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Optimum Operating Conditions for Steady-State Two-Phase Flow in Pore Networks: Conceptual Justification Based on Statistical Thermodynamics

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Abstract

The mechanistic model *DeProF* considers steady-state two-phase flow in porous media as a composition of three flow patterns: connected-oil pathway, ganglion dynamics and drop traffic flow. Their key difference is the degree of disconnection of the non-wetting phase which affects the relative magnitude of the rate of energy dissipation caused by capillary effects compared to that caused by viscous stresses. An appropriate mesoscopic scale analysis defines the process independent variables to be the capillary number, Ca, and the oil-water flowrate ratio, r, and leads to the determination of all the internal flow arrangements that are compatible with the externally imposed flow conditions. The observed macroscopic flow is an average over the canonical ensemble of the internal flow arrangements at mesoscopic scale. Extensive simulations using the *DeProF* algorithm revealed that there exist a continuous line, $r^*(Ca)$, in the domain of the process operational variables, (Ca, r) on which the efficiency of the process (oil produced per kW dissipated in pumps) attains a local maximum. The locus r*(Ca) defines the process *optimum operating conditions*. These findings are consistent with the phenomenology already presented in many experimental works.

The scope of the present work is to introduce a rational justification of the existence of the locally optimum operating conditions predicted by the *DeProF* theory.

Steady-state two-phase flow in porous media is a stationary process maintained in dynamic equilibrium on the expense of energy supplied to the system (an off-equilibrium process). The efficiency of the process depends on its spontaneity, measurable by the rate of global entropy production. The latter is the sum of two components: the rate of mechanical energy dissipation at constant temperature and a conformational entropy production component, directly related to the number of internal flow arrangements.

The DeProF algorithm simulations indicate that: for every oil-water-pore network system, *optimum operating conditions* exist for the $r^*(Ca)$ values for which the rate of global entropy production becomes maximum, i.e. when the process is *as spontaneous as physically possible*.

The conceptual statement introduced here is an initial approach towards implementing aspects of statistical thermodynamics to elucidate further the underlying physics of the process.

Introduction

Two-phase flow in porous media (2 φ FPM) occupies a central position in physically important processes with practical applications of industrial and environmental interest. Some examples are [Tsakiroglou *et al.*, 2007]: the oil and gas production from underground reservoirs; the groundwater and soil contamination by organic compounds and relevant methods of subsurface restoration; the operation of multiphase trickle-bed reactors; the drying of hygroscopic capillary porous media; the gas/water flow and transport in the cathode of proton exchange membrane fuel cells (PEMFC). It has been experimentally observed [Avraam & Payatakes, 1995 & 1999, Tallakstad *et al.*, 2009] that during two-phase flow the disconnected oil contributes significantly (and in certain cases of practical interest even exclusively) to the flow. Furthermore, the flowrate vs pressure gradient relation is found to be strongly non-linear, and to be strongly affected by the physical parameters that pertain to the fluid-fluid interfaces.

The mechanistic model DeProF developed by Valavanides & Payatakes [Payatakes & Valavanides, 1998, Valavanides & Payatakes, 1998, 2000, 2001], predicts the relative permeabilities using the concept of decomposition in prototype flows; it accounts for the pore-scale mechanisms and the network wide cooperative effects, and is sufficiently simple and fast for practical purposes. The sources of non-linearity (which are caused by the motion of interfaces) and other complex effects are

modeled satisfactorily. The quantitative and qualitative agreement between existing sets of data and the corresponding theoretical predictions of the DeProF model is excellent [Valavanides & Payatakes, 2000 & 2001].
In the DeProF model it is assumed that, in the most general case, the macroscopic flow can be decomposed into two prototype flows, Connected-oil Pathway Flow (CPF) and Disconnected Oil Flow (DOF). The latter comprises Ganglion Dynamics (GD) and Drop Traffic Flow (DTF), regimes which have been observed experimentally [Avraam & Payatakes, 1995 & 1999, Tallakstad *et al.*, 2009]. Each prototype flow has the essential characteristics of the corresponding flow patterns in suitably idealized form, and so the pore scale mechanisms are incorporated in the prototype flows.
Using the DeProF model, one can obtain the solution to the problem of steady-state two-phase flow in porous media (SS2φFPM) in the form of the following transfer function

$$x = x\left(Ca, r; \kappa, \theta_A^0, \theta_R^0, \mathbf{x}_{pm}\right) \tag{1}$$

where, $x = \left(-\partial\tilde{p}/\partial\tilde{z}\right)\tilde{k}\left(\tilde{\gamma}_{ow}Ca\right)^{-1}$ is the reduced macroscopic pressure gradient, $\tilde{k}$ is the absolute permeability of the porous medium, Ca is the capillary number, defined as $Ca = \tilde{\mu}_w\tilde{U}^w/\tilde{\gamma}_{ow}$ ($\tilde{\mu}_w$ is the viscosity of water, $\tilde{U}^w$ is the superficial velocity of water, and $\tilde{\gamma}_{ow}$ is the interfacial tension), $r = \tilde{q}_o/\tilde{q}_w$ is the oil/water flowrate ratio, $\kappa = \tilde{\mu}_o/\tilde{\mu}_w$ is the oil/water viscosity ratio, θ_A^0 and θ_R^0 are the advancing and receding contact angles and $\mathbf{x}_{pm}$ is a parameter vector composed of all the dimensionless geometrical and topological parameters of the porous medium affecting the flow (e.g. porosity, genus, coordination number, normalized chamber and throat size distributions, chamber-to-throat size correlation factors, etc). Note that in equation (1) S^w is not considered to be an independent variable; actually, S^w is one of the dependable variables in the system of DeProF equations. A typical dependence of x on Ca & r is presented in Figure 2(b) for a system with o/w viscosity ratio $\kappa = 1{,}45$.
Simulations implementing the DeProF theory, suggest that conditions of optimum operation (read: improved efficiency) exist for processes of steady-state two-phase flow in pore networks. The term 'optimum operating conditions' (OOC) is introduced to interpret those values of Ca & r (the operating parameters) for which the process efficiency, expressed in terms of "oil transport per kW of mechanical power supplied to the process" or "oil produced per kW of mechanical power dissipated in pumps" or "oil flowrate per unit energy cost", takes one (or many) locally maximum values (Valavanides & Payatakes, 2003). Detecting and setting such conditions in a real process could eventually increase the process efficiency; that could provide potentially large marginal benefits in industrial applications, such as EOR (Taber et al., 1997, 1 & 2). It is therefore imperative to challenge the DeProF theory claims regarding the existence of OOC in such processes.
As a first step towards the potential exploitation of the DeProF theory findings, the scope of the present work is to furnish a conceptual justification of the existence of optimal operation conditions in steady-state two-phase flows in pore networks.

Basics of the DeProF model

In the general case of SS2φFPM of Figure 1(a), the physical system, comprising the porous medium, oil and water, is characterized by the values of the physicochemical parameters, namely $\tilde{\gamma}_{ow}, \tilde{\mu}_o, \tilde{\mu}_w, \theta_A^0, \theta_R^0, \mathbf{x}_{pm}$. Oil and water are continuously supplied along the macroscopic flow direction, $\tilde{z}$, with constant flowrates $\tilde{q}^o$ and $\tilde{q}^w$, so that the operational (dimensionless) parameters Ca & r have constant values.
In the CPF region the oil retains its connectivity and flows with virtually one-phase flow. The porous medium volume fraction occupied by the connected oil is denoted by β. The DOF regime is defined as the region composed of the rest of the unit cells, so the DOF volume fraction equals $(1-\beta)$. Water is the wetting phase and always retains its connectivity. DOF implicitly represents the connected-water pathway flow. A microscopic scale representation (a snapshot) of a typical DOF region is shown in Figure 1(b). An oil ganglion having a typical "cruising" configuration [Valavanides & Payatakes, 2000, 2001, 2002] is shown at the center. All the cells that accommodate parts of this (or any other) oil ganglion are called ganglion cells and are demarcated with a thick dashed line. The rest of the cells in the DOF region are cells containing water and oil drops. These cells comprise the regions of the GD and DTF domains respectively.
The fraction of all the ganglion cells over all the DOF region cells is denoted by ω, and is called the GD domain fraction. The DTF domain fraction in the DOF region equals $(1-\omega)$. S^w, β and ω are called *flow arrangement variables* (FAV) because they give a coarse indication of the prevailing flow pattern. One of the objectives of DeProF is to determine the values of S^w, β and ω that conform with the externally imposed conditions (Ca,r).
The flow analysis is carried out at two length scales, a macroscopic scale (10^{12} pores, or more) and a microscopic scale, and produces a system of equations that includes macroscopic water and oil mass balances, flow arrangement relations at the macroscopic scale, equations expressing the consistency between the microscopic and macroscopic scale representations in the DOF region and an equation that is obtained by applying effective medium theory [Kirkipatrick, 1973] to the "equivalent one-phase flow" in the DOF (GD&DTF) region -implicitly representing the transfer function for this region [Valavanides & Payatakes, 2000 & 2001]. The system is closed by imposing an appropriate type of distribution function for the ganglion

volumes, which is dictated by the physics of ganglion dynamics and experimental observations [Avraam & Payatakes, 1995 & 1999, Tallakstad *et al.*, 2009] and numerical simulations [Valavanides *et al*, 1998].

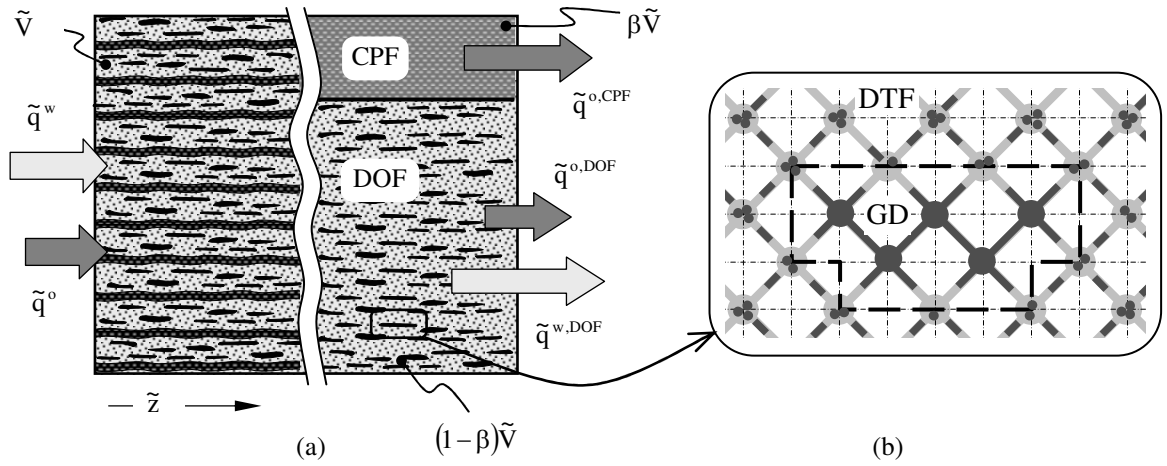

Figure 1 (a) "Actual" flow and its theoretical decomposition into prototype flows: CPF & DOF. (b) A microscopic scale representation (snapshot) of a DOF region. An oil ganglion of size class 5 is shown. For simpler representation, all cells are shown identical and the lattice constant is shown expanded. The dashed line separates the GD cells domain and the DTF cells domain. In reality chambers and throats have prescribed size distributions.

Physically admissible flow configurations

A core feature of the DeProF model is the detection of all flow configurations that are physically admissible under the imposed macroscopic flow conditions. On a mesoscopic scale (say 10^4-10^9 pores), the actual flow at a given region of the porous medium 'wanders' over the domain of physically admissible flow configurations 'visiting' any one with equal probability, or frequency (ergodicity).

To detect these flow configurations we partition the domain $\{S^w, \beta, \omega\}$ of all possible flow arrangement parameter values using sufficiently fine steps to obtain a 3D grid. Then, we select any triple of values for the flow arrangement parameters $\{S^w, \beta, \omega\}$ from this grid, and solve the system of the DeProF equations to compute the reduced macroscopic pressure gradient x' corresponding to that triple of f.a.p. values. Now, if a solution to the DeProF equations that is compatible with the selected $\{S^w, \beta, \omega\}$ values, exists, this is allowed as a physically admissible solution (PAS) and is denoted as $x'(S^{w}{}', \beta', \omega')$. Otherwise, the set of $\{S^w, \beta, \omega\}$ values is rejected as a possible flow arrangement. The process is repeated until all the grid points have been so characterized. In the end, we have a domain of the $\{S^w, \beta, \omega\}$ space, denoted Ω_{PAS}, that corresponds to the physically admissible solutions, x'. (The diagrams in Figure 4 provide images of detected physically admissible solutions for fixed Ca=1,2×10^{-6} and various r (0,1≤r≤10).

The measure ("volume") of Ω_{PAS} is given by

$$V_{\Omega_{PAS}}(Ca,r) = \iiint_{\Omega_{PAS}(Ca,r)} dS^w d\beta d\omega \tag{2}$$

where Ω_{PAS} (Ca,r) stands for integration carried over the physically admissible ranges in (S^w, β, ω) for the imposed Ca, r values. The volume of Ω_{PAS} is a measure of the degrees of freedom of the process at the mesoscopic scale; it is also related to the rate of entropy production at the mesoscopic scale (conformation entropy).

By assuming that each physically admissible solution is visited with the same probability, or frequency (assumption of ergodicity), and averaging over their domain, Ω_{PAS}, a unique solution for the macroscopic flow is obtained. For any quantity, Φ', the corresponding expected mean macroscopic flow quantity, Φ is defined as

$$\Phi(Ca,r) = \langle \Phi' \rangle = \frac{\iiint_{\Omega_{PAS}(Ca,r)} \Phi'(Ca,r) dS^w d\beta d\omega}{\iiint_{\Omega_{PAS}(Ca,r)} dS^w d\beta d\omega} = \frac{1}{V_{\Omega_{PAS}}(Ca,r)} \iiint_{\Omega_{PAS}(Ca,r)} \Phi'(Ca,r) dS^w d\beta d\omega \tag{3}$$

A prime is used to denote physically admissible values of any quantity. The symbol without a prime is reserved for the expected value of the quantity.

As with any macroscopic physical quantity, unique set of values for S^w, β, ω can be obtained by averaging over the PAS domain. These values define the flow configuration of the mean macroscopic flow (ergodicity).

Simulations of Steady-State Two-Phase Flow in Pore Network

A number of simulations of steady-state two-phase flow in a three-dimensional (3D) pore network of the chamber-and-throat type were carried out using the DeProF model. The simulations covered a rectangular domain in (Ca, r), from (Ca, logr)=(10-7, -1) to (Ca, logr)=(10-5, 2). The domain was covered in successive steps of Ca=10-6 (10 steps in the Ca range) and of logr=0,1 (32 steps in the logr range).

Pore Network

The network is cubic with lattice constant $\tilde{\ell} = 1221\,\mu\text{m}$. Chambers and throats are sited at the nodes and branches of the network. There are 5 classes of chamber sizes and 5 classes of throat sizes (see Table 1) and we assume that there is no correlation between the classes of chambers and throats. The chambers are spheres and the throats are right cylinders. The geometry of the 3D pore network is identical to the geometry of the pore network used in the DeProF model simulations of Valavanides & Payatakes (2002, 2003 & 2004).

Table 1 Occurrence probabilities, fj, and respective reduced size diameters for the 5 classes of chambers, D_{Cj}, and throats, W_{Tj}, of the 3D pore network used in the DeProF simulations. All dimensions are normalized to the lattice constant

j	1	2	3	4	5
fj (%)	16	21	26	21	16
D_{Cj}	0,2703	0,3849	0,4996	0,6143	0,7289
W_{Tj}	0,0929	0,1036	0,1127	0,1192	0,1251

This pore network is isotropic with volume porosity $\varepsilon = 0{,}0464$ and absolute permeability $\tilde{k}$ =8,965 μm^2. In all simulations, the pressure gradient (and the direction of macroscopic flow since the network is isotropic) is parallel to the cubic diagonal of the network.

Oil / water systems

Three typical oil/water systems were examined, with system parameter values $\tilde{\gamma}_{ow} = 25\times10^{-3}\,\text{N/m}$, $\theta_A^0 = 45\,\text{deg}$ and $\theta_R^0 = 39\,\text{deg}$, and $\kappa = 0{,}66$, 1,45 & 3,35.

Discretization scheme

For every set of (Ca,r) values, corresponding to one complete DeProF simulation, the entire flow configuration space $[S^w, \beta, \omega] \equiv [0,1]^3$ was swept in 50 successive steps in the S^w range and in 100 successive steps in the β & ω ranges.

Results

Results of simulations are presented in Figures 2, 3 and 4. For economy of space results are only presented for simulations pertaining to o/w systems with viscosity ratios κ =1,45. Results from all the simulations (pertaining to all examined viscosity ratios) show a systemic consistency. The (Ca, r) domain for which two-phase flow is not sustainable or physically admissible is also mapped.

The DeProF model predictions for the reduced macroscopic pressure gradient, x, are presented in Figure 2(b). It is clear that the effects of capillarity and contact angle hysterisis are significant up to at least 1 order of magnitude,

Predictions for the reduced rate of mechanical energy dissipation, W, calculated as the weighted sum of the respective rates in each prototype flow:

$$W \equiv \tilde{W}\tilde{k}\tilde{\mu}_w\left(\tilde{\gamma}_{ow}Ca\right)^{-2} = \beta rU^{o,CPF} + \left[(1-\beta)rU^{o,DOF} + 1\right]x \qquad (4)$$

are presented in Figure 2(a). The rate of mechanical energy dissipation equals the mechanical power that is externally supplied to the system. Mechanical energy dissipation is caused interstitially: (a) by bulk viscous stresses in combination with the local rates of deformation, and (b) by capillary pressure in combination with the velocities of moving menisci and contact angle hysteresis effects. Clearly, the relative magnitude of the two contributions depends -among other factors- on the degree of disconnection of oil (the non-wetting phase).

Optimum Operating Conditions for SS2φF in Pore Networks

The efficacy of the process with respect to the maximization of the oil transport per kW of mechanical power supplied to the system may be assessed by the values of the energy utilization coefficient, f_{EU}, a macroscopic quantity defined by Valavanides & Payatakes [2003] as

f_{EU}=r/W (5)

The effect of Ca and r on the energy utilization factor f_{EU} (=r/W) is depicted by the hump-shaped surfaces in the top row diagrams of Figure 3. A continuous line exists in the (Ca, r) domain for which the energy utilization factor takes locally maximum values. This line appears when the r/W surface ridge is projected on the (Ca, r) plane.

The DeProF model calculations show that for every fixed value in Ca there exists a unique value in r, r*(Ca), for which f_{EU} (=r/W) attains a locally maximum value. Therefore, a continuous line $r = r^*\left(Ca; \kappa, \theta_A^0, \theta_R^0, \mathbf{x}_{pm}\right)$ in the domain of (Ca, r) values exists, along which the system is at its most efficient operation in terms of oil flowrate per unit energy cost.

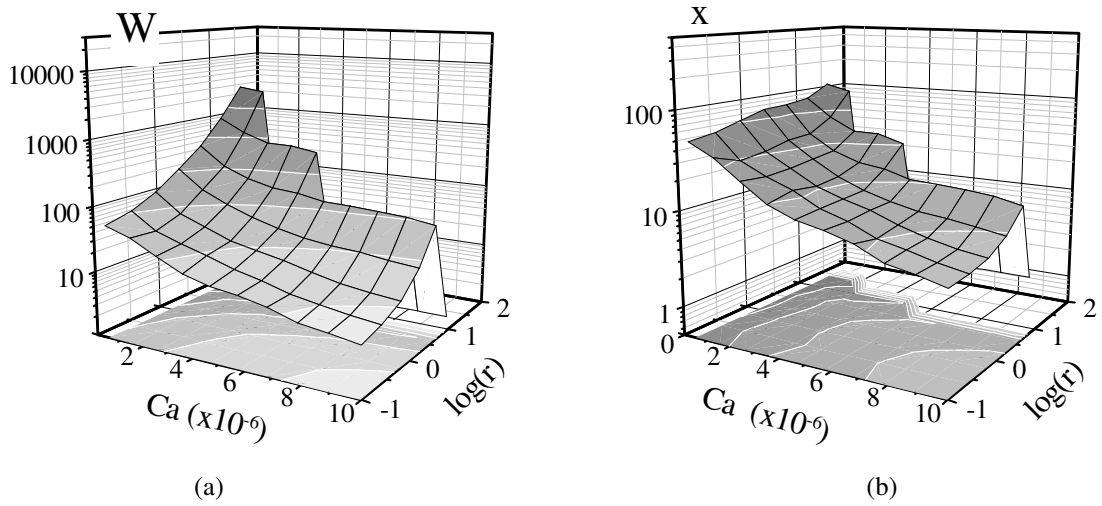

Figure 2 (a) Reduced mechanical power dissipation, W, and (b) Reduced pressure gradient, x, of the total flow, as a function of Ca and r. The diagrams pertain to 3D pore network simulations for an o/w system with viscosity ratio κ = 1,45

Conceptual justification of the existence of optimal operation conditions

The consistency of DeProF model predictions pertaining to optimal operation conditions (OOC) was examined against phenomenological arguments by Valavanides & Payatakes [2003]. Still, a careful examination of the dependency of W on Ca & r, in Figure 2(a), reveals that for any fixed Ca value, and while r takes relatively small values, W(Ca,r) increases slower than r does, therefore the ratio f_{EU}=r/W increases with increasing r. The relative increase in W over r is inverted after a certain point, r*(Ca), henceforth the denominator grows faster than the nominator, the ratio f_{EU}=r/W decreases with increasing r and a local maximum is formed. This outcome is based on the specific form of W(Ca,r) as predicted by DeProF. In that sense, internal consistency of DeProF has been satisfactorily assessed.

Nevertheless, one needs to benchmark the consistency of the DeProF model predictions with axioms and/or laws of physics that are not incorporated in the DeProF theory. The present work elaborates upon this task. In addition, a retrospective examination of the universal relative permeability curves for SS2φFPM, in light of the DeProF theory predictions, reveals that the existence of optimum operating conditions is also an inherent characteristic of steady-state two-phase flows in *real* porous media (Valavanides, 2010 in preparation).

In the next paragraph the correlation between optimum operating conditions and the domain of the physically admissible mesoscopic flow arrangements will be examined.

Affinities between OOC and the PAS domain

An intrinsic characteristic of SS2φFPM is the variety of flow configurations -observed at a mesoscopic scale- that are consistent with the externally imposed macroscopic flow conditions. The PAS domain, Ω_{PAS}, is a function of Ca and r.

The effect of r, under constant Ca, on the PAS domain is illustrated in the sequence of diagrams in Figure 4. The diagrams pertain to a gradual increase of the o/w flowrate ratio by 2 orders of magnitude ($-1 \le \log r \le 1$) against a fixed value of the capillary number, Ca ($Ca=1{,}2\times10^{-6}$). The PAS domain is depicted by the swarm of small/red ballpoints. Each ballpoint corresponds to a mesoscopic flow configuration, pinpointed in the space of the flow arrangement variables by a set $\{ S^w{}', \beta', \omega' \}$. The configuration of the mean macroscopic flow, $\{ S^w, \beta, \omega \}$, is depicted by a large sphere and it pivots against the 3 planes.

For any fixed value of Ca and as r gradually increases, the PAS domain progressively swells, extends to a maximal size and then shrinks to zero just as the two-phase flow cease to be sustainable. When the PAS domain attains a maximal volume

(for Ca=1,2×10^{-6}, at r~2,5), the macroscopic two-phase flow is as rich as possible in different flow configurations. A similar (systemic) behavior is observed for the other o/w systems examined (with $\kappa = 0{,}66$ & 3,35).

In Figure 3 (bottom row diagrams) the number of physically admissible solutions, detected by the DeProF algorithm, $N^{\#}_{PAS}$, is plotted against Ca & r, for two o/w systems with $\kappa = 0{,}66$ & 1,45. Note here that if a different discretization scheme of the flow configuration space $[S^w, \beta, \omega] \equiv [0,1]^3$ was implemented, a different population of PAS would be detected, nevertheless, the volume and envelope of $\Omega_{PAS}(Ca, r)$ would remain the same. The correlation between the measure (volume) of Ω_{PAS}, and the $N^{\#}_{PAS}$ needs to be defined for every discretization scheme.

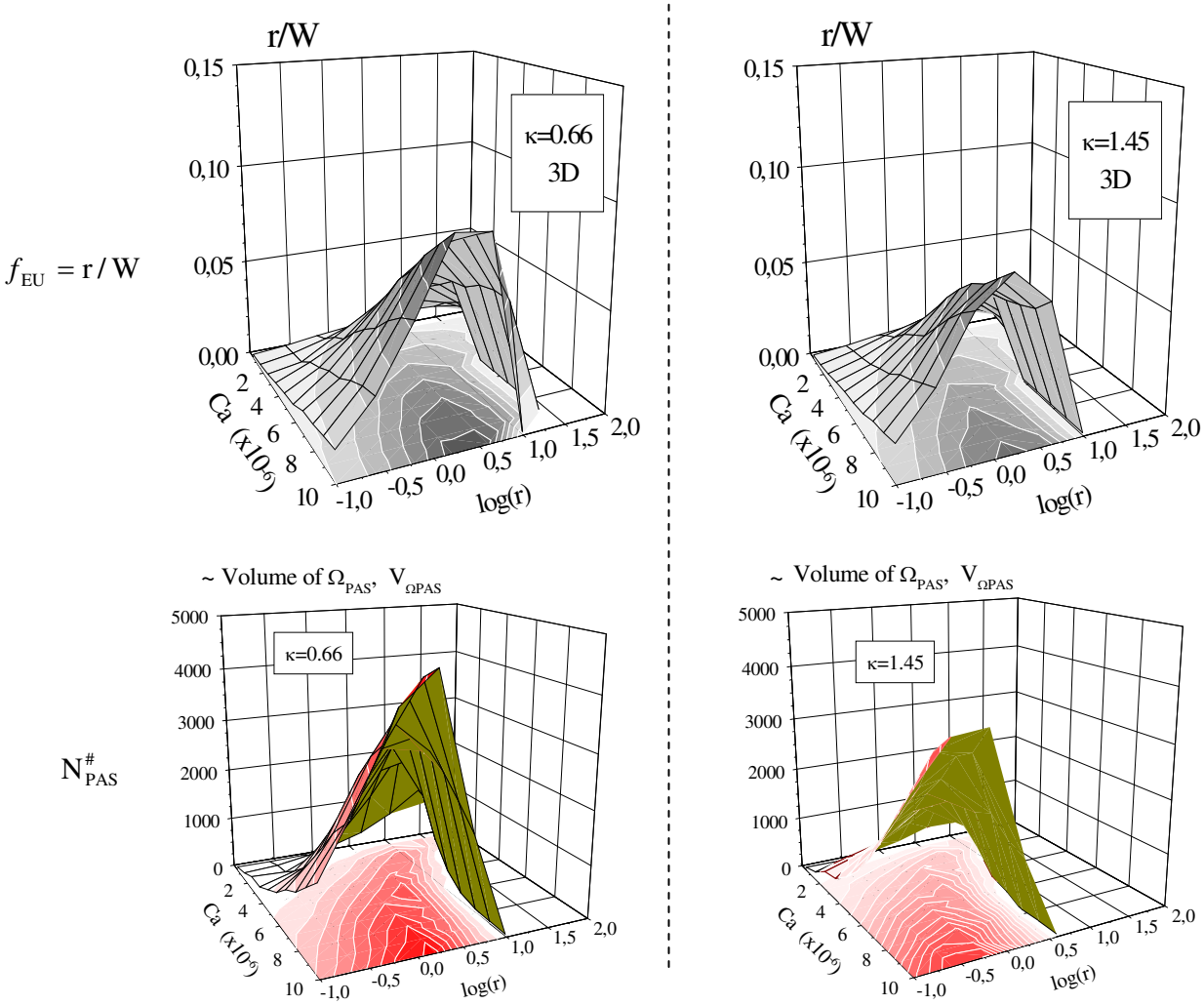

Figure 3 Energy utilization factor, f_{EU}, and number of physically admissible solutions detected by the DeProF algorithm, $N^{\#}_{PAS}$, as a function of Ca and r. The diagrams pertain to 3D pore network simulations for two o/w systems with viscosity ratio $\kappa = 0{,}66$ and 1,45

Comparing the diagrams of same κ in Figure 3 we note that f_{EU} and $N^{\#}_{PAS}$ show a similar trend with Ca and r. Again, as is the case with f_{EU}, there exists a continuous line in the (Ca, r) domain for which the $N^{\#}_{PAS}$(Ca,r) surface takes locally maximum values. A locus may be defined by projecting the ridge of the $N^{\#}_{PAS}$(Ca,r) surface on the (Ca, r) plane. For any fixed value of Ca, there exists a particular value of the flowrate ratio, r'(Ca), for which the number of numerically detected PAS, $N^{\#}_{PAS}$, and, consequently, the volume of Ω_{PAS}, take locally maximum values. Nevertheless, apart from any trend similarities of the two loci, a discernible, systematic shift between r*(Ca) and r'(Ca) exists for all systems examined, i.e. r*(Ca)>r'(Ca).

Each one of the $N^{\#}_{PAS}(Ca,r)$ flow configurations are equally likely to occur with probability $1/N^{\#}_{PAS}$. The main difference between these flow configurations is the degree of disconnectedness of the oil phase, which, in turn, affects the relative magnitude of the rate of energy dissipation caused by capillary effects compared to that caused by viscous stresses. A careful observation of the layout (volume, extent, topography) of the PAS domain as it "flows" -for increasing r values- within the domain of the flow arrangement variables (S^w,β,ω), reveals that for any fixed value of Ca and as r increases, the PAS domain starts from (S^w,β,ω) areas of low values of β ($\beta \to 0^+$ and the macroscopic flow is just DOF), then it swells (the number of PAS increase), then swells further and shifts into (S^w,β,ω) domains of increased β (where CPF is pronounced), to end shrinking (the number of PAS decrease significantly) in (S^w,β,ω) domains with relatively high values in β (where CPF dominates).

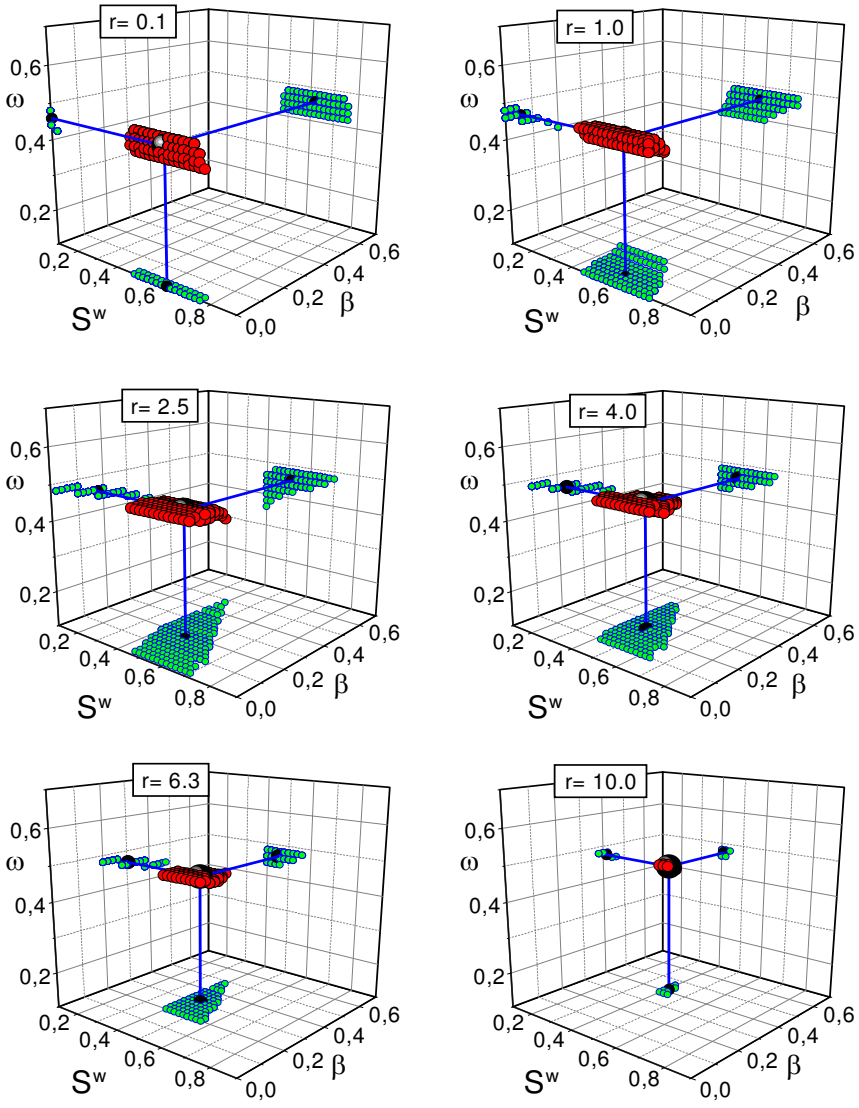

Figure 4 The concept of physically admissible solutions (PAS): For any fixed pair of externally imposed Ca & r values, the two-phase flow visits a continuum, Ω_{PAS}, of physically admissible flow configurations, outlined by the swarm of small/red ballpoints and its projections on the S^w,β,ω planes. Each larger/black ball (with its 3 pivots), pinpoint the macroscopic flow arrangement -determined by a set of $\{S^w,\beta,\omega\}$ values computed by averaging over Ω_{PAS}. The diagrams pertain to 3D pore network simulations for an o/w system with viscosity ratio $\kappa = 1{,}45$ operating at fixed capillary number $Ca=1{,}2\times10^{-6}$ and for increasing values of the flowrate ratio, r (spanning over 2 orders of magnitude).

Let now consider the case where the process is set to operate under a fixed value of the capillary number and a stepwise increasing of the o/w flowrate ratios until a limiting value of r, above which, two-phase flow is no longer sustainable. The corresponding PAS domains are determined within the flow configuration space, along with the "trajectory" of the macroscopic flow configuration. Then, the irreversibility characteristics of the process can be traced along r.

Initially, at low r values, irreversibility stems mainly from capillary pressure in combination with the velocities of moving menisci and contact angle hysterisis effects, while bulk viscosity has a less significant effect. Near the limiting value of r the main cause of irreversibility are the bulk viscous stresses in combination with the local rates of deformation whereas capillarity effects are now less significant (since oil has connected into pathways, the o/w interphase area has decreased significantly). At a certain point r=r*(Ca) between the span of r values considered, the irreversibility of the process is reduced to a minimum and it is there that f_{EU} attains a maximal value $f_{EU}(\mathrm{Ca}, \mathrm{r}^*) = \max[f_{EU}(\mathrm{Ca}, \mathrm{r})]$ and conditions of optimal operation are set.

Statistical Thermodynamics aspects of OOC

Steady-state two-phase flow in porous media is an off equilibrium process. One needs to provide energy to the process to keep it stationary at fixed operating conditions, i.e. to maintain its operation at fixed values of Ca and r (and a fixed temperature, say T_0).

A justification of the existence of optimum operating conditions will be proposed along the lines of the following postulate [Atkins, 1984]:

The efficiency of a stationary process in dynamic equilibrium, is proportional to its spontaneity. (P)

Spontaneity (the notional inverse for irreversibility) may be quantitatively assessed by the amount of entropy produced globally. Therefore, what the postulate implies is that, in order to maximize the efficiency of a process under specified operational constraints, one should maximize the process spontaneity (or, minimize its irreversibilty).

To proceed, we need first to notionally represent the physical domains in which the process of steady-state two-phase flow in p.m. (Process) takes place. We define as

- System: the porous medium and the two fluids
- Surroundings: the heat reservoir in which the System resides and with which it exchanges heat at constant temperature. The heat reservoir can absorb all the heat released by the system.
- Universe: it comprises the System and the Surroundings

Postulate (P) implies that the energy utilization coefficient, $f_{EU} = \mathrm{r}/\mathrm{W}$, and the global entropy production, S_{UNIV}, (process spontaneity) must show similar dependencies on the operational parameters Ca and r, i.e.

$$S_{UNIV}(\mathrm{Ca}, \mathrm{r}) \propto f_{EU}(\mathrm{Ca}, \mathrm{r}) \tag{6}$$

The consequence of this analogy is that the locus of optimum operating conditions r*(Ca) would coincide with the locus of maximization of global entropy production, say r"(Ca), i.e.

$$\mathrm{r}^*(\mathrm{Ca}) \equiv \mathrm{r}''(\mathrm{Ca}) \tag{7}$$

and, therefore

$$\max[S_{UNIV}(\mathrm{Ca}, \mathrm{r})] \Rightarrow \max[f_{EU}(\mathrm{Ca}, \mathrm{r})] \tag{8}$$

an implication that is consistent with the postulate (P).

The analogy in (6) relates two physical quantities. Of these, f_{EU}, has been already derived from classical mechanics (mass and momentum balances) and computed numerically by use of the DeProF model algorithm, while S_{UNIV} needs first to be derived analyticaly and then numerically by DeProF.

The entropy produced globally (within the Universe), S_{UNIV}, is the sum of two terms: a term representing the entropy released from the System to the Surroundings, S_{SUR}, and a term representing the entropy produced within the System, S_{SYS}. The former is actually produced in the Surroundings from the Process occurring within the System (see below); the latter may be directly related to the respective production of chaos due to the multitude of the mesoscopic flow configurations (the PAS of DeProF theory) that are maintained for so long as the (stationary) process is kept at conditions of dynamic equilibrium.

Therefore

$$S_{UNIV}(\mathrm{Ca}, \mathrm{r}) = S_{SUR}(\mathrm{Ca}, \mathrm{r}) + S_{SYS}(\mathrm{Ca}, \mathrm{r}) \tag{9}$$

One may proceed by interpreting each source of entropy production as follows.

The rate of entropy production in the Surroundings (maintained at constant temperature T_0) is due to the rate with which mechanical energy is dissipated within the System, W, irreversibly transformed into heat, Q, and then released to the Surroundings. Therefore,

$$S_{SUR}(Ca,r) = \frac{Q(Ca,r)}{T_0} = \frac{W(Ca,r)}{T_0} \tag{10}$$

The second source of entropy is due to the multitude of the mesoscopic flow arrangements maintained within the System Process (configuration entropy). It can be expressed similar to the Boltzmann entropy formulations in statistical mechanics:

$$S_{SYS}(Ca,r) = k_{DeProF} \ln\left[N_{PAS}(Ca,r)\right] \tag{11}$$

where

k_{DeProF} is a constant quantity to be derived in accordance with the DeProF theory on SS2 φ FPM (to be derived) and

N_{PAS} is the actual number of different mesoscopic flow arrangements (reduced per unit volume of porous medium) consistent with the macroscopic flow at (Ca,r)

Therefore, expression (6) may be rewritten in terms of quantities that can be evaluated by means of the DeProF algorithm as

$$\frac{W(Ca,r)}{T} + k_{DeProF} \ln\left[N_{PAS}(Ca,r)\right] \quad \propto \quad f_{EU}(Ca,r) \tag{12}$$

Implications of analogy (12)

In order to maximize the efficiency of the process one should increase/maximize the sum on the left side of (10). Of the sum components, the first term represents the cost of energy irreversibly transformed into heat and dumped to the surroundings; any increase of this term should be avoided -even better, this term should be decreased as much as possible. To do so, and, in parallel, increase as much as possible the entropy in the Universe -in order to increase the efficiency of the process, one may arrange or even "force" the process to operate in conditions for which the flow is as rich as possible in different physically admissible mesoscopic flow arrangements.

Conclusions

The predictive capability of the DeProF model was used to investigate the existence of optimum operating conditions in steady-state two-phase flow in pore networks. For every fixed value in Ca there exists a unique value in r, r*(Ca), for which the efficacy of the process with respect to the maximization of the oil transport per kW of mechanical power supplied to the system, quantitatively evaluated by the energy utilization factor f_{EU} (=r/W), attains a locally maximum value. Thus, there exists a continuous line $r = r^*\left(Ca; \kappa, \theta_A^0, \theta_R^0, \mathbf{x}_{pm}\right)$, in the domain of (Ca, r) values for which two-phase flow is sustainable, along which the operation of the system is at its most efficient in terms of oil flowrate per unit energy cost.

The existence of 'optimum conditions' for oil transport in steady-state two-phase flow in pore networks is a consequence of the remarkable internal adaptability of the flow to externally imposed flow conditions (Ca, r) and its inherent characteristic in trading-off between connected pathway flow, ganglion dynamics and drop traffic flow and self adjusting the connected versus disconnected moving-oil balance.

The domain of physically admissible mesoscopic flow configurations, compatible with the externally imposed macroscopic flow conditions, was examined and correlated to the efficiency characteristics of the process in the domain of (Ca, r) values for which two-phase flow is sustainable.

Two-phase flow in porous media is burdened (a) with the tendency of oil to disconnect and induce the capillarity effects that restrain or inhibit -to a certain extent- the superficial transport of oil & water (b) the bulk viscosities of oil & water. Applied engineering tackles problems invoking improvement of process efficiency under various techno-economical constraints.

The present work indicates that process engineers have the opportunity to take advantage of the intrinsic characteristics of 2 φ FPM, namely the multitude of physically admissible esoteric flows that act as -potentially beneficial- degrees of freedom against the imposed macroscopic constraints. Metaphorically speaking, the process designer may trade with the Daemon -avid for chaos in any form, an amount of configurational chaos (created from the multitude of intrinsic flow arrangements) in exchange for microscopic chaos (created by the rate of dissipation of mechanical energy into heat released within the jostling motion of molecules).

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