Transport and adsorption under liquid flow: the role of pore geometry

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I. COMPUTATION OF POROSITY AND SPECIFIC SURFACE AREA

The porosity (Φ) is simply computed as the ratio between the number of fluid nodes and the total number of nodes. The specific surface area is computed simply by counting the number of interfacial nodes. An interfacial node is define as a fluid node having at least one neighbouring solid node considering the Lattice-Boltzmann speed model D3Q19.

II. SLIT PORE GEOMETRY WITH RANDOM ROUGHNESS

The Figure 1 present 3 typical cut views of the slit pores with roughness generated here for the three aggregation conditions ($A_c = 1/8, 1/16, 1/32$). Grey nodes corresponds to the solid part and blue nodes corresponds to the fluid part. Some solid nodes seems to "fly" in the fluid part. Their connection with the walls exist but is in another plane behind or ahead of the one presented here.
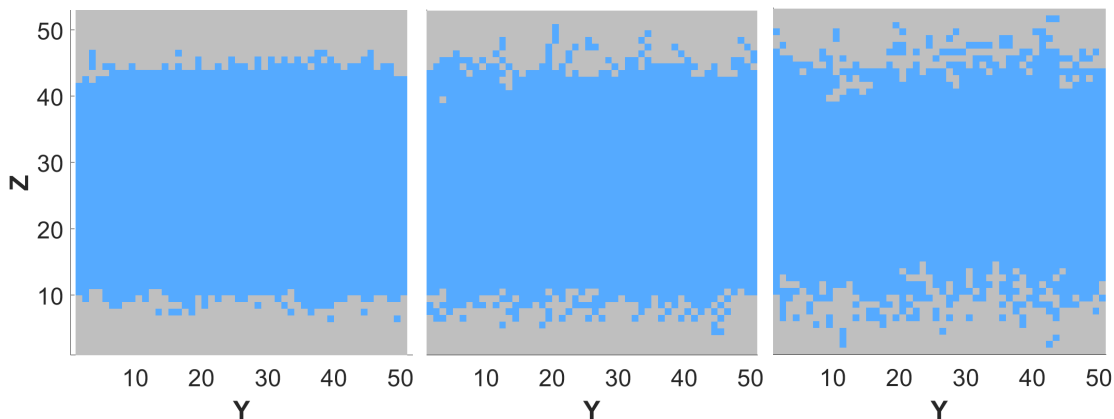

Figure 1. Slit pore with random roughness. Left: $A_c = 1/8$. Center: $A_c = 1/16$. Right: $A_c = 1/32$.

III. METHOD: HOW TO COMPUTE PORE SIZE DISTRIBUTION

The pore size distribution is defined, according to IUPAC[1], as *"the distribution volume with respect to the pore size"*. Experimentaly, the mercury porosimetry and the nitrogen adsorption measure are casualy employed to measure the pore size distribution of a material. The pore size distribution computation algorithm depends mainly on the modelisation method we are dealing with. However the basic principle remain the same. The ideer consists in discretising the void part of the material into a finite number of points and measure the biggest sphere we can introduce in the pore containing this point (P) (see. Fig 2). For atomistic simulation methods (Monte Carlo, Molecular Dynamics...) the Gubbins *et al.*[2] algorithm is the most commonly used.
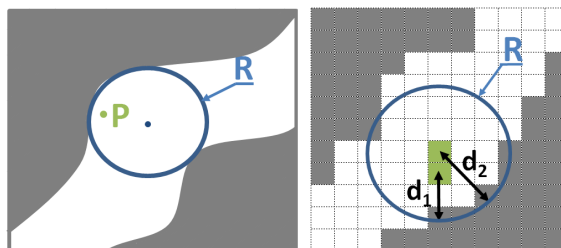

Figure 2. a. Pore size distribution measurement. b. Pore size distribution computation on lattice.

In the present case the discrete base of the the Lattice-Boltzmann gives a useful framework to compute the sphere size (see Fig 2b. The algorithm starts with the computation of the distance between each liquid nodes to its closest solid neighbour. The diameter of the sphere is twice this length. Then for each node we compare the size of the

sphere with the one of its liquid neighbours. If one of them has a bigger sphere we move to this node and compare again the sizes of the spheres with its neighbours. When the nodes has the highest size of sphere, we assign this size to all the nodes we have been passing through and included inside the sphere of this node.

IV. INPUT PARAMETERS OF THE GEOMETRY COMPARISON

Inputs values: $F_{ext} = 2\ 10^8$ Pa, $D_b = 6.04\ 10^{-8}$ m^2.s^{-1}, $K_a = 6.04$ m.s^{-1}, $K_d = 6.04\ 10^6$ s^{-1}, $\nu = 1.007\ 10^{-6}$ m^2.s^{-1}, $\rho_f = 1000$ kg.m^{-1}, $\rho_s = 4970$ kg.m^{-1}, $C_i = 1$ g.L^{-1}.

Porosity	Type	Mesh size(Δx)	Geom. param.(Δx)	Δx (m)	S_s (m^2)	V_p (m^3)	S_s/V_p (m^{-1})
65%	spinodal dec.	$70 \times 70 \times 70$	$\sigma_c = 0.4$	$1.44\ 10^{-7}$	$2.51\ 10^{-9}$	$6.26\ 10^{-16}$	$4.00\ 10^6$
	inv. opal	$99 \times 99 \times 99$	$d_{\text{int}} = 100, d_s = 108$	$1.38\ 10^{-8}$	$6.80\ 10^{-12}$	$1.70\ 10^{-18}$	$4.02\ 10^6$
	honeycomb	$118 \times 116 \times 1$	$a = 30, w = 15$	$2.55\ 10^{-8}$	$5.88\ 10^{-13}$	$1.47\ 10^{-19}$	$4.00\ 10^6$
70%	spinodal dec.	$70 \times 70 \times 70$	$\sigma_c = 0.4$	$1.07\ 10^{-7}$	$1.15\ 10^{-9}$	$2.88\ 10^{-16}$	$4.00\ 10^6$
	inv. opal	$97 \times 97 \times 97$	$d_{\text{int}} = 98, d_s = 108$	$1.31\ 10^{-8}$	$5.64\ 10^{-12}$	$1.41\ 10^{-18}$	$4.00\ 10^6$
	honeycomb	$118 \times 116 \times 1$	$a = 30, w = 13$	$2.48\ 10^{-8}$	$5.73\ 10^{-13}$	$1.43\ 10^{-19}$	$4.00\ 10^6$
73%	spinodal dec.	$70 \times 70 \times 70$	$\sigma_c = 0.4$	$8.25\ 10^{-8}$	$5.68\ 10^{-10}$	$1.42\ 10^{-16}$	$4.00\ 10^6$
	inv. opal	$94 \times 94 \times 94$	$d_{\text{int}} = 95, d_s = 108$	$1.29\ 10^{-8}$	$5.24\ 10^{-12}$	$1.33\ 10^{-18}$	$4.00\ 10^6$
	honeycomb	$118 \times 116 \times 1$	$a = 30, w = 11$	$2.41\ 10^{-8}$	$5.6\ 10^{-13}$	$1.40\ 10^{-19}$	$4.00\ 10^6$

Table I. Inputs values for the design of geometries: spinodal decomposition, inverse opal and honeycomb.

"Geom. param." (geometric parameters) stands for the specific parameters we employed to generate each of the geometries. In the case of spinodal decomposition ("spinodal dec.") σ_c corresponds to the threshold value employed for the Ostwald ripening algorithm. In the case of inverse opal ("inv. opal"), d_{int} corresponds to the distance between the spheres and d_s to the spheres diameter. In the case of honeycomb geometry, a correspond to the characteristic length of the hexagons and w to the thickness of the profile.

V. ADSORPTION ISOTHERMS OF THE GEOMETRY COMPARISON

The Fig. 3 shows the isotherms for the three geometries (honeycomb, inverse opal and spinodal decomposition) keeping adsorption capacity constant for low and high concentration in solute. The adsorption isotherms are exactly the same, and reflect the Langmuir model of adsorption introduced at the microscopic scale in the Lattice Boltzmann scheme. It confirms that keeping Φ and S_s/V_p constant gives the same adsorption capacity for all the concentrations.
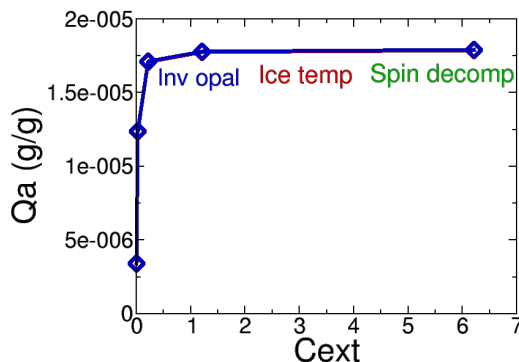

Figure 3. Adsorbed quantity considering the saturation of the adsorption sites.

VI. RELATION BETWEEN REDUCED UNITS AND SCIENTIFIC INTERNATIONAL UNITS IN LATTICE BOLTZMANN SIMULATIONS

The Lattice Boltzmann model used here runs in reduced units (also called LB units). We present below the relation to transform the adimensional results in scientific international units (SI units). The Table II summarize the symbols and their units used here. In LB units the distance between two nodes of the grid corresponds to x_{lb}. The time step corresponds to t_{lb}. In the algorithm, the viscosity of the fluid is constant ($\nu_{lb} = 1/6$ in lattice units)[3]. The density of the fluid is also dimentionless. It has be considered constant, corresponding to an incompressible fluid ($\rho_{lb} = 1$ lattice units). Translating to real units first requires defining the real distance between two nodes x_r and the real viscosity of the fluid ν_r (in SI units). The resulting time step can then be calculated as:

$$t_r = t_{lb} \frac{\nu_{lb} x_r^2}{\nu_r x_{lb}^2} \ . \tag{1}$$

The real external force density $Fext_r$ can be computed when we further specify the real density of the fluid ρ_r:

$$\frac{Fext_r}{Fext_{lb}} = \frac{P_r x_{lb}}{P_{lb} x_r} = \frac{f_r x_{lb}^3}{f_{lb} x_r^3} = \frac{m_r x_{lb}^2 t_{lb}^2}{m_{lb} x_r^2 t_r^2} = \frac{\rho_r x_r}{\rho_{lb} x_{lb}} \left(\frac{t_{lb}}{t_r} \right)^2 \tag{2}$$

or:

$$Fext_r = Fext_{lb} \frac{\rho_r x_r}{\rho_{lb} x_{lb}} \left(\frac{t_{lb}}{t_r} \right)^2 \tag{3}$$

Similarly, the average velocity of the fluid is computed using:

$$\bar{v}_r = \bar{v}_{lb} \frac{x_r t_{lb}}{x_{lb} t_r} \ , \tag{4}$$

for the bulk diffusion coefficient:

$$Db_r = Db_{lb} \frac{x_r^2 t_{lb}}{x_{lb}^2 t_r} \ , \tag{5}$$

for the adsorption coefficient:

$$ka_r = ka_{lb} \frac{x_r t_{lb}}{x_{lb} t_r} \ , \tag{6}$$

and for the desorption coefficient:

$$kd_r = kd_{lb} \frac{x_r^2 t_{lb}}{x_{lb}^2 t_r} \ . \tag{7}$$

The pore volume and specific surface area are simply given by $V_p = N_f x_r^3$ and $S_s = N_{\text{ads}} x_r^2$, respectively. For the total concentration of species in the fluid:

$$C_{tot} = \frac{Dmax_r x_r^2}{Dmax_{lb} V_p x_{lb}^2} \tag{8}$$

For the external concentration of species *i.e.* the contration of species present in the fluid at the adsorption equilibrium:

$$C_{ext} = C_{tot}(1 - F_a) \tag{9}$$

For the maximum amount of adsorbed tracers for each adsorption site:

$$Dmax_r = Dmax_{lb} \frac{V_p C_i x_{lb}^2}{x_r^2} \tag{10}$$

Description	Name in LB units	LB units	Name in SI units	SI units
Distance between two nodes	x_{lb}	Δx	x_r	m
Time step	t_{lb}	Δt	t_r	s
Mass	m_{lb}	Δm	m_r	kg
Force	f_{lb}	$\Delta f = \Delta m.\Delta x.\Delta t^{-2}$	f_r	N
Pressure	P_{lb}	$\Delta p = \Delta f.\Delta x^{-2}$	m_r	Pa
Viscosity	ν_{lb}	$\Delta x^2.\Delta t^{-1}$	ν_r	m^2. s^{-1}
Density	ρ_{lb}	$\Delta m.\Delta x^{-3}$	ρ_r	kg.m^{-3}
External force density	$Fext_{lb}$	$\Delta p.\Delta x^{-1}$	$Fext_r$	Pa.m^{-1}
Average speed	$\bar{v}_{lb}$	$\Delta x.\Delta t^{-1}$	$\bar{v}_r$	m.s^{-1}
Bulk diffusion coefficient	Db_{lb}	$\Delta x^2.\Delta t^{-1}$	Db_r	m^2.s^{-1}
Adsorption coefficient	ka_{lb}	$\Delta x.\Delta t^{-1}$	ka_r	m.s^{-1}
Desorption coefficient	kd_{lb}	Δt^{-1}	kd_r	s^{-1}
Maximum amount of adsorbed tracers for each adsorption site	$Dmax_{lb}$	-	$Dmax_r$	kg.m^{-2}
Initial concentration	-	-	C_i	kg.m^{-3} or g.L^{-1}
External concentration	-	-	C_{ext}	kg.m^{-3} or g.L^{-1}
Porous volume	N_f	-	V_p	m^3
Specific surface area	$Nads$	-	S_s	m^2

Table II. Description of the different variables used in LB units and SI units

Refinement	$\ell_x(\Delta x)$	$\ell_y(\Delta x)$	$\ell_z(\Delta x)$	$\Delta x(m)$	$F_{ext}(Pa/m)$	$\langle v_y \rangle(m/s)$	$K_\Phi(m^2)$
1	50	50	52	5.10^{-8}	5.10^9	1.15	$2.3.10^{-13}$
2	100	100	104	$2.5.10^{-8}$	5.10^9	1.12	$2.2.10^{-13}$
3	150	150	156	$1.7.10^{-8}$	5.10^9	0.9	$1.8.10^{-13}$
4	200	200	208	$1.25.10^{-8}$	5.10^9	0.9	$1.8.10^{-13}$

Table III. Effect of mesh refinement on fluid behavior in a slit pore with random roughness on wall ($A_c = 1/8$).

VII. EFFECT OF MESH SIZE ON PERMEABILITY IN SLIT PORE WITH AGGREGATED RANDOM ROUGHNESS

This section presents the results on the investigation of the effect of the size of the mesh in the case of a slit pore with aggregated roughness on the wall ($A_c = 1/8$). This investigation comes from the interrogation about the origin of the surprisingly higher permeability with a roughness with $A_c = 1/8$ compared with a slit pore.

To increase the mesh refinement we take the aggregated geometry (with roughness) lets say with the refinement factor equals to 1 and scale it up. For example, for a refinement factor of 2, each node of the initial geometry gives its value to four nodes of the refined geometry. For a refinement factor of 3 each node becomes 9 nodes in the refined geometry. For each refinement factor we adapt the value of the distance between the nodes Δx to keep the global size of the geometry constant and the pore size constant.

Table III presents the results and highlights an influence of the mesh refinement on the properties of the fluid creating in the case of less refined mesh some artefact. The permeability decreases with the mesh refinement meaning that the initial geometry is sensitive to simulation artefact. More over the permeability of the equivalent slit pore is $2.1.10^{-13}$ m^2 which is higher than the permeability with the refined mesh. The unexpected effect is a simulation artefact.

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