Q_{irr} = TdS \text{ at } T \text{ constant.} \quad (23)$$

But in the Carnot cycle, where we should necessarily have temperature variations, if $Q = TS$, then what should be the meaning of the other term of the full differential dQ : $\delta Q = SdT$ at S constant?

According to Romani³ (Volume I, p. 68, 1975), the full differential would consist of the heat amount being (supposedly) irreversibly exchanged at T constant: $\delta Q_{irr} = TdS$ – and the heat amount (supposedly) reversibly exchanged at S constant: $\delta Q_{rev} = SdT$, with the term $Q = TS$ representing then the Total Energy, which is constant, just in accord with the 1st principle of thermodynamics⁴).

Indeed, by deriving the energy equation using what we know from its terms, we obtain:

$$d(TS) = TdS + SdT = Td\left(\frac{V_t}{V_m}\right) + SdT = \frac{T}{V_m}dV_t - \frac{TV_t}{V_m}d\ln V_m + SdT \quad (24)$$

³ Lucien Romani, French physicist engineer, inventor of the “absolute dimensional analysis” in the 1970s, the author of “Théorie générale de l'univers physique” (reduction to kinematics) 1975; Volume 1: principles and methods, plus Volume 2: Applications; Albert Blanchard Bookstore. He supports the thesis that the Ether is a perfect fluid, constituting all particles starting with the electron and the positron (its antiparticle), which should be considerable the perfect Ether vortex rings.

⁴) Please note: The cycle Carnot has introduced nicely represents an ingenious theoretical model to prove that SOMETHING does render the *Perpetuum Mobile impossible*. On the other hand, this cycle is a nice example of *theoretically motivated metaphysics*. In fact, the heat machine behind this cycle has *no friction*, as well as none of any possible hindrances/obstacles/resistances of any other realistic sort. Remarkably, but the *very cyclicity* of this heat device’s *working chart* should also be viewable as a pure idealism – because NOTHING IS to 100% PERFECTLY REVERSIBLE in our Universe. The problem Carnot had posed – and successfully solved – in going his purely logical way, without using any mathematical tools, was to prove that SOMETHING REALISTIC should but *render any Perpetuum Mobile a Mission Impossible*. To persuasively demonstrate this – Carnot could estimate the efficiency coefficient for his purely ideal heat device having its ideal cyclic working chart, which we should be actually expecting to become equal to 100%. Carnot’s result had been but fully unexpected: maximum 25%. Consequently, the reaction of most colleagues was comprehensible, while not fully consequent: ‘*Sure, we shall not concentrate our efforts on clarifying what should be the realistic roots of Carnot’s result; instead, we would physicalize Carnot’s idealistic model, in that we declare the latter to be the skillfully hidden basis of the entire Physical Universe*’. So, this is just how such metaphysical misnomers as ‘reversibility’, ‘adiabaticity’ have started to stubbornly invade all the fields of the Natural Sciences...

where we may identify:

$$\delta Q_{rev} = SdT \quad (25)$$

and

$$\delta Q_{irr} = d(TS) - SdT = TdS = \frac{T}{V_m} dV_{mt} - \frac{TV_{mt}}{V_m} d \ln V_m = PdV_{mt} - TSd \ln V_m \quad (26)$$

$$\delta Q_{irr} = -TSd \ln V_m \quad (27)$$

because $dV_{mt} = 0$ at *constant temperature* (Eq. 15). Bearing this in mind we have:

$$\delta Q_{irr} = TdS = -TSd \ln V_m = -E_{mt}d \ln V_m \quad (28)$$

δQ_{irr} is not a heat transfer but just a change of internal molecular configuration in the absence of any external work, and this is how we may explicitly embody the idea of irreversibility into the scheme of ours.

We deduce, after dividing each member of the equality by T :

$$dS = \frac{\delta Q_{irr}}{T} = -Sd \ln V_m \text{ and } d \ln S_\alpha = -d \ln V_{m\alpha} \quad (29)$$

at constant temperature.

Indeed, the relative entropy variation of some fluid phase at constant temperature is directly related to the inverse of the relative variation of the volume occupied by the internal energy of a molecule within the phase, to energy and volume, which are the sums of its atomic energies and volumes, respectively.

At this point, we do arrive at Clausius inequality: $dS \geq 0$.

Specifically, within the soil at constant temperature, the migration of water to the soil surface is spontaneous and irreversible – only with an entropy production ($dS > 0$), but without any apparent external work to carry out, until the system would have achieved some balance of the water pressures among the fluid phases of the pedostructure – and the gas phase outside – at this point, $dS = 0$ holds.

Thus, we could herewith represent the basic second law of thermodynamics in its explicit form – as it is naturally applicable to soil water: *There is a spontaneous production of entropy in the system until the equilibrium among the tensions (pressures) of the soil water phases – and the environmental pressure – might get achievable.*

3.2. Entropy of the gaseous phase

Across a single molecule, we might define its Entropy as the ratio of its total energy (the sum of its vibrational energy and kinetic energy) to its vibrational energy (temperature) T_i , just to arrive at the following expression⁺⁾ :

⁺⁾ In our water molecule model, we separate what we dub ‘*Kinetic Energy*’ (this is just the sum of the energies of translating the molecule as a whole in the three space directions, plus the energies of rotating the molecule as a whole around its principal inertia axes) from what we may dub ‘*Oscillatory Energy*’ (this is just the energy of atomic oscillators within the molecule. It is conventionally known as the *Intramolecular Vibrational Energy*). This is in full accordance with the conventional molecular physics.

$$S = \frac{V_{mt\alpha}}{V_{m\alpha}} = \frac{P_t V_{mt_i}}{P_{m_i} V_{m_i}} = \frac{T_i + T_c}{T_i} = \frac{\frac{1}{2}mv^2 + \frac{1}{2}m\lambda^2 v^2}{\frac{1}{2}m\lambda^2 v^2} = \frac{v^2 + \lambda^2 v^2}{\lambda^2 v^2} \quad (30)$$

as the internal $P_{m_i} = \frac{T_i}{V_{m_i}}$ and external molecular pressures $P_{mv_i} = \frac{T_c}{V_{mv_i}}$ are equal to each other at equilibrium.

Now, it is all the more judicious to distinguish between the two energies, for T_i – unlike T_c – should correspond to some emitter of electro-magnetic waves, which renders it possible to identify the temperature of a molecule in the space.

On the other hand, if we monitor raising or lowering of the temperature T_i , it is obvious that such changes might, in fact, come from two channels: the one, electromagnetic, which corresponds to the resonance of the intramolecular vibration with the beams of the incident waves – and the other, mechanical, which would result from an increase in the molecular kinetic energy, that is, from the thermal excitation energy T_c . Meanwhile, the latter is well known to increase with a decrease in the occupancy volume (under the action of any mechanical work from outside) – or due to contacts of the fluid phases with some warmer body (i.e., a body having higher temperature), or with the solid walls of the vessel containing the system under study, as the molecular vibrations of these walls do get more intense.

Our viewpoint in regard to the heat transfer is totally different from the conventional one: It is the thermal state of the medium at each of its points (the molecules) that may change – either by the direct individual contact between every molecule and its outside, or by contact the entire phase does get with a body of different temperature. But in these both cases a simultaneous “mechanical” equilibrium should be achievable between the two temperatures T_i and T_c – so that, this should both reconcile any pressure gap – and, consequently, nullify the entropy excess in the medium as well.

Hence, we are rather far both from the classical thermodynamic vision and from Boltzmann’s statistical theory of gases. The entropy of an isolated molecule goes from 1, when its velocity is equal to zero in the observer’s reference frame – and increases to become > 1 , when molecules do acquire their non-zero velocities in the medium, which they are in equilibrium with. Sure, this has nothing to do with the statistical mechanics – and we might now calculate entropy in a straightforward way, via the pressure of the medium, because at equilibrium we do get the following expressions:

$$P = P_m = P_{mv} = \frac{T_i}{V_m} = \frac{T_c}{V_{mt} - V_m} = \frac{\frac{1}{2}mv^2}{V_{mt} - V_m} \quad (31)$$

The ‘*Kinetic Energy*’ might indeed correspond to REVERSIBLE events, as soon as we skip INTERMOLECULAR COUPLING.

Meanwhile, the ‘*Oscillatory Energy*’ should sometimes correspond to IRREVERSIBLE events, because higher amplitudes of the atomic oscillators might lead to the chemical degradation of the molecule.

Still, ‘*Kinetic Energy*’ should sometimes also correspond to IRREVERSIBLE events, if we would wish to properly take into account the INTERMOLECULAR COUPLING – because very intensive collisions among molecules might also lead to their chemical degradation.

Physically-chemically, water is well known as an ‘unusual’ liquid, for the H_2O entity must be chemically unstable – unless it is both in vacuo and at zero absolute temperature, which is but technically inaccessible.

This is why our idea to build up a *multilevel* (having both molecular and atomic levels) systemic model for soil water should properly reflect the actual physical properties of the water.

$$v^2 = 2 \frac{T_i}{m} \frac{V_{mt} - V_m}{V_m} = 2\mu_m(S_g - 1) \quad (32)$$

$$\text{Thus, } S_g \geq 1 \text{ and } dS_g = \frac{v dv}{\mu_m} \quad (33)$$

To sum up, we arrive at the expression for the entropy of the gas phase – taken at a constant temperature, so that entropy is directly related to the velocity of gas molecules divided by the atomic and/or molecular chemical potential (Eq. 33), which is equal everywhere in the system, whatever the value of the molecular mass.

3.3. Entropy variation of soil water molecules in contact with surface air

After contacts environmental unsaturated air makes with the surface of the soil system, a number of water molecules per unit of time do leave the soil and evaporate into the environmental air. What happens to the internal energy of these molecules, their internal volume concentration (i.e., pressure) and their entropy in the novel medium?

After leaving the soil system, the water molecules regain the volumes they had in the saturated state of the soil in equilibrium with the external air pressure, and also their vibrational amplitudes and frequencies without but the need for any external energy supply. On the other hand, the molecules do experience a considerable increase in their occupational volume (cf. Fig. 6) – after changing in such a way their medium – and it is logical to assume that the same holds for all the molecules of the air. They do gain an additional entropy – but **without any priori change in their velocities**: indeed, the frequency of intermolecular shocks should be related to the occupational volume V_{mt} being the same for all the molecules present in the air – and this is directly related to the number of the molecules available. The intramolecular vibrational spectrum of a water molecule newly arrived at the environmental air should be adjustable to the shock frequency of the air molecules. This results in a change of the volume $V_{m_{wg}}$ together with the pertinent change in the water molecule's intramolecular vibrational spectrum. To sum up, just by leaving the soil medium, the water molecule does gain the power to adapt itself to the occupational volume available to it in the air – without but any external energy release or supply. This adjusts the thermodynamic equilibrium between the air and the incoming water molecules: their intramolecular vibrations do get in tune with air without any energy change. The opposite pathways of water molecules, namely of those getting from the air into the soil through the surface of the latter, may be conceivable in the same way, i.e., as an adaptation of their vibration frequencies and volumes $V_{m_{wl}}$ without any energy input or release. Hence, the balance – or imbalance – in one direction or the other, that is, between the number of the water molecules entering or leaving the soil medium, might well be representable by a probability that depends directly on the volume concentration of water molecules in the air, i.e., the water partial pressure in the air. Just in line with the latter, Braudeau (2020) has clarified the relationship (9) between the water retention pressure in the surficial layer of the soil – and the relative humidity of the air at the soil surface.

4. CONCLUSION

We have shown how the systemic approach, as it may be understood and practiced by pedologists for the study of the hydric and agronomic functioning of the soil in its natural or managed environment, led first of all to recognize the need for a paradigm shift in the way of describing and modeling the water-soil couple: identify the scales of hydro-functional

organization of the representative pedon and establish the appropriate systemic descriptive variables for each level of scale. This paradigm shift later led (2014) to the discovery of the exact thermodynamic equation of the characteristic soil moisture curve (19), long sought after in the field of water sciences.

More specifically, we show how the systemic thermodynamic theory of soil water recently published by the author – and based upon the study of the molecular and atomic organization of the two aqueous phases of the pedostructure – is in perfect continuity with the systemic approach stepping down to the level of the two aqueous phases. Such a continuity does provide us with the fundamental meaning the entire set of the description variables we employ, such as temperature, the internal energy (molar) of the water molecule, in Joule, the chemical potential of any aqueous phase, which is equal to the squared molecular velocity at any point of this phase, etc.

Finally, the correction of the Gibbs-Duhem equation does enable us to visualize and explain the immense agreement between the two laws of thermodynamics in the case of spontaneous water evaporation from the soil surface into the surrounding air.

Philosophically, our consideration does indicate why our ancestors were treating soil (Earth), Water, Air and fire (Energy) as the four truly Basic Elements of Creation, with the extensive properties as defined here being apprehensible up to the level of the atom within the Cartesian Physics. Here, we could have seen that it is at these two levels, molecular and atomic, that the extensive (material) and intensive (informational) characteristics of the systemic description variables are definable. If we now adopt the philosophic standpoint of L. Romani⁴, our Cartesian-Physical standpoint should be applicable up to the level of the electron and its antiparticle, the positron, which are the first particles formable of Ether (to be describable as ether vortices), with the Ether being a perfect fluid to build up the Matter.

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⁴ See note page 20

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