

Systemic Modelling of Soil Water Thermodynamics under Natural Conditions of Air Temperature and Pressure

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ABSTRACT

Following the recent theorization of the systemic approach of natural organizations such as soils, we give in this article the systemic definition of three fundamental variables of thermodynamics: temperature (T_α) as the internal energy of molecules constituting a fluid phase " α "; entropy (S_α), as the ratio of two organization variables of the phase that are: the occupational volume of molecules (V_{mt}) and their own volume V_m in the phase of volume V_α ; and the internal molecular chemical potential (μ_{m_i}) as the ratio of the temperature of a molecule to its mass (T_i/m_i).

This allowed the following conceptual advances that could not be done using the two principles of thermodynamics: i) establishing the definitional equations of the 3 equivalent forms of the Gibbs free energy of the system, ii) establishing that the general equilibrium criterion of the system is the internal molecular potential μ_m rather than the temperature, iii) removing the confusion between internal and external pressures of the system that did not allow to distinguish the two types of energy of a molecule: internal (T_i) and external ($T_i(S_\alpha - 1)$), then iv) correcting accordingly the differential equations of thermodynamic potentials as well as the Gibbs-Duhem equation. Application to the soil water air system is given followed by some comments about this new vision of thermodynamic equilibrium modeling.

1 Introduction

Water is the fluid responsible for the morphology and the internal functionality of soil organizations, at every hydro-functional scales of the natural environment, from the soil pedostructure and geomorphological units in the watershed.

Cependant, la physique de l'eau du sol ne s'est pas développée avec la même ampleur ni la même pertinence à ces différents niveaux d'échelles d'organisations : l'hydrologie et l'hydropédologie ont pris en charge la description des phénomènes hydriques à la surface du sol (érosion, infiltration, évaporation) mais ont toujours considéré le milieu sol comme un milieu homogène du point de vue de la structure : les phases solide, liquide et gazeuse du milieu sol sont indiscernables, formant une mixture homogène dans des volumes représentatifs élémentaires (REV) dont les surfaces limites n'ont, par conséquent, pas de relation hydrostructurale avec le volume interne. Les équations de transfert de l'eau dans le sol sont alors issues des équations de la mécanique des fluides dans les milieux poreux continus, science qui est basée sur le concept de REV (Volume Représentatif Élémentaire). C'est pour cette raison, comme l'ont montré Braudeau et Mohtar (2009), que ces équations ne pouvaient prendre en compte le rôle de la structure du sol dans l'interaction hydrostructurale du sol et de l'eau qui fait l'identité d'un sol et est à l'origine de toutes ses propriétés

physiques. Ainsi, pour distinguer les organisations internes du milieu sol et leur associer les variables descriptives pertinentes, Il a été nécessaire de remplacer le concept de REV par celui de SREV (structural representative elementary volume) que ces auteurs ont établi dans l'approche systémique des organisations du sol (Braudeau et Mohtar, 2009, Braudeau et al. 2016). Une nouvelle physique de l'eau du sol a pu se développer sur la base de ce nouveau concept de l'approche systémique des organisations. Les équations physiques exactes de l'interaction entre l'eau et la phase solide de la structure du sol, ont pu être établies (B et al. 2014), notamment celles de l'équilibre thermodynamique constant entre les deux phases aqueuses de la pédosstructure aboutissant à la formulation thermodynamique exacte de la très connue courbe de rétention du sol $h(W)$ appelé encore courbe caractéristique d'humidité du sol. L'approche systémique était le cadre scientifique nécessaire pour définir fondamentalement les variables d'organisation propres à chaque échelle d'organisation hydro-fonctionnelle du sol.

La théorisation de l'approche systémique qui en a découlé, comme approche humaine des organisations du milieu naturel et humain (Braudeau et al. 2016), ainsi que les avancées conceptuelles la physique de l'eau du sol qui ont eu lieu dans cette approche, justifient entièrement la naissance d'une nouvelle discipline en sciences de la terre : la pédologie hydrostructurale. Celle-ci offre un nouveau paradigme de caractérisation, de recherche et de modélisation du sol en tant que milieu physique organisé, siège des processus biologiques chimiques et hydro physiques dans un contexte d'équilibre thermodynamique et hydrostructural du milieu sol.

L'équilibre hydrostructural du sol étant maintenant bien défini avec la mise en évidence des deux phases aqueuses de la pédosstructure et de leurs propriétés physiques macroscopiques (Braudeau et Mohtar, 2014), nous voulons, dans la première partie essentiellement théorique de cette étude, définir et comprendre fondamentalement les termes (variables, paramètres fonctions) de l'équilibre thermodynamique de l'eau de la pédosstructure du sol ; ceci pour être en mesure d'appréhender, dans une deuxième partie, la dynamique de l'eau dans ce milieu physique en état d'équilibre thermodynamique et soumis à l'évaporation de l'eau en surface.

Dans ce premier article il s'agira d'appliquer l'approche systémique jusqu'aux niveaux moléculaires et atomiques des deux phases aqueuses de la pédosstructure afin de définir les variables descriptives de l'équilibre thermodynamique de ces deux phases en fonction de la teneur en eau et d'en comprendre la signification physique exacte.

2 Theory: Systemic Modelling of the Thermodynamic Equilibrium of the Fluid Phases of the Pedostructure

2.1 The Hydrostructural Pedology Paradigm

The physical formulation of the hydrostructural equilibrium of the pedostructure (Braudeau et al., 2014a, b), coming from experimentation and interpretation of results in the systemic paradigm of the hydrostructural pedology, constitutes a fundamental progress in soil water physics. They compel the physical sciences of the natural environment, particularly thermodynamics of soil water, to take into account two fundamental findings:

1) The systemic approach as it was redefined and theorized by Braudeau et al. (2016) to be applied to soil science. It constitutes the theoretical and methodological framework (Braudeau et al. 2014k) necessary for the physical and systemic description of the nested and multiscale organization of the natural environment. This allows providing an exhaustive list of the descriptive hydro-functional variables of this natural organization with their precise physical definition. Having these variables

makes it possible to write the correct physical equations that describe the thermodynamic equilibrium of the soil water pools (phases) within the soil structure (solid phase); and this, at each scale level of the hydro-functional organization of the soil structure (pedon, horizon, pedostructure and primary peds (Fig. 1).

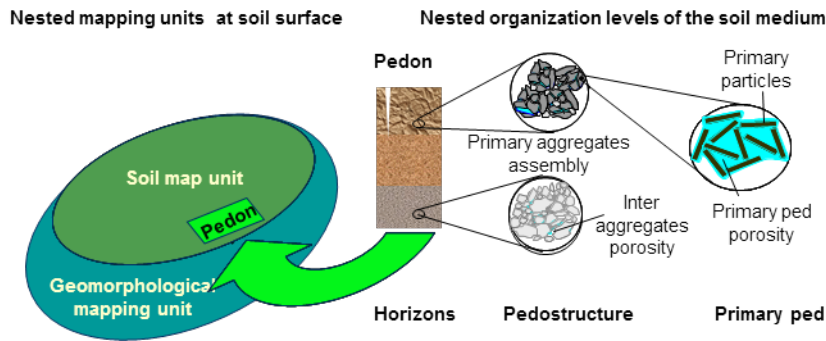


Figure 1 : Nested hydro functional systems and sub-systems recognized in the system approach of the natural environment in the hydrostructural pedology paradigm

2) The experimental discovery that the Gibbs free energies of the micro and macro-aqueous phases, written $\bar{G}_{mi}$ and $\bar{G}_{ma}$ (eq.1), are equilibrium constants, independent of the water content of the pedostructure, as we succinctly detail it hereafter.

Equation (1) shows $\bar{G}_{mi}$ and $\bar{G}_{ma}$ as written under their Eulerian form and reported to the structural mass of the pedostructure system taken as reference; they are equal respectively to $\bar{E}_{mi}$ and $\bar{E}_{ma}$, the surface charge potential energies of clay particles, positioned inside (subscript: mi) and at the surface (subscript: ma) of primary-peds of the pedostructure:

$$\begin{aligned}\bar{G}_{ma} &= \mu_{ma} W_{ma} = \mu_{maSat} W_{maSat} = \bar{E}_{ma} \\ \text{and} \\ \bar{G}_{mi} &= \mu_{mi} W_{mi} = \mu_{miSat} W_{miSat} = \bar{E}_{mi}\end{aligned}\quad (1)$$

where μ_{mi} and μ_{ma} are the water chemical potential of the pedostructural water phases “micro” and “macro” respectively, of which W_{mi} and W_{ma} are the corresponding water contents such that $W_{mi} + W_{ma} = W$, the total water content of the pedostructure.

The important and new result that could be deduced from equation (1) was the water retention pressure¹ h equation for each of the aqueous phases of the pedostructure (Figure 1) according to the corresponding water content, as:

$$\begin{aligned}h_{ma} &= \rho_w (\mu_{ma} - \mu_{ma^\circ}) = \rho_w \bar{E}_{ma} \left(\frac{1}{W_{ma}} - \frac{1}{W_{maSat}} \right) \\ \text{and} \\ h_{mi} &= \rho_w (\mu_{mi} - \mu_{mi^\circ}) = \rho_w \bar{E}_{mi} \left(\frac{1}{W_{mi}} - \frac{1}{W_{miSat}} \right)\end{aligned}\quad (2)$$

¹ μ_{mi} and μ_{ma} were considered negative in Braudeau et al. (2014) article so the suction pressure was written such as: $h_\alpha = -\rho_w (\mu_\alpha - \mu_{\alpha^\circ})$. We are showing here that μ_α is always positive, like the retention pressure h . So we will do this correction automatically thereafter.

At equilibrium of the pedostructure system, the water retention pressures are equal, so we have:

$$h_{ma}(W_{ma}) = h_{mi}(W_{mi}) = h(W) \quad (3)$$

Assuming that the equilibrium equation (3) holds with a slow change in total water content W , the change in W_{mi} and W_{ma} is such that the resulting suction pressures of both phases (equations 2) stay equal during this change, according to equation (3).

This equality of pressures determines the distribution of the water contents: W_{mi} and W_{ma} at equilibrium according to the total water content W of the pedostructure (Braudeau et al., 2014a, c):

$$W_{ma}^{eq}(W) = \frac{1}{2} \left(W + \frac{\bar{E}}{A} \right) + \frac{1}{2} \sqrt{\left[\left(W + \frac{\bar{E}}{A} \right)^2 - \left(4 \frac{\bar{E}_{ma}}{A} W \right) \right]} \quad (4)$$

and

$$W_{mi}^{eq}(W) = W - W_{ma}^{eq} = \frac{1}{2} \left(W - \frac{\bar{E}}{A} \right) - \frac{1}{2} \sqrt{\left[\left(W + \frac{\bar{E}}{A} \right)^2 - \left(4 \frac{\bar{E}_{ma}}{A} W \right) \right]} \quad (5)$$

Where A is a constant representing the difference of chemical potentials of the two types of water at the saturated state:

$$A = (\mu_{maSat} - \mu_{miSat}) = \frac{\bar{E}_{ma}}{W_{maSat}} - \frac{\bar{E}_{mi}}{W_{miSat}} \quad (6)$$

$$\bar{E} = \bar{E}_{mi} + \bar{E}_{ma} \quad (7)$$

Thus, W_{maSat} , W_{miSat} , $\bar{E}_{ma}$, and $\bar{E}_{mi}$ are four intrinsic characteristics of the soil pedostructure that determine all the descriptive variables of the pedostructure: the chemical water potentials (μ_{ma} and μ_{mi}) as functions of the corresponding water content (W_{mi} or W_{ma}) which are themselves, at equilibrium, univocal functions of the total water content W (equations 4 and 5). Equations (2) to (5) were fully validated by experience, which confirmed the starting equation (1).

The question is now how to integrate these two new facts of the soil water science, theoretical and experimental, into a fundamental theory of soil water thermodynamics?

2.2 Defining the thermodynamic system

2.2.1 Two kinds of physical modelling of a process

Like any modeling of a physical phenomenon, thermodynamics requires a set of well-defined variables that are necessary for it to simulate and describe the phenomenon (as well as the processes involved) in time and space; in this case the thermodynamic equilibrium of a thermodynamic system. Two options are possible as Braudeau and Mohtar (2009) have shown by contrasting the concepts of REV (Representative Elementary Volume) and SREV (Structural Representative Elementary Volume) on which these two types of modeling are based.

The concept of REV was set up by soil hydrodynamicists (Bear, 1972) to consider the aggregated medium of the soil as homogeneous, to be allowed for modelling the hydraulic functioning of this medium without having to take into account of the internal structure of this REV of soil. This kind of modeling based on the REV principle is, in fact, double-edged: it allows modelling the external behavior of the system but it prevents modelers from understanding the internal processes leading to the external behavior and so, from establishing the exact equations describing these processes.

Indeed, establishing exact equations requires an exhaustive list of exact organizational and functional variables of the medium.

The concept of SREV was set up by Braudeau and Mohtar (2009) to overcome the impossibility with the REV concept to define these exact variables of the internal organization of the soil medium. This concept has been considered further as one of the basic concepts of the systemic approach theory applied to natural organizations like soils (Braudeau et al., 2016). Physical modeling based on this concept of SRV is termed systemic, and uses a set of systemic variables quite different from the non-systemic set of variables used by the classical modeling.

2.2.2 Postulates and principles at the basis of the current thermodynamics

The current modeling of the thermodynamic equilibrium of the liquid or aqueous phases of a thermodynamic system proceeds, as we will show, from the same macroscopic (or non-systemic) approach as the current modeling of soil hydrodynamics. It is based on two postulates.

The first postulate of the thermodynamics, which can be called the general principle of thermodynamics because it is at the basis of all thermodynamics and determines its domains of validity (Bazarov, 1983), is stated as follows: "In thermodynamics, we postulate that the isolated system possesses a thermodynamic equilibrium state that it reaches with time and that it can never leave spontaneously".

The second postulate concerns the existence of temperature as a particular state function of a system in equilibrium (Bazarov, 1983 p.20): "all internal parameters of a system at equilibrium are functions of the external parameters and the temperature". So, "the energy of the system being its internal parameter, it will be, at the equilibrium, function of the external parameters and the temperature. "

These two statements postulate only the existence of two characteristic variables: the internal energy U as internal parameter of the system and the temperature T as state function characteristic of the equilibrium state of the system.

The two principles of thermodynamics establish the notions of heat, temperature and entropy without however providing any information on the physical dimension of the last two variables, T and S . Heat ΔQ or δQ has the dimension of a work quantity ΔW or δQ , in Joule, according to the first principle while the entropy is defined as the conjugate variable of T in the relation postulated by the 2nd principle such as: $\delta Q = TdS$. Thus the product we only know that the product TS has dimensions of an energy (ML^2T^{-2}) like ΔQ and ΔW .

The temperature is generally interpreted as an index of the internal energy state U (internal parameter) of the system; so it would be S which would have the dimension of energy. This essential question about the physical dimensions of temperature and entropy has not yet been decided.

Despite this lack of information on the internal variables of the system, it is the generalized variables of Lagrangian mathematics that have been used to define the thermodynamic potentials and their exact total differences such as for example the differential of the internal energy $U(S, V, m_i)$:

$$dU = TdS - pdV + \sum_i \mu_i dm_i \quad (8)$$

where p is the external pressure, V the volume, μ_i the chemical potential of element i and m_i the mass of component i of the system

We believe that the Lagrangian mechanics used here at the macroscopic level of the phase where the internal state variables have no precise definition, is not adequate. Indeed, the generalized forces,

generalized work, generalized coordinates etc. are mathematical variables without physical definition. The internal organization of the aqueous or gaseous phase, made of vibrating molecules which are themselves the assembly of their atoms in oscillatory motions, is not at all taken into consideration in these equations. This is why the current thermodynamics is typically a REV type (black box) modeling since the only level of perception scale is external to the volume of the phase and that nothing that happens inside this volume can be described and taken into account.

2.2.3 Expectations in the application of the systemic approach to thermodynamics

The modeling of the thermodynamic equilibrium of an aqueous or gaseous phase of the system requires defining the internal organization variables of the phase which is composed of molecules, and the molecules from atoms. These two levels of organization are not considered in the equilibrium equations and need the systemic approach of hydrostructural pedology to be defined and at the same time keep the link with the higher scale levels (pedostructure, horizon, pedon, parcel, etc.).

The systemic modeling of a thermodynamic system will be to define first the descriptive variables of the internal organization of homogeneous fluid phases of a "thermodynamic system" as defined by the two postulates seen above. This is to correctly and exhaustively define the descriptive variables of the functional organization levels of these phases: molecules and their atoms. We think that it is only at this level of molecular scale that the Lagrangian mechanics could support the modeling of the dynamics of a thermodynamic system out of equilibrium.

2.3 Defining the thermodynamic variables according to the system approach

2.3.1 Temperature and pressure in the perfect gases equation

The fundamental variable of a system is its volume, which must be defined as containing exactly all the functional volumes of its component subsystems. In thermodynamics, the constituent subsystems of an aqueous or gaseous phase are the molecules in motion, each of which are characterized by a volume of occupation which we will note V_{mt} and a specific volume V_m .

These two organizational variables are currently not distinguished and used in the current thermodynamic equations whereas they are essential to the definition of thermodynamic system as we will see.

Let us start with the case of perfect gases. Let a non-structural system (no structured solid phase) of volume V , enclosing n molecules of perfect gases (without attracting the molecules to each other), in equilibrium under an external pressure P and at a temperature T .

The van der Waals' works highlighted the real existence of a volume characteristic of each type of molecule: V_m . Without having the means to measure it, we postulate its existence as a functional volume containing the oscillatory energy of the molecule: E_m , due to the periodic oscillations of its atoms. This molecular volume "expresses" the oscillatory energy of the molecule as a pressure: $P_m = E_m/V_m$, applied to its surface, separating the inside with the outside of the molecule that we define as the intermolecular void space: $V_v = V - nV_m$. Similarly, we can define in this intermolecular void space a pressure: $P_v = E_v/V_v$, due to the Brownian motion of molecules maintained by this molecular oscillation which opposes the crowding of the molecules under the effect of their weight. The equilibrium is reached when the two intra- and inter-molecular pressures are equal. And if the gas system is in equilibrium with the outside air at the pressure P (no material delimitation of the system which is virtually closed for its n molecules component), we have:

$$P_m = P_v = P. \quad (9)$$

Three functional volumes can thus be defined unambiguously at the level of a molecule of chemical species "i"; these are respectively: the molecular volume V_{m_i} , the external void volume V_{mv_i} , and the total volume V_{mt_i} of the molecule "i" which is the occupational volume of the molecule in the gas phase of volume V_g , such that we have :

$$n_i V_{m_i} = V_g \text{ and } V_{mt_i} = V_{m_i} + V_{mv_i} = \frac{\sum_i n_i V_{mt_i}}{n_g} \quad (10)$$

n_i and n_g being, respectively, the number of molecules of chemical species "i" and the total number of molecules in the gaseous phase.

Let us consider now the implications of recognizing the reality of these functional volumes. We suppose in a first time hereafter that there is only one species of molecule, so that $n_i = n_g$.

The volume composition relationship of the gaseous system is:

$$V_g = n_g(V_m + V_{mv}) = n_g V_{mt} \quad (11)$$

Each volume component of V_g in equation (11) can be considered as a particular type of energy volume, that is to say a volume whose internal energy comes from a particular type of process, like the atoms oscillation in V_m . Confined in a volume, this energy acts as a pressure on the enveloping surface of the volume, in Joule / m³ (ML⁻¹T⁻²). The following pressures corresponding to each type of volume of energy in equation (11) are thus defined as:

$$P_g = \left(\frac{E_t}{V_g}\right); P_m = \left(\frac{nE_m}{nV_m}\right); P_{mv} = \left(\frac{nE_{mv}}{nV_{mv}}\right) = P_v; \text{ and } P_{mt} = \left(\frac{nE_{mt}}{nV_{mt}}\right) = P_g \quad (12)$$

where P_g is the internal pressure of the volume V_g of the gaseous phase. By multiplying each member of equation (11) by the corresponding pressure defined in (12):

$$\left(\frac{E_t}{V_g}\right) V_g = n_g \left(\frac{E_m}{V_m}\right) V_m + n_g \left(\frac{E_v}{V_v}\right) V_v = n_g \left(\frac{E_{mt}}{V_{mt}}\right) V_{mt} \quad (13)$$

We obtain the equation of energy distribution of the system at equilibrium:

$$E_t = n_g E_m + n_g E_v = n_g E_{mt} \quad (14)$$

which corresponds to the volume distribution in equation (11). This is possible if and only if all pressures are equal, which is the only condition of equilibrium of the gas phase:

$$P_g = \left(\frac{E_t}{V_g}\right) = P_m = \left(\frac{E_m}{V_m}\right) = P_{mv} = \left(\frac{E_{mv}}{V_{mv}}\right) = P_{mt} = \left(\frac{E_{mt}}{V_{mt}}\right) \quad (15)$$

It is an obvious equilibrium law which derives from 3 things: i) the definition of the functional volumes of molecules in the gaseous phase (equation (11)), ii) the physical definition of a pressure as a volumetric concentration of energy and iii) the mathematical property of equal fractions: $\frac{a}{b} = \frac{c}{d} = \frac{a+c}{b+d}$. Equation (15) simply means that energy, whatever its form, is homogeneously distributed in space and that the only source is the internal energy of molecules of the gaseous phase system.

Each of the 2 functional volumes of a molecule has its own type of energy, so that their internal pressures which are like volume concentrations of energy, are different in nature but are quantitatively equal at equilibrium. Each of both is associated to a particular energy production mechanism: E_m is the sum of oscillatory energies of type $1/2 m \omega^2 \lambda^2$ of atoms inside the molecular volume V_m ; E_{mv} is the kinetic energy ($1/2 m v^2$) of the Brownian motion of the molecule in the

gaseous phase. Equilibrium is reached when an equal pressure is reached in the two volumes: V_m and V_{mv} . Accordingly, the total energy of all the n gas molecules can be written under different forms:

$$E_t = P_g V_g = n(E_m + E_{mv}) = n(P_m V_m + P_{mv} V_{mv}) \quad (16)$$

Since all pressures are equal in the phase at equilibrium, we can write:

$$E_t = P_g V_g = \left(\frac{E_m}{V_m}\right) V_g = E_m \left(\frac{V_g}{V_m}\right) = n_g E_m \left(\frac{V_{mt}}{V_m}\right) \quad (17)$$

where V_{mt} is the occupational volume of a molecule in the gaseous phase. V_{mt} is the average volume occupied by the Brownian motion of one molecule in the volume V_g of the gaseous phase of the system:

$$V_{mt} = V_m + V_{mv} = \frac{\sum V_{mt_i}}{n_g} = V_g / n_g \quad (18)$$

Equation (17) seems like the state equation of perfect gases:

$$E_t = P_g V_g = N R T_k = (n_g / N_A) \left(\frac{V_{mt}}{V_m}\right) (N_A E_m) \quad (19)$$

where N is the number of moles contained in V_g , N_A is the Avogadro number; $(R T_k)$ is the molar energy (Joule mole⁻¹) of the system (V_g), the product of two variables of which the fundamental physical meanings are unspecified until now: namely, the Kelvin temperature T_k and the perfect gases constant R (Joule mole⁻¹ K⁻¹).

However, such as E_t has been developed in equation (19), R could be interpreted as the fraction $\frac{V_{mt}}{V_m}$ and T_k as the internal energy of N_A molecules: $T_k = N_A E_m$.

If we name T_i the internal energy of one molecule i , equation (19) can be written such as:

$$P_g V_g = n_g \left(\frac{\sum V_{mt_i}}{\sum V_{m_i}}\right) \left(\frac{\sum T_i}{n_g}\right) = n R T_g \quad (20)$$

so, at the phase level, the constant R would be identified with $R = \left(\frac{\sum V_{mt_i}}{\sum V_{m_i}}\right)$ and T_g with the average temperature of the phase: $T_g = \frac{\sum T_i}{n_g}$.

And at the molecule level, because of equality of pressures at equilibrium (eq. 15), the fraction $\frac{V_{mt_i}}{V_{m_i}}$ is, at equilibrium in the gas phase, equal to the ratio of the total energy of the molecule to its internal energy. Calling this ratio entropy, S_i , we have according to (15), at the molecular level:

$$S_i = \frac{E_{mt_i}}{E_{m_i}} = \frac{V_{mt_i}}{V_{m_i}} \quad (21)$$

and:

$$P_g V_{mt_i} = T_i S_i = \frac{T_i}{V_{m_i}} V_{mt_i} = P_m V_{mt_i} \quad (22)$$

$$\text{In this equation } P_g = \frac{T_i S_i}{V_{mt_i}} = \frac{T_i}{V_{m_i}} = P_m \quad (23)$$

We can see from equation (23) that, if molecules have the same entropy in the phase, which is homogeneous in pressure and temperature, then the equality: $\frac{V_{mt_i}}{V_{m_i}} = \frac{\sum_i n_i V_{mt_i}}{\sum_i n_i V_{m_i}}$ holds. This equality holds even in case of mixing of different chemical species i , like atmospheric air. Thus, the gas constant

R can be identified to the entropy of the gas phase, which is observed constant, independent of temperature and pressure.

This implies that each molecule of the gaseous system carries two different kinds of energy: its internal energy, $T_i = E_{m_i}$ which is vibrational and characteristic of the molecule, and a kinetic energy $T_{c_i} = E_{mv_i} = T_i(S_i - 1)$ resulting from its linear movement between two chocks within the intermolecular space of the gas phase ($V_{mv} \equiv V_g/n_g - V_m$). Equilibrium is reached when all pressures, which are physically equal to the quantity of any particular energy occupying a part of space divided by its occupation volume, are equal everywhere in the gaseous phase sub system:

$$P_m = \frac{E_m}{V_m} = \frac{E_{mv}}{V_{mv}} = \frac{E_{mv}+E_m}{V_{mv}+V_m} = \frac{E_{mt}}{V_{mt}} = \frac{nE_{mt}}{nV_{mt}} = \frac{E_g}{V_g} = P_g \quad (24)$$

2.3.2 Entropy and chemical potential as state variables in the Gibbs-Duhem equation and thermodynamic potentials

In thermodynamics of aqueous solutions, the Gibbs-Duhem equation is just as well known as the perfect gas equation is for the gaseous phases. Sposito (1981) presented this equation, for a single phase α of a soil, like:

$$S_\alpha dT - V_\alpha dP + \sum_i m_{i\alpha} d\mu_{i\alpha} = 0 \quad (25)$$

where S_α , T , V_α , P , $m_{i\alpha}$, and $\mu_{i\alpha}$ are the set of the six basic thermodynamic variables for a soil phase in absence of external fields. They are listed in table I along with their quality (extensive or intensive) and units.

Table 1. Summary of thermodynamic state variables for a soil in the current thermodynamics theory (Sposito, 1981)

Variables	Symbol	Extensive	Intensive	Units
Temperature	T		X	K
Entropy	S	X		J K ⁻¹
Pressure	P		X	N m ⁻²
Volume	V	X		m ³
Chemical potential of i^{th} element	$\mu_{i\alpha}$		X	J kg ⁻¹
Mass of i^{th} element	$m_{i\alpha}$	X		kg

Sposito (1981) said, about the Gibbs-Duhem equation (25): « This expression is an identity relationship among the differentials of the intensive variables that describe a soil.” It “could have been derived just as well, by choosing, the Euler equation for U and comparing its total differential U_α with the differential form of $U_\alpha(S, V, \{m_{i\alpha}\})$ ”

$$\text{The Euler equation for } U \text{ is: } U = TS - PV + \sum_\alpha \sum_i \mu_{i\alpha} m_{i\alpha} \quad (26)$$

$$\text{and for the Gibbs energy } G: G = \sum_\alpha \sum_i \mu_{i\alpha} m_{i\alpha} \quad (27)$$

The differential form of $U_\alpha = U_\alpha(S, V, \{m_{i\alpha}\})$ is, according to the First and Second Law of thermodynamics:

$$dU_\alpha = TdS_\alpha - PdV_\alpha + \sum_\alpha \sum_i \mu_{i\alpha} dm_{i\alpha} \quad (28)$$

Total differential of U for a phase α gives:

$$dU_\alpha = TdS_\alpha - PdV_\alpha + \sum_i \mu_{i\alpha} dm_{i\alpha} + (S_\alpha dT - V_\alpha dP + \sum_i m_{i\alpha} d\mu_{i\alpha}) \quad (29)$$

The comparison of (29) with the differential form of $U_\alpha(S, V, \{m_{i\alpha}\})$, which is a total exact differential according to the 2 thermodynamics principles, shows that the expression in parentheses is necessarily null. This expression is the Gibbs-Duhem equation (25).

Knowing that the derivative of the Gibbs free energy written in its Eulerian form (27) is:

$$dG_\alpha = \sum_i (\mu_{i\alpha} dm_{i\alpha} + m_{i\alpha} d\mu_{i\alpha}) \quad (30)$$

introducing (30) into the Gibbs-Duhem equation (25) leads to:

$$dG_\alpha = -S_\alpha dT + V_\alpha dP + \sum_i (\mu_{i\alpha} dm_{i\alpha}) \quad (31)$$

which is the Gibbs free energy equation written in its exact partial differential form. That shows that G_α , as function of the state variables $(T, P, \{m_{i\alpha}\})$, is a thermodynamic potential equivalent in all respects to the internal energy $U(S, V, \{m_{i\alpha}\})$ based on the two principles of thermodynamics (Sposito, 181).

However, these thermodynamic potentials equations involve a variable that is not mentioned in the perfect gas equation, namely the chemical potential, $\mu_{i\alpha}$. The corresponding energy form is the product of this potential by a mass, $\mu_{i\alpha} m_{i\alpha}$. Unlike the energy form (TS_α) of which the 2 variables are not clearly defined, the energy form $(m_i \mu_{m_i})$ is a product of two variables of which one, the mass, is well identified as the mass of the molecule indicating that the second variable is a potential: the internal energy of the molecule divided by its mass.

Thus, in the same way that we could define the types of pressure corresponding to the different types of energy of the molecule (15), we can define the corresponding types of molecular chemical potential as follows:

The internal molecular chemical potential μ_{m_i} :

$$\mu_{m_i} = \frac{E_{m_i}}{m_i} = \frac{T_i}{m_i} = \frac{T_i}{V_{m_i}} \frac{V_{m_i}}{m_i} = \frac{P_{m_i}}{\rho_{m_i}} \quad (32)$$

The external molecular chemical potential:

$$\mu_{mv_i} = \frac{E_{mv_i}}{m_i} = \frac{T_i(S_i - 1)}{m_i} = \frac{P_{m_i}}{\rho_{mv_i}} \quad (33)$$

The total molecular chemical potential:

$$\mu_{i\alpha} = \frac{E_{mt_i}}{m_i} = \frac{T_i S_i}{m_i} = \frac{P_{m_i}}{\rho_{i\alpha}} \quad (34)$$

where ρ_{m_i} , ρ_{mv_i} and $\rho_{i\alpha}$ are the corresponding densities of the energetic volumes, V_{m_i} , V_{mv_i} et V_{mt_i} .

With the molecular definition of the chemical potential, we have defined a third form of writing the energy of a set of moving molecules which corresponds to the Gibbs free energy. According to the definition equations of variables used in writing this energy, It is completely equivalent to the first two forms of energy previously studied for the gas phase: $n_g T_g S_g$ and $n_g P_g V_{mt_g}$. Thus, for all fluid (free) phases α of a thermodynamic system, we have the following equivalence relationships:

$$G_\alpha = n_\alpha m_\alpha \mu_\alpha = n_\alpha T_\alpha S_\alpha = P_\alpha V_\alpha \quad (35)$$

where variables : n_α , m_α , μ_α , T_α , S_α , P_α and V_α are the state variables of the phase, used for writing the partial differentials of the thermodynamic potentials of the phase, like dU_α and dG_α .

2.3.3 The conceptual model of the thermodynamic equilibrium

Figure 2 shows the conceptual model of a vibrating molecule of volume (V_m) in the space (V_{mt}) created and maintained by its vibrations against the van der Waals attraction forces of the medium and the environmental pressure. We assume that we have the same model of molecular vibration in the liquid phase than in the gas phase and so that the molecular volumes V_{mt} and V_m exist just as well in the gas phase as in the liquid phase.

At equilibrium, the oscillation motion of a molecule inside the created volume V_{mt} , identified as the occupational volume of this molecule in its phase, constitutes what we called the external kinetic energy of the molecule, E_{mv} , which is precisely contained in external volume: $V_{mv} = (V_{mt} - V_m)$. The

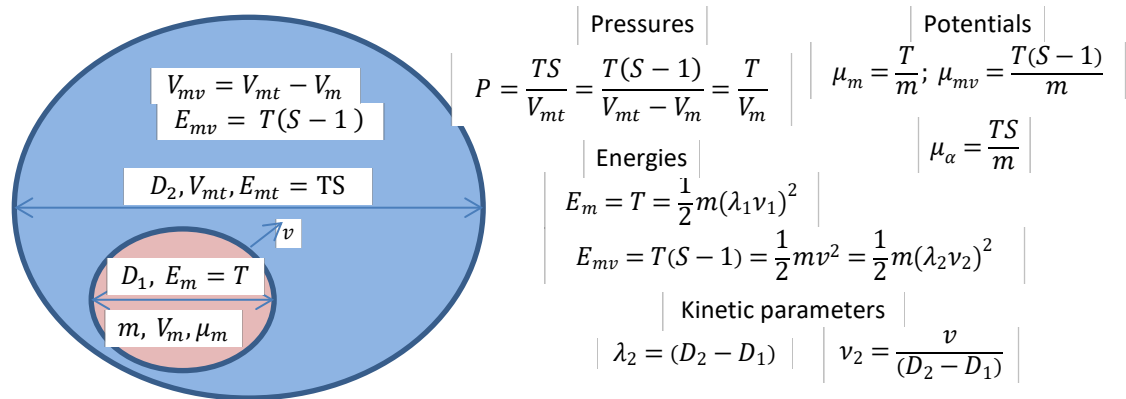


Figure 2. Conceptual model of the thermodynamic equilibrium at molecule organization scale; v is the celerity of the molecule and v_2 is the number of shocks per unit of time

current error is to consider that this kinetic energy is the only one existing in V_{mt} , forgetting then the vibrating energy of molecules E_m in V_m . Thus, even if the total molecular volume V_{mt} is not of the same nature for the liquid and gaseous phases, this volume is accounted for in the same way in that it is the total volume containing both the kinetic energy of the molecule (linear momentum, inertial forces) and its internal vibrational energy, E_{m_i} .

We saw that the macroscopic variables are averages, or ratios of averages, of molecular characteristics and that molecules (or ions) are the primary source of energy of the phase. They manifest this energy homogeneously in the phase, according to equilibrium principles such as the equality of the molecular pressures, the internal chemical potential, or temperature, which are here defined at the microscopic level of the molecules in relation with their masses. We must therefore study these principles of equilibrium by including now the internal organization of the molecule that says, its atomic organization.

2.3.4 Characteristic variables at the atoms-molecule level

In our conceptual model of the thermodynamic equilibrium of fluid phase at macroscopic level, we have introduced the descriptive variables of the internal organization of a molecule considered as an exact assembly of its functional subsystems (vibrators) that are its atoms. Like any system, the subsystems are defined by a functional envelope defining a volume $V_{ma_{ij}}$ and a homogeneous content of mass $m_{a_{ij}}$ and energy $E_{ma_{ij}}$ of oscillatory type. The systemic variables of the molecule i are then:

$$V_{m_i} = \sum_j V_{ma_{ij}} ; m_i = \sum_j m_{a_{ij}} \text{ and } T_i = E_{m_i} = \sum_j E_{ma_{ij}} \quad (36)$$

We deduce automatically from these definitions (36) two fundamental variables that are necessary for defining the internal / external thermodynamic equilibrium of the molecule: the internal molecular pressure ($P_{m_i} = \frac{T_i}{V_i}$) and the molecular chemical potential ($\mu_{m_i} = \frac{T_i}{m_i}$), ratio of the internal energy of the molecule to its mass. We have, indeed, the following equalities:

$$P_{m_i} = \frac{T_i}{V_{m_i}} = \frac{\sum_j E_{ma_{ij}}/n_{a_i}}{\sum_j V_{ma_{ij}}/n_{a_i}} = \frac{E_{ma_i}}{V_{ma_i}} = P_{a_i} \text{ and } \mu_{m_i} = \frac{T_i}{m_i} = \frac{\sum_j E_{ma_{ij}}}{\sum_j m_{a_{ij}}} = \frac{E_{ma_i}}{m_{a_i}} = \mu_{a_i} \quad (37)$$

where E_{ma_i} , V_{ma_i} , and m_{a_i} , are the averages of the oscillation energy, volume and mass values of the n_{a_i} atoms of the molecule i .

Equation (37) shows that the internal pressures of molecules and their atoms have the possibility of being equal; and that it is the same for the chemical potentials and the densities of molecules and their atoms. This comes from the simple fact of the fractional nature (38) of these variables:

$$\frac{a}{b} = \frac{c}{d} = \frac{a+c}{b+d} \quad (38)$$

By analogy with the principle of least action, it may be thought that the criterion of thermodynamic equilibrium leading to a homogeneous distribution of the oscillatory energies of atoms in the molecule is that all the atoms of the molecule each acquire the same pressure and same chemical potential as their assembly, the parent molecule.

$$P_{m_i} = \frac{\sum_j E_{ma_{ij}}}{\sum_j V_{ma_{ij}}} = P_{a_{ij}}; \mu_{m_i} = \frac{\sum_j E_{ma_{ij}}}{\sum_j m_{a_{ij}}} = \mu_{a_{ij}} \text{ and } \rho_{m_i} = \frac{\sum_j m_{a_{ij}}}{\sum_j V_{ma_{ij}}} = \rho_{a_{ij}} \quad (39)$$

We will then assume that, *at thermal equilibrium, the constituent atoms of a molecule all have the same values in pressure and in chemical potential as the mother molecule*, because of the properties of the equivalent fractions. It follows that the density is the same everywhere in the molecule.

Moreover, the oscillation energy being of the form: $E_{ma_i} = \frac{1}{2} m_{a_{ij}} \omega_{a_{ij}}^2 \lambda_{a_{ij}}^2$, the atomic volume $V_{a_{ij}}$ and the atomic density $\rho_{a_{ij}}$ are in direct relationship with $\lambda_{a_{ij}}^2$ and the chemical potential: $\frac{E_{ma_{ij}}}{m_{a_{ij}}}$ with $\frac{1}{2} \omega_{a_{ij}}^2 \lambda_{a_{ij}}^2 \equiv L^2 T^{-2}$.

2.3.5 Characteristic variables at the molecule - phase level

We have seen above that S for liquids and R for gas have the same role, which is that of extending the intra-molecular vibrational energy in the external space of the molecule so that internal and external molecular pressures are equal (24). To establish equations of equilibrium and distribution of molecular energies in the phase, we must first define the systemic variables of the molecular organization of the phase.

Thus, for a molecule i , in the α , liquid or vapor phase, two well-differentiated compartments or energy volumes of the molecule are defined that are: its internal volume $V_{m_{i\alpha}}$ and its external volume: $V_{mv_{i\alpha}}$. The sum of these two volumes is the total volume $V_{mt_{i\alpha}}$ of the molecule which is in fact its occupation volume in the phase. The corresponding molecular energies are: $E_{m_{i\alpha}}$, $E_{mv_{i\alpha}}$ and $E_{mt_{i\alpha}}$, respectively, such that:

$$E_{mt_{i\alpha}} = E_{m_{i\alpha}} + E_{mv_{i\alpha}} \quad (40)$$

where $E_{mt_{i\alpha}}$ is the total molecular energy, $E_{m_{i\alpha}}$, the internal molecular energy, and $E_{mv_{i\alpha}}$, the external molecular energy of the species chemical molecules i in the phase α .

Equation (40) corresponds to:

$$T_{i\alpha}S_{i\alpha} = T_{i\alpha} + T_{i\alpha}(S_{i\alpha} - 1) \quad (41)$$

where $T_{i\alpha}$ is the temperature of molecules i in the phase α and $S_{i\alpha}$ their entropy. So we have, by definition:

$$T_{i\alpha} = E_{m_{i\alpha}} \text{ and } S_{i\alpha} = \frac{V_{mt_{i\alpha}}}{V_{m_{i\alpha}}} \quad (42)$$

At the phase level, temperature $T_{i\alpha}$ like the other molecular characteristics such as the molecular mass $m_{i\alpha}$ and the molecular volumes $V_{m_{i\alpha}}$ and $V_{mt_{i\alpha}}$, can be called “primary organizational variables” of the phase.

2.4 The different qualities of the systemic variables of a phase

2.4.1 Pseudo-intensive variables: average of primary organizational variable

We can then define two kinds of representative average molecule, one (with subscript i) is representative of the set of molecules of chemical species i in the phase, and the other (subscript α) is representative of the mixture of all molecules of (fluid) phase:

- Organizational molecular variables of the phase α relative to the chemical component i , are:

$T_{i\alpha}$, $m_{i\alpha}$, $V_{m_{i\alpha}}$ and $V_{mt_{i\alpha}}$

We can consider them as *pseudo-intensive variables* because each point of the phase is characterized by this partial average molecule homogeneously distributed in the phase:

$$T_{i\alpha} = \frac{\sum_i T_i}{n_{i\alpha}}; m_{i\alpha} = \frac{\sum_i m_i}{n_{i\alpha}}; V_{m_{i\alpha}} = \frac{\sum_i V_{m_i}}{n_{i\alpha}}; V_{mt_{i\alpha}} = \frac{\sum_i V_{mt_i}}{n_{i\alpha}} \quad (43)$$

where $n_{i\alpha}$ is the number of molecules of species i in the phase.

- Organizational molecular variables of the total mixture of the phase are:

T_α , m_α , V_{m_α} and V_{mt_α}

which are averages of organizational variables of all molecules over the phase:

$$T_\alpha = \frac{\sum_i n_{i\alpha} T_{i\alpha}}{n_\alpha} = \frac{\sum_i \sum_\alpha T_i}{n_\alpha}; m_\alpha = \frac{\sum_i n_{i\alpha} m_{i\alpha}}{n_\alpha} = \frac{\sum_i \sum_\alpha m_i}{n_\alpha}; \quad (44)$$

$$V_{m_\alpha} = \frac{\sum_i n_{i\alpha} V_{m_{i\alpha}}}{n_\alpha} = \frac{\sum_i \sum_\alpha V_{m_i}}{n_\alpha}, V_{mt_\alpha} = \frac{\sum_i n_{i\alpha} V_{mt_{i\alpha}}}{n_\alpha} = \frac{\sum_i \sum_\alpha V_{mt_i}}{n_\alpha} \quad (44)$$

where n_α is the total number of molecules in the phase: $n_\alpha = \sum_i n_{i\alpha}$.

As for the previous case, these variables can be said “pseudo-intensive” because they are those of the same averaged molecule that represents all points (molecules) of the phase.

2.4.2 True intensive variables: Pressure, Entropy and Chemical potential

Accordingly, three true intensive variables can be deduced as fractional numbers from the primary (molecular) variables or the pseudo-intensive variables as well (for mixtures of different chemical types of molecules):

$$\mu_{m_\alpha} = \frac{T_\alpha}{m_\alpha} = \frac{\sum_i n_{i\alpha} T_i / n_\alpha}{\sum_i n_{i\alpha} m_i / n_\alpha} \quad (45)$$

$$S_\alpha = \frac{V_{mt_\alpha}}{V_{m_\alpha}} = \frac{\sum_i n_{i\alpha} V_{mt_i} / n_\alpha}{\sum_i n_{i\alpha} V_{m_i} / n_\alpha} \quad (46)$$

$$P_{\alpha} = \frac{T_{\alpha}}{V_{m_{\alpha}}} = \frac{\sum_i n_{i\alpha} T_i / n_{\alpha}}{\sum_i n_{i\alpha} V_{m_i} / n_{\alpha}} \quad (47)$$

As intensive variables, they have the same value at each point of the phase and at each organization level of the phase: atomic, molecular and macroscopic (the phase level). This property makes them differentiable.

The chemical potential of the phase, μ_{α} , is also a true intensive variable as the product of both true intensive variables, $\mu_{m_{\alpha}}$ and S_{α} .

$$\mu_{\alpha} = \mu_{m_{\alpha}} S_{\alpha} = \frac{T_{\alpha} V_{mt_{\alpha}}}{m_{\alpha} V_{m_{\alpha}}} \quad (48)$$

They have the important property of the fractional equivalent numbers (equation 32) that we used above to show that a molecule and its atoms necessarily have the same pressure and the same chemical potential. This property also applies to the relationship between the phase and its constituent molecules, indeed we have:

$$P_{\alpha} = \frac{T_{\alpha}}{V_{m_{\alpha}}} = \frac{\sum_i n_{i\alpha} T_i}{\sum_i n_{i\alpha} V_{mt_i}} = \frac{T_{i\alpha}}{V_{m_{i\alpha}}} = P_{m_{i\alpha}} \quad (49)$$

showing that : $P_{\alpha} = P_{m_{i\alpha}}$ at each point (molecule) of the medium (the phase)

And since $P_{\alpha} = \frac{T_{\alpha}}{V_{m_{\alpha}}} = \frac{T_{\alpha} S_{\alpha}}{V_{mt_{\alpha}}}$ and $P_{m_{i\alpha}} = \frac{T_{i\alpha} S_{i\alpha}}{V_{mt_{i\alpha}}}$, we should have also $\frac{T_{\alpha}}{V_{m_{\alpha}}} = \frac{\sum_i T_{i\alpha} / n_{\alpha}}{\sum_i V_{mt_{i\alpha}} / n_{\alpha}} = \frac{T_{i\alpha}}{V_{m_{i\alpha}}}$ and:

$$S_{\alpha} = \frac{V_{mt_{\alpha}}}{V_{m_{\alpha}}} = \frac{\sum_i n_{i\alpha} V_{mt_i}}{\sum_i n_{i\alpha} V_{m_i}} = \frac{V_{mt_{i\alpha}}}{V_{m_{i\alpha}}} = S_{i\alpha} \quad (50)$$

Regarding the molecular chemical potential of the phase: $\mu_{m_{\alpha}}$, it is of the same nature as pressure and entropy: a fractional number which is the ratio of the mean temperature of the molecules of the phase to the average of their masses (eq. 45).

For saying that the equality: $\frac{T_{\alpha}}{m_{\alpha}} = \frac{T_{i\alpha}}{m_{i\alpha}}$ is probably true, we have to note two things: i) that the simplest energetic solution for obtaining an ordered equilibrium of the vibrating molecules of a fluid phase is that the chemical potential is the same for all the molecules of the phase, whatever their chemical species; and ii) that the temperature of a phase (T_{α}) is an average of the different temperatures of the phase and so cannot be the equilibrium criteria of the phase, unlike $\mu_{m_{\alpha}}$ which is already a criterion of equilibrium at intra molecular level, as we have shown above.

We will therefore advance the highly probable hypothesis that the molecular chemical potential of the phase: $\mu_{m_{\alpha}}$ is the equilibrium criterion of the phase. It is a true intensive variable of the fluid phase and, just like P_{α} and S_{α} , represents as well the average molecule α representative of the phase, as the average molecule i representative of the chemical species i present in the phase or the single molecule i of the phase:

$$\mu_{m_{\alpha}} = \frac{T_{\alpha}}{m_{\alpha}} = \frac{\sum_i n_{i\alpha} T_{i\alpha} / n_{\alpha}}{\sum_i n_{i\alpha} m_{i\alpha} / n_{\alpha}} = \frac{T_{i\alpha}}{m_{i\alpha}} = \mu_{m_{i\alpha}} \quad (51)$$

It is the same for the phase chemical potential μ_{α} .

$$\mu_{\alpha} = \mu_{m_{\alpha}} S_{\alpha} = \frac{T_{\alpha} S_{\alpha}}{m_{\alpha}} = \frac{E_{mt_{\alpha}}}{m_{\alpha}} = \frac{E_{mt_{i\alpha}}}{m_{i\alpha}} = \mu_{i\alpha} \quad (52)$$

Thus, the 4 fractional variables of the phase: P_{α} , S_{α} , $\mu_{m_{\alpha}}$ and μ_{α} have the same physical value at the two levels of scale, macroscopic (phase) and punctual (molecule), everywhere in the phase. This is why these 4 fractional variables are called "true intensive variables", compared to pseudo-intensive

variables: T_α , $V_{mt\alpha}$, m_α and $V_{m\alpha}$ that are only averages. These last also have the same values at every point of the phase but these values are averages, and are not equal to the exact physical values at each point of the phase as are the true intensive variables.

2.4.3 Extensive and partial extensive variables

Let us call $E_{t\alpha}$ the total free energy of a fluid phase α of volume V_α , and $E_{t_{i\alpha}}$ the total free energy of the partial volume $V_{i\alpha}$, occupied by molecules of chemical species i in the same phase. We have, by definition:

$$E_{t\alpha} = n_\alpha E_{mt\alpha} \text{ and } E_{t_{i\alpha}} = n_{i\alpha} E_{mt_{i\alpha}} \quad (53)$$

Where n_α is the total number of molecules in phase α of volume V_α and $n_{i\alpha}$ is the number of molecules of chemical species i in same volume V_α .

Using the particular property of the true intensive variables highlighted above, we can obtain the following equalities:

$$E_{t\alpha} = \sum_i E_{t_{i\alpha}} = \sum_i n_{i\alpha} V_{mt_{i\alpha}} P_{m_{i\alpha}} = P_\alpha \sum_i n_{i\alpha} V_{mt_{i\alpha}} = P_\alpha \sum_i V_{i\alpha} = P_\alpha V_\alpha = P_\alpha n_\alpha V_{mt\alpha} \quad (54)$$

These relationships define $V_{mt\alpha}$ since $V_\alpha = \sum_i V_{i\alpha}$ and $n_\alpha = \sum_i n_{i\alpha}$:

$$V_{mt\alpha} = \sum_i V_{i\alpha} / \sum_i n_{i\alpha} = V_\alpha / n_\alpha \quad (55)$$

The same for

$$E_{t_{i\alpha}} = n_{i\alpha} T_i S_\alpha \text{ leading to } E_{t\alpha} = \sum_i E_{t_{i\alpha}} = n_\alpha S_\alpha T_\alpha \quad (56)$$

and

$$E_{t_{i\alpha}} = n_{i\alpha} m_i \mu_\alpha \text{ leading to } E_{t\alpha} = \sum_i E_{t_{i\alpha}} = n_\alpha m_\alpha \mu_\alpha \quad (57)$$

By multiplying the intensive or pseudo-intensive state variables by $n_{i\alpha}$, there is obtained the extensive variables of the partial energy of the phase with respect to the chemical species concerned.

By multiplying by $n_{i\alpha}$ the intensive or pseudo-intensive state variables of a phase α of volume V_α , we obtain the extensive variables of the partial energy of the phase relative to the chemical species i in the partial volume $V_{i\alpha}$ of V_α .

These extensive properties, partial and total, are recapped hereafter, developed according to their definition:

At the molecule level:

$$V_{i\alpha} = n_{i\alpha} V_{mt_i} ; M_{i\alpha} = n_{i\alpha} m_i ; V_{i\alpha} = n_{i\alpha} V_{mt_i} ; E_{t_{i\alpha}} = n_{i\alpha} E_{mt_{i\alpha}} \quad (58)$$

$$E_{t_{i\alpha}} = (n_{i\alpha} S_\alpha) T_{i\alpha} = P_\alpha V_{i\alpha} = M_{i\alpha} \mu_{i\alpha} \quad (59)$$

and at the phase level

$$V_\alpha = n_\alpha V_{mt\alpha} = \sum_i n_{i\alpha} V_{mt_i} ; M_\alpha = n_\alpha m_\alpha = \sum_i M_{i\alpha} = \sum_i n_{i\alpha} m_i ; \quad (60)$$

$$E_{t\alpha} = n_\alpha E_{mt\alpha} = (n_\alpha S_\alpha) T_\alpha = P_\alpha V_\alpha = M_\alpha \mu_{w\alpha} \quad (61)$$

3 New understanding of the thermodynamics

3.1 Significant differences between the two approaches

Let us summarize below the clarifications provided by the systemic description of the molecular organization of a "free" (aqueous or gaseous) phase of a thermodynamic system (such as soil).

- All systemic variables characterizing the molecular organization and energy state of the fluid (liquid or gaseous) phases of a natural thermodynamic system at equilibrium are summarized as follows:

- S_α , P_α , μ_{m_α} and μ_α , are true intensive variables of the phase, i.e. fractional numbers which have the same values at the level of the molecule as at the level of the phase, and this, in every point (molecule) of the phase.

- T_w , T_α , V_{mt_w} , V_{mt_α} , V_{m_w} , V_{m_α} , m_w and m_α , are pseudo-intensive, i.e. equal to the average molecular variable of a particular chemical element of the phase (here water) or of all the molecules of the phase;

- $\{E_{t_{w\alpha}}, (n_{w\alpha}S_\alpha), V_{w\alpha}$ and $M_{w\alpha}\}$ and $\{E_{t_\alpha}, (n_\alpha S_\alpha), V_\alpha$, and $M_\alpha\}$ are, respectively, partial extensive variables and total extensive variables of the phase according to equations (59) and (61).

- The temperature T_α of a phase α is a *pseudo-intensive variable*, like all the extensive molecular variables (energies, volumes, masses) divided by the number of molecules concerned. T_α represents the average temperature of the constituent molecules of the phase that says the average internal molecular energy of the phase (ionized or not) E_{m_α} . This is why two different composition phases, at equilibrium, cannot have the same average temperature, contrary to what is currently thought.

- The molecular chemical potential (μ_{m_α}) is the real thermodynamic equilibrium criterion for the whole system. It has the same value in the different phases of the system ($\mu_{m_\alpha} = \mu_m$), contrarily to the temperature (T_α) which is different from one phase to another.

- However, the temperature of water, T_w , can also be taken as equilibrium criterion like μ_m , since $T_w = \mu_m m_w$ and that m_w is a constant (mass of a water molecule) contrarily to m_α in $T_\alpha = \mu_m m_\alpha$.

- The entropy S_α of a phase α is a true intensive variable: a fractional variable that is the ratio of two molecular variables which has the same value at all points (molecules) of the phase. That is also to define the entropy of a molecule as the ratio of its total energy to its internal energy, or the ratio of its full chemical potential to its internal potential since we have, for the molecule of water:

$$S_w = \frac{T_w S_w}{T_w} = \frac{\mu_w}{\mu_{m_w}} = \left(\frac{(\lambda\omega)^2 + v^2}{(\lambda\omega)^2} \right)_w \quad (62)$$

where λ and ω are the amplitude and pulsation of vibration of the molecule and v , its velocity in the medium.

We have to note that the entropy S , as used in the thermodynamic potential equations or in the Gibbs-Duhem equation (Sposito, 1981), is written alone, without the multiplicative term $n_{i\alpha}$ or n_α . That shows that S , in these equations, means in fact $n_\alpha S_\alpha$ which is then an extensive variable.

This is why we chose to consider the product $n_\alpha S_\alpha$ as the extensive variable S used in classical thermodynamics, and keep the term entropy for the intensive variable S_α for the case of a phase and S_i for the case of a molecule. Thus, the temperature T_α stays intensive and is the conjugate variable of $n_\alpha S_\alpha$.

- The Gibbs free energy G_α defined in its Euler form by equation (19, 27), is equal to the total molecular energy E_{t_α} of the fluid phases. Therefore, according equalities (59) and (61), it can be written under

three equivalent forms of writing, representing the different expressions of the partial free energy $G_{w\alpha}$ (of water) and total free energy G_α (of the phase):

$$G_{w\alpha} = n_{w\alpha}m_w\mu_{w\alpha} = M_{w\alpha}\mu_{w\alpha} = E_{t_{w\alpha}} = (n_{i\alpha}S_\alpha)T_{i\alpha} = P_\alpha V_{i\alpha} \quad (63)$$

and

$$G_\alpha = n_\alpha m_\alpha \mu_\alpha = M_\alpha \mu_\alpha = E_{t_\alpha} = (n_\alpha S_\alpha)T_\alpha = P_\alpha V_\alpha \quad (64)$$

It becomes clear that the Gibbs free energy of these fluid phases, generally known in its differential form (27, 31), is exactly the total energy of all the motions (displacements, vibrations, oscillations, rotations) of the n_α particles (molecules, ions) of these phases, in equilibrium with each other.

We now have to confront our conceptual model of the Gibbs free energy (molecular energy of the fluid phases of a thermodynamic system at equilibrium) with the thermodynamic potentials equations of the classical thermodynamics, like equations (25) to (31).

3.2 Internal energy U and the equivalent forms of writing the Gibbs free energy

Equations (58) to (64) define the 3 equivalent forms of writing G as the internal and external motion energy of molecules of a fluid (liquid or gaseous) phase. These equations are valid at all three levels: that of the molecule alone in its environment, the phase; that of a chemical species present in the phase (water for example); and finally the macroscopic one of the phase itself. Compared with the internal energy U of a thermodynamic system, it constitutes the free part of U which also contains a fixed part, U_0 , constituted by energies of constitution of molecules of the phase. So that we can write, for a fluid phase " α ", according to our molecular model of free energy :

$$U_\alpha - U_{0\alpha} = (TS)_\alpha = (PV)_\alpha = G_\alpha \quad (65)$$

Therefore, using our nomenclature, we can rewrite (65) like:

$$U_\alpha - U_{0\alpha} = n_\alpha T_\alpha S_\alpha = P_\alpha V_\alpha = n_\alpha m_\alpha \mu_\alpha \quad (66)$$

or, taking the water temperature T_w as reference:

$$U_{w\alpha} - U_{0w\alpha} = n_{w\alpha} T_w S_\alpha = P_\alpha V_{w\alpha} = n_{w\alpha} m_w \mu_\alpha \quad (67)$$

where $U_{w\alpha}$ is the partial internal energy, relative to the molecule of water and defined by the relation. We have indeed

$$U_\alpha - U_{0\alpha} = \sum_i (U_{i\alpha} - U_{0i\alpha}) \quad (68)$$

and following the definition of the free Gibbs energy by equations (61) and (62), equation (65) of the internal energy U_α can be written as :

$$U_\alpha - U_{0\alpha} = G_\alpha \text{ and } U_{i\alpha} - U_{0i\alpha} = G_{i\alpha} \quad (69)$$

That says that the internal energy U_α is composed of two kinds of energy: one, fixed, is the formation energy of molecules and the other, subject to variation, is the free energy which is the motion energy of molecules and their atoms. Consequently, the differentials of U_α and G_α or $U_{w\alpha}$ and $G_{w\alpha}$ are the same:

$$dU_\alpha = dG_\alpha = d(n_\alpha T_\alpha S_\alpha) = d(P_\alpha V_\alpha) = d(n_\alpha m_\alpha \mu_\alpha) \quad (70)$$

$$dU_{w\alpha} = dG_{w\alpha} = d(n_{w\alpha} T_w S_\alpha) = d(P_\alpha V_{w\alpha}) = d(n_{w\alpha} m_w \mu_\alpha) \quad (71)$$

To report the extensive variables to a fixed reference of the system, in general its structural mass M_s which is a unique and constant reference, we divide all the variables "number of molecules", like $n_{i\alpha}$ or n_α , by the structural mass of the system M_s . Any referenced extensive variable is then written with a horizontal bar above it. We thus have:

$$\bar{n}_\alpha = \frac{n_\alpha}{M_s}, \bar{S}_\alpha = \bar{n}_\alpha S_\alpha; \bar{V}_\alpha = \bar{n}_\alpha V_{mt_\alpha} \text{ and } \bar{M}_\alpha = \bar{n}_\alpha m_w \quad (72)$$

and, if the temperature of water is taken as reference:

$$\bar{n}_{w\alpha} = \frac{n_{w\alpha}}{M_s}; \bar{S}_{w\alpha} = \bar{n}_{w\alpha} S_\alpha; \bar{V}_{w\alpha} = \bar{n}_{w\alpha} V_{mt_\alpha} \text{ and } \bar{M}_{w\alpha} = \bar{n}_{w\alpha} m_w \quad (\text{bb}) \quad (73)$$

The two internal energy equations U_α and $U_{w\alpha}$ become

$$\bar{U}_\alpha - \bar{U}_{0\alpha} = T_\alpha \bar{S}_\alpha = P_\alpha \bar{V}_\alpha = \bar{M}_\alpha \mu_\alpha \quad (\text{aaa}) \quad (74)$$

$$\bar{U}_{w\alpha} - \bar{U}_{0w\alpha} = T_w \bar{S}_{w\alpha} = P_\alpha \bar{V}_{w\alpha} = \bar{M}_{w\alpha} \mu_\alpha \quad (75)$$

Note here that we made the choice to take T_α as the intensive variable and $\bar{S}_\alpha$ as the extensive variable for being in the same terms of comparison with the classical equations.

3.3 Exact total differential of the internal energy $\bar{U}_\alpha$

There are three possible ways to add the 3 writing forms of G to obtain the internal energy $\bar{U}_\alpha$ of the phase (positive quantity) so that all the state variables are represented:

$$\bar{U}_{\alpha 1} - \bar{U}_{0\alpha} = T_\alpha \bar{S}_\alpha - P_\alpha \bar{V}_\alpha + \mu_\alpha \bar{M}_\alpha \quad (\text{dd}) \quad (76)$$

$$\bar{U}_{\alpha 2} - \bar{U}_{0\alpha} = T_\alpha \bar{S}_\alpha + P_\alpha \bar{V}_\alpha - \mu_\alpha \bar{M}_\alpha \quad (78)$$

$$\bar{U}_{\alpha 3} - \bar{U}_{0\alpha} = -T_\alpha \bar{S}_\alpha + P_\alpha \bar{V}_\alpha + \mu_\alpha \bar{M}_\alpha \quad (79)$$

Take for example the total derivative of $\bar{U}_{\alpha 1}$

$$d\bar{U}_{\alpha 1} = T_\alpha d\bar{S}_\alpha - P_\alpha d\bar{V}_\alpha + \mu_\alpha d\bar{M}_\alpha + (\bar{S}_\alpha dT_\alpha - \bar{V}_\alpha dP_\alpha + \bar{M}_\alpha d\mu_\alpha) \quad (80)$$

If we assert that, according to the two principles of thermodynamics, $\bar{U}_{\alpha 1}$ is a function of the extensive variables: $\bar{S}_\alpha$, $\bar{V}_\alpha$ and $\bar{M}_\alpha$, we assert at the same time that the partial differential of $\bar{U}_{\alpha 1}$ in these 3 variables is an exact total differential and so that the expression in parenthesis is null:

$$d\bar{U}_{\alpha 1} = T_\alpha d\bar{S}_\alpha - P_\alpha d\bar{V}_\alpha + \mu_\alpha d\bar{M}_\alpha \quad (81)$$

and

$$(\bar{S}_\alpha dT_\alpha - \bar{V}_\alpha dP_\alpha + \bar{M}_\alpha d\mu_\alpha) = 0 \quad (82)$$

The classical forms of the exact total differential of the internal energy U of a system and the associated Gibbs-Duhem equation (31) are well recognized in (81) and (82).

The problem is that there are 3 combinations of possible signs (2 signs + for sign -) whereas the classical thermodynamics imposes the choice of one of them. Since there are 7 variables for 3 equations (74, 75) and two known variables (M_α and V_α), the 2 equations (81) and (82) coming from $\bar{U}_{\alpha 1}$, impose the sign of variations of the variables relative to each other; and in particular with variations of $\bar{M}_\alpha$ and $\bar{V}_\alpha$ that is to say, in fact, with $\bar{n}_\alpha$ and ρ_α , the molecules number and the density of the phase.

We must therefore study the significance of these three possible forms of Gibbs Duhem's equation, which we will call GD1, GD2 and GD3, and confirm or refute the choice of $\bar{U}_{\alpha 1}$ and GD1 of classical thermodynamics for our molecular model of a thermodynamic phase at equilibrium.

The Gibbs Duhem equations GD2 and GD3 corresponding to $\bar{U}_{\alpha 2}$ and $\bar{U}_{\alpha 3}$ are:

$$GD2 \equiv \bar{S}_\alpha dT_\alpha + \bar{V}_\alpha dP_\alpha - \bar{m}_\alpha d\mu_\alpha = 0 \quad (83)$$

$$GD3 \equiv -\bar{S}_\alpha dT_\alpha + \bar{V}_\alpha dP_\alpha + \bar{m}_\alpha d\mu_\alpha = 0 \quad (84)$$

Let us study the meaning of each of these Gibbs-Duhem equations in relation to the internal variation of the hidden variables V_{m_α} and V_{mt_α} , knowing that $T_\alpha/P_\alpha = V_{m_\alpha}$ and $\mu_\alpha/P_\alpha = V_{mt_\alpha}$ by definition.

Since $\bar{S}_\alpha dT_\alpha = \bar{V}_\alpha dP_\alpha = \bar{m}_\alpha d\mu_\alpha$ we can rewrite the functions GD1, GD2 and GD3 by dividing each term by the corresponding energy form, which gives

$$GD1 \equiv d\log(T_\alpha) - d\log(P_\alpha) + d\log(\mu_\alpha) = 0 \quad (85)$$

$$GD2 \equiv d\log(T_\alpha) + d\log(P_\alpha) - d\log(\mu_\alpha) = 0 \quad (86)$$

$$GD3 \equiv -d\log(T_\alpha) + d\log(P_\alpha) + d\log(\mu_\alpha) = 0 \quad (87)$$

From each of these equations we deduce the constraints of variation that it imposes:

- In the case of GD1 (85) :

$$d\log(\mu_\alpha) = -d\log(T_\alpha) + d\log(P_\alpha) = -d\log(V_{m_\alpha}) \quad (88)$$

The two state variables μ_α and V_{m_α} are inversely proportional . However, knowing that $d\log(\mu_\alpha) = d\log(T_\alpha S_\alpha)$, equation (86) implies a second constraint, between the temperature and V_{mt_α} :

$$d\log(T_\alpha) = -d\log(V_{mt_\alpha}) \quad (89)$$

which is contrary to the observation (dilation of water with temperature above 3 ° C).

- Case of GD2 (86):

$$d\log(\mu_\alpha) = d\log(T_\alpha) + d\log(P_\alpha) = 2d\log(T_\alpha) - d\log(V_{m_\alpha}) \quad (90)$$

The direction of variation of μ_α with V_{m_α} is the same as in the previous case and by developing $d\log(\mu_\alpha)$ in equation (90) result in:

$$d\log(T_\alpha) = d\log(V_{mt_\alpha}) \quad (91)$$

which is consistent with the observation.

- Case of GD3 (87):

$$d\log(\mu_\alpha) = d\log(T_\alpha) - d\log(P_\alpha) = d\log(V_{m_\alpha}) \quad (92)$$

The μ_α and V_{m_α} variations are directly proportional, unlike the previous two cases. By developing $d\log(\mu_\alpha)$ we get:

$$d\log(T_\alpha) = d\log(V_{m_\alpha}) - d\log(S_\alpha) \quad (93)$$

However, the fact that, at constant temperature, the pressure and the chemical potential vary in opposite directions in the GD3 equation (87), whereas they should vary in the same direction, both having the variable V_{m_α} at the denominator, does not allow to retain this constraint of variation.

Therefore, among the three possible forms of Gibbs Duhem equation, the only one consistent with experiment is GD2, corresponding to the writing of the internal energy in the form:

$$d\bar{U}_{\alpha 2} = d(T\bar{S})_\alpha + d(P\bar{V})_\alpha - d(\mu_\alpha \bar{M}_\alpha) = T_\alpha dS_\alpha + P_\alpha d\bar{V}_\alpha - \mu_\alpha d\bar{M}_\alpha \quad (94)$$

$$\text{with } GD2 \equiv \bar{S}_\alpha dT_\alpha + \bar{V}_\alpha dP_\alpha - \bar{m}_\alpha d\mu_\alpha = 0 \quad (95)$$

The latter requires that P and μ vary in the same direction that is inversely proportional to the internal molecular volume of the phase; and secondly that there is dilatation of water with increasing temperature.

Note that, by introducing $d\bar{G}_\alpha = \bar{M}_\alpha d\mu_\alpha + \mu_\alpha d\bar{M}_\alpha$ into equation (95), the equation of the total differential of Gibbs free energy becomes, rather than the classical equation (31):

$$d\bar{G}_\alpha = \bar{S}_\alpha dT_\alpha + \bar{V}_\alpha dP_\alpha + \mu_\alpha d\bar{M}_\alpha \quad (96)$$

By replacing the term $\bar{S}_\alpha dT_\alpha$ by $(d(\bar{S}_\alpha T_\alpha) - T_\alpha d\bar{S}_\alpha)$ we obtain the total differential of enthalpy $H(S, P, M)$; it is equal to zero since $d(\bar{S}_\alpha T_\alpha) = d\bar{G}_\alpha$.

$$dH_\alpha = -T_\alpha d\bar{S}_\alpha + \bar{V}_\alpha dP_\alpha + \mu_\alpha d\bar{M}_\alpha = 0 \quad (97)$$

Similarly, by replacing $\bar{V}_\alpha dP_\alpha$ by $(d(\bar{V}_\alpha P_\alpha) - P_\alpha d\bar{V}_\alpha)$ in (95), we obtain the total differential of Helmholtz energy $A(T, V, M)$ which is also equal to zero.

$$dA_\alpha = \bar{S}_\alpha dT_\alpha - P_\alpha d\bar{V}_\alpha + \mu_\alpha d\bar{M}_\alpha = 0 \quad (98)$$

Thus, the simple use of the systemic molecular model of a fluid phase, at thermodynamic equilibrium, leads to GD2 instead of the classical Gibbs-Duhem equation GD1 for being in agreement with experiment.

3.4 Discrepancy between equations coming from the two approaches

The main reason for this discrepancy is of course that the variables T , μ and P do not exactly cover the same meanings in the two approaches, systemic and non-systemic, of a thermodynamic system. The fact that the organizational volumes of the system are not definitively taken as internal state variables, as in the classical thermodynamics, did not allow establishing an inside and an outside for the system and its sub-systems, as properties of the system. This has not allowed classical thermodynamics to take into account the two types of energy carried by each molecule: T_i and $T_i(S_\alpha - 1)$ within the phase; while these energies and their volumes of occupation are recognized in the new systemic vision of thermodynamics. Moreover, the pressure variable cannot mean another type of pressure than the atmospheric pressure, which is currently seen as due to the thermal agitation: the only one of the two energies carried by molecules, the kinetic energy of molecules. The statistical theory of Boltzmann gases is based on this representation and cannot apply to the internal pressure in liquid phase.

On the contrary, in the systemic vision of the molecular phase organization, any thermodynamic system is defined as a macroscopic object having a determined volume (envelope) containing a very large but finite number of organized sub-systems (molecules). The confusion between the external and internal energy of the system is avoid. According to conceptual model Figure 3, the external energy of the object-system is that of the atmospheric environment: $P_\alpha V_\alpha = N_\alpha RT_\alpha$, while the internal free energy of the object-system can be written exactly under the three equivalent forms of energy highlighted here ($P_\alpha V_{w\alpha} = n_{w\alpha} S_\alpha T_w = M_{w\alpha} \mu_{m_w} S_\alpha$).

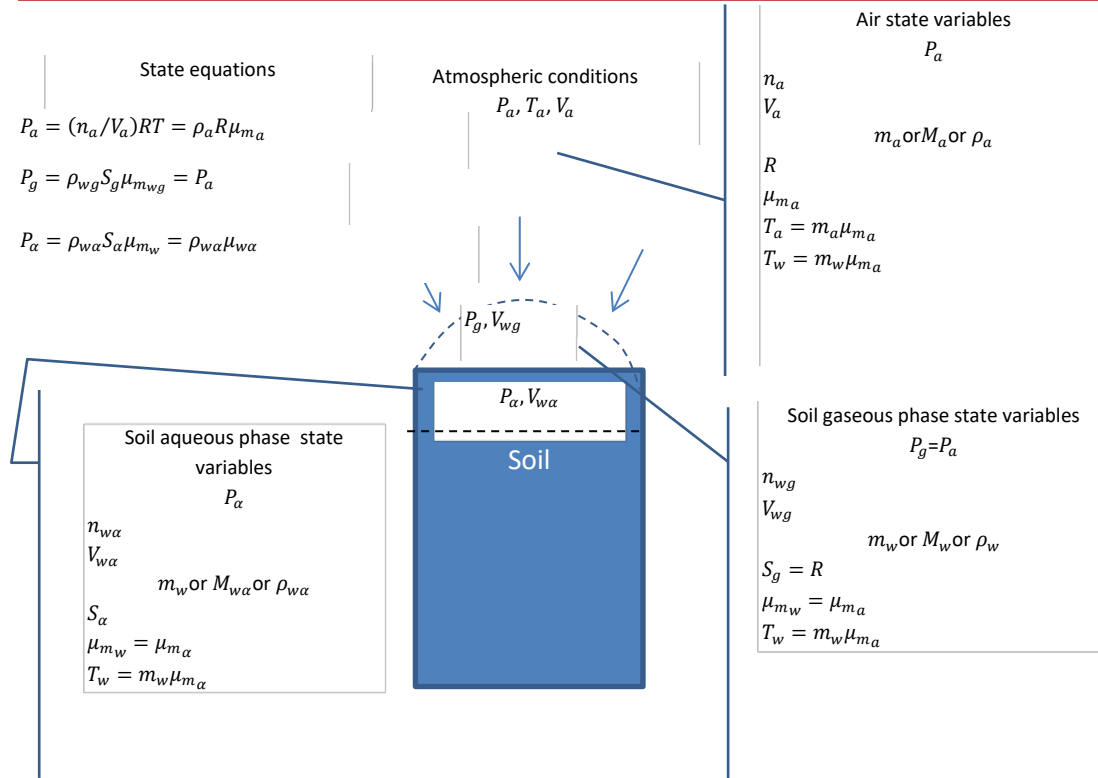


Figure 3. Conceptual model of the soil surface system at thermodynamic equilibrium under atmospheric conditions. The molecular chemical potential, μ_m , is the criteria of equilibrium instead of temperature and have the same value everywhere in the system at equilibrium.

4 Application to soil water air system at equilibrium

4.1 The soil water retention pressure equation

Unlike free water, the soil's pedostructural water is trapped in the electric field developed by the surface charges of the clays composing the aggregates. That is to say that the 2 aqueous phases of the pedostructure, inter- and intra-primary aggregates, have their free energy $\bar{G}_\alpha$ remaining constant despite the change in the amount of water of each phase (eq. 1).

Equations 1 rewritten using the new terminology give:

$$\bar{G}_{w\alpha 1} = \bar{m}_{w\alpha 1} \mu_{\alpha 1} = \bar{E}_{\alpha 1} \text{ et } \bar{G}_{w\alpha 2} = \bar{m}_{w\alpha 2} \mu_{\alpha 2} = \bar{E}_{\alpha 2} \quad (99)$$

where $\bar{E}_{\alpha 1}$ and $\bar{E}_{\alpha 2}$ are energy constants that are thought to be due to the surface charges of the clays with which the aqueous phases $\alpha 1$ and $\alpha 2$ are in contact and at equilibrium together in the intra and inter primary aggregates spaces.

According to the Gibbs-Duhem equation (GD2), at constant temperature we have:

$$\bar{V}_{w\alpha 1} dP_{\alpha 1} = \bar{m}_{w\alpha 1} d\mu_{\alpha 1} \quad (100)$$

so,

$$dP_{\alpha 1} = \rho_w d\mu_{\alpha 1}$$

We also know that, at constant temperature, $V_{mt\alpha 1}$ is constant and therefore $\rho_{w\alpha 1}$ too. Only $V_{mt\alpha 1}$ is changing inversely proportionally to the concentration of water $\bar{m}_{w\alpha 1}$. Indeed, since $G_{\alpha 1}$ and $G_{\alpha 2}$ are constant: $dG_{\alpha 1} = \bar{m}_{w\alpha 1} d\mu_{\alpha 1} + \mu_{\alpha 1} d\bar{m}_{w\alpha 1} = 0$, and we have the following relations:

$$d\log(\mu_{\alpha 1}) = -d\log(\bar{m}_{w\alpha 1}) \text{ and } d\log(\mu_{\alpha 2}) = -d\log(\bar{m}_{w\alpha 2})$$

Starting from the saturated state where no suction h is observed, the evaporation of water causes the internal pressure of the aqueous phases to pass from $P_{\alpha 1 sat}$ to $P_{\alpha 1}$; that says from the equilibrium pressure at the saturated state ($\bar{m}_{w\alpha 1^\circ}$) to the increasing internal pressure of the phase $P_{\alpha 1}$ at water content ($\bar{m}_{w\alpha 1}$). The water retention pressure, $h \geq 0$, is defined by $h_{\alpha 1} = P_{\alpha 1} - P_{\alpha 1 sat}$ as follows:

$$h = \int_{sat}^{m_{\alpha 1}} dP_{\alpha 1} = \rho_w \int_{sat}^{m_{\alpha 1}} d\mu_{\alpha 1} = \rho_w \int_{sat}^{m_{\alpha 1}} d\left(\frac{\bar{E}_{\alpha 1}}{\bar{m}_{w\alpha 1}}\right) \quad (101)$$

Hence the equation of the suction pressure in the aqueous phases of the pedostructure (Braudeau et al. 2014²)

$$h_{\alpha 1} = P_{\alpha 1} - P_{\alpha 1^\circ} = \rho_w \bar{E}_{\alpha 1} \left(\frac{1}{\bar{m}_{w\alpha 1}} - \frac{1}{\bar{m}_{w\alpha 1^\circ}} \right) \quad (102)$$

$$h_{\alpha 2} = P_{\alpha 2} - P_{\alpha 2^\circ} = \rho_w \bar{E}_{\alpha 2} \left(\frac{1}{\bar{m}_{w\alpha 2}} - \frac{1}{\bar{m}_{w\alpha 2^\circ}} \right)$$

During evaporation, the pedostructure remaining at equilibrium and at constant temperature, the suction pressure in the pedostructure (subscript ps) is $h_{ps} = h_{\alpha 1} = h_{\alpha 2}$ and corresponds to the water content $W_{ps} = \bar{m}_{w\alpha 1} + \bar{m}_{w\alpha 2}$. Considering these equalities allows us to calculate the water content in each of the two phases ($\bar{m}_{w\alpha 1}$ and $\bar{m}_{w\alpha 2}$) as well as the water retention pressure h_{ps} according to the overall water content W_{ps} (Braudeau et al., 2014c).

The agreement experiments with theory is exemplary (Figure 3)

Let us now see the equilibrium of the aqueous phase with its vapor phase.

4.2 Equilibrium of the soil water phase with atmosphere

Suppose the soil water is in equilibrium with its vapor (Figure 3). The aqueous phase of the pedostructure in contact with the air is its macroscopic (inter aggregates) aqueous phase $\alpha 1$.

As there is equilibrium between the liquid phase and the vapor phase of water, the energy variation due to a variation in the number of molecules must be the same in both phases:

$$(\Delta G_{wg})_{T,P} = (\Delta G_{wl})_{T,P}$$

$$\mu_{wl} d\bar{m}_{wl} = \mu_{wg} d\bar{m}_{wg} = RT_w d\bar{n}_{wg} \quad (104)$$

However, we know that for the liquid phases of soil:

$$d(\mu_{wl} \bar{m}_{wl}) = \mu_{wl} d\bar{m}_{wl} + \bar{m}_{wl} d\mu_{wl} = 0 \quad (105)$$

Thus, equation (101) can be written:

$$RT_w d\bar{n}_{wg} = -\bar{m}_{wl} d\mu_{wl} \quad (106)$$

Let us seek to obtain the relation between $\bar{n}_{wg}$ and $\bar{n}_{wl}$, the numbers of water molecules in the two respective phases. It is known that, starting from the equilibrium in the saturated state, a decrease in the water content in the aqueous phase results in an increase in the retention pressure h , the corresponding water retention energy of the phase passing from 0 to $h\bar{V}_{wl}$. Similarly, a decrease in the number of water molecules in the gas phase results in a decrease in the partial volume of the

² Note that the chemical potential in these publications Braudeau et al. 2014 was considered negative.

water under constant pressure P_a (Fig. 2). The equilibrium is respected if the energy differences in the two phases between the saturated and unsaturated states are equal:

$$\bar{V}_{wl}\Delta h = P_g\Delta\bar{V}_{wg}$$

$$h\bar{V}_{wl} = P_g(\bar{V}_{wg^\circ} - \bar{V}_{wg}) \quad (107)$$

where, as we know, $h = \rho_w(\mu_{wl} - \mu_{wl^\circ})$ and varies in the opposite direction of n_{wl}

Knowing that $E_{wl} = \mu_{wl}\bar{m}_{wl} = \mu_{wl^\circ}\bar{m}_{wl^\circ}$, the first term of (104) can be written as :

$$h\bar{V}_{wl} = \rho_w(\mu_{wl} - \mu_{wl^\circ})\bar{V}_{wl} = \bar{m}_{wl}(\mu_{wl} - \mu_{wl^\circ}) = E_{wl} - \mu_{wl^\circ}\bar{m}_{wl} = \mu_{wl^\circ}(\bar{m}_{wl^\circ} - \bar{m}_{wl}) \quad (108)$$

The second term can be written as :

$$P_g(\bar{V}_{wg^\circ} - \bar{V}_{wg}) = RT_w(\bar{n}_{wg^\circ} - \bar{n}_{wg}) \quad (109)$$

That gives the relationship between the water contents of the two phases:

$$RT_w(\bar{n}_{wg^\circ} - \bar{n}_{wg}) = \mu_{wl^\circ}(\bar{m}_{wl^\circ} - \bar{m}_{wl}) \quad (110)$$

At T_w constant,

$$\bar{n}_{wg}RT_w = \bar{n}_{wl}m_w\mu_{wl^\circ} \quad (111)$$

By introducing $\bar{n}_{wg}$ according to $\bar{n}_{wl}$ (108) in equation (103), we obtain:

$$d\mu_{wl} = -\mu_{wl^\circ}d \log(\bar{n}_{wg}) \quad (112)$$

$$\mu_{wl} - \mu_{wl^\circ} = \mu_{wl^\circ} \log\left(\frac{n_{wg^\circ}}{n_{wg}}\right) = \mu_{wl^\circ} \log\left(\frac{p_{w^\circ}}{p_w}\right) = \mu_{wl^\circ} \log\left(\frac{V_{wl^\circ}}{V_{wl}}\right) \quad (113)$$

$$h_l = \rho_w(\mu_{wl} - \mu_{wl^\circ}) = \rho_w\mu_{wl^\circ} \log\left(\frac{n_{wg^\circ}}{n_{wg}}\right) = P_{wl^\circ} \log\left(\frac{n_{wg^\circ}}{n_{wg}}\right) \quad (114)$$

Equation (111) is the relationship between the water retention pressure in the soil surface layer and the relative humidity of the air at the soil surface.

5 General comments

5.1 Position statement for the choice of internal state variables

A first statement, consistent with the systemic approach, was to define the functional volumes of the system and its subsystems as state variables of the thermodynamic system. The volumes of the fluid phase, of its molecules and of each of their atoms, and finally the occupation volume of each molecule (V_{mti}), are called the organizational variables of the medium (aqueous or gaseous phase) and are clearly defined on Figure 2.

The second statement, consistent with the two postulates of thermodynamics (Bazorov) , was to define the temperature as the average of the internal energy of all stable particles of more than one atom (molecules, ions) present in a fluid phase homogeneous at thermodynamic equilibrium.

These statements are based on the fact that the internal energy of a molecule is the sum of the oscillation energies of its atoms, just as its mass and its volume are the sums of the masses and volumes of its atoms. It follows that, at equilibrium state, the internal chemical potential of a molecule is naturally the same as that of its atoms. Since any molecule of the phase is vibrant and is characterized by three independent characteristics: mass, volume and its temperature, the internal molecular properties of the phase can be calculated, namely, the internal molecular chemical

potential T/m , internal molecular pressure $T/V_m = TS/V_{mt}$ and the internal molecular density $r = m/V_{mt}$.

The second statement leads to distinguish the two types of molecular energies coexisting in the form of energetic bubbles (of total volume V_{mt}) at same pressure within the fluid phase. We thus have two types of pressure (T/V_m and $T(S-1)/(V_{mt}-V_m)$) and two types of chemical potential (T/m and $T(S-1)/m$).

All this led us to put forward a strong hypothesis, having value of principle, that there exists a process of thermal equilibrium of the phases of the system whose two equilibrium criteria, characteristic of the phases, are:

- The molecular chemical potential $\mu_m = T/m$ is everywhere equal in the system, it is the first equilibrium criterion, intra and inter phases (instead of temperature) of the system and between its inside and outside. Cf Figure 2
- the two types of pressures, internal and external, of a molecule in a fluid phase, involving the entropy of the phase, have equal value everywhere in the phase:

$$\frac{T}{V_m} = \frac{T(S-1)}{V_{mt}-V_m} = \frac{TS}{V_{mt}} \quad (115)$$

The internal pressure of a molecule, $\frac{T}{V_m}$, is equal to its external pressure, $\frac{T(S-1)}{V_{mt}-V_m}$, and so to the total pressure $\frac{TS}{V_{mt}}$ of the molecule, as volumetric energy contents.

This equality of pressures is the in-phase equilibrium criterion (replaces the equipartition theorem of energy). This is the in-phase equilibrium criterion (replaces the equipartition theorem of energy).

5.2 Comments on the physical meaning of entropy

The definition of entropy S in terms of energies could result from this hypothesis since S intervenes in the distribution and equilibrium of these two types of energy via the pressure and the chemical potential

In fact, the definition of entropy as the ratio of the molecular volumes $V_{mt\alpha}/V_{m\alpha}$ is only suitable in the case of the liquid or gaseous phases where this ratio characterizes the organizational state of molecules of the phase at equilibrium. However, entropy can be defined across a single molecule as the ratio of its total energy (the sum of its oscillatory energy and kinetic energy) to its oscillatory energy T , either:

$$S = \frac{T_i + T_c}{T_i} = \frac{\frac{1}{2}mv^2 + \frac{1}{2}m\lambda^2\sigma^{-2}}{\frac{1}{2}m\lambda^2\sigma^{-2}} = \frac{v^2 + \lambda^2\sigma^{-2}}{v^2} \quad (116)$$

Within a thermodynamic liquid or gaseous phase, entropy of a molecule becomes:

$$S = \frac{T_c + T_i}{T_i} = \frac{v^2 + \lambda^2\sigma^{-2}}{v^2} = \frac{V_{mt\alpha}}{V_{m\alpha}} \quad (117)$$

It is all the more judicious to distinguish the two energies that it is T_i and not T_c which is emitter of electro-magnetic waves making it possible to identify the temperature of a molecule in space.

On the other hand, concerning the raising or lowering of the temperature T_i , it becomes obvious that it can come from two channels: the one, electromagnetic, which would be the resonance of the internal molecular vibration with a beam of incident waves, and the other, mechanics, resulting from an increase in the kinetic energy of molecules, that is the thermal agitation energy T_c . It is known that

the latter increases with the decrease in the occupancy volume (under the action of any mechanical work from outside) or by contact of the fluid phases with a warmer body (higher temperature) or with the solid walls of the vessel of which molecular vibrations have increased.

The point of view on heat transfer is totally different from usual: it is the thermal state of the medium at each of its points (the molecules) which can change, either by a direct wave connection of the molecules individually with the outside, or by contact of the phase with a body of different temperature. In both cases, however, there is simultaneously a "mechanical" equilibrium of the two temperatures T_i and T_c which homogenizes the pressures and therefore also the entropy of the medium.

We are therefore far from the classical thermodynamic vision and from Boltzmann's statistical theory of gases. The entropy of an isolated molecule goes from 1 when its speed is zero in the observer's frame of reference and increases > 1 with the speed acquired in the medium with which it is in equilibrium. This is determined and can be calculated via the pressure of the medium since we have, at equilibrium:

$$P = \frac{T_c}{V_{mt}-V_m} = \frac{T_i}{V_m} = \frac{1}{2} \frac{mv^2}{V_{mt}-V_m} \quad (118)$$

$$v^2 = 2 \frac{T_i}{m} \frac{V_{mt}-V_m}{V_m} = 2\mu_m(S_g - 1) \quad (119)$$

5.3 Comparison with the variables T and P from the kinetic theory of gases

In comparison, pressure and temperature in classical thermodynamics are so-called kinetic pressures and temperatures linked by the equation:

$$PV = NRT \leftrightarrow PV = \frac{2}{3} n \left[\frac{1}{2} mv^2 \right]$$

Which leads to the expression of T:

$$T_c = \frac{2}{3} \frac{n}{NR} \left[\frac{1}{2} mv^2 \right] = \frac{2}{3} \frac{1}{k} \left[\frac{1}{2} mv^2 \right] \quad (120)$$

where k is Boltzmann's constant, R is the ideal gas constant per mole of gas, n is the number of molecules and N is the number of moles. The same equation formulated according to our definitions is:

$$nP(V_{mt} - V_m) = n \frac{2}{3} kT_c = n \frac{2}{3} kT_i(S_i - 1) \quad (121)$$

$$nP V_{mt} = nP \frac{(V_{mt}-V_m)}{V_{mt}-V_m} V_{mt} = n \frac{2}{3} kT_c \frac{S_i}{S_i-1} = n \frac{2}{3} kT_i S_i \quad (122)$$

The ideal gas equation is written for us as:

$$P_g V_g = n_g S_g T_g \quad (123)$$

où doit être calculé en fonction des données expérimentales etc. et non en fonction de k

where S_g must be calculated according to the experimental data and not according to k; that is to say that PV is actually:

$$(P_g V_g - n_g T_g) = n_g T_g (S_g - 1) = N S_g T_c = \frac{2}{3} n_g \left[\frac{1}{2} v^2 \right] \quad (124)$$

We know that $S_g = R$ and T_c is the kinetic temperature of N_A molecules, therefore:

$$T_c = \frac{1}{3k} [mv^2] \text{ et } T_c = T_g \frac{S_g^{-1}}{S_g} \quad (125)$$

$$\frac{1}{3k} [mv^2] = T_g \frac{S_g^{-1}}{S_g} \quad (126)$$

$$v^2 = 3k \frac{T_g}{m_g} \frac{S_g^{-1}}{S_g} = 3k \mu_m \frac{S_g^{-1}}{S_g} \quad (128)$$

By comparing with the equation for v^2 given above, we have $k = \frac{2}{3} S_g$, i.e., since the ideal gas constant is given for N_A molecules, $k = \frac{2}{3} R/N_A$.

6 Conclusion

The classical thermodynamics bases the modeling of all the thermal phenomena (heat transfer, Carnot cycles, notions of work and its thermal equivalent heat, etc.) on a modeling principle which is that of the "black box" where the internal organization of the object to be modeled, here the phase at thermodynamic equilibrium, is unknown and so, ignored. Systemic thermodynamics, on the contrary, is based on the principle of systemic modeling, which establishes the prior recognition of the levels of internal and hierarchical organization of the object to be modeled in order to exhaustively define the corresponding organizational variables, called systemic variables, and to use them in the multiscale transfer equations.

We have shown in this article that classical thermodynamics, the one we know with its 2 or 3 laws or principles to define the internal and external variables and parameters of the system that will fit into the standard equations of the discipline, is in fact the mathematical modeling of the macroscopic phenomenon due to physical processes that occur at the microscopic scale of molecules. This macroscopic phenomenon is the achievement by the system of stable and unique state of thermodynamic equilibrium, which occurs within a black box called thermodynamic phases of the system. This same type of modeling (black box) is practiced in soil hydrodynamics where, in the same way, their internal organization, the soil structure, is ignored and overstepped by the REV hypothesis. The state equations used are thus semi-empirical and cannot represent the physical processes that are the basis of the state functions.

Faced with this type of black box modeling, we propose the systemic modeling that defines exactly and exhaustively variables of the functional organization of the thermodynamic system. That is, first and foremost, the total functional volume considered and that of its subsystems all reported to the structural mass of the system. We have shown in this article that we could introduce in the classical theory of thermodynamic potentials (sposito, 1981), the organizational variables describing molecules and their atoms and then correct the classical equilibrium equations established according to the two principles of thermodynamics. The gain is a better understanding in the specific terms used in thermodynamics, such as "intensive or extensive variables", "partial volume" or "partial pressure", and especially the terms of temperature and entropy which appear in the thermodynamic potentials equations.

We move from a macroscopic modeling (that we could say "Aristotelian") since it satisfies the results of experiment globally without taking care of the internal processes which are at the origin and which consists only of "saving appearances", to a systemic modeling of molecular organizations, entirely mechanistic (Cartesian physics), without any statistics that would mix the scales. All equations of state and functioning are physically exact and involve well-defined systemic variables. These variables are universal in the case of natural thermodynamic systems such as soils because it is those of the pedostructure which is the driving element of the soil horizon and which is accounted for in terms of

the volume percentage of the horizon (compared to other fixed components of the horizon such as pebbles, biological macropores, roots etc.).

We have shown that the systemic formalism of the thermodynamics that we have constructed has justified in depth (at the molecular and atomic level) the exact equations of the hydro-thermodynamic equilibrium of the liquid and gaseous phases of the pedostructure which had been found previously. This deepening of the field of the systemic approach allowed us, moreover, to give the exact equilibrium relation between the two phases, liquid and gaseous, of the soil water under the atmospheric pressure of the air, thus explaining the one of the aspects of Henry's law.

Systemic modeling up to the atomic level has brought to light the hidden properties of molecular organizations such as entropy and chemical potential as fractional intensive variables. This type of variable crosses the scales keeping the same physical value which is that of the molecule (representative point of the phase). This property opens the door to a new science that is that of the harmonization of the structures of water, emitting and receiving temperature waves through the wave character of one of the two molecular volumes that make up entropy.

Thus, the two major questions to be solved from this new conceptual basis of thermodynamics are: i) the heat transfer understood as what causes the temperature variation (internal energy of the molecules) and ii) the soil water transfer which is a migration of the water molecules under the effect of a potential difference in the aqueous phases of the soil.

The solutions given to these two research questions will find their place directly in the Kamel model of the hydrostructural and hierarchical properties of a soil pedon, defined as the elementary representative system of a soil mapping unit, under controlled natural atmospheric conditions or not. The systemic approach of the natural environment, the methodology of soil pedostructural characterization and the systemic mapping of soils and the Kamel model, which makes it possible to articulate the different sciences of the agro environment around the question of the soil, are the objects and tools of this new discipline called hydrostructural pedology.