We thank Michael Roderick (MR in the following) for his thoughtful comments on the proposed paper. We agree that the proposed definitions of internal/ total energy and free energy in our paper ((Eq.1) and Eq. 5)) are not conventional and that the revised paper should clearly explain the link and the difference to classical approaches in textbooks. These definitions in the last version suggest that Eq. 5 can be inserted into Eq.1, this does as outlined by MR, not produce a meaningful term. We agree that this has to be fixed in the revised paper and thank again for. We want to stress that most of the critique points in MR review are, though being important, not relevant for the main findings of this study.

Due to the structure of MR's review, we regard a line to line response as in appropriate. In the following we develop the background that is necessary to respond to the major comments of his review and highlight the responses in bold.

Mass flow related flows of (free) energy in the hydrological system and the link to thermodynamics.

Given the definitions of the upper and lower boundary of the critical zone/hydrological system (soil surface and ground water surface) it receives during rainfall events (as correctly states by MR) free energy in form of kinetic energy. Parts of this free energy input (we define free energy below) is dissipated into heat and partly dissipated by breaking up soil aggregates. The remaining part becomes potential energy of surface water and of soil water (depending on the balance between infiltration and rainfall intensity).

Potential energy of surface water is transformed into kinetic energy of overland flow, which includes again dissipation of free energy into heat, performs work on sediments, or is exported from the catchment (Kleidon et al. 2012). **As correctly pointed out by MR (Page 3 suggestions), this should be accounted for in the free energy balance of the system. It is correct that we currently overestimated the export of kinetic energy in the paper, because not the entire potential energy in surface water is transformed into kinetic energy overland flow. We will fix that in the revised paper.**

Soil wetting is associated with reduction of capillary binding energy of water in soil that is associated with the release of "heat of immersion (Hillel 1995)" (it is a matter of taste to relate this either to chemical energy as suggested in Kleidon and Schymanski 2008 or to surface energy as done in this manuscript).

Although, these mass fluxes are not associated with large heat fluxes, they nevertheless reflect the overall conservation of energy as well as the second law, so that they require a thermodynamic treatment, because tiny amounts of kinetic energy and potential energy are dissipated into heat which implies irreversibility.

We regard the internal process of soil wetting in contrary to MR (Page 3 suggestions) as highly relevant due to two main reasons. The first is that capillary binding energy of soil water is much larger than the potential energy of soil water in fine porous soils during dry spells. Small changes in soil moisture due to infiltration may change capillary binding energy drastically due to strongly nonlinear shape of the soil water retention curve. (In other words “soil” water flows against much steeper gradients than surface water at the land surface). Secondly, soil hydraulic equilibrium arises from a balance in potential and capillary binding energy in soil. Soil water potential (defined as matric potential + gravity potential) is, in equilibrium, zero everywhere and thus vertically uniform, this is well known. This hydraulic equilibrium is a state of maximum entropy as the potential gradient is zero. This state should thus also correspond to a state of minimum (Helmholtz or Gibbs) free energy. Hydraulic equilibrium cannot be related to thermodynamic equilibrium when neglecting internal redistribution of water, as suggested by MR.

The revised manuscript will better explain this point and distinguish between entropy production due to fluxes across the boundaries and entropy production due to fluxes against internal gradients. **One of the main advantages of the proposed approach is that we can quantify internal and external power/entropy production and thus explore the tradeoff that arises from the tradeoff between overland flow and infiltration and subsequent soil water flow.** This tradeoff causes a thermodynamic optimum in the surface density of macropores in the Weiherbach, which is the most important findings of this study. Connected flow paths (macropores and the river net) enhance velocities of mass fluxes thus power in associated mass fluxes by enhancing the flow against driving gradients. Macropores affect the trade of between overland flow formation and infiltration and thus the tradeoff between the amount of kinetic energy input of rainfall that is converted in to power associated with overland flow and power associated with soil water flows. Due to steepness of the gradients in soil water potential and the nonlinear dependence of soil water potential we find a macropore density (represented by the macroporosity factor) which maximizes power generation in soil water flows. When using this value in an uncalibrated simulation of rainfall-runoff of the catchment we come close to the best fit found in a calibration exercise. When approaching this question along an alternative avenue by calculating dynamics of free energy (which will be defined in a minute), we again find a macropore density (represented by the macroporosity factor) that maximizes reduction of total free energy in the system during a long term simulation of rainfall runoff in the Weiherbach. An uncalibrated simulation with this value perform even better.

Different meanings of free energy and the first law: conventional formulation and our formulation

We are familiar with the conventional formulation of the first law;

$$dU = \delta Q - \delta W \quad \text{(E1)}$$

This equation relates the change of the internal energy to a change in heat and work performed by the system. In case of a closed system (without mass exchange) it is exclusively mechanical work that is performed by the system. Mechanical work is PdV. (The idea of Clausius was that gas molecules knock at the walls confining the system, PdV was thus originally introduced for small changes in dV which imply small and slow changes in pressure P, we come back to this later). The minus is necessary for satisfying energy conservation but also to assure that entropy production during an isoenergetic and irreversible expansion of an ideal gas into a vacuum (dU=0) is positive. Hence, we have (as pointed out by MR).

$$dU = TdS - PdV \quad \text{(E2)}$$

The term free energy is in physics unfortunately used for slightly different things. On one hand there are the definitions of Helmholtz free energy (*F*) and Gibbs free energy (*G*) as ” thermodynamic potentials” that can be derived from the conventional formulation of the first law using the following Legendre transformations:

$$\begin{aligned} &G = U - TS + PV \Rightarrow dG = dU - d(TS) + d(PV) = -SdT + VdP + \mu dN \\ &F = U - TS \Rightarrow dF = dU - d(TS) = -SdT - PdV + \mu dN \end{aligned} \quad \text{(E3)}$$

The last term μdN is change in chemical energy to change in number of molecules in the system

On the other hand electrical energy, kinetic energy, gravitational energy, surface energy and nuclear energy are frequently referred to as different forms of free energy. Different forms of free energy can be used to perform work without dissipative losses (or more precisely the losses can be neglected): to perform work means for instance to accelerate mass or an electric charge, to lift mass in the gravity field or to build up a gradient of an intensive state variable (chemical potential, velocity, surface tension).

Let us have a look at dissipation and the idea of free energy for the hydrological system. Why does water not flow uphill although this would not violate conservation of energy, when the system cooled down at certain rate and transferred this amount of thermal energy per time into power to push the water at a certain velocity upwards the hillslope. This is not possible, because heat is thus not a form of free energy and this would violate the second law. The explanation for this is that we can dissipate kinetic energy into heat without violating energy and momentum conservations because momentum is vector. As temperature T represents the average kinetic energy of the molecules in a system of interest, kinetic energy of water flow can be converted into heat, by increasing the average kinetic energy and thus the average velocity magnitude of through elastic collisions of water and soil molecules. (This will lead to a tiny increase of soil temperature). At the same time momentum can be conserved, because the loss in macroscopic momentum of water molecules (which had a net direction of movement) is dissipated, by distributing this in an isotropic manner to all different directions. This dissipated momentum does not change the momentum of the center of mass of the molecules at the soil surface, i.e. it does not create macroscopic movement. Reversing this procedure in a sense that isotropic momentum of the molecules at the soil surface is converted into anisotropic momentum of surface water - to accelerate it uphill and perform thus work by cooling down the surface is a very, very unlikely process.

Heat is thus not a form of free energy. The forms of free energy which are related to our study are kinetic and potential energy and surface energy (the latter performs work against gravity by capillary rise). A change in free energy is always associated with the performance of work in the above specified sense or vice versa. That is why we formulated the first law.

$$dU = dQ + dF \quad \text{(E4)}$$

In fact the first law could also look like this dU = dQ –dF, as long as the definition of changes of different forms of free energy that are hidden behind dF, especially their signs, are consistent with conservation of energy, the second law and the degrees of freedom of the system of interest. Within a catchment as a hydrologic system, the work is performed within the system, so it is important to trace the total amount of energy within the system to ensure energy conservation.

Our first oversight in this context was to name U as internal energy, although our formulation is motivated by the work of Kleidon (2012), who expressed the change of the total energy of the earth system U as

$$dU = d(ST) - d(PV) + d(\sum_i \mu_i M_i) + d(\sum_j \Phi_j M_i) + d(\vec{v} \cdot \vec{p}) + d(\sigma_w A_w)\ldots \quad \text{(E5)}$$

(Eq. E5 is identical to Kleidons eq. 3.5 except that we added the terms –d(PV) (mechanical work) and d($\sigma_w A_w$) (surface energy) here).

The first term of the right hand side is heat, the third is change of chemical energy, the forth term is change in gravitational energy and the fifth one is change in kinetic energy. All terms except the first one name different forms of free energy. Eq. E5 is similar to Gibbs fundamental formula, although the latter is not introduced as total differential. This is one of the main reasons why Eq. E5 is difficult to reconcile with formulations of conventional thermodynamics (Major point on page 2 of MRs review). We pick this up later.

Much of the confusion outlined in MRs review, including the question were to add kinetic and potential gravitational energy to the first law comes due to (Falk und Ruppel 1976) from the term internal energy. In fact we meant with U the total energy of the critical zone and will revise the paper accordingly.

The second oversight that occurred in the definition of free energy is that the manuscript defines, due to an oversight the change in free energy as (Eq. 5):

$$dF = -d(\underset{I}{ST}) - d(\underset{II}{pV}) + d(\underset{III}{\sum_i \mu_i M_i}) + d(\underset{IV}{\sum_j \Phi_j M_i}) + d(\underset{V}{\vec{v} \cdot \vec{p}}) + d(\underset{VI}{\sigma_w A_w})\ldots$$

This is, however, not correct: -d(TS) is heat and heat is no free energy. In this form Eq. 1 and Eq. 5 cannot be combined in a manner that conserves energy (Major point that the proposed theory does not conserve energy page 2 of the review). We totally agree that when doing this Eq. 1 and Eq. 5 do not add up in a meaning full manner and we thank MR for this important point.

A consistent definition is to define the change in free energy based on the forms that are relevant for mass flows in the hydrological system:

$$dF = -d(\underset{II}{p}V) + d(\underset{III}{\sum_i \mu_i M_i}) + d(\underset{IV}{\sum_j \Phi_j M_i}) + d(\underset{V}{\vec{v}} \cdot \vec{p}) + d(\underset{VI}{\sigma_w} A_w)\ldots \tag{E6}$$

The change in total energy dU as in E5 and first law in the conventional manner either as dU=δQ-δW.

Allow us to stress again that the numerical experiments and the main findings of our study are not touched by this oversight, because we neglected all terms in the free energy definition expect term IV and VI in our analysis (E6).

However, Eq. E6 and Eq. E5 are total differentials. This is not standard and difficult to reconcile with classical formulations in textbooks. This needs thus additional clarification. We think a closer look at the term mechanical work and the first law helps here.

Mechanical work and the first law: classical definition and thermodynamic definition

Mechanical work W is in classical mechanics defined as the scalar product of the force F (gravity) and a displacement r in the force field.

$$\begin{aligned} W &= \mathbf{F} \bullet \mathbf{r} \\ W &= m\mathbf{g} \bullet \mathbf{r} \end{aligned} \tag{E7}$$

Work is maximum and positive if the displacement of the point mass is parallel to the force, negative if the displacement is antiparallel and zero, when the displacement is orthogonal to the force. The link to Clausius' definition of mechanical work in thermodynamics is obvious, as force is the product of mechanical pressure and area, either of the walls that bound for instance an ideal gas or of a moveable wall that is located between two gases of different pressures let's say P_1 and P_2. In case of a small displacement dx we get.

$$\delta W = PAdx = PdV \quad \text{(E8)}$$

The usual idea, as expressed above, to account for the mechanical work performed by the knocking of the molecules against a fixed boundary (implying small dV and that the change in P might be neglected)-

As the gas performs work when expanding into (net) direction of the force PA, the internal/total energy of the gas U is reduced by this term, as correctly pointed out by MR. The classical definition of the first law of thermodynamics relates thus, as correctly stated by MR, the change of internal energy to exchange of work and heat as in Eq. E1 and E2.

When expanding the first two terms in the total energy expression in Eq. E5 we obtain however:

$$dU = SdT + TdS - PdV - VdP \quad \text{(E9)}$$

If we assume T and P are constant during this expansion, that terms SdT and VdP are zero: Eq. E9 and E 2 are equivalent. However, this assumption is in many cases not correct. An expansion of a gas implies a net displacement of the wall (lets pick up the example of moveable wall between two gases of different pressures. This implies necessarily a net force to be consistent with Eq. E7. This in turn implies a pressure difference to the gas on the other side of the moveable wall. The displacement/expansion will stop, when the net force acting on the wall is zero, which implies that the pressure of the expanding gas decreases during the expansion. P is in fact not constant during such an expansion. The classical formulation of the first law of thermodynamics acts as if it was constant, and defines U is a function of V and S only. However, when it comes to treatment of expansions the pressure change is not neglected, but calculated by using a diagnostic equation (for instance of the ideal gas law). This works when the pressure change is slow against the change in volume. To be honest I always wondered why this should be, when I attended lectures on thermodynamics during my time at university.

The formulation of the change in total energy as total differential proposed by Kleidon (2012) accounts for the fact that during most processes in the earth system the state variables in the conjugated pairs characterizing heat or different forms of free energy are not constant. We admit, however, that the formulation of dU (Eq. E5) and dF (Eq.E6) as total differentials are difficult to reconcile with classical formulations of Helmholtz and Gibbs free energy. Eq. E5 is not to be meant as being valid in a universal sense. Depending of the constraints and degrees of freedom of the system, one might have to change the sign of different terms (as in conventional thermodynamics too). We feel that this point cannot be clarified in the revised manuscript but deserves a study of its own.

Response to MRs comment "Adding new terms to the conventional formulation" on page 3 first paragraph of his review).

We agree with MR that there has been confusion on which side the terms for kinetic energy **vdp** and gravitational energy ϕdM should be added to the conventional formulation of the first law (Eq. E1), where U is internal energy. Stephan (1975) provides a nice discussion on this topic reviewing several authors who added either - ϕdM or -Mdϕ to the right hand side of Gibbs fundamental formula, where U is internal energy. The problem here is that intensive state variables P, T and μ are defined as partial derivatives of internal energy with respect to V, S and N. In case one added for instance ϕdM on the right hand side of the conventional first law (dealing with internal energy), this would surrogate that the gravity potential ϕ=gz is defined as derivative of the internal energy with respect to M, which is of course nonsense.

Kondepudi and Prigogine (1998), which introduce dU as total energy, add the term + φdQ (electrical energy) on the right hand side of Gibbs fundamental formula (page 43).

$$dU = TdS - PdV + \mu dN + \sigma dA + \mathbf{v} \bullet d\mathbf{p} + \varphi dQ + \phi dM \ldots \text{(E10)}$$

(we added the terms vdp, ϕdM and σdA here), describing the change in total energy as function of heat exchange, mechanical work and additional forms of free energy exchange, which are defined by products of conjugated pairs of an intensive state variable and the change of an extensive state variable (surface energy σdA, kinetic energy **vdp**, electrical energy φdQ, gravitational energy ϕdM). If we regard mass as analogue to the electrical charge (Coulomb's law for electrostatic forces and Newton's gravitational law have the same mathematical structure), we have an electric potential difference (φ) times a flow in charge dQ (which is an electrical current) or gravitational potential difference (which is constant) times a mass flow. ϕdM is thus gravitational work that belongs to the right hand side of the first law in Eq. 3 as well as of to the right hand side of Gibbs fundamental formula (Eq. 10), as long as U is total energy instead of internal energy.

Similarly, Kleidon adds the term vdp (velocity times the change in momentum) for kinetic energy to the right hand side of his formulation of the first law, where U is also total energy of the system. A temporal change in momentum is per definition a force, multiplying this by velocity is close to the expression of mechanical power as defined in classical mechanics (scalar product of force and velocity). We thus think vdp affects free energy and should appear at the right hand side of Eq. E5 and Eq. E6..

We think that the terms in the definition of free energy should assure that thermodynamic equilibrium should, when neglecting all the terms expect those who deal with free energy dynamics arising from soil water dynamics, correspond to hydraulic equilibrium. This depends on the signs of ϕdM and σdA and we will double check this for the revision of this manuscript. As stressed above, we need to account for all energy terms within the system, and the work done by one form of energy yields a different form of energy. Hence, we must consider all terms that are involved in the energy conversions that are considered in hydrology.

Suggestions of MR

MR’s comment that internal details/ redistribution of water do not have to be accounted for.

We have – of course – a different view. In our manuscript we follow two avenues to shed light on the role of preferential pathways from a self-organizing perspective: analyzing power/entropy production associated with water mass fluxes during rainfall driven conditions and analyzing the trajectories of free energy of the critical zone. One key mass flux that affects power generation is, in this respect, infiltration, because it depletes the gradient in soil water potential and affects at the same time overland flow production. This can be seen as production of entropy due to mass exchange at the upper boundary (dSe according to Kondepudi and Prigogine 1998). As the unsaturated zone is in permanent disequilibrium additional entropy is produced by redistributing water against internal gradients of soil water potential. The use of a distributed model allows thus to quantify additionally entropy production due to internal processes. We consider this as an important add on, as the state of maximum entropy (assuming steady state soil texture and structures) is to our understanding hydraulic equilibrium, which corresponds to a zero vertical gradient in soil water potential.

Another strong argument that these internal details matter is that the macroporosity factors that maximize power production and reduction of free energy during numerical experiment 2 are almost identical and thus consistent. This would not be the case, if we neglected power/entropy production associated with depletion of internal gradients in soil water potential.

MRs suggestion of an input output analysis of "power".

In this context we do not exactly understand what is meant with the initial comment about steady flow equation. The proposed analysis is not based on something like this, but on dynamic simulations with a fully distributed thermodynamically consistent model. We mention terms like steady state or stationarity exclusively in connection to the MEP principle and we stress that a steady state is difficult to define for the critical zone.

Concerning the proposed input output analysis of power, we think that the proposed analysis goes much further than this. What is meant by MR is an input - output analysis of free energy. Power is a source term of free energy (Kleidon 2012) as it is energy per time. A balance requires integration over time, which yields the free energy input and outputs into/ from the system. This is exactly what we do along the second avenue.

In this respect we like to stress, that the balance of stream flow generation and water storage is strongly affected by the surface density of preferential pathways, because Hortonian overland flow dominates (as explained in the manuscript). Increasing storage by increasing infiltrability of the surface does not simply increase base flow here.

Best regards,

Erwin Zehe

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