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Number of Microstates and Configurational Entropy for Steady-State Two-Phase Flows in Pore Networks

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Abstract. Steady-state two-phase flow in porous media is a process whereby a wetting phase displaces a non-wetting phase within a pore network. It is a stationary, off equilibrium process -in the sense that it is maintained in dynamic equilibrium on the expense of energy supplied to the system. The efficiency of the process depends on its spontaneity, measurable by the rate of global entropy production. The latter has been proposed to comprise two components: the rate of mechanical energy dissipation at constant temperature (a thermal entropy component, Q/T, in the continuum mechanics scale) and a configurational entropy production component (a Boltzmann-type statistical-entropy component, klnW), due to the existence of a canonical ensemble of flow configurations, physically admissible to the externally imposed macrostate stationary conditions.
Here, the number of microstates, lnW, in steady-state two-phase flows in pore networks is estimated in three stages: Combinatorics are implemented to evaluate the number of identified microstates per physically admissible internal flow arrangement compatible with the imposed stationary flow conditions. Then, "Stirling's approximation limiting procedure" is applied to downscale the computational effort associated with the operations between large factorial numbers. Finally, the number of microstates is estimated by contriving a limiting procedure over the canonical ensemble of the physically admissible flow configurations. Counting the microstates is a prerequisite for estimating the process configurational entropy in order to implement the Maximum Entropy Production principle and justify the existence of optimum operating conditions.

Keywords: two-phase flow in porous media, configurational entropy, microstates, Boltzmann-Gibbs entropy, maximum entropy production principle.

INTRODUCTION

Two-phase flow in porous media is a physical process whereby a wetting phase ("water") displaces the non-wetting phase ("oil") within a porous medium. The process has many industrial applications such as enhanced oil recovery, soil remediation, characterization of porous media, etc. The majority of those applications are based on inherently transient processes. Nevertheless, to understand the physics of such processes in a deeper context, we need first to understand the stationary case, steady-state flow in macroscopically homogeneous p.m. or pore networks, whereby the two immiscible phases, "oil" & "water", are forced to flow at pre-selected, constant flowrates.

To this play, the *DeProF* theory [1] implements hierarchical mechanistic modelling - scaling-up from pore- to core- to fracture scales- to predict relative permeabilities in terms of the values of the operational parameters, i.e. the capillary number, Ca -expressing the relative contribution of viscous over capillary forces, and the flowrate ratio, r, given the values of the system physicochemical and topologic parameters. Many strands of evidence support the *DeProF* theory specificity. *DeProF* model predictions are proven through consistent physical interpretation and empirical/experimental verification. Recently, the modelling provision for the existence of a locus of optimum operating conditions i.e. conditions whereby process efficiency – considered as the "amount of oil extracted per kW of power dissipated in the pumps"- attains locally maximum values, has been confirmed by a re-examination of laboratory studies [2], describing the process macroscopic behaviour under

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controlled laboratory conditions.

Detecting and setting optimum operating conditions in the sought process could provide potentially large marginal benefits in industrial applications. It is therefore imperative to challenge the *DeProF* theory claims regarding the existence of optimum operating conditions in this type of processes. As a first step, a conceptual justification of the existence of optimal operation conditions in steady-state two-phase flows in pore networks has been recently furnished [3]. The proposed concept is based on the generalized *maximum entropy production* (MEP) principle. The sources of entropy have been identified to reside in multiple scales, from the continuum scale at molecular lever to the *configurational* scale of canonical ensembles of physically admissible internal flow arrangements, consistent to the macrostate stationary flow conditions. The scope of the present work is to identify, detect and count the process microstates at the configurational scale domain.

DEFINITION AND COUNTING OF MICROSTATES

Process, Pore Network and Discrete Fluidic Elements

Steady-state immiscible two-phase flow in pore networks is manifested by the stationary exchange of positions and momenta between discrete fluidic elements as they move downstream within a pore network at constant flowrates.

The pore network where the process takes place comprises interconnected pore unit cells forming an orthonormal (cubic) lattice of constant $\widetilde{\ell}$. Each unit cell occupies an equilateral octahedron of pore network space with diagonal lengths all equal to $\widetilde{\ell}$, edge lengths equal to $\widetilde{\ell}\sqrt{2}/2$ and volume $\widetilde{\ell}^3/6$. The pore network volume density of unit cells is $\widetilde{\mathrm{M}} = 6/\widetilde{\ell}^3$.

The macroscopic flow of the two phases is set parallel to one of the main diagonals of the cubic lattice. The discrete fluidic elements are formed by the disconnection and immiscible dispersion of a non-wetting phase (oil) within a wetting phase (water), due to the physicochemical properties of the two phases (fluids) in the pore network. Water is continuous and oil is discontinuous, therefore the fluidic elements mainly comprise discontinuous oil blobs separated by continuous water. Their size extends from one- to infinite- many pore unit cells. There are three categories of discrete fluidic elements: *connected-oil pathways* comprising the connected pathway prototype flow (CPF), *oil ganglia unit cells* comprising the ganglion dynamics (GD) prototype flow and *unit cells containing water and dispersed oil drops* comprising the drop traffic prototype flow (DTF). These occupy all the pore network space in corresponding volume fractions. The partitioning and classification of any fluidic elements in the three classes depends on the degree of disconnectedness of the non-wetting phase (oil) [1].

The *DeProF* model assumes that all fluidic elements attain a zig-zag shape (infinitely long, snake-like, for connected-oil pathways and short, worm-like, for ganglia); this is because the macroscopic flow direction is parallel to the network lattice diagonal.

Along the main diagonal of the pore network, virtual zig-zag corridors (or pathways) are formed by concatenations of unit cells aligned to the macroscopic flow. These pathways correspond to the shortest distance between any two points aligned to the lattice diagonal, so, each one is virtually confined within a normal triangular prism with sides equal to $\widetilde{\ell}\sqrt{2}$ and a frontal p.m. area equal to $\sqrt{3}\widetilde{\ell}^2/2$. The frontal area density of pathway corridors is $\widetilde{\mathrm{K}} = 2/\left(\widetilde{\ell}^2\sqrt{3}\right)$.

Consider now a network reference volume (orthogonal parallelepiped) comprising $M_z \times (M_x \times M_y)$ unit cells with z indicating the direction of macroscopic flow and x, y the other two directions perpendicular to z. This reference volume comprise $M=M_z M_x M_y$ pore unit cells in total. Considering the actual dimension of the reference pore network lattice [1, 4], $\tilde{\ell} = 1{,}221\text{mm}$, an adequate magnitude of this reference volume is 1lt. There are $M = 3{,}296129 \times 10^6$ unit cells per lt of network space and $K = 0{,}7745296 \times 10^4$ pathways per square decimeter (dm^2) of network frontal area. These figures are increased to $3{,}296129 \times 10^9$ of unit cells and $0{,}7745296 \times 10^6$ of corridors if the reference volume and frontal area are extended to $1m^3$ and $1m^2$ respectively.

Of the total number of the unit cells in the reference volume, $\beta M_x M_y M_z = \beta M$ unit cells are occupied by connected oil (comprising the CPF prototype flow). Connected-oil pathways (COP) are actually connected-oil unit cells with infinite length. These occupy $\beta M_x M_y$ part of the frontal area (perpendicular to the macroscopic flow) and allow the rest $(1-\beta)M$ of the p.m. unit cells to host the disconnected oil flow (DOF unit cells). These DOF cells are again partitioned into two subpopulations. The p.m. unit cells occupied by (or hosting) ganglion unit cells (GUC) count to $(1-\beta)\omega M$, whereas the remaining $(1-\beta)(1-\omega)M$ host drop traffic flow (DTF) unit cells. The DTF unit cells are all indistinguishable. The ganglion unit cells are not indistinguishable in the sense that each ganglion unit cell is part of certain ganglion size class.

Configurational Entropy and Definition & Counting of Microstates

The global (total) entropy production (pertaining to the system & its environment [3]) is considered over two scales: thermal entropy is estimated over the continuum mechanics scale (thermodynamics) whereas configurational entropy is considered over a discrete (and countably finite) scale whereby the microstates have been grouped together to obtain a countable set.

The process microstates are countable. In the system examined here, the pore network (the medium) comprises discrete classes of unit cells in which discrete fluidic elements exchange momentum. A microstate is specified by the positions and momenta of all the fluidic elements – mainly ganglia and drop-traffic flow cells. Ganglia can only occupy countably-many unit cells and their mass is considered as integer multiple of a conceptual elemental void space (CEVS, see [4], whereas their velocity –albeit a function of the macrostate conditions (Ca,r)- is also classified into velocity classes on a one-to-one correspondence to their size. Drop-traffic flow cells are identical (momentum-wise) since they contain water and uniformly dispersed oil droplets. We count two microstates as different if the respective "virtual snapshots" are different. i.e. the fluidic elements are arranged in different layouts. The aforementioned coarse-graining is inherent in the *DeProF* model algorithm therefore any eventual counting of microstates in the present work is fully consistent with the modelling of the process.

For every set of externally imposed conditions (Ca,r) there corresponds a set of physically admissible arrangements of prototype flows, comprising a canonical ensemble. The ensemble is determined by triplet values of *flow arrangement variables* $\{S^{w}{}', \beta', \omega'\}$, namely, the water saturation, $S^{w}{}'$, the volume fraction of connected pathway flow cells, β', and the volume fraction of ganglion unit cells within the disconnected oil flow unit cells, ω' [1]. Each of these flow

arrangements has a countable set of microstates (or degrees of freedom) that may be evaluated by combinatorics. In the following, we will focus on the estimation of the configurational (discrete scale) microstates stemming from the different arrangements of the fluidic elements for every physically admissible flow configuration.

Counting of microstates in the Connected Pathway Flow regime

Accounting for the reference frontal area, for any physically admissible flow arrangement provided by the *DeProF* model, $N_{COP} = \beta K$ of the pathways are occupied by identical connected-oil pathways that may take any possible arrangement parallel to the macroscopic flow (recall that K is the number of the pore network virtual pathways). By implementing the combinatorics approach in placing N_{COP} identical balls (the connected-oil pathways) into K identical boxes (the pore network virtual pathways), the number of different arrangements of the connected-oil pathways is given by

$$P_{COP} = \begin{pmatrix} K \\ N_{COP} \end{pmatrix} = \frac{K!}{N_{COP}!(K - N_{COP})!} \tag{1}$$

Counting of microstates in the Disconnected Oil Flow regime

We must also count the number of different ways that a population of ganglia of various sizes (i.e. of a given size distribution) may be arranged to occupy the available pore network unit cells. The question is equivalent to how many different ways a variety of short-length chains (ganglia), each one of size ranging from 1 to I_{max} links (ganglia unit cells), may engage onto an available number of barbs (unit cells).

Every physically admissible flow arrangement, comprises also a reduced ganglion size distribution, $\{ n_i^G ; i=1, 2, ..., I_{max}\}$, i.e. a population density distribution of an integer multiple (i) of linked ganglion unit cells (oil saturated unit cells). Every n_i^G, i=1; I_{max}, is equal to the ratio of the total number of i-class ganglion cells over the total number of all ganglion cells in the DOF region. All n_i^G are unknown variables, which can be determined by the DeProF model /algorithm [1, 4]. Ganglia of different size classes may arrange themselves anywhere within the $(1-\beta)$ volume fraction of the pore network unit cells occupied by disconnected oil flow (DOF). Counting the number of different ways ganglia cells may be arranged within this volume fraction, follows.

The ganglion unit cells may be considered as "links" being used to construct "chains" of different sizes, i.e. ganglia of different sizes, with their size ranging from 1 to a certain number I_{max} (provided by the *DeProF* model solution). The distribution of the population of chains of size i, per reference volume, is given by the expression:

$$N_i = M(1-\beta)\omega \times \begin{cases} n_i^G & , \quad i = 1,2 \\ n_i^G \zeta^{(i-2)} & , \quad 3 \le i \le I_{max} \\ 0 & , \quad i > I_{max} \end{cases} \tag{2}$$

with n_1^G, n_2^G, I_{max} & ζ given (better, determined as a physically admissible solution from the *DeProF* model algorithm), $0<\zeta<1$, e.g. $\zeta \in \{0,3, 0,5, 0,7\}$) and $I_{max}<<M_z$.

The total number of chains (of all sizes), N_C, the total number of links in these chains (ganglion unit cells), N_{GUC}, and the total number of DTF unit cells, N_{DTF}, are given by

$$N_C = \sum_{i=1}^{I_{max}} N_i = M(1-\beta)\omega \sum_{i=1}^{I_{max}} n_i^G \tag{3}$$

$$N_{GUC} = \sum_{i=1}^{I_{max}} iN_i = M(1-\beta)\omega \sum_{i=1}^{I_{max}} in_i^G = M_x M_y M_z (1-\beta)\omega = M(1-\beta)\omega \tag{4}$$

$$N_{DTF} = M(1-\beta) - N_{GUC} = M(1-\beta) - M(1-\beta)\omega = M(1-\beta)(1-\omega) \tag{5}$$

In this context, the N_{GUC} links can be placed in $M(1-\beta)$ unit cells available for hosting the DOF=GD+DTF prototype flow cells. After the links have taken their place in the elementary cells, there will be N_{DTF} "unoccupied" identical (drop traffic flow) unit cells.

There is no restriction in ordering the chains, the links, the empty cells e.t.c. The only requirement is that all the chains are parallel to the z-direction (of the macroscopic flow). Therefore, the network unit cells available for DOF(=GD+DTF) can be notionally (re-)ordered (aligned) in just a single row of size $M(1-\beta) = N_{GUC} + N_{DTF}$.

The problem of counting the different number of ways that ganglia unit cells may be arranged within the DOF unit cells is partitioned into two parts. In the 1st part, we find the number of ways we can choose N_C empty cells from a total of N_{DTF}+N_C cells. In the 2nd part, we find the number of different ways we can choose the N_C chains, one at a time (we make the assumption that, the 1st chain chosen is placed in the 1st of the N_C empty cells picked and so on). Finally, by applying the so called "basic counting principle"[a] [5], the result stems by multiplying these two numbers.

1st part: The problem of placing a chain of size i, in i empty unit cells (continuously), each one containing one link, is equivalent to replacing the i empty unit cells with one single cell ("icell") and placing all these i links (the i-chain) in this "icell". Doing this, we have N_{DTF} empty unit cells plus N_C empty "icells" and we have to place, in these cells, N_C chains (of various sizes) in such a way that each "icell" can contain at most one i-chain. Since the cells are identical, the number of ways we can choose N_C cells from a total of N_{DTF}+N_C cells is equal to (order does not matter):

$$P_1 = \binom{N_{DTF}+N_C}{N_C} = \frac{(N_{DTF}+N_C)!}{N_C!\,(N_{DTF}+N_C-N_C)!} = \frac{(N_{DTF}+N_C)!}{N_C!\,N_{DTF}!} \tag{6}$$

2nd part: There are N_1 chains of size 1, N_2 chains of size 2 and so on N_{Imax} chains of size I_{max}. In other words, there are N_C objects and N_1 are identical, N_2 are identical and so on, N_{Imax} are identical. The number of ways we can choose (order) the N_C objects (chains) is equal to:

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[a] *Basic Counting Principle*: Suppose that a task involves a sequence of *k* choices. Let p_1 be the number of ways the first stage or event can occur and p_2 be the number of ways the second stage or event can occur after the first stage has occurred. Continuing in this way, let p_k be the number of ways the k^{th} stage or event can occur after the first (k-1) stages or events have occurred. Then the total number of different ways the task can occur is: $p_1 p_2 ... p_k$

$$P_2 = \binom{N_C}{N_1\ N_2 \cdots N_{Imax}} = \frac{N_C!}{N_1!\,N_2! \cdots N_{Imax}!} \tag{7}$$

Finally, by implementing the basic counting principle [5], the number of ways of placing the N_C chains in the $N_{DTF}+N_C$ empty cells or (equivalently) the number of different ways that the given population of ganglia may be arranged to occupy the available empty p.m. unit cells, P_{DOF}, is equal to the multiplication of P_1 by P_2:

$$P_{DOF} = P_1 \times P_2 = \frac{(N_{DTF} + N_C)!}{N_{DTF}!\,N_C!} \times \frac{N_C!}{\prod_{i=1}^{I_{max}} N_i!} \tag{8}$$

Counting of microstates per physically admissible condition

Implementing once more the basic counting principle [5], the number of different microstates, P', pertaining to a physically admissible prototype flow arrangement determined by the triplet of flow arrangement variables $\{S^w', \beta', \omega'\}$, is given by

$$P' = P_{COP} \times P_{DOF} = \frac{K_{CP}!}{N_{COP}!(K_{CP} - N_{COP})!} \times \left(\frac{(N_{DTF} + N_C)!}{N_{DTF}!\,N_C!} \times \frac{N_C!}{\prod_{i=1}^{I_{max}} (N_i!)} \right) \tag{9}$$

Now, considering the magnitude of the numbers in (9), computation of the factorials requires copious effort. Nevertheless, instead of P', it is possible (and advisable as well) to tackle its logarithm, $\ln P'$,

$$\begin{aligned} \ln P' \;=\; & \ln(K_{CP}!) - \ln(N_{COP}!) - \ln((K_{CP} - N_{COP})!) \\ & + \ln[(N_{DTF} + N_C)!] - \ln(N_{DTF}!) - \sum_{j=1}^{I_{max}} \ln(N_j!) \end{aligned} \tag{10}$$

Then, implementing the "Stirling's approximation limiting procedure" formula

$$\ln(n!) \cong n\ln(n) - n \tag{11}$$

the equality being true in the sense that $\ln(n!)$ & $n\ln(n) - n$ are almost identical, results

$$\ln P' = K_{CP}\ln K_{CP} - N_{COP}\ln N_{COP} - (K_{CP} - N_{COP})\ln(K_{CP} - N_{COP}) + (N_{DTF} + N_C)\ln(N_{DTF} + N_C) - N_{DTF}\ln N_{DTF} - \sum_{i=1}^{Imax} N_i \ln(N_i) \quad (12)$$

Now, replacing $N_{COP} = \beta K_{CP}$, and using expressions (2)-(5) yields (by straightforward algebra) a form similar to the Boltzmann-Gibbs entropy [6] expression

$$\ln P' = K_{CP}\left[-\beta\ln\beta - (1-\beta)\ln(1-\beta)\right] + M(1-\beta)\left[-(1-\omega)\ln(1-\omega) - \left(\omega\ln\omega - \omega\sum_{i=1}^{Imax} n_i^G \ln n_i^G\right)\right] \quad (13)$$

Note two contributions in the number of microstates: (a) the extensive contribution of the reference volume size & frontal area, expressed by "user-selected" parameters M and K_{CP} respectively, depending on the reference volume aspect ratio and the network topology; (b) the non-extensive contribution of the actual flow configuration, expressed by reduced variables, namely the flow arrangement variables β, ω, and the reduced ganglion size distribution n_i^G, i=1; I_{max}. For the sought network, considering a cube as reference volume, parameters K_{CP} and M are related as $K_{CP} = 2{,}349816\times10^{-3} M$.

Expression (13) can be interpreted as follows. There are two different domains where microstates "live": the frontal reference area and the reference volume. On the reference area there are two entities with identical size (areal footprint), connected-oil pathways that may arrange within the β fraction and DOF pathways that may arrange within the complementary fraction, $(1-\beta)$, in any possible way. The other microstate domain comprises the $(1-\beta)$ volume fraction that is shared by two entities: the DTF unit cells –all of identical size- within the $(1-\omega)(1-\beta)$ fraction of the reference volume and the ganglia that live within the complementary domain, $\omega(1-\beta)$, but have a size distribution and deprive vital space from the DTF unit cells and singlet ganglia. If all ganglia were equally partitioned in singlets, then the number of microstates would equal $(-\omega\ln\omega)$; nevertheless this number is actually reduced by the accumulated number of microstates of ganglia of size i, $(-n_i^G \ln n_i^G)$, for i=1 to I_{max}.

ESTIMATION OF THE CONFIGURATIONAL ENTROPY

To proceed with the computation of the configurational entropy of the process for any particular macrostate flow condition (Ca, r), S_{SYS}, we use a Boltzmann type expression for the entropy in every physically admissible flow arrangement, $j \in \{1,..., N_{PAS}\}$, $S'_{SYS,j}$, and sum over all j.

$$S_{SYS}(Ca,r) = \sum_{j\in I}^{N_{PAS}(Ca,r)} S'_{SYS,j} = \sum_{j\in I}^{N_{PAS}(Ca,r)} \left(k_{DeProF}\ln P'_j\right) = k_{DeProF}\sum_{j\in I}^{N_{PAS}(Ca,r)} \ln P'_j \quad (14)$$

In this context, the contribution of microstates within *each* physically admissible flow arrangement, P'_j, as well as the contribution of other microstates stemming from the plurality of *all* physically admissible flow arrangements, $N_{PAS}(Ca,r)$, have been taken into account.

CONCLUSIONS

To evaluate the global (total) entropy production of steady-state two-phase flow in pore networks processes we need to consider two scales: (a) molecular level entropy is accounted as thermal entropy within the continuum mechanics scale; (b) configurational entropy lurks within a discrete (and presumably countable) scale of flow microstates inherent in every flow configuration that is physically admissible with any stationary macrostate flow condition.

An analytical scheme has been furnished -based mainly on combinatorics- to estimate (count) the population of the complete set of (discrete scale) microstates stemming from the different arrangements of the fluidic elements for every physically admissible flow configuration.

An open problem that still needs to be addressed is the delivery of an expression for the constant k_{DeProF} appearing in expression (14). To this end, the work of Campisi and Kobe [7] may be implemented. To the authors confidence, delivery of an appropriate expression for k_{DeProF}, would eventually provide a sound theoretical justification of the phenomenology of steady-state two-phase flow in porous media.

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