<u>**HESS Manuscript Review**</u>

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Title: Connected flow paths as first order control on critical zone water flows: coincidence or self-organized optimality?

Authors: Zehe et al.

This manuscript describes an analysis of two catchments in terms of the 2^{nd} law of thermodynamics. The topic is important and suitable for HESS.

I struggled to understand the formulation of the problem that is presented here. In particular I did not understand the terminology or formulation of the "Free Energy". Let me explain.

Eqn 1 reads as dU = dQ + dF. That is (more or less) conventional with dU defined as the change in internal energy while dQ is the "heating". All that is fine so far. On that definition, the classical approach would identify the dF term as the work. I would write the equation as dU = δQ + δW where the "δ" symbol denotes that heat and work are dependent on the path whilst dU is the change in a state variable and does not depend on the path.

In the manuscript dF is called free energy. As noted above, the conventional terminology I am familiar with would call dF the work. There is, to my knowledge, no strict terminology for Free Energy but most equate it with the Gibbs Free Energy (= H – TS, where H = enthalpy, S = entropy) or sometimes to the Hemholtz Free Energy. This difference in terminology could potentially be reconciled by the definitions in Section 2.3 but I did not understand how that expression (per the definition in Eqn 5 and subsequent equations) could be used?

According to conventional thermodynamics, the formulation presented here does not, as far as I can tell, appear to conserve energy. Let me explain using a simplified example for the change in internal energy in a single component hydrostatic system. This system is only capable of doing PV work but that simple example is sufficient to make the point about conserving energy.

CONVENTIONAL THERMODYNAMICS

$$dU = \delta Q + \delta W \qquad \text{(C1)}$$

In this simplified example, the heat is defined by,

$$\delta Q = TdS \qquad \text{(C2)}$$

as per Eqn 2 in the manuscript and the work done is given by,

$$\delta W = -PdV \qquad \text{(C3)}$$

The negative sign in Eqn C2 ensures that when *dV* is positive, *dU* will decrease and the system is said to have done work on the surroundings. Note that when a system is capable of other forms of work (e.g. surface work, chemical work, electrical work, etc.,) then Eqn C3 must be extended to include explicit expressions for that work as well. See chapter 3 in Zemansky & Dittman (1997) Heat and Thermodynamics, 7th Edition, McGraw Hill for details on how additional work terms are included in the conventional formulation.

Following the classical definitions as per the above we have,

$$dU = TdS - PdV \qquad \text{(C4)}$$

That equation can be found in any textbook.

THERMODYNAMICS IN THE MANUSCRIPT

Combining Eqns 1 and 2 in the manuscript we have,

$$dU = TdS + dF \qquad \text{(1 \& 2)}$$

and for the purposes of this example, we only consider the TS and PV terms from Eqn 5, i.e,

$$dF = -d(TS) - d(PV) + ... \qquad \text{(part of 5)}$$

Combining (1 & 2) with (part of 5) we have,

$$dU = TdS - d(TS) - d(PV) = TdS - TdS - SdT - PdV - VdP = -SdT - PdV - VdP$$

The problem is immediately apparent. This is not consistent with the conventional statement of the conservation of energy (C4). I tried various ways of reconciling the manuscript formulation with conventional thermodynamics but could not do so. For example, one could ignore the TS term and write,

$$dF = -d(PV) + ... \qquad \text{(alternative part of 5)}$$

and combining with (1 & 2) we would have,

$$dU = TdS - d(PV) = TdS - PdV - VdP$$

But doing that does not reconcile the statements with the conventional approach.

The central issue here is that even if we ignore differences in terminology, the formulation presented in the manuscript does not appear to conserve energy.

ADDING TERMS TO THE FUNDAMENTAL EQUATION USING THE CONVENTIONAL APPROACH

A second general problem is how other terms are added to the fundamental equation. In conventional thermodynamics, dU includes all forms of energy that are internal to the system.

They are lumped together and no attempt is made to identify them explicitly. On that convention, if one were to add say gravitational potential energy (E_g) or kinetic energy (E_k) then these are added to the left hand side of Eqn C1. Hence we have the energy on the left hand side and the "heating" and "working" on the right hand side, i.e.,

$$dE_g + dE_k + dU = \delta Q + \delta W \qquad \text{(C5)}$$

This is the approach developed originally by Willard Gibbs but adding different energies can, and has, led to confusion. For example, see Roderick (2001 *Australian Journal of Plant Physiology* 28: 729-742) for an example of adding the gravitational potential energy following the Gibbs approach. Of relevance here is that in the current manuscript the gravitational potential energy is added to the right hand side (as a work term) instead of the left hand side as an energy term.

Note that one need not follow the conventional approach and one could define the total energy differently but then one would also need to re-derive all the other intermediate results.

SUGGESTIONS

I agreed in a qualitative sense with the general discussion about the processes in section 2.3 – I just did not understand the formal quantitative definitions. Those processes all describe important aspects of local mass and energy transfers. However, in the fundamental equation, heat and work are distinguished by what happens at the boundary of the system. The internal details of mass fluxes, etc., are just that – internal details. To consider the internal details you need to have a whole lot of smaller sub-systems all enclosed by individual boundaries and distinguish the heat and work at each of those sub-system boundaries. But following that approach seems to negate the advantage of the thermodynamic approach.

Most analysis of flow systems start with the so-called steady flow equation. That is awkward in hydrology because the steady flow is used for the analysis of machines where the mass entering and leaving is identical. In a catchment you have mass leaving via evaporation as well. In that context I wondered whether it was possible to simply investigate the input and output of power, e.g. you have a power input via the mass flux (rainfall). You need to know the velocity of the rainfall but I imagine you could have at least get a reasonable estimate of that. Some of that rainfall is retained and ultimately, after some variable amount of time, becomes streamflow and you can calculate the power output in the streamflow (from the kinetic energy). That might be a useful practical way of making a start on the problem. Note that not all of the gravitational potential energy would be converted to kinetic energy at the outlet and this difference means that some of the "potential work" was destroyed and will re-appear as frictional heating or dissipation more generally and is related to the generation of entropy.

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