

## ***Interactive comment on “Energy states of soil water – a thermodynamic perspective on storage dynamics and the underlying controls” by Erwin Zehe et al.***

**G.H. de Rooij (Referee)**

gerrit.derooij@ufz.de

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Review comments on ‘Energy states of soil water - a thermodynamic perspective on storage dynamics and the underlying controls’ by Erwin Zehe et al. MS No.: hess-2018-346

The paper attempts to derive a thermodynamic expression for the total potential energy of solute-free, slow-moving water in a rigid porous medium. Taking hydrostatic equilibrium as the equilibrium state of a soil it uses this expression to examine if a soil has excessive or insufficient water to see in which direction the soil water status will naturally evolve. An extensive test on two different catchments in a temperate climate

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is carried out to illustrate the practical application of the equation and demonstrate how it can show the dynamics within a catchment and the differences between catchments.

Major comments

The second part of the paper is clearly the strongest, and my comments are limited to some suggestions for improvement and requests for clarifications. I was impressed by the potential of the method, and liked the way the demonstration was set up.

I am quite critical of the first part though, and the vast majority of my comments focus on that section because I believe older literature (including my own) was not acknowledged adequately, which could have saved the authors some time. I agree with the other reviewer that the presentation of that part has a certain pompousness that the contents do not justify. The second part of the paper makes clear that this is an interesting contribution to an on-going debate in the literature to which several authors of the paper have contributed over the past years, partially within the CAOS project, and to which I too have made some contributions. If the paper presents the material as the next leg of this on-going journey without too much further ado, it will be much more compelling. As a case in point, quoting Aristotle while overlooking the literature of the last century on the thermodynamics of soil water does not create a favourable impression. I provided a set of references and a detailed discussion of some of those in my detailed comments that hopefully will be of help to the authors.

Why did you choose the Helmholtz free energy instead of the Gibbs free energy? According to the formal definitions of both (Callen, 1985, p. 146-147),  $J = U - TS$  and  $G = U - TS + PV$ , where  $J$  is the Helmholtz free energy,  $G$  is the Gibbs free energy,  $U$  is the internal energy,  $T$  is the temperature,  $S$  is the entropy,  $P$  is the pressure, and  $V$  is the volume. Pressure seems to me to be a relevant variable, so why leave it out? The second part of the paper is quite interesting. The thermodynamical analysis leading up to it either needs to be cleaned up or removed. As I point out in several detailed comments it lacks the rigour that is required and overstates its novelty, as the other reviewer also

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states. The thermodynamical analysis of soil water and groundwater was essentially completed in the 1940s to 1960s, and I provide numerous references to those works. The authors quote only Iwata (1995), whose older work highlights the variation of various thermodynamical quantities within a single pore. I recommend using the work of Bolt and colleagues for the catchment scale instead. That would allow the removal of several weaknesses in the current write-up: the scale ambiguity, the lack of terms for the interaction with the solid phase and for the groundwater pressure, the absence of a geometry term, the strange discussion of a water sphere, the reliance on cylindrical pores, and the choice for the Helmholtz free energy instead of the Gibbs free energy.

I would even go so far as to recommend to let go of the thermodynamics completely and instead adhere to the terminology adopted in all major soil physics text books in which the potential energy of solute-free soil water in a rigid soil without overburden pressure consists of gravitational potential energy and matric potential energy - kinetic energy being many orders of magnitude smaller in nearly all cases. The equations for the total potential energy and its components of a body of subsurface water of arbitrary size are already in the literature (de Rooij, 2009), and with those you can develop your entire theoretical framework without unnecessary distractions.

As stated above, I developed equations for average matric, gravitational, and hydraulic potential and average water content for large volumes, as well as their expressions for hydrostatic equilibrium and unit gradient flow, in de Rooij (2009). I also wrote in that paper that 'An upscaled  $h$  sub  $V$  (  $\theta$  sub  $V$  ) relationship according to Eqs. (19) and (20) incorporates spatial heterogeneity and allows  $h$  to vary with elevation under hydrostatic equilibrium conditions. The relationship for megascopic  $V$  (e.g., a soil layer within a field plot, or an entire field) will be of little use to calculate actual flow, but by comparing the actual  $h$  sub  $V$  and  $\theta$  sub  $V$  to the equilibrium curve, the deviation from equilibrium can be asserted, and the tendency of  $V$  to absorb or release water from or to its surroundings (e.g., the groundwater, or a stream) can be established with a more or less quantitative measure.' Thus, it is clear that the central thesis of the

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current paper was already formulated 9 years ago. I believe the paper as it stands does not accurately reflect this. Note that I limited the potential application to a field because assuming hydrostatic equilibrium in an entire catchment leads to a lake in the lower reaches and unrealistically dry conditions near the watershed. In this paper, this is resolved using the height over nearest drainage instead of the height with respect to a fixed reference height. This is the innovative theoretical element of the paper.

Please consult the guide for authors regarding the use of footnotes.

Detailed comments

I. 49. The authors appear to be unaware of a body of work on the thermodynamics of soil water and groundwater in the 1940s to 1960s that I believe to be highly relevant to this work. I particularly recommend the rigorous treatment by Bolt, Groenevelt, and coworkers (Bolt and Frissel, 1960; Groenevelt and Bolt, 1969). The references in these papers provide access to other papers. By not acknowledging the earlier work by several authors, the novelty of the work is overstated. It is also apparent that the level of rigour does not match that of the work around the middle of last century.

The authors quote Iwata (1995) (reference in the paper). I read Iwata's earlier work (Iwata, 1972a,b,c, 1974a,b) but found it not easy to penetrate. He argues that the thermodynamic status of the soil water depends on the distance to charged clay particles, which he treats strictly in one dimension (distance to the surface of a single clay plate) and therefore advocates to treat the soil water as a series of thin layers that are all homogeneous, but with different values for the various thermodynamic variables. Yet, when discussing the effect of the air-liquid meniscus he assumes a cylindrical pore without attempting to resolve the obvious discrepancy between the two geometries.

Iwata's line of thought culminates in the necessity to adopt the chemical potential of soil water as its true thermodynamic state, even going so far as to call the matric potential meaningless. The water pressure is a component of the chemical potential as defined by Iwata. The practical application of the concept is hampered by the necessity to

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divide the water in an individual pore in an unspecified number of layers. This also made it difficult for me to fully grasp the critique on the matric potential, which can realistically only be measured at scales far beyond the pore scale. I am willing to accept a complicated interplay between various forces in the diffuse double layer that make the composition of the soil solution vary with distance from the clay surface. Nevertheless, I am also willing to accept that water flow and movement of ions over a few centimeters (Representative Elementary Volume scale – Bear and Bachmat, 1991, p.14-29) is fast enough to establish an equilibrium in which the sum of the components of the soil water potential is essentially the same everywhere, or at least exhibits a gradient that is observable at that scale. I am not sure how to reconcile that with Iwata's work, but the authors seem confident this can be done. If the thermodynamical framework remains part of the paper, an elaboration of the mathematical formalization of that reconciliation by the authors would strengthen the work, all the more since they use the matric potential themselves, albeit under another name – see my comment about I. 185.

I. 52, 57. What is the definition of power in this context?

I. 59. See also the minimization of energy dissipation during groundwater flow discussed by van der Molen (1989).

I. 84-87. The phrasing seems to suggest that the internal redistribution of water in response to external forcing (differences in rainfall, incoming and outgoing radiation, and potential evapotranspiration; gravity for sloping areas) is much faster than the fluctuations in the forcings, but is this truly the case? One could argue that the system (groundwater/soil water) is always running behind, being in a state of perpetual perturbation. How do you find the reference state in that case? Furthermore, it is quite possible that the system is still responding to a previous stimulus, and therefore seems to react to the current stimulus in the wrong way. Case in point: sunshine after heavy rain. Water should be moving upward to respond to the radiative forcing, but apart from the top few centimeters, the infiltrated rain water is still moving down. The subsurface

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has a degree of inertia that increases with depth, and the inertia of an aquifer increases quadratically with its size. For simple aquifers this inertia can even be quantified by their characteristic times, which can be in the order of centuries for extensive systems (de Rooij, 2013). Without an inertia term I think the theory remains incomplete.

The matric potential is highly dissipative over distances of the order of  $< 1$  m, but not at all for catchment-relevant distances  $> 102$  m. One can reasonably argue that a well developed root system of an individual organism (tree) offers a dissipative mechanism over tens of meters. Less direct but not entirely baseless would be to argue that the root network of a crop or a natural ecosystem also dissipates the matric potential, even though a direct communication over the root network of an individual does not exist. In this case, the dissipation can be argued to occur from similarity of the atmospheric boundary condition experienced by the entire plant community in combination with variations in water stress, that are then evened out by their effect on the local actual evapotranspiration. In the absence of vegetation, this subsurface communication effect breaks down. The only horizontal transfer of information in that case is the reduction in the potential evapotranspiration brought about by the water transmitted to the atmosphere from moist areas. This process gives rise to the complementary relationship between actual and potential evapotranspiration (Brutsaert, 2005, p. 136-137 and references therein), and is typically considered to operate on scales much larger than that of the catchments discussed here.

I. 87. The term water stock used here is used casually, but really needs careful consideration. From Fig. 1 it is readily clear that thermodynamic equilibrium as used in this paper corresponds to hydrostatic equilibrium, i.e., a spatially uniform hydraulic head throughout the catchment. The value of this hydraulic head is a function of the water stock. Note that this function is neither unique nor monotonically increasing because of hysteresis. A catchment's water stock at any given time is a function of past external forcings, internal geomorphological processes, and the catchment biota (through canopy interception, vegetation effects on infiltration, root water uptake, creation of

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macropores by flora and fauna, and a myriad of other processes). Furthermore, it varies in time. Once the water stock is determined for a catchment at a given time, and if the geohydrological make-up of a catchment is known in sufficient detail, it is possible in principle to determine the hydraulic head corresponding to hydrostatic equilibrium. Especially in sloping areas this will correspond to flooded lower reaches of the catchment and dried out streams and absent groundwater in higher elevations. You essentially have one or more lakes surrounded by a flat groundwater level and no streams. This state is therefore wholly unrealistic.

Yet you need it to determine the equilibrium groundwater level because you need to know the current status of your catchment given the amount of water that it currently holds. If the average groundwater level is lower, the average depth of the unsaturated zone is larger, and it will hold more water. By necessity that extra soil water has to replenish the groundwater, so the catchment is in the P-stage. If the average groundwater level is higher, the unsaturated zone on average is thinner and drier. The catchment is in the C-stage. I can see the logic of this, but as I explained above, catchment-wide hydrostatic equilibrium is not a useful reference state in any meaningful way. It might be of use to describe the status of soil profiles in the catchment. This ties in with my argument above that lateral exchange of water in the unsaturated zone is often small and operates at scales far smaller than that of a catchment. Later on in the paper you explain the HAND approach, which I consider to be a rather practical way to circumvent these problems. Perhaps it would be good to move that to the front, because I really got bogged down in reconciling hydrostatic equilibrium with perpetual flow in a sloping catchment. Nevertheless, the dynamic nature of the water stock remains a problem that the theory cannot easily deal with. Am I overseeing something? If so, please elaborate on this. If not, this is a limitation that should be mentioned.

There are additional problems though. I do not believe you can calculate the water fluxes entering and leaving the catchment from catchment-scale variables alone, thermodynamic or otherwise. To keep track of the catchment's water stock you therefore

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have to rely on hydrological modelling, monitoring data, or both. That being the case, what is the added value of the thermodynamic description of the catchment? The water stock and the groundwater level as a function of time are crucial for determining in which state the catchment is, which in turn is key for your approach. Yet you can calculate neither of these variables with your model. The models that can also calculate the fluxes your model is supposed to calculate, so I have a hard time understanding what your model contributes. Even though I like the match with experimental data that you show later on I still find it hard to pinpoint to a meaningful addition to the hydrologist's toolbox that this research provides or at least has the potential of providing in the future. Can you tell us crisply why we need this stuff?

I. 96. How do you define (and measure) the capillary surface energy of soil water? The term suggests it is strictly limited to the potential energy arising from the gas-liquid interface.

I. 96-97. The potential energy due to matric forces is reflected in the matric potential. The gravitational potential energy is due to its elevation. I assume that the capillary surface energy is incorporated in the matric potential, which also includes the potential energy associated with the interactions along the liquid-solid interface. But if that is true, the sentence seems to have a tautology in it. Also, the qualifier 'in absolute terms' appears misplaced. Surely the sign of the difference in the two energies is crucial.

I. 98. From my comments above it is clear that I do not believe capillary surface energy differences are the dominant driver of soil water dynamics. I think the total hydraulic head is the main driver: gravitational + matric + osmotic + overburden + pneumatic potential. I do agree that under sufficiently dry conditions, the gravitational contribution becomes negligible, but I am less willing to dismiss the role of the liquid-solid interface. By ignoring it, one is unable to discuss the effect of soil wettability on the formation of preferential flow paths during infiltration, to name an extreme example.

I. 100. The energetic distance to equilibrium is not the only factor that determines the

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amount of necessary recharge. The pore architecture and the phase distribution in it also factor in. Bolt and Frissel (1960) therefore included a geometry factor in their equations, which is missing in this paper. I expect that a good deal of theoretical work will go into deriving this geometry factor for an entire catchment. At the scale of a plot I analyzed a special case (rainfall while the top of the capillary fringe initially was near the soil surface) in detail in a paper (de Rooij, 2011) that was inspired by an earlier paper by members of the current group of authors and is part of the debate that the current paper continues. In the terminology of this paper, the test case was concerned with a very rapid transition from a C-regime to a P-regime. It demonstrated with how little water a large energetic distance could be overcome in mere seconds given the right circumstances. By doing so, de Rooij (2011) implicitly warned against using the energetic distance as the main criterion. The architecture of the pore space and distribution of the liquid and the gas phase in it cannot be ignored.

Fig. 1 The figure has an R-regime that I suspect should be the P-regime.

l. 118-119. Preferential flow paths by definition bypass relatively dry areas in the top soil, and provide a conduit through which infiltrating water reaches the groundwater, or at least the wetter subsoil, more quickly. Thus, a dry area of the soil is to some degree shut off the terrestrial part of the hydrological cycle. The vegetation suffers, which is why farmers mix in clay or apply surfactants to eliminate soil hydrophobicity to eliminate preferential flow. But you argue the other way: preferential flow paths accelerate recharge of the dry soil. If this were the case, would farmers not promote hydrophobicity instead, to encourage the development of preferential flow paths? p. 6, footnote. Not only do you not consider volumetric change of the pore space, you assume a rigid soil. No deformation of any kind is permitted.

l. 151 (Eq. 1) From this equation it becomes clear that the term 'potential energy' only referred to the gravitational potential energy of the water. This goes against established terminology in the soil physics literature. Equation (1) lacks terms for the external pressure, for the forces resulting from the contact with the solid phase, and for the ionic

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composition of the soil solution. Furthermore, the authors do not state if the equation is local (microscopic) or applies to the entire water phase. The text is ambiguous in that respect. Bolt and Frissel (1960) present the full equations for both cases, but for the Gibbs free energy instead of the Helmholtz free energy.

l. 164-183. This derivation is only valid if the water is stored in radially symmetric pores that are fully saturated with water behind the air-liquid interface, because the two principal radii of curvature are set to be equal to one another. Pendular rings and water films on pore walls or in corners are not covered by this derivation.

l. 177 (Eq. 5). A further simplification appears in Eq. (5), where, for reasons that are not explained, the water is assumed to occur in a sphere, which would cause the water pressure to be higher than the atmospheric pressure, which is not typically the case in an unsaturated hydrophilic soil. A more logical approach would have been to calculate the volume in the cup-shaped air pocket enclosed by the liquid-air meniscus and the plane through the air-solid-liquid contact line at its outer boundary, and see how that volume changes when the pressure difference across the interface changes. This would then have to be done for different pore sizes to find something meaningful at the sample scale and all scales beyond that. Defining the populations of pore sizes and the required range of pressure variations for which to carry out the calculations may be conceivable at the sample scale but on first sight seems to be daunting for the catchment scale.

This simplification is too extreme for the result to be meaningful I believe. The geometry factor introduced 58 years ago by Bolt and Frissel (1960) seems to offer a better starting point.

l. 182 (Eq. 6) The end result of the derivation in Eq. (6b) is the conventional expression for the hydraulic head (multiplied by  $\rho g$  to obtain the potential with units  $\text{Nm}^{-2}$  (Jury and Horton, 2004, p. 54)) if only the gravitational force and the matric forces in the vadose zone are accounted for and kinetic energy can be ignored. You can arrive there by

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a Newtonian analysis of the forces acting on the water in a much more straightforward way than presented here. I believe your initial reliance on the interface being a section of a sphere made you arrive at a correct result despite requiring water to be residing in a sphere. You made two assumptions that happened to cancel each other out. But because the pressure difference between the liquid and the air is opposite because the direction of curvature of a spherical water droplet and water in a axisymmetric pore is opposite, I suspect you dropped or added a minus sign along the way.

I. 185. The term matric potential is well-defined and has been in use for decades. Why do you want to change it to the much less accurate capillary surface energy?

I. 186-188. In the analysis above you included the effect of a single meniscus. Implicitly, you defined the control volume to be so small as to envelope only a single pore. Here you invoke the continuity approach in which the macroscopic water content can be defined, which requires the control volume to be the size of the representative elementary volume, i.e. a very large number of pores (Bear and Bachmat, 1991, p. 14-29). A rigorous treatment can be carried out for the scale at which the phases can be separated or at the continuum scale, but not by switching from the one to the other. Bolt and Frissel (1960) developed equations for both analyses.

I. 192 (Eq. 7). From thermodynamics, the expansion of  $dV \sub \theta$  is familiar, but what does the term  $\theta dV$  signify here? Your explanation only holds over incremental changes because the water content is held constant, so your phrase 'moving up scale' appears to be too broad. In thermodynamics the differentials typically stem from external inputs/outputs of energy or work done by the system or being done to the system. I do not see how any of these possibilities lead to a change of volume in a rigid soil.

I. 194. It is called the Richards equation.

I. 207-217. These insights are not particularly new. Also, the definition of linear behaviour is ambiguous as the driver of the behaviour and the response are not clearly defined. I presume one could adopt the uptake/release of water with a change in the

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total hydraulic potential for different combinations of gravitational and matric potential energy. In that case, the capillary fringe creates a very non-linear trajectory even when gravity is supposed to dominate: zero response when the matric potential is larger (less negative) than the air-entry value, and a significant response when it is just below the air-entry value. In hydrophobic soils things become even weirder.

I. 258 deriving -> taking the derivative

Section 2.2 Section 2.2 does not offer any new insights in my view, but it phrases it in an unconventional way. With the rather large depth to groundwater deployed in the discussion, the limitations of the minimum free energy concepts at these scales become clear. Have the authors ever measured hydrostatic equilibrium in such deep profiles? The only area where the assumption of hydrostatic equilibrium is applied is in the sub-sealevel part of the Netherlands, where the groundwater is maintained at about 1.5 m depth. At the end of winter/early spring, when rain is not so frequent, the agricultural soils are still barren, and the potential evapotranspiration is very low, the soil may approximate hydrostatic equilibrium reasonably well. When the groundwater is deeper, a good portion of the soil profile below the root zone may exhibit near-constant unit gradient flow, during which the matric potential is constant with depth, and the purely gravity driven flow occurs at a water content for which the hydraulic conductivity equals the long-time average net drainage rate. This does not meet your minimum free energy criterion but nevertheless seems to reflect a relaxed state in which the soil hydrology has adapted to external forcings.

Section 2.3. You present families of curves at equidistant intervals of elevation above nearest drainage (HAND). You can take this one step further by characterizing a catchment through the probability density function of HAND, dividing the range in intervals with equal probability mass and then plot the curves that are representative for each of these intervals. These plots will then convey useful information about the catchment that the current Fig. 4 does not.

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l. 349. In most climates, the total fraction of time with rainfall is much smaller than the complementary fraction without rain. The only exceptions that I can think of are cloud forests. Furthermore, rainfall involves generally higher flux rates as evapotranspiration, and are not influenced by the soil moisture status of the soil at the time the rain is falling. Finally, wet soils are more conductive than dry soils and therefore can move back to hydrostatic equilibrium more quickly than dry soils. Without formal analysis we therefore can conclude that the C-regime occurs more often than the P-regime in the top soil. The deeper we get, these fluctuations between wetting and drying are damped ever more strongly. At some depth that depends on soil properties and climatic conditions, a nearly constant downward flow occurs, with a vertically uniform matric potential. Within 1-2 m from the groundwater level the matric potential profile responds to the phreatic level. The section of soil under unit gradient conditions is permanently in the P-regime, I believe. Depending on the flux density this is somewhere between hydrostatic equilibrium and unit-gradient flow. This seems to imply that the installation depth of your tensiometers/water content sensors may affect the status that you assign to the free-energy regime of the catchment. I would like to see that discussed in the paper.

l. 375. Optioned?

l. 375-377. I am not convinced that fitting a single retention curve through the data points of a number of samples gives you the catchment-scale retention curve. Of prime concern is the conservation of mass when moving from the sample scale to the catchment scale (de Rooij, 2009, 2010). This dictates that the hypothetical representative soil profile should have the average depth (distance between the soil surface and the phreatic level), and that its saturated water content equals the weighted average of that of the samples, with the weighting factors equal to the fraction of the catchment soil volume represented by the individual sample. If one prefers to have the catchment-scale groundwater table at a different depth for whatever reason, the saturated water content must be multiplied by the ratio between the average groundwater depth and

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this chosen depth to ensure mass conservation. Furthermore, if all soils are saturated, the catchment as a whole will start losing water when the first sample reaches the air-entry value and upon further drying will stop losing water when the final sample is dry. (The fact that the van Genuchten function captures neither of these points will be saved for another day.) The latter requirement is of no practical value because this situation will never be reached. Complete saturation is also unlikely, but the catchment can realistically come close, for instance after prolonged rain shortly after snow melt. Thus, mass conservation forces us to fix the catchment-scale saturated water content and its air-entry value at a weighted average of all samples and the value of a single sample, respectively. Optimizing these parameter values based on goodness of fit will lead to mass balance discrepancies. If one devotes some thought to the matter, other critical matric potential levels can probably be defined. The catchment scale water content at hydrostatic equilibrium should be correctly represented by the catchment-scale retention curve as well. Perhaps unit gradient conditions at different matric potentials can also provide useful values. Straight-forward parameter fitting is not the best approach for 'what the authors have in mind.

Note that in Fig. 5 (l. 393-394) you state that you used energy-conserving averaging, which seems to contradict the text. Can you give the equations of the averaging operation?

l. 430 Is an observations the sum of an observed matric potential and an elevation multiplied by the locally observed water content?

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