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Shannon entropy of transport self-organization due to dissolution–precipitation reaction at varying Peclet numbers in initially homogeneous porous media

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S1. Thermodynamic system in a stationary nonequilibrium state

To illustrate how an open thermodynamic system can be maintained in a stationary nonequilibrium state through an inflow of energy, let us consider a simple heat transfer example: an open system that consists of a pair of thermal reservoirs, a hot thermal reservoir at a temperature T_h and a cold thermal reservoir at a temperature T_c, linked by heat transfer that occurs between the two reservoirs. In accordance with the second law of thermodynamics, a diffusive heat flux will occur from T_h to T_c, driven by the temperature difference of the reservoirs. In a stationary state, a constant amount of heat per unit time dQ will be removed from the hot reservoir and transferred to the cold reservoir. Recall the definition by Clausius of a change in entropy dS due to amount of heat dQ added or removed at the temperature T of the system

$$dS = \frac{dQ}{T} \tag{S1}$$

Therefore, the entropy of a warm reservoir would decrease by dQ/T_h, whereas the entropy of a cold reservoir would increase by dQ/T_c. The net entropy change within the system is $dS = -dQ/T_h + dQ/T_c$ (notice that $dS > 0$ since $T_h > T_c$) (net entropy production within system due to irreversible heat transfer processes). In a stationary state, a constant heat flux $J = dQ/dt$ will flow through the system, resulting in the rate of internal entropy production of the system

$$\frac{dS_p}{dt} = J(\frac{1}{T_c} - \frac{1}{T_h}) > 0 \tag{S2}$$

For the system to remain in a stationary state, its total entropy must remain constant, therefore entropy excesses have to be exported to the surroundings. In a stationary state, the rate of change of the total entropy of the system, equal to the sum of the rate of the internal entropy production in the system dS_p/dt and the rate of the entropy export to the surroundings dS_e/dt, is zero, thus

$$\frac{dS_e}{dt} = -\frac{dS_p}{dt} \tag{S3}$$

To maintain this nonequilibrium stationary state, an energy must be invested, for example in the form of a heat pump, operating outside the system, that will transfer the heat from the cold reservoir back to the hot one in order to maintain their temperatures at constant values, otherwise the system will eventually (asymptotically) arrive at an equilibrium state. For more details on the topic of nonequilibrium thermodynamics, see Kondepudi and Prigogine (1998).

S2. Information entropy

To acquire the basic concept of the information entropy, let us consider a single probabilistic event, having a number of possible outcomes that are assumed equally probable. For example, in case of a single symbol, transmitted in the Morse code, we have two possible outcomes (realizations) for this event - a dash and a dot (omitting the intermission between the transmitted letters). Employing the indices 0 and 1 to denote parameters before and after the event realization, initially we have $N_0 = 2$ equally possible outcomes of the message transmission event and zero initial information $I_0 = 0$. Following the transmission of a single symbol, we have a single realization of the event - a dash or a dot, thus $N_1 = 1$, and a non zero information due to the receipt of a symbol $I_1 \neq 0$.

In case of a sequence of events enumerated $1...n$, having respective number of outcomes $N_{0_1}, N_{0_2}, ..., N_{0_n}$ (consider a word that consists of n symbols in the Morse alphabet), the total number of possible outcomes is $N = N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n}$. Intuitively, we would expect the information measure to be an additive parameter, so that the amount of information contained in a word transmitted with the help of the Morse code would equal to the sum of the amounts of information for each symbol that constitutes the word, that is $I(N) = I(N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n}) = I(N_{0_1}) + I(N_{0_2}) + ... + I(N_{0_n})$. This can be fulfilled by choosing $I = b \ln N$, where b is a an arbitrary constant parameter, that amounts to a choice of a unit of measure (in fact, Shannon (1948) gave a formal proof that the logarithm function is the only possible relation between I and N that possesses, in addition to additivity, also continuity and monotonicity properties). For a binary system that consists of only two symbols, such as the dash and the dot in the Morse alphabet, a transmitted word of a total n symbols has $N = N_{0_1} \cdot N_{0_2} \cdot ... \cdot N_{0_n} = 2^n$ possible realizations. Taking a single transmitted symbol as one unit of information, we demand that $I = b \ln N = n$ to obtain $b = \log_2 e$ and $I = \log_2 N$. Since a single position in a sequence of symbols in a binary system is defined as a bit, the corresponding units of information I will be called $bits$ (an abbreviation from *binary digit*).

Now, assume that each of the final amount of different symbols that constitute a message has its own relative occurrence frequency (the respective probability of finding a specific symbol at a specific place in a sequence), such as the case of different letters in an alphabet. In the case of a Morse code, assume that the transmitted n-symbol word consists of n_1 dashes and n_2 dots, so that $n_1 + n_2 = n$. Using some results from combinatorics, it can be shown that

$$S = I/n = -\Sigma_i \, p_i \log_2 p_i \tag{S4}$$

where S is the information entropy (also referred to as the Shannon entropy) per symbol and $p_i = n_i/n$, $i = 1, 2$ are the relative occurrence frequencies of both symbols. Maximum Shannon entropy obtained during the transmission of a message is when the relative occurrence frequency of each symbol is identical $p = 1/2$. It is easily shown that this maximum value equals to

$S_{max} = -\log_2 p = 1$. The relation S4 can be easily generalized for any number of possible outcomes per event.

Thus, a definition of the information entropy is obtained that possesses an additivity property, similarly to physical properties such as entropy, energy, and mass. An example that may be seen as a consequence of the results obtained with the help of the information theory is that in modern communication methods the more common alphabet letters are encoded in such a way that their information content is minimized in order to facilitate the transmission process. Thus, in a Morse code a letter E is encoded by a single dot, while J is a dot followed by three dashes. For more details on the topic of Shannon entropy, see Shannon (1948).

S3. Lagrangian particle tracker validation

In the current work, a Lagrangian particle tracker (LPT) model is employed to simulate the dynamics of the reaction-transport interaction in an initially homogeneous porous medium. We use the Langevin stochastic differential equation (SDE) to simulate the solute transport inside the medium. To be used in the context of a numerical simulation, the Langevin SDE is discretized using the straightforward Euler-Maruyama method [Kloeden (1992)]. To perform validation of the model against a known analytical solution, the equivalence property between the Langevin SDE and the Advection-diffusion differential equation (ADE), that takes place when the statistical ensemble of particles considered in the solution of the Langevin SDE is large enough, was employed [Risken (1996), Perez et al. (2019)]. For the one-dimensional problem of instantaneous solute injection into a homogeneous medium, the solution for ADE is well-known and is given by the Gaussian distribution of solute concentration [Kreft and Zuber (1978), Table 2]. To validate the model, a quantity of $1e5$ non-reactive particles was injected at the inlet of the field and then allowed to move along the X axis of the field, while their motion was governed by the one-dimensional Langevin SDE. The equivalence of the Lagrangian and Eulerian (ADE) approaches to this problem was established by comparing the numerical particle tracking simulations to the analytical solution for the one-dimensional ADE equation as follows: the spatial distribution of the injected particles at different times was converted into the probability density function (PDF), which was then compared to the analytical solution for the ADE equation for identical flow conditions, such as flow velocity and diffusion coefficient (see Figure S1).

Recall that for the analytical ADE solution for the one-dimensional instantaneous injection case, the expectation of the spatial distribution of the injected particles μ corresponds to the distance passed by the flow of velocity v during the time t since the injection $\mu = vt$. The statistical deviation of the spatial particle distribution is $\sigma = \sqrt{2Dt}$, where D is the diffusion coefficient [Kreft and Zuber (1978), Table 2]. The pairs μ, σ were calculated for the spatial particle distribution at different times and then compared to the analytical values. For the computational time $t = 3.3784[min]$, the values $\mu, \sigma = 10.980, 0.008235$ were obtained from the statistical analysis of the spatial particle distribution, as opposed to $\mu, \sigma = 10.9799, 0.00822$ for the ADE

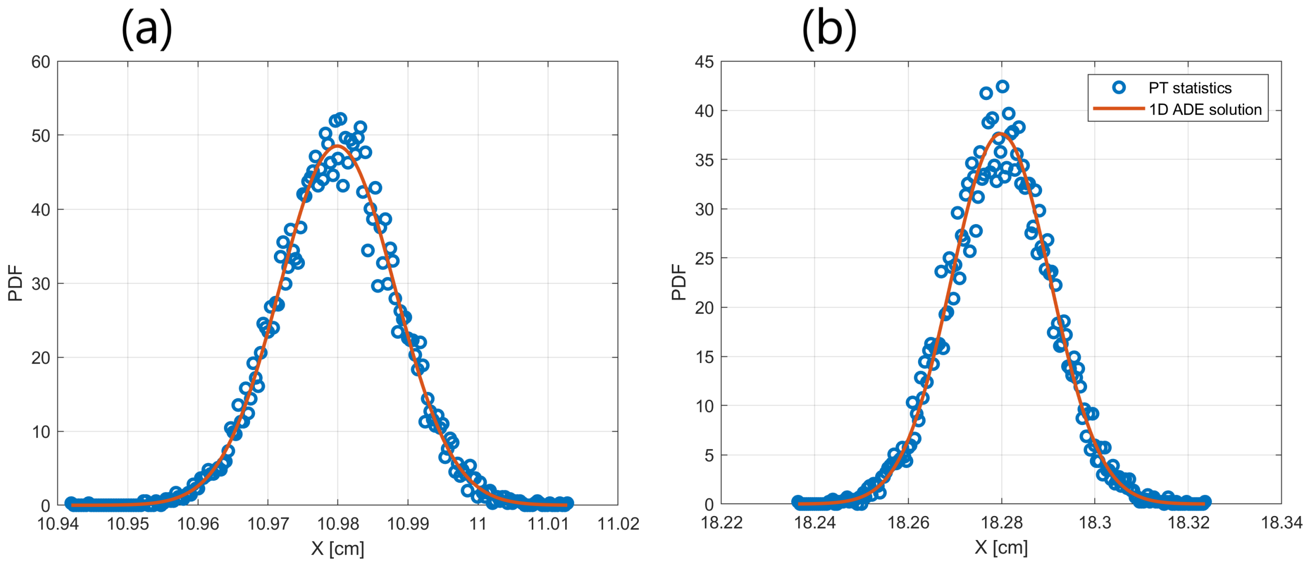

Figure S1. Validation of the Lagrangian particle tracker model using the ADE analytical solution for one-dimensional instantaneous injection into a homogeneous medium: (a) $t = 3.3784[min]$, (b) $t = 5.6246[min]$. Blue circle markers show particle tracking experiment results while solid red lines show the analytical ADE solution.

analytical solution (Figure S1a). For the computational time $t = 5.6246[min]$, statistical analysis of particle tracking gave $\mu, \sigma = 18.2798, 0.010768$, as opposed to $\mu, \sigma = 18.2798, 0.010606$ for the ADE analytical solution (Figure S1b). The high degree of agreement between these two approaches is evident, thus showing a satisfying degree of equivalence between the Lagrangian particle tracker model and the analytical ADE solution for the validation scenario.

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