**Referee Report on Shavelzon and Edery, "Shannon entropy of Transport Self-Organization Due to Dissolution/Precipitation Reaction at Varying Peclet Number in an Initially homogeneous Porous Media," submitted for publication in HESS.**

Reviewer 3: I found this manuscript very interesting. The use of Shannon entropy to measure emergent structures is nice and makes sense. The manuscript is well written and easy to follow, even for those that do not have a background in statistical physics.

We sincerely thank the author for giving valuable feedback on the manuscript draft, as well as for endorsing it for publication. Please find our reply below in red.

The way that the Shannon entropy is measured does not consider spatial correlations. It is therefore an incomplete measure of this entropy. It is equivalent to measuring the Shannon entropy of a language based solely on the frequency of its use of each letter, thus missing the information attached to larger correlated structures such as the appearance of the letter "q" almost always being followed by the letter "u." Hence, the measurement of the Shannon entropy is incomplete. It is, however, probably a good first approximation to it.

We thank the reviewer for pointing out the incompleteness of the Shannon entropy when used as a measure of transport self-organization in the field due to the fact that it does not take into account spatial correlations. However, we believe that for the specific case of an initially homogeneous field, presented in the manuscript draft, it should be accurate enough, since in this case the transport self-organization mimics the form of straight parallel channels from inlet to outlet.

Thus, estimating the spatial correlation of the solute distribution in the field will not bear any additional information in this case, as no larger-scale structures are expected to emerge in the field. However, we would like to stress an importance of taking spatial correlation into account when assessing transport self-organization in the more complex situations, such as highly heterogeneous fields where larger-scale structures can be expected to emerge.

I disagree with the arguments that internal and external entropy should add up to zero. There is viscosity in the system and total entropy, both from the emerging structures and that attached to the microscopic flow, is being produced continuously. The information entropy, which reflects macroscopic structures, is a very small part of the entire entropy budget, so the connection between the two is tenuous. The increase in conductivity as the dissolution process proceeds leads to an increase in entropy *production*. That is not the same as there is an increase in entropy as the entropy leaks away from the system in the form of heat, and this also increases.

We sincerely thank the reviewer for pointing out inaccuracies in the manuscript draft. To our best understanding, there are a few points in the manuscript draft that require further clarification:

1. The presented study does not intend to construct a complete thermodynamic formalism for the problem under investigation, such as the one that is presented in *Hansen et al 2018, 2023*. The thermodynamic framework presented in the current study is aimed at providing only the qualitative dependencies / trends between the three parameters of interest, that are the entropy of the transport self-organization, the entropy of the breakthrough curve and the hydraulic power, dissipated in the field, similar to Zehe et. al. 2021. Thus, when the relationship between the pair of entropies is considered, we only state that a decrease in the entropy of the transport self-organization leads to an increase in the breakthrough curve

entropy. Under no circumstances do we state that these two entropies should construct the entire entropy budget and, thus, give a zero sum. However, we are currently working on a complete thermodynamic formalism for the reactive flow in porous medium, where we will consider the full thermodynamic budget of all the components in our system.

Please see the following quote from the manuscript draft (l.652-657):
*…since the transport entropy within the field is decreasing for lower Peclet values and, according to the second law of Thermodynamics, the overall entropy of the system and its surroundings cannot decrease, the entropy, produced within the field needs to be exported outside (see Appendix A); this is reflected in the increased entropy of the breakthrough curve. This statement should be regarded on a qualitative level only, as, due to different spatial and temporal discretizations, changes in the Shannon entropies of the field transport and the breakthrough curves with the passage of time do not comply.*

2. To analyze the emergence of self-organization in our computational field, we consider snapshots of the field in terms of hydraulic conductivity distribution, taken at different computational times as the reactive process in the field evolves (see the description in the beginning of Section 3.1). We consider each snapshot as an open thermodynamic system and perform a non-reactive tracer test by injecting *non-reactive* solute particles at the field's inlet to quantify the transport self-organization in the field at that specific time. In such a tracer test, no changes in the hydraulic conductivity distribution occur and the non-reactive solute transport in each of these field snapshots is considered as a steady state.

To clarify these aspects, we propose the following amendments to the manuscript draft (in the beginning of Section 3.1):

*<u>l. 336:</u> The computational setting described in the previous section mimics the dynamics of a coupled dissolution-precipitation reactive process in a calcite porous medium, leading to an emergence of heterogeneity in an initially homogeneous field. Previous studies have shown that self-organization of the solute transport in the field is expected to emerge in such a situation in the form of preferential flow paths that lead to solute concentration gradients in the direction transverse to flow, yet the details of this self-organization emergence and evolution are critical to understanding the large-scale dynamics of the coupled reactive process in the field.*

*To analyze the emergence of self-organization in our computational field, we consider snapshots of the field in terms of hydraulic conductivity distribution, taken at different computational times as the reactive process in the field evolves. We consider each snapshot as an open thermodynamic system and perform a non-reactive tracer test by injecting non-reactive solute at the field's inlet.*

*Along the lines of Section 1.2, we argue that organized states, characterized by reduced entropy, can emerge in an open system, driven away from equilibrium due to exchange of energy or matter with surroundings. Such a system may persist in a stationary nonequilibrium state. Since, according to the second law, overall entropy cannot decrease, in such a case entropy must be exported from the system outside, leading to an increase in the entropy of its surroundings.*

<u>l. 459:</u> *We emphasize that the presented study does not intend to construct a complete thermodynamic formalism for the problem under investigation, such as the one that is presented in Hansen et al 2018, 2023. The thermodynamic framework presented in the current study is aimed at providing qualitative dependencies / trends between the parameters of interest, such as the entropy of the transport self-*

*organization, the hydraulic power, dissipated in the field, etc. It is our intent to arrive at a more complete thermodynamic formalism for the reactive flow in porous medium in the course of the research work.*

A recent paper considers Shannon entropy in connection with immiscible two-phase flow in porous media, defining it in a way similar to that of Equation (13) in the manuscript, see https://doi.org/10.1016/j.advwatres.2022.104336. However, rather than connecting the information entropy to the molecular entropy, these authors build a statistical mechanics around it. I believe that the same ideas would be applicable in the present manuscript.

We thank the reviewer for suggesting the work of *Hansen et al 2018, 2023* for our further consideration. The thermodynamic formalism presented therein is indeed of interest for our current research direction. We will add references to *Hansen et al 2018, 2023* to the manuscript, as both of the publications are relevant to our current research direction. We will also consider the derivation presented in these papers for our current work on the complete thermodynamic formalism for dissolution\precipitation reactive transport in porous media, as parallels can be drawn between the immiscible two-phase flow in porous medium and our setup.

Despite my disagreement with the analysis of the authors with respect to the entropy budget, I will endorse publication. However, the authors should address my concern.

We sincerely thank the reviewer for identifying the merit of our work, despite our differences in the analytical aspects of it. We aim at deriving a complete thermodynamic formalism, as suggested by the reviewer, and this work is the first building block towards this goal. We believe that we have responded faithfully and in a complete fashion to the reviewer concerns, and truly appreciate the work invested in the review process, and the enlighten comments and references.

<u>References:</u>


- Alex Hansen, Santanu Sinha, Dick Bedeaux, Signe Kjelstrup, Magnus Aa. Gjennestad, Morten Vassvik. *Relations Between Seepage Velocities in Immiscible, Incompressible Two-Phase Flow in Porous Media*, 2018.

- Alex Hansen, Eirik Grude Flekkøy, Santanu Sinha, Per Arne Slotte . *A statistical mechanics framework for immiscible and incompressible two-phase flow in porous media*, 2023.

- Erwin Zehe, Ralf Loritz, Yaniv Edery, and Brian Berkowitz. *Preferential pathways for fluid and solutes in heterogeneous groundwater systems: self-organization, entropy, work, 2021.*