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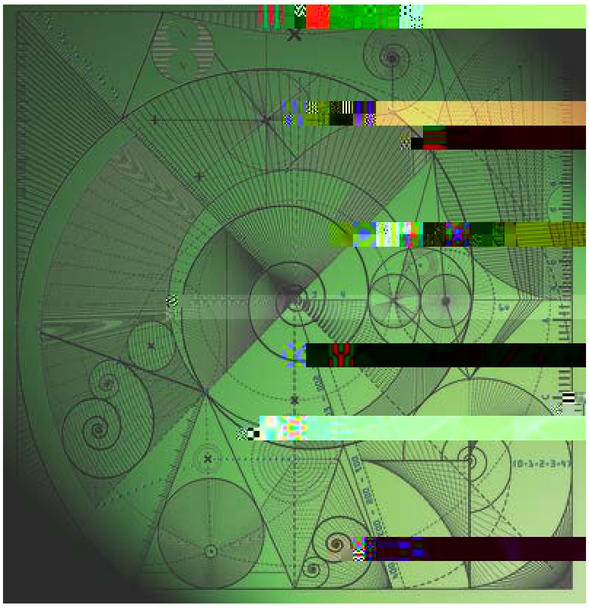

Capillary transport in paper porous materials at low saturation levels.

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The problem of capillary transport in fibrous porous materials at low levels of liquid saturation has been addressed. It has been demonstrated, that the process of liquid spreading in this type of porous materials at low saturation can be described macroscopically by a similar super-fast, non-linear diffusion model as that, which had been previously identified in experiments and simulations in particulate porous media. The macroscopic diffusion model has been underpinned by simulations using a microscopic network model. The theoretical results have been qualitatively compared with available experimental observations within the witness card technique using persistent liquids.

I. INTRODUCTION

Liquid distributions and transport in particulate porous media, such as clay, loam and sand, at low saturation levels was found to have very distinctive features resulting in a special class of mathematical problems, superfast non-linear diffusion [1–4]. It has been established, both experimentally and theoretically, that any time any wetting liquid naturally (that is when there is no force wetting regime involved) spreads in a dry (or a nearly dry) porous particulate matrix, the moving front dynamics follows, after some time, the power evolution law dictated by the super-fast non-linear diffusion mechanisms.

The special character of this non-linear diffusion process is caused by the loss of global, pore-scale connectivity at low levels of saturation. In this case the liquid transport only occurs over the surface elements of the porous matrix, sand particles for example, while the liquid is mostly located in the capillary bridges formed at the point of particle contacts.

Apparently, liquid spreading in dry porous materials is not just characteristic for particulate porous media, such as sand, but also frequently occurs in other porous materials. Therefore, in this paper, the previously develfurther used to obtain a macroscopic, average model. The macroscopic model will be compared with a microscopic network setup. In the end, we consider a set of available experimental data, and compare the general trends expected from the macroscopic formulation with the experimental results.

A. Quasi-steady liquid distribution in fibrous materials at low saturation levels

The morphology of the liquid structures formed between the crossing fibres in the wetting case is found to be in general more complex than that observed between the particles [13–18].

In particulate porous media, isolated bridges only exist below a certain critical level of saturation s s_c 8 10%, where the saturation s is defined as the ratio of the liquid volume V_L to the available volume of voids V_E,

$s =$ V_L

First, an average coordination number, that is the average number of crossings per unit volume N_c is to be defined. The value of L_e in a random paper network allows to estimate the mean distance l_f between the nearest fibre crossings, as in [11], $l_f \quad \frac{2}{L_e}$. That is, typical values of l_f are expected in the range 8 m $\quad l_f \quad 13$ m. Using $R = 7$ m and $L_e = 50\,\mathrm{mm}^{\;1}$, one can obtain an estimate of the coordination number with a typical value $N_c = \frac{L_e^2}{2R} \quad 5{:}6 \quad 10^5\,\mathrm{mm}^{\;3}$.

To parametrize saturation, we split, similar to [4], average liquid content in a sample volume $V = S_0 R$ of thickness R and surface area S_0 into two parts: the liquid contained on the rough surface of fibres and in the intrafibre pores of volume $V_r = L_e S_0 \, {}^{2}_{R}$ and the liquid contained in the capillary bridges at the fibre crossings $V_c = V_B N_c V$. The parameter ${}_R$ has the dimension of length and can be interpreted as the characteristic length scale of the surface roughness (intrafibre pore size), which could be considered as the fitting parameter of the model. We further assume that the smaller details (on the length scale $L \quad R$) of fibres are fully saturated, as it is commonly found on the rough surfaces [21], such that the amount of the liquid stored on the rough surface of fibres and in the intrafibre pores is independent of the liquid pressure, that is constant. This approximation is well fulfilled if the capillary pressure is on the scale of $p \quad p_0$.

Combining both contributions, saturation

$$s = \frac{V_c + V_r}{V}$$

can be presented as

$$s = V_B V_0^{\;1} + s_0; \quad V_0 = \frac{}{N_c}; \qquad (2)$$

where

$$s_0 = \frac{L_e \, {}^{2}_{R}}{R}$$

is the saturation level when all liquid bridges cease to exist.

Then, using (2), the average capillary bridge pressure $P = < p >^{l}$

$$P = \quad p_0 \; \frac{R^3}{V_0}^{\,1=2} \; \frac{1}{(s \quad s_0)^{1=2}}; \qquad (3)$$

where $< ::: >^{l} = V_l^{\;1} \, \mathrm{R}_{V_l} \, d^3x$ is intrinsic liquid averaging, V_l is liquid volume within the sample volume V. Using $L_e = 50\,\mathrm{mm}^{\;1}$, ${}_R = 1$ m, $R = 7$ m and $= 0{:}7$ as the typical parameters, one can estimate that the residual saturation level $s_0 \quad 10^{\;2}$, that is about 1% as expected.

Consider now local transport on the surface of fibres and in the intrafibre pores. The surface flux density q, according to the previous study of liquid spreading on of diffusion D_0, which is defined by the connectivity of the porous network of fibres, while in particulate porous media, there is a weak logarithmic dependence on saturation, and the diffusivity is driven by the shape of the particles and their contact area, details can be found [1–4]. In a way, the situation is simpler in the case of fibrous materials than that in particulate media, since the connectivity parameter can be quite accurately found via a network model. This will be done in the next part of this study. On the other hand, the question of the liquid amount stored in the intrafibre space is still open, and down to simplifying assumptions at this stage.

To address a moving boundary value problem set in an open domain with a smooth boundary ∂ moving with velocity v, the governing equation (9) can be complemented with the boundary conditions

$$s|_{\partial} = s_f; \quad s_f > s_0 \tag{10}$$

and

$$v \quad n = \quad D_0 \frac{n \quad \nabla s}{s(s \quad s_0)^{3/2}}; \tag{11}$$

where n is the normal vector to the boundary ∂.

D. The boundary value of saturation and steady states

The existence of a sharp boundary during the wetting of a dry porous material has been established experimentally in the case of particulate porous media [1, 4], in the experiments with the paper porous materials, a sharp boundary was also observed, though there are some differences discussed below.

As we have shown previously, the boundary value of saturation s_f is defined by the capillary pressure developed at the moving front, which in turn is conditioned in particulate porous media by the formation of bottleneck regions at the point of particle contacts [4]. In the fibrous porous media, such clear separation of the length scales generating the capillary pressure is not expected in a general case. Indeed, while the contact area between two particles vanishes when the bridge size shrinks and bottleneck regime of the contacts is achieved, the contact area between the fibres is expected to be still of the order of the fibre diameter R. In particulate porous media, this leads to a sharp cut off when propagation of the moving front practically stops. In the fibrous materials, this transition should be smoother to the mode, when the transport will be mostly conditioned by the smaller details of the fibres, for example intrafibre pores or other smaller elements of a fibre. Further in the model development, we consider only the regime when the liquid bridges still exist, so that the minimal level s_0 is defined by fully saturated intrafibre structure. The boundary value then is always supposed to be larger then the minimal value $s_f > s_0$ and should be defined by the length scale of the fibre details, $_R$.

To get an estimate of the typical values of the boundary pressure and the saturation, we assume that the pressure is generated by the capillaries with characteristic size of the order of $_R$. Then, for example for water, taking characteristic value of the surface tension $= 72\,\mathrm{mN}/$

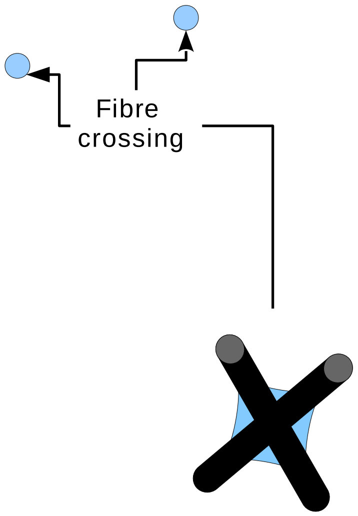

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FIG. 1. Illustration of the fibre crossing and the microscopic network.

of crossings per unit area in a porous layer of thickness R, that is $N_s = N_c R$.

In what follows, we will use non-dimensional forms by normalizing distance, pressure, flux density and flux by R, p_0, $q_0 = \frac{R}{R}\frac{k_m p_0}{R}$ and $I_0 = \; R\frac{k_m p_0}{}$ respectively. Then in non-dimensional form, designating non-dimensional variables by a bar,$N_s = N_c = \frac{8}{}(1 \quad)^2$.

We further assume, according to (1), that at any node the liquid pressure is defined by the amount of the liquid in the bridge, that is

$$p_m = \frac{1}{V_B^m} \; {}^{1=2} ;$$

where V_B^m is the normalized liquid volume at node m. At the same time, at non-equilibrium, the liquid flux between the nodes connected through the links is defined by the pressure difference. That is the liquid flux from node m to node n connected by the filament of length L_{mn} is proportional to the pressure difference between the nodes

$$I_{mn} = \; {}_{mn}\frac{p_n \quad p_m}{L_{mn}} :$$

The coefficient of proportionality here is a non-dimensional adjusting parameter $_{mn}$, which takes into account the average shape of the fibres and their average ability to transport the liquid. In our simulations, parameter $_{mn}$ is either a constant, $_{mn} = 1$, or is a random number uniformly distributed in the interval $0 \quad {}_{mn} \quad 1$, such that the average$< \; {}_{mn} >= 1{=}2$. Note, if all links would be of a cylindrical shape of diameter DJ/F11 9.9626 Tf 98 0 T(.re)-G8 0 T(.re)-G8 0 T(.re)-G8 0 T(.r profiles of $s(x)$ to get C_1. So that the ratio of the area of entrances and exits S_e/S, the main connectivity parameter, is parametrized by the non-dimensional parameters $_R/R$ and , since $N_c = N_c(\ )$.

Steady state distributions and the network connectivity factor

In the simulations, the quasi one-dimensional network setup corresponding to the macroscopic model (12) evolved in time till the flux density arrived at a uniform distribution in the bulk within the tolerance of 5 10%. We used different total number of points in the fixed simulation domain (side size $X = 100$) n_T and two types of networks, with three neighbours (triangular tessellation) and four neighbours (quadrilateral tessellation) per each node, namely, $n_T = 2300$, $N_c = 0.23$ and $= 0.7$, and $n_T = 6400$, $N_c = 0.64$ and $= 0.5$. The boundary values of saturation have been set to $s_1 = 0.1\%$ and to $s_2 = 20\%$ to cover the whole range, where the super-fast regime may be expected. We have also used two different models for the link permeability parametrised by the non-dimensional coefficients $_{ij}$, when either all $_{ij} = 1$ or they were randomly, but uniformly distributed in the interval 0 $_{ij}$ 1, such that the average $< _{ij} > = 1/2$.

What do we observe in simulations with the microscopic model? After reaching a steady state, when the flux density is constant in the flow domain, the distribution of pressure as a function of saturation, Fig. 2, was found to be in very good agreement with that anticipated in the macroscopic model (3), which is in a non-dimensional form

$$P = \frac{\sqrt{s}}{N_c}\;\frac{1}{\sqrt{s}} : \qquad (14)$$

the velocity at the time of the impact, Fig. 4. In the current study, we used two characteristic values of the impact velocity $u = 0{:}2$ m/s and $u = 3{:}1$ m/s.

The test liquid was neat tributyl phosphate (TBP, molar weight 266:32 g/mol), a low-volatility organophosphate compound, dyed with Calco red or blue oil (0:11% 0:5% mass concentration respectively). To introduce non-Newtonian effects and variations of viscosity, the neat (dyed) TBP solution was mixed with 3:8% (mass concentration) of Poly(Styrene-Butyl Methacrylate) (PSBMA).

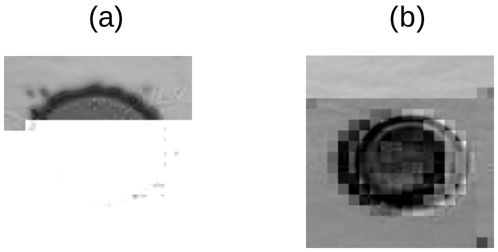

FIG. 4. Drop impact at $t = 1{:}6$ ms after the initial contact at the impact velocity $3{:}1$ m/s: (a) neat TBP (b) TBP with 3.8% of PSBMA.

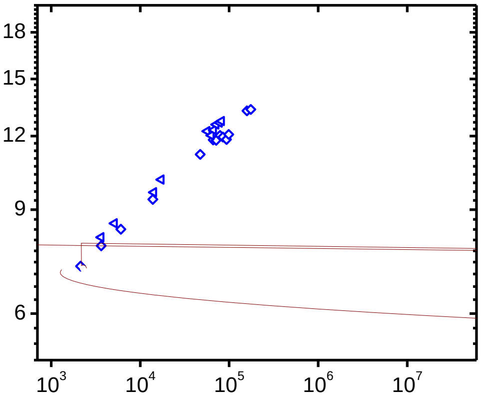

FIG. 5. The spot diameter D as a function of the reduced time $t{=}t_0$. Experimental data are shown by symbols at different impact velocities ($u = 0{:}2$ m/s and $u = 3{:}1$ m/s), for different liquids (neat TBP and TBP with 3.8% PSBMA), different dyes (the Calco blue and red oils at 0:5% and 0:11% mass concentrations respectively) and different paper matrices (Epson, Filter and Watercolor papers). The solid line (brown) is the power-law t $D = A(t{=}t_0 \quad t_C)^{1=3} + D_0$ at $A = 0{:}16$ mm, $t_C = 10^3$ and $D_0 = 5{:}2$ mm. The data collapsed into a master curve by using the characteristic time scale: for the Filter paper and TBP+PSBMA $t_0 = 1{=}9$ s, the Watercolor paper and TBP+PSBMA $t_0 = 3$ s, for the Epson paper and TBP+PSBMA $t_0 = 1$ s and for the Filter paper and neat TBP $t_0 = 1{=}900$ s.

The neat TBP solution has liquid viscosity $=$ 3:88 mPa s and surface tension $= 28 \quad 1$ mN=m measured in our laboratory at 20 C. The addition of the polymer into the pure TBP liquid resulted in substantial increase in the liquid viscosity $_P$ 340 mPa s at practically identical values of the surface tension 27 mN=m, basically introducing non-Newtonian behaviour during the first, short lasting stage of the impact to avoid formation of satellite droplets, the so-called corona of the splashing droplet, Fig. 4. The details of the properties of the polymer solution, also used in viscoelastic aerobreakup studies, can be found in [29].

B. Results and discussions

As we have already discussed, the detailed description of the liquid dispersion process in the papers, which requires microscopic information on the porous paper matrix, will be the subject of future research, so that here, we only analyse the general trend by observing the wetting spot diameter $D(t)$ as a function of time. Our prime concern is the long-time evolution of the spot diameter, which is shown in Fig. 5.

In the experiments, all drops were of a fixed volume of 2:2 L . There were three different fibrous substrates: Epson paper (80g=m^2), Watercolour paper (300g=m^2) and Filter paper (70g=m^2). It appears, though not surprisingly, that the long-time evolution of the wetting spot diameter (after some initial relaxation time t_C, that is at $t > t_C$) on all samples in different conditions can be effectively reduced to a single master curve by renormalizing time $t{=}t_0$, where the characteristic time t_0 only depends on the liquid viscosity and the substrate material, Fig. 5, but, essentially, is independent of the initial conditions, such as the impact velocity, and the visualization materials (red or/and blue oils).

As one can clearly see from the figure, the spreading law $D(t{=}t_0) \, / \, (t{=}t_0 \quad t_C)^{1=3}$ is well observed at $t{=}t_0 \quad t_C$ indicating that indeed the process of spreading after some initiation time t_C follows the super-fast non-linear diffusion model. As one can also observe, the long-time evolution characteristic behaviour (the exponent) is insensitive to the impact drop velocity, the type and concentration of the visualization liquid (red or blue Calco dyes), the substrate and liquid properties despite obvious difference in the initial conditions and the substrate and liquid properties, Fig 4. One may also note that in spite of the non-Newtonian character of the polymer solution, the observed effect while switching from the neat TBP to its 3:8% polymer solution is simply down to the change in the zero shear rate viscosity from $= 3{:}88\,\mathrm{mPa}$

[28] J. Xiao, H.A. Stone and D. Attinger, Source-like Solution for Radial Imbibition into a Homogeneous Semi-infinite Porous Medium