

1 **Pore network modeling of thin water film and its influence on**
2 **relative permeability curves in tight formations**

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14 **Abstract**

15 The thin water film stabilized by disjoining pressure is non-negligible in tight
16 formations which results in significant difference in multiphase flow behavior
17 compared with that in conventional formations. In this work, a pore network model is
18 proposed to simulate two phase flow in tight formations to highlight the contribution of
19 thin water film on multiphase flow. The newly developed pore network model includes
20 the influence of thin water film on fluid configuration, capillary entry pressure, fluid
21 conductance and connectivity during multiphase flow in pore space. Our approach is
22 first validated with the existing pore network model and then the influence of thin water
23 film on two-phase flow is investigated extensively. The results show that the connate
24 water saturation increases and its associated oil relative permeability decreases as the
25 average pore radius decreases. It also suggests that in water-wet systems, the influence
26 of thin water film on both oil and water phases becomes significant when the average
27 pore radius is smaller than 100 nm. Existence of thin water film will increase the
28 proportion of film water and corner water, resulting in an increasement in oil phase

29 relative permeability and a slight decline of water phase relative permeability in tight
30 porous media dominated by angular pores and throats; while in porous media
31 dominated by circular shaped pores and throats, oil and water phase relative
32 permeability are both enhanced due to better connectivity caused by thin water film; at
33 the same time swelling of water film results in lower residue oil saturation and higher
34 end point of water relative permeability. We also found higher water relative
35 permeability when porous media has more irregular pores.

36 Keywords: Water film, Tight formation, Pore-network modeling, Quasi-static,
37 Multiphase flow

38 **1. Introduction**

39 Tight oil reservoirs have been attracting considerable interests in recent years due
40 to the increasing energy demand and production depletion in conventional reservoirs
41 [1, 2]. Water flooding, which is considered as one of the most feasible secondary
42 recovery approaches, has been adopted to extract hydrocarbon from tight oil reservoirs.
43 However, even implemented with advanced horizontal well and volumetric fracturing
44 strategies, the recovery factor is still not promising as the limitation of relatively poor
45 formation properties of tight formation [3, 4]. Compared with conventional sandstone
46 reservoirs, the pore sizes of tight formations are much smaller and span from micro- to
47 nano-scale [5-8]. Therefore, a rigid understanding of oil-water flow behavior in
48 nano/micro scale pore space plays an important role in evaluating the efficiency of
49 water flooding and favorable production strategy design in tight formation [9].

50 During primary drainage, a thin water film is often deposited on the water-wet
51 solid surface [10]. Li and He [11] conducted a large amount of experiments to
52 investigate the dependence of water film thickness on pressure gradient and capillary
53 radius in microtubes, and they found that the thickness of water film increases as
54 capillary tube radius or pressure gradient decreases. Based on experimental data,
55 empirical correlations are also established to quantify the thickness of water film [12].
56 These studies have shown that the thin water film could contribute up to 60% volume
57 of nano-scale pore throat. Furthermore, the stability and thickness of nano-scale thin
58 water film strongly depend on the solid-liquid interaction. In a rock/brine/oil system,

59 the stability and thickness of thin water film are significantly influenced by chemical
60 characteristics of the system including water salinity [13, 14], crude oil composition
61 [14, 15], surface texture [16, 17], temperature [18], pH [19] and so on. Even though the
62 thin water may collapse under some conditions, many researchers have demonstrated
63 that the thin water film could remain stable after primary drainage and the reservoir
64 remain water-wet, especially in tight reservoir [14, 16, 20]. Roman et al. [10] measured
65 the water film thickness and investigated the water film dynamics during drainage
66 process. Results showed that the residing water film leads to snap-off during imbibition
67 process. In addition, using molecular dynamic (MD) simulations, Zhan et al. [21]
68 investigated the effect of water film on oil flow in quartz nanopores. They found that
69 liquid-liquid slip phenomenon could be non-negligible in small nanopores and the thin
70 water film is capable of flowing. These studies have shown that the thin water film has
71 a significant effect on dynamics of the fluid flow in micro/nano tube. Due to the
72 relatively high percentage and reduction of effective flowing space in nanopores, the
73 influence of thin water film on multiphase flow behavior becomes non-negligible [22-
74 25]. Therefore, the impact of thin water film on multiphase flow in tight formation has
75 to be considered properly.

76 Relative permeability is the key parameter to describe the multiphase flow
77 behaviors, which could be investigated by many methods, such as experiments (steady-
78 state or unsteady-state core flooding tests) [26-29], analytical modeling [22, 30-35],
79 simulations (Lattice-Boltzmann (LB) method, finite element method and pore network
80 modelling [36-39]). For tight formations, the core flooding test method is time
81 consuming and may fail to work due to its low permeability [40]. As analytical methods,
82 capillary bundle model is usually used to determine the relative permeability. Based on
83 capillary bundle model, Zhang et al. [22] investigated the effect of water film on gas-
84 water relative permeability, and they found that water film has a negative impact on
85 both the gas and water phase relative permeability in nano-porous media. Tian et al.
86 [12] improved Purcell's model to estimate oil-water relative permeability in tight oil
87 reservoirs with incorporation of thin water film effect while they didn't consider its
88 flow capability. Wang et al. [32] employed fractal theory to predict gas-water relative

89 permeability in nanoporous media with consideration of interfacial effects. They
90 quantified the contribution of different surface force components and the interfacial
91 effects is proven to promote the fluid flow in the nanoporous media. These analytical
92 models simplified the porous media to capillary tubes with given pore size distribution.
93 However, they fail to capture the topology and complexity of pore space [31, 41, 42].
94 As simulation methods, Lattice-Boltzmann (LB) method [43, 44] and finite element
95 method could capture the complexity and topology of pore space with time consuming
96 and requires large computation resources [45]. In contrast, pore network modelling
97 representing pore space as nodes interconnected by throats, finds an efficient way to
98 take the complexity of porous media into consideration with acceptable cost of time
99 and resources and has been used extensively to estimate relative permeability curves
100 with the development of recent advanced imaging techniques[46-52].

101 The pore network modeling could be classified into quasi-static model and
102 dynamic model according to the ratio between viscous force and capillary force during
103 the multiphase flow. When capillary pressure dominates the flow (with capillary
104 number less than 10^{-6}), the quasi-static pore network model is accurate enough to
105 simulate two-phase flow in porous media [45, 53, 54]. To our knowledge, the flow in
106 tight formations is dominated by capillary pressure, therefore the quasi-static pore
107 network model is chosen here. Over the last few decades, the quasi-static pore network
108 model has been proven to be successful in predicting steady-state relative permeability
109 in conventional sandstone [39, 47, 55, 56]. Ruspini et al. [57] and Raeini et al. [38]
110 incorporated more advanced methods into a quasi-static pore network model to
111 calculate cooperative pore-filling pressure. However, these pore network models only
112 took corner water into consideration because of the negligible amount of thin water film
113 attached to the solid surface. As mentioned before, the proportion of thin water films
114 become comparable to non-wetting phase and have flowability in unconventional
115 formations. Thus, it is no longer reasonable to overlook the contribution of these thin
116 water films in tight formations. In order to apply network model to unconventional
117 porous media, some nano-scale phenomena have been introduced into a quasi-static
118 model [58-60]. Nevertheless, no effort has been made about pore network modeling the

119 influence of thin water film on multiphase flow, which is essential in tight formations
120 [12, 61].

121 Concludingly, the influence of thin water film on multiphase flow is limited in
122 relatively simplified models, such as bundle of capillary tube model, which overlook
123 the pore connectivity and phase trapping. In this work, we aim to include thin water
124 film into quasi-static pore network model to investigate its influence on relative
125 permeability and improve its capacity in predicting oil-water two phase flow in tight
126 formation. First, we introduce the thin water film into the classic quasi-static pore
127 network model; and then we validate the extended pore network model in a Berea
128 sandstone. Subsequently, the effect of pore size and pore shape on relative permeability
129 is studied, from which we can see at what scale the effect of thin water film are
130 unavoidable. Furthermore, the influence of thin water films on relative permeability in
131 tight formation has been investigated thoroughly in terms of connectivity, fluid
132 configuration and flow capability. Our work is then finalized with a short summary and
133 conclusion.

134 **2. Pore network model for tight formations**

135 Quasi-static pore network modeling of multiphase flow requires to adopt an
136 analytical capillary entry pressure as well as fluid conductance together with invasion
137 percolation algorithms to describe displacement in the pre-determined pore network.
138 Previously, pore network modeling has been used extensively to simulate multiphase
139 flow in intermediate and highly permeable rock samples with analytically derived
140 capillary entry pressure and fluid conductance for drainage and followed imbibition
141 processes. In these works, the influence of thin water film on capillary entry pressure
142 and fluid conductance is neglected due to its limited thickness compared with the pore
143 size. It is true that the conductivity of the water film attached on the rock surface is very
144 limited compared with bulk phase flow if the pore size is relatively larger than the water
145 film thickness. While the flow in film couldn't be neglected when the pore size goes
146 down to nano-scale; this has been supported by amount of previous studies, such as
147 molecular simulation results [21], experimental results [62] and analytical model results
148 [63]. On the other hand, the stability and thickness of thin water film are significantly

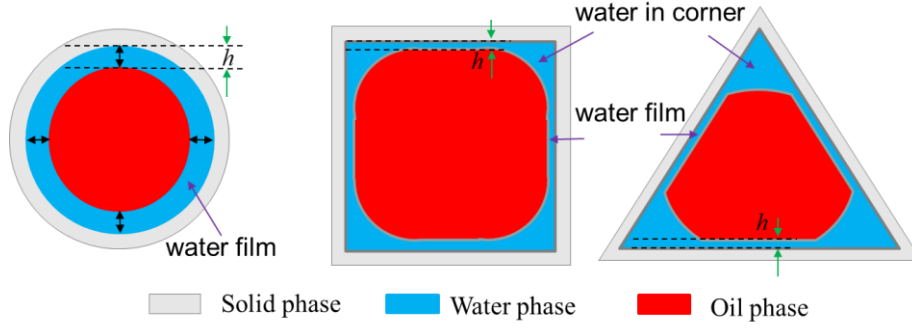
149 influenced by water salinity and this could be down by adding salinity into the
150 disjoining pressure model [13, 14]. Because we primarily focus on the scale that water
151 film starts to affect multiphase flow in tight formation, the influence of water salinity
152 is neglected in our study.

153 In this section, we first describe the qualification of thin water film thickness and
154 the fluid configuration in circular and angular pore throats. And then we include the
155 thin water film thickness into the calculation of capillary entry pressure and fluid
156 conductance during primary drainage and imbibition processes.

157 2.1. Thin film thickness in nano-scale pore space

158 The thin water film is often deposited on the water wet solid surface after oil
159 invading into pore space. The residing thin water film could collapse after primary
160 drainage process, and then the oil contact with solid surface directly, which could lead
161 to wettability alteration due to adsorption of polar compounds, the deposition of organic
162 matter and roughness of solid surface and so on [17, 20]. While many researchers have
163 demonstrated that the thin water film could remain stable after primary drainage and
164 the reservoir remain water-wet, especially in tight reservoir [14, 16, 20]; this is because
165 it takes much longer time for the polar molecules in oil phase to adhesive on pore
166 surface through diffusion across the thin water film [64]. The existence of the thin water
167 film (especially in the tight formation) plays a key role in multiphase flow behavior in
168 porous media; this is because first the thin water films increase water film connectivity
169 and thus lead to fluid rearrangements [65], and second the swelling of water films and
170 subsequent snap off displacement during imbibition process reduce oil connectivity
171 [66].

172 For water-wet circular and angular pore geometry (square or triangular cross
173 section), Fig. 1 presents the possible fluid configurations after primary drainage with
174 water film present. As shown in this figure, the oil phase doesn't contact with solid
175 surface directly due to the existence of thin water film.



176

177 Fig. 1 Schematic of possible fluid configurations, (a) circular pore (b) square pore (c) equilateral
178 triangular pore. Grey: solid, blue: water and red: oil.

179 The water film shown in Fig. 1 is very thin and is stabilized by the disjoining
180 pressure if the capillary number is very small and the multiphase flow process is
181 dominated by capillary pressure [67]. Due to technical challenge to perform thin film
182 thickness measurement in nano/micro capillary tubes at low capillary number, we have
183 adopted the approach proposed by Derjaguin et al. [68] to estimate the thin water film
184 thickness attached to the water-wet solid wall. This model is based on including the
185 disjoining pressure and capillary pressure with the well-known DLVO theory [13, 68,
186 69] as below:

$$187 \quad \Pi(h) = \Pi_m(h) + \Pi_{el}(h) + \Pi_{st}(h) \quad (1)$$

188 Eq. (1) simulates the disjoining pressure as a sum of electrostatic forces between
189 charged surfaces ($\Pi_{el}(h)$), the van der Waals force ($\Pi_m(h)$), and the structural force
190 ($\Pi_{st}(h)$) [70]. In contrast to gas/water/solid system, the Van der Waals force becomes
191 attractive and correspondingly, contributes to negative disjoining pressure and leads to
192 destabilization of the water film [15, 71, 72]. Thus, the other two forces becomes more
193 important in stability of thin water film. The three forces can be formulated as follows:

$$194 \quad \Pi_m(h) = \frac{-A_{ows}(15.96h/l+2)}{12\pi h^3(1+5.32h/l)^2} \quad (2-a)$$

$$195 \quad \Pi_{el}(h) = n_b k_B T \left(\frac{2\zeta_1 \zeta_2 \cosh(\kappa h) - \zeta_1^2 - \zeta_2^2}{(\sinh(\kappa h))^2} \right) \frac{\epsilon \epsilon_0 (\zeta_1 - \zeta_2)}{8\pi h^2} \quad (2-b)$$

$$196 \quad \Pi_{st}(h) = A_k e^{-\frac{h}{\lambda}} \quad (2-c)$$

197 where A_{ows} is the Hamaker constant in an oil-water-solid system, given by Eq.(3),
198 h is the water film thickness; l is the London wavelength; n_b is the ion density in bulk
199 phase; k_B is the Boltzman constant; T is the temperature; ζ_1 and ζ_2 are the zeta potential
200 at solid/water and water/oil interface respectively; A_k is the coefficient for the structural

201 force; λ is the decay length. κ is the Deby-Huckel reciprocal length and can be given
 202 by Eq.(4).

$$203 \quad A_{ows} \approx (\sqrt{A_{oo}} - \sqrt{A_{ww}})(\sqrt{A_{ss}} - \sqrt{A_{ww}}) \quad (3)$$

204 where A_{oo} , A_{ww} , and A_{ss} are the Hamaker constants of oil/oil, water/water and
 205 solid/solid via vacuum, respectively.

$$206 \quad \kappa = \frac{\sqrt{2e^2z^2n_b}}{\sqrt{\epsilon\epsilon_0k_B T}} \quad (4)$$

207 where e is the electron charge; ϵ_0 is the dielectric permittivity of vacuum; ϵ is the
 208 relative permittivity of water; z is the ion valence.

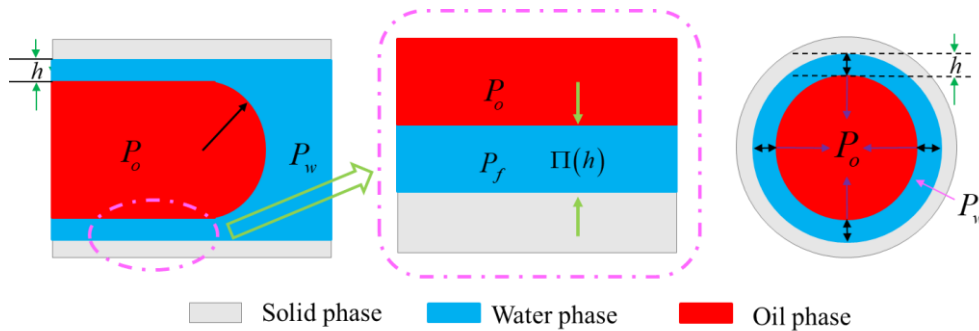
209 As shown in Fig.2, for a circular pore, the pressure difference between oil and
 210 water caused by arc meniscus and the disjoining pressure effect is described as [22]:

$$211 \quad \Delta P = P_o - P_w = \frac{\sigma}{R-h} + \Pi(h) \quad (5)$$

212 Combined with the pressure difference caused by terminal arc meniscus, the
 213 relationship between disjoining pressure and thin water film thickness at capillary entry
 214 pressure can be formulated as [22]:

$$215 \quad \frac{\sigma}{R-h} = \Pi(h) \quad (6)$$

216 where P_o and P_w is the oil phase pressure and water phase pressure, respectively;
 217 σ is the oil/water interfacial tension; R is the radius of tube; h is the water film thickness.
 218 However, once oil is displaced, the terminal meniscus no longer exists. Eq. (5) will be
 219 used to describe the relationship between disjoining pressure and thin water film
 220 thickness.



221

222 Fig. 2 Schematic diagram of force analysis during drainage process in a circular tube

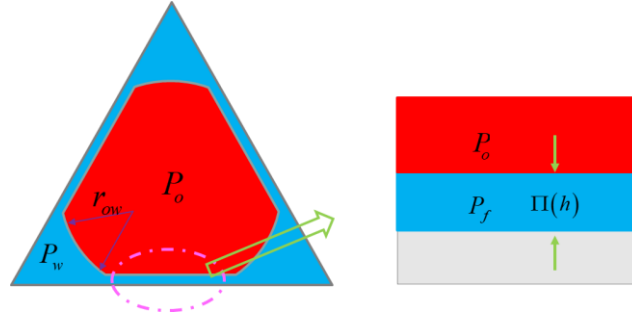
223 As shown in Fig. 3, the relationship between pressure difference and disjoining
 224 pressure in angular pores can be expressed as [73]:

225

$$\frac{\sigma}{r_{ow}} = \Pi(h) \quad (7)$$

226

where r_{ow} is the capillary radius of arc meniscus.



227

228

Fig. 3 Schematic diagram of force analysis during drainage process in an angular pore

229

From Eqs. (1-7), it can be seen that film thickness is a function of pore radius and

230

capillary pressure which is consistent with that obtained by experiments [61]. In the

231

calculation of water film thickness, the values of these parameters are shown in Table

232

1 with reference to previous experimental studies.

233

Table 1 Summary of parameters used in the calculation

Parameter	Symbol	Unit	Value
Hamaker constant of oil/oil	A_{oo}	J	5×10^{-20} [70]
Hamaker constant of water/water	A_{ww}	J	3.7×10^{-20} [70]
Hamaker constant of solid/solid	A_{ss}	J	6.5×10^{-20} [70]
London wavelength	l	nm	100 [70]
Ion valence	z	Dimensionless	1
Electron charge	e	C	1.6×10^{-19}
Boltzmann constant	k_B	J/K	1.38×10^{-23}
Temperature	T	K	298
Dielectric permittivity of vacuum	ϵ_0	F/m	8.854×10^{-12} [13]
Relative permittivity of water	ϵ	Dimensionless	78.4 [13]
zeta potential at solid/water interface	ζ_1	mV	-80 [19]
zeta potential at water/oil interface	ζ_2	mV	-70 [19]
Coefficient for the structural force	A_k	Pa	3.3×10^{10} [19]
Decay length	λ	nm	0.6 [19]
Interfacial tension	σ	mN/m	25 [16]

234

235

2.2. Capillary entry pressure calculation

236

Pore network modeling requires the capillary entry pressure as a priority to be

237

implemented for fluid invasion in the pore network [74]. Here in this work, we

238

considered the thin water film attached on the water-wet rock surface, and we first

239

simulate the primary oil displaces water in water-filled pore networks, which is referred

240 to as primary drainage process. The primary drainage process is then followed by
 241 waterflooding process until the capillary pressure reaches its minimum or the water
 242 saturation reaches the target water saturation. Saturation can be calculated at any point

$$243 \quad S_{w,t} = \frac{\sum_{i=1}^N V_i S_{w,i}}{V_t} \quad (8)$$

244 where $S_{w,t}$ is the water saturation of the network, $S_{w,i}$ and V_i are the water
 245 saturation and volume of a pore throat, N is the total number of pores and throats, and
 246 V_t is the total volume of the network.

247 Applying mass conservation at every pore, the flow rate of each phase is then
 248 estimated by solving the pressure distribution throughout the network

$$249 \quad \sum_j q_{ij} = \sum_j g_{ij}(P_i - P_j) = 0 \quad (9)$$

250 where j is the number of throats connected to pore i , q_{ij} and g_{ij} are flow rate
 251 and flow conductance respectively between pore i and pore j , P_i and P_j are pressure
 252 of pore i and pore j .

253 The conductance between two pore elements g_{ij} can be calculated by harmonic
 254 mean method as follows

$$255 \quad \frac{L_{ij}}{g_{ij}} = \frac{L_i}{g_i} + \frac{L_t}{g_t} + \frac{L_j}{g_j} \quad (10)$$

256 where t indicates the connecting throat, L_i and L_j are the lengths from the pore-
 257 throat interface to the pore center.

258 2.2.1. Drainage process

259 The capillary entry pressure of oil invades a water saturated circular capillary tube
 260 could be estimated by the Young-Laplace equation [73]:

$$261 \quad P_{entry} = \frac{2\sigma \cos \theta_{ow}}{R-h} \quad (11)$$

262 where σ is oil-water interfacial tension, R is radius of element, θ_{ow} is the contact
 263 angle and h is the thin water film thickness.

264 The MS-P method [75-82] was initially proposed to calculate capillary entry
 265 pressure in straight tubes based on free energy balance. For polygon geometry, the
 266 capillary entry pressure for oil invasion could be estimated by Eq. (12) and the details
 267 of the calculation are shown in the Appendix. It has to be noticed that the new analytical
 268 model has a similar expression with the previous models which possess simple and

269 concise forms. Specifically, the effect of thin water film is incorporated to calculate the
 270 capillary entry pressure.

$$271 \quad P_c = \frac{\sigma(\sqrt{1+4GD}+1)}{r_a} \quad (12)$$

272 where $G=A/L^2$ is the shape factor, $r_a = R-h$ is the oil inscribe maximum radius and
 273 D is defined as:

$$274 \quad D = \sum_{k=1}^n \left\{ \frac{\pi}{2} - \theta_{ow} - \alpha_k \right\} + \cos \theta_{ow} \sum_{k=1}^n \frac{\cos(\theta_{ow}+\alpha_k)}{\sin(\alpha_k)} \quad (13)$$

275 where n is corner number of the pore; α_k is the corner half angle.

276 2.2.2. Imbibition process

277 In the water imbibition process, piston-like displacement is a major displacing
 278 mechanism. As capillary pressure decreases gradually, due to contact angle hysteresis
 279 the oil-water interface in corner remains pinned at the initial position of imbibition with
 280 hinging contact angle $\theta_{h,k}$. When advancing contact angle θ_a is reached, the oil-water
 281 interface starts to move. When the capillary pressure is positive, the threshold capillary
 282 pressure for piston-like displacement can again be calculated based on the principle of
 283 interfacial energy balance. The following formula can be solved iteratively to obtain
 284 the capillary entry radius.

$$285 \quad r_{ow} = \frac{A_o}{L_{ow}+L_{os} \cos \theta_a} \quad (14)$$

$$286 \quad A_o = \frac{r_a^2}{4G} - \sum_{k=1}^n r_{ow}^2 \left\{ \theta_{h,k} + \alpha_k - \frac{\pi}{2} + \cos(\theta_{h,k}) \frac{\cos(\theta_{h,k}+\alpha_k)}{\cos(\alpha_k)} \right\} \quad (15)$$

$$287 \quad L_{os} = 0 \quad (16)$$

$$288 \quad L_{ow} = 2r_{ow} \sum_{k=1}^n \text{asin} \left(\frac{b_k \sin \alpha_k}{r_{ow}} \right) + \frac{r_a}{2G} - 2 \sum_{k=1}^n b_k \quad (17)$$

$$289 \quad b_k = r_{ow} \frac{\cos(\theta_a+\alpha_k)}{\sin \alpha_k} \quad (18)$$

290 where A_o is the area occupied by oil, L_{ow} is the length of oil-water interface, L_{os} is
 291 the length of the solid-water interface, $\theta_{h,k}$ is the hinging contact in a corner, b_k is
 292 the length from three phase contact point to corner apex as shown in Fig. A 1, and θ_a
 293 is the advancing contact angle.

294 Besides piston like displacement, cooperative pore-filling plays an important role
 295 during the imbibition process. The capillary entry pressure for filling a pore depends
 296 on the number of adjacent oil filled throats and contact angle [54, 83, 84]. Recently

297 Ruspini et al. [57] presented a new algorithm to calculate pore filling capillary pressure
 298 which overcomes the uncertainty of stochastic models. Since we mainly focus on the
 299 effect of thin water film on relative permeability, for simplicity we include the thin
 300 water film in the well-known pore filling model proposed by Blunt et al. [85] to estimate
 301 the entry pressure for pore filling events:

$$302 \quad P_c = \frac{2\sigma \cos \theta_a}{(R-h)} - \sigma \sum_{i=1}^m B_i x_i \quad (19)$$

$$303 \quad B_2 - B_m = \frac{0.03}{\sqrt{K}} \quad (20)$$

304 where m is the number of adjacent non-wetting phase filled throats, x_i are random
 305 weight coefficient numbers ranging from zero to one, B_i are arbitrary numbers and K is
 306 the permeability.

307 2.3. Conductance calculation

308 In order to calculate single and multiphase permeability during drainage and
 309 imbibition, the phase conductance should be cooperated with given a fluid
 310 configuration determined using capillary entry percolation algorithm. The conductance
 311 for single-phase flow in a capillary tube with no-slip boundary has been described as a
 312 linear function or second-order polynomial equation of shape factor [56, 86]. In this
 313 work, the linear correlation is used to calculate the single-phase conductance as below:

$$314 \quad g_p = k \frac{A^2 G}{\mu_p} \quad (21)$$

315 where $k=0.5$ for circular, $k=3/5$ for triangles and $k=0.5623$ for squares [45], A is
 316 area of cross-section and μ_p is the fluid viscosity.

317 2.3.1. Conductance of two-phase flow in circular pores

318 The water-oil distribution in micro/nano pores is assumed to be that water phase
 319 flows in the outer annulus and oil phase in the core as shown in Fig. 1a. The volume
 320 flux of each phase can be given by following expression respectively [87]:

321 For simplicity, we can define oil radius in tube as $r_a=R-h$.

$$322 \quad q_o = \frac{\Delta p \pi r_a^4}{L 8\mu_o} + \frac{\Delta p \pi (R^2 - r_a^2) r_a^2}{L 4\mu_w} \quad (22-a)$$

$$323 \quad q_w = \frac{\pi \Delta p}{8\mu_w L} (R^2 - r_a^2)^2 \quad (22-b)$$

324 where $r_a=R-h$ is the radius of oil phase.

325 From Eq. (22) we can get conductance of each phase as follows:

$$326 \quad g_{co} = \frac{\pi r_a^4}{8\mu_o} + \frac{\pi(R^2 - r_a^2)r_a^2}{4\mu_w} \quad (23-a)$$

$$327 \quad g_{cw} = \frac{\pi}{8\mu_w} (R^2 - r_a^2)^2 \quad (23-b)$$

328 where μ_w denotes for water viscosity and μ_o denotes for oil viscosity.

329 The water saturation is presented as follows:

$$330 \quad S_{w,i} = 1 - \frac{r_a^2}{R^2} \quad (24)$$

331 2.3.2. Conductance of two-phase flow in angular pores

332 During drainage process oil phase occupies the central area of the pore throat,
 333 while water phase exists in the corner and as thin film along the water-wet surface (see
 334 Fig. 3). During imbibition process oil layers doesn't exist under assumption of water-
 335 wet network according to oil layer formation criteria [86, 88]. So taking scenario shown
 336 in Fig. 3 as an example, we calculate area and conductance for bulk oil, corner water
 337 and water films respectively.

338 The correlation proposed by Oren [56] is adopted in our work to describe the flow
 339 of corner water. With consideration of water film, the area of the water phase in the
 340 corner needs to be revised by adding the trapezoid part as shown in Fig. A 1 and formula
 341 is given by:

$$342 \quad g_{pc} = C \frac{A_c^2 G_c}{\mu_w}, C = 0.364 + 0.28 \frac{G_c^*}{G_c} \quad (25)$$

$$343 \quad A_c = r_a^2 \left\{ \theta_{ow} + \alpha_k - \frac{\pi}{2} + \cos(\theta_{ow}) \frac{\cos(\theta_{ow} + \alpha_k)}{\sin(\alpha_k)} \right\} + h(2b_i + h \cot \alpha_k) \quad (26)$$

344 where G_c is the shape factor for the pore throat which contains the film, G_c^* is the
 345 shape factor with zero curvature on the oil-water interface, A_c is corner water area and
 346 μ_w is the water viscosity.

347 Conductance of thin water films could be estimated by the slit flow equation [89]:

$$348 \quad g_{pf} = \frac{A_f h^2}{12\mu_w} \quad (27)$$

$$349 \quad A_f = L_{of} h \quad (28)$$

350 where A_f is water film area and L_{of} is length of water film.

351 The bulk oil phase conductance is estimated by multiplying the single-phase
 352 conductance by the percentage the bulk phase occupies [88].

353
$$g_{po} = \frac{A_o}{A} g_p \quad (29)$$

354
$$A_o = A - A_c - A_f \quad (30)$$

355 The water saturation is given by

356
$$S_{w,i} = 1 - \frac{A_o}{A} \quad (31)$$

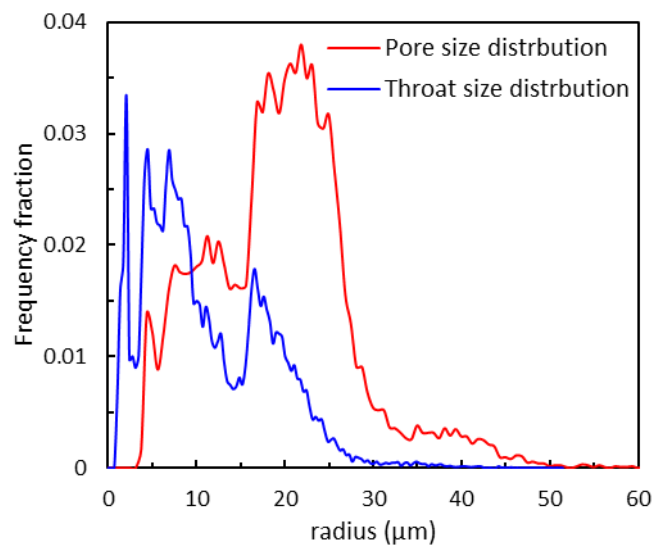
357 **3. Results and discussion**

358 We first validate our extended pore network model using the measured relative
359 permeability curves in Berea sandstone core samples. To better analyze the effect of
360 thin water film on relative permeability, the influence of thin water film on capillary
361 entry pressure, fluid configuration and fluid conductance in a single pore are is
362 investigated. And then we qualify the dependency of relative permeability on average
363 pore size and pore shape and illustrate the effect of thin water film on relative
364 permeability.

365 **3.1. Model validation**

366 Here we use the network generated from reconstructed Berea sandstone [90] to
367 validate our pore network model, the pore network is generated with the well know
368 maximum ball algorithm proposed by Dong et al [91]. The pore throat size distribution
369 is shown in Fig. 4. Relative permeability curves during drainage and imbibition process
370 are predicted using our extended model and Valvatne's model [88]. During primary
371 drainage process the network is assumed to be strongly water wet with an intrinsic
372 contact angle of zero degree. During imbibition process, due to wettability alteration
373 and surface roughness [92], the advancing contact angles have a significant influence
374 on relative permeability prediction [93] and we assign it a uniform distribution between
375 50 and 60 degrees as in Valvatne's prediction [88]. The simulated and experimental
376 relative permeability curves are shown in Fig. 5. It can be seen that curves simulated
377 by our proposed model achieve good agreement with experimental data and Valvatne's
378 prediction, especially for the oil phase relative permeability. Therefore, the validation
379 results prove the reliability of the proposed pore network model. It can also be observed
380 that in this case effect of thin water film on relative permeability is negligible. This is
381 because the thin water films have thicknesses ranging from 10nm to 40nm (see Fig. 6),

382 and thus they have very limited influence on multiphase flow behavior as the thin water
383 film is much smaller than the pore size as given in Fig. 4.

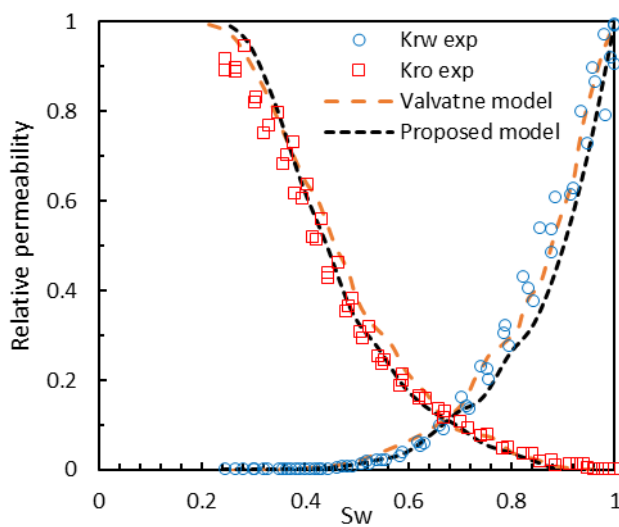


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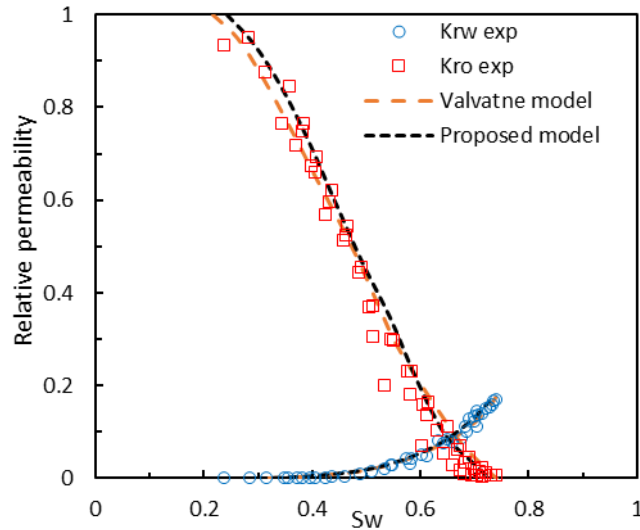
Fig. 4 Pore throat size distribution curves of the Berea sandstone [90]



387

388

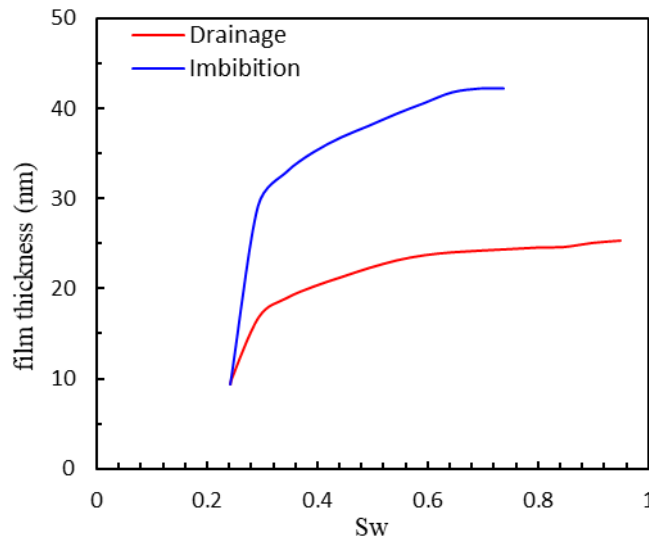
(a) in drainage process



389
 390
 391
 392
 393

(b) in imbibition process

Fig. 5 Relative permeability curves: experiment data by Oak [94] and predicted results from the proposed network model



394

Fig. 6 Thickness of thin water film during drainage process and imbibition process

395

396 3.2. The influence of thin water film on flow behavior in capillary tube

397

397 3.2.1. The influence of thin water film on fluid distribution

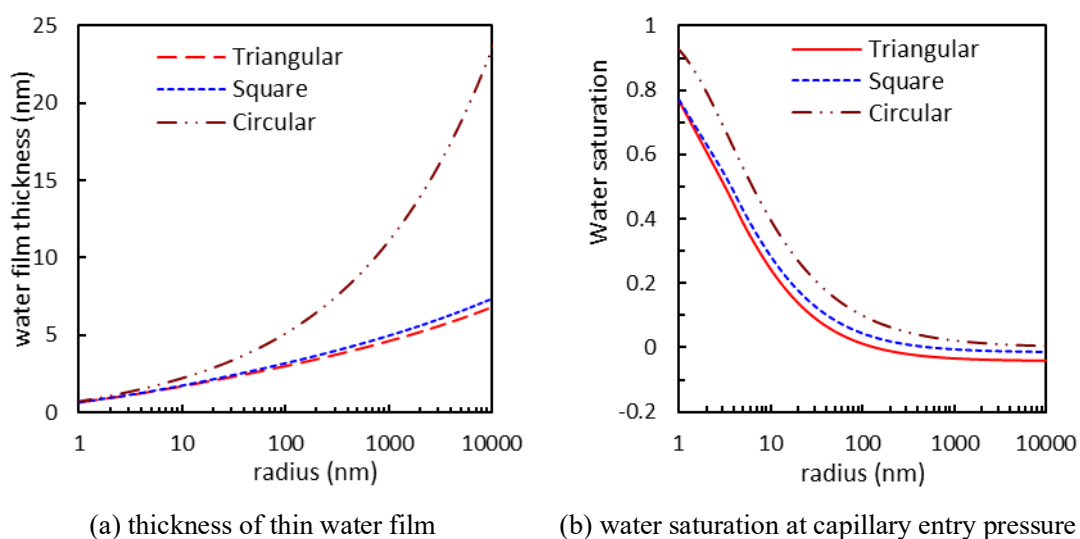
398

398 In order to characterize the effect of thin water film on fluid distribution, we
 399 investigate the thickness of thin water film at capillary entry pressure. The effect of pore
 400 throat radius on thin water film thickness and water saturation at capillary entry pressure
 401 during drainage process is shown in Fig. 7. As pore radius increases, the thickness of
 402 water film at capillary entry pressure attached to solid wall becomes thicker, and as
 403 expected the water saturation becomes smaller. When the radius reaches 100 nm, the

404 influence of thin water film on water saturation can be negligible. At the same inscribed
 405 radii, pores with circular-cross section have thicker water films than that with angular
 406 cross-section, and the difference increases when pore radius increases. However, the
 407 relationship between water film thickness and pore size at a given capillary pressure
 408 value varies in circular pores and polygonal pores. For circular pores, the water film
 409 thickness will decrease with increasement of pore radius. However, for polygonal pores,
 410 the water film thicknesses are identical due to the same capillary pressure.

411 Besides, the contributions of thin water film and corner water to the total water
 412 saturation for angular pores are shown in Fig. 8. In this figure, the water saturation
 413 curves without thin water films are also presented to compare the influence of thin water
 414 film on water saturation. It can be seen that the thin water film is critical for evaluating
 415 water saturation in small-sized pores (e.g. $r < 100\text{nm}$). The traditional model (without
 416 considering the thin water film) underestimates the total water saturation in small pores
 417 due to the existence of thin water film. While on contrast, it slightly overestimates the
 418 total water saturation in large pores. That's because the water saturation contributed by
 419 thin water film gradually approaches zero in large pores. However, the thin water film
 420 slightly increases the threshold capillary pressure and thus slightly decreases the
 421 saturation of corner water.

422



(a) thickness of thin water film (b) water saturation at capillary entry pressure
 Fig. 7 Thin water film thickness residing on the wall at capillary entry pressure and its influence
 on water saturation

423

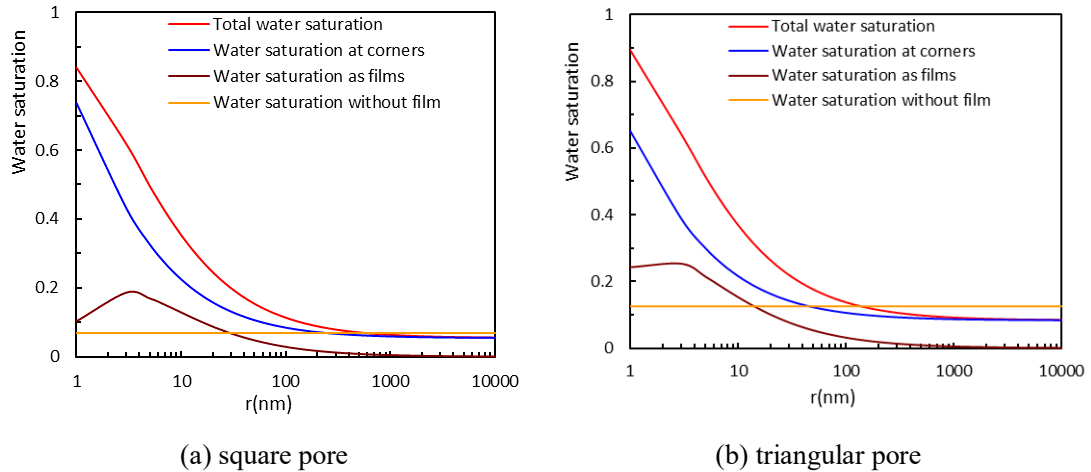


Fig. 8 Contribution of water at corners and water film on total water saturation for (a) square pores (b) triangular pores

424 Previous studies have shown that the thickness of thin water film is not a constant
 425 value during displacement, for example it strongly depends on applied pressure gradient
 426 [11]. In quasi-static pore network model, the fluid configuration is estimated for each
 427 pre-set capillary during the displacement processes. Thus, the relationship between thin
 428 water film thickness and capillary pressure in various shaped pores is discussed for
 429 three cases with pore radii equal to 10, 50 and 100 nm.

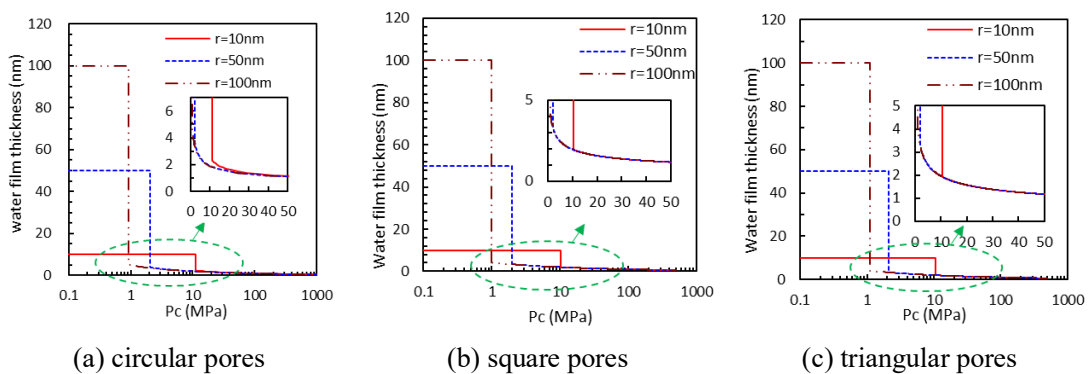
430 Fig. 9 presents that the effect of capillary pressure on thin water film during
 431 drainage process can be basically divided into three stages. When less than threshold
 432 pressure P_{entry} (the stage I), the capillary pressure has no effect on thin water film
 433 thickness. It is because that there exists only wetting phase in the pores. Non-wetting
 434 phase invades into pores only if capillary pressure reaches capillary entry pressure.
 435 When the capillary pressure exceeds entry pressure (the stage II), the water film
 436 thickness drops straightly due to invasion of non-wetting phase and after that they
 437 decrease dramatically with an increase in capillary pressure. Eventually, when the thin
 438 water film becomes thin enough (the stage III), the capillary pressure has little effect on
 439 water film thickness. The reason is that at this time the film is mainly controlled by
 440 attraction force between water molecular and solid surface. Correspondingly the
 441 relationship between capillary pressure and water saturation is shown in Fig. 10. When
 442 the capillary pressure reaches entry pressure, water saturation decreases suddenly, and
 443 with further increasement of capillary pressure it has a dramatic decrease. Eventually,

444 near the irreducible water saturation, the capillary pressure curves become nearly
 445 vertical.

446 In imbibition process, the relationship between thin water film thickness and
 447 capillary pressure is similar to that of drainage process. Corresponding to the non-
 448 wetting phase invasion, the wetting phase collapse is essential in imbibition process.
 449 The thin water film becomes unstable at the critical thickness and results in spontaneous
 450 coalescence. The collapse of water film occurs when the pressure partial differential
 451 $\partial p/\partial h < 0$ [95] [96]. Based on Eq. (5) and Eq. (7) the critical thickness of thin water film
 452 can be expressed by Eq. (32) for circular pores and Eq. (33) for angular pores. Its
 453 relationship with pore throat radius is shown in Fig. 11. Compared with Fig. 7, it can
 454 be observed that the critical thickness of thin water film during imbibition process is
 455 larger than that at capillary entry pressure during drainage process. This is because the
 456 non-wetting phase needs larger capillary pressure to invade into pores which means
 457 thinner thin water film thickness. It also has to be noted that that critical thickness inside
 458 circular pores is larger than that inside angular pores which follows the same trend with
 459 Li et al.'s study [73] in the gas-water system.

460
$$\frac{\sigma}{(r-h)^2} + \Pi'(h) = 0 \quad (32)$$

461
$$\frac{\sigma}{R-h} = \Pi(h) \quad (33)$$



(a) circular pores (b) square pores (c) triangular pores
 Fig. 9 Effect of capillary pressure on thin water film thickness during drainage process in various shaped pores

462

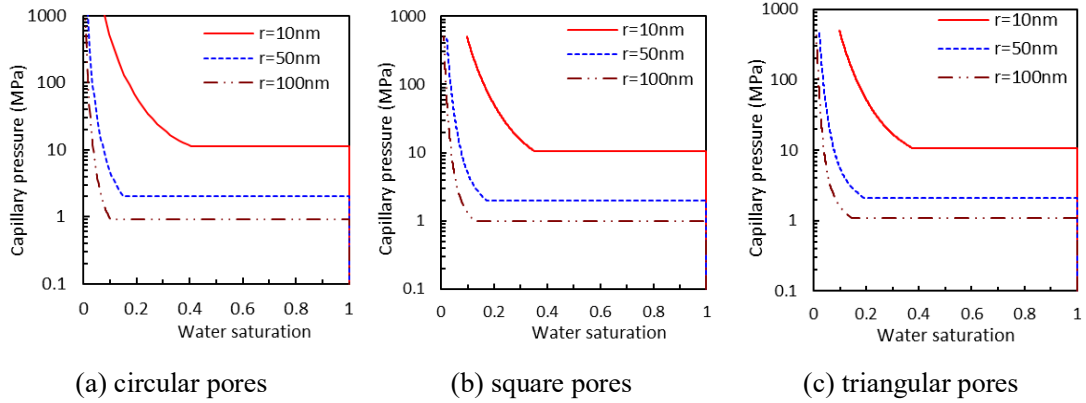


Fig. 10 Capillary pressure curves in various shaped pores

463

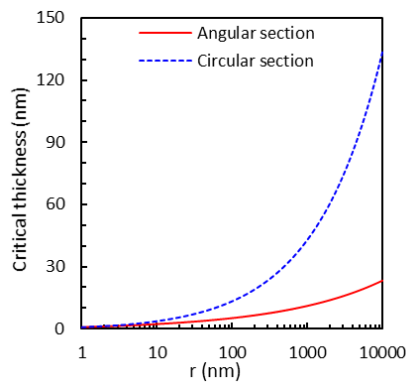


Fig. 11 Critical thickness of thin water film during imbibition process

464

465

466 3.2.2. The influence of thin water film on capillary entry pressure

467 The effect of thin water film on capillary entry pressure is analyzed here, as shown
 468 in Fig. 12. As shown in this figure, the influence of thin water film on capillary entry
 469 pressure is unavoidable if the pore size is smaller than 20 nm. Without considering the
 470 thin water film, the traditional models underestimate the capillary entry pressure
 471 dramatically. This is because due to the existence of thin water film, the effective flow
 472 radius is less than the actual radius of the pore.

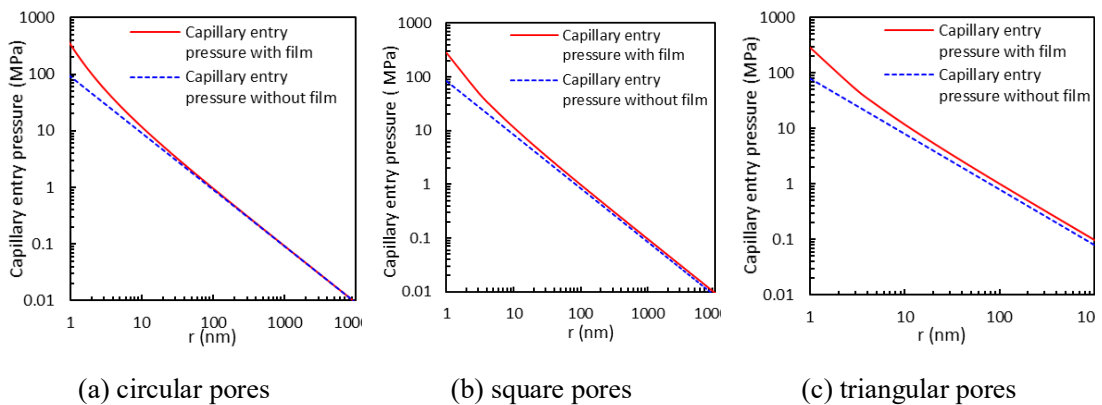


Fig. 12 Effect of water film on capillary entry pressure inside various shaped pores

473 3.2.3. The influence of thin water film on phase conductance in pore throat

474 In order to evaluate the water-oil flow capacity in a single pore with different
 475 cross-sections, relative conductance of each phase is defined as:

476
$$C_t = C_w + C_o \quad (34)$$

477
$$C_{rw} = \frac{C_w}{C_t} \quad (35)$$

478
$$C_{ro} = \frac{C_o}{C_t} \quad (36)$$

479 The effect of thin water film on relative conductance of each phase and its
 480 sensitivity to pore radii is plotted in Fig. 13. Here the film thickness is assumed to be at
 481 entry condition. We can find that the water relative conductance is approximately zero
 482 without consideration of water film existence, while the oil conductance approaches to
 483 the conductance of single-phase flow through the pore throat. In larger pores this
 484 assumption might be appropriate (e.g. for angular pore larger than 20 nm, and for
 485 circular pores larger than 100 nm). However, the thin water film plays an important role
 486 in smaller pores, especially if the pore size is smaller than 10nm for angular pores and
 487 20nm for circular pores. The relative water conductance increases with a decrease in
 488 pore radius while for oil phase decreases.

489

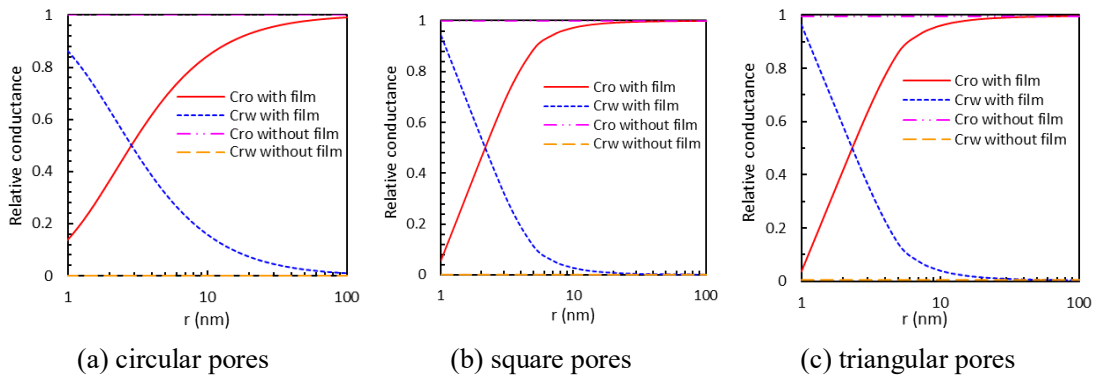


Fig. 13 Effect of water film on relative conductance inside single pore with various shaped cross-section

490 3.3. The influence of pore size on relative permeability

491 As discussed in previous sections, the thin water film influences the capillary entry
 492 pressure as well as phase conductance significantly when the pore throat reaches to tens
 493 of nanometers, while it is still not clear to us how the thin film affects the multiphase
 494 flow process in a complicated pore network. Here, the pore-network extracted for the

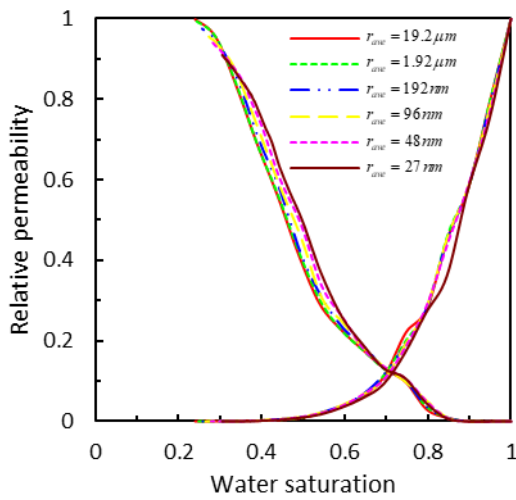
495 Berea sandstone and its downscaled pore-networks are used to understand the influence
 496 of thin water film on multiphase flow process at different average pore sizes. The
 497 original extracted pore network using the maximum ball algorithm [90] is scaled down
 498 by multiplying its physical size by $1/10^{\text{th}}$, $1/100^{\text{th}}$, $1/200^{\text{th}}$, $1/400^{\text{th}}$ and $1/700^{\text{th}}$
 499 respectively. As a result, all networks have the same porosity which is 0.183 and
 500 connectivity, and other basic properties for these rescaled networks are listed in Table
 501 2.

502 Table 2 Fundament properties for the scaled-down pore networks

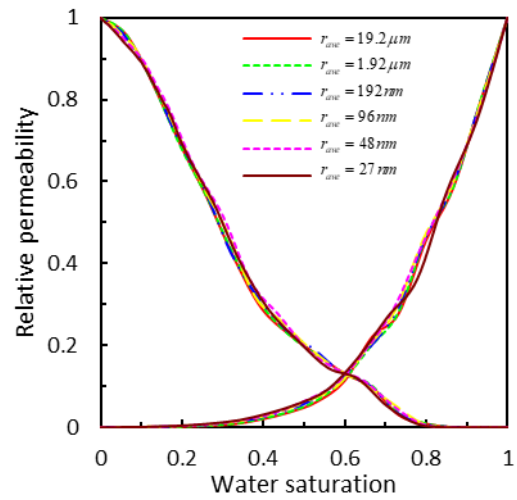
Network	Permeability (mD)	Mean pore radii (μm)	Mean throat radii (μm)
Original pore network	2551.6	19.2	11.0
Scaled-down by $1/10^{\text{th}}$	2.836	1.92	1.10
Scaled-down by $1/100^{\text{th}}$	0.709	0.192	0.110
Scaled-down by $1/200^{\text{th}}$	0.315	0.096	0.055
Scaled-down by $1/400^{\text{th}}$	0.177	0.048	0.028
Scaled-down by $1/700^{\text{th}}$	0.005	0.027	0.016

503
 504 The relative permeability curves predicted from our extended pore network model
 505 during drainage and imbibition process are plotted in Fig. 14. It can be seen that pore
 506 size has little effect on relative permeability during drainage process, which is shown
 507 in Fig. 14a, b. However as shown in this Fig. 14c, in imbibition process, when the
 508 average pore radius increase, the two-phase flow region shifts to the left. High
 509 permeable rock sample tends to yield more shrunk relative permeability curve, as the
 510 proportion of water film becomes lower. However, pore size has a very limited
 511 influence on normalized relative permeability curves (see Fig. 14d). In addition, we
 512 also employ Valvatne's model [88] to predict relative permeability for these scaled
 513 down networks. However, the relative permeability curves of scaled-down networks
 514 predicted by Valvatne's model are the same as that of no-scaled down Berea sandstone
 515 which implies it fails to capture the dependence of relative permeability curve on pore
 516 size. That's because if there's no water film, similar fluid configuration and relative
 517 conductance will be obtained for a given saturation if capillary dominated flow is
 518 assumed even pore size varied, but it will be at different capillary pressure. In order to
 519 compare the performance of these two models in tight formation, we take the

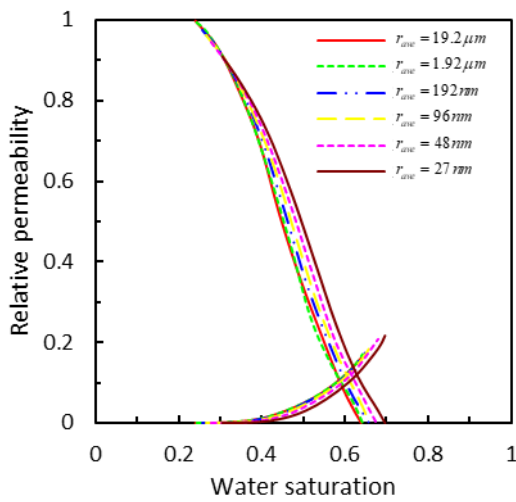
520 downscaled pore-network by 1/700th as an example and compare the results predicted
 521 by these two models. As shown in Fig. 14e, the connate water saturation and end-point
 522 relative permeability to water are higher in our proposed model than Valvatne's model
 523 due to existence of water film. Our extended model successfully captures the
 524 characteristics of relative permeability in tight formations.



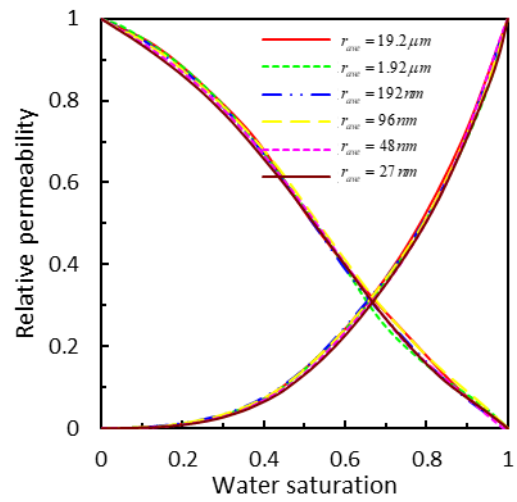
(a) curves of drainage



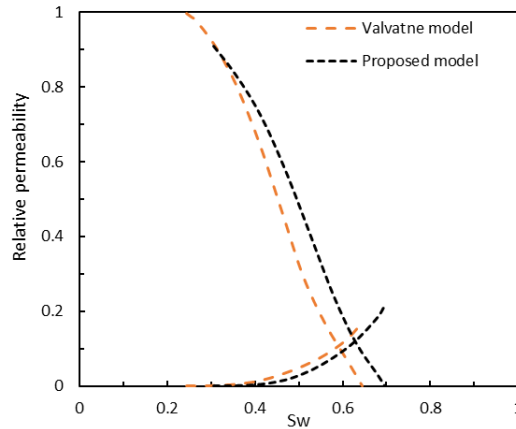
(b) normalized curves of drainage



(c) curves of imbibition



(d) normalized curves of imbibition



(e) relative permeability curves of imbibition for Berea downscaled pore-network by 1/700th

Fig. 14 The influences of pore size on relative permeability curves

525 The result also shows that the pore size primarily changes the endpoints of relative
 526 permeability as shown in Fig. 15. When the average pore size is smaller than 100 nm,
 527 the connate water saturation increases dramatically while oil relative permeability at
 528 connate water saturation decreases significantly. This is mainly caused by the fluid
 529 configuration distribution in pores. In order to compare fluid configuration in different
 530 average pore size cases, we normalize pore throat radius according to the maximum
 531 and minimum radius. Fig. 17a shows the water saturation distribution at connate water
 532 saturation in different average pore sizes. As average pore size decreases, the water
 533 saturation increases which is more conspicuous in small pores. This finding is
 534 consistent with previous research by Torskaya et al. [97]. Using lattice-Boltzmann
 535 method, they studied the relationship between irreducible water saturation and
 536 permeability. They found that permeability decreases with increasing irreducible water
 537 saturation.

538 Meanwhile higher connate water saturation means lower initial oil saturation
 539 which leads to lower residual oil saturation as shown in Fig. 16 and this is reasonable
 540 under the same porous medium structure. From Fig. 17c, d we can see that in the
 541 imbibition process water mainly displaces oil in the sequence of from small pores to
 542 large pores due to the dominance of capillary pressure. As average pore size decreases,
 543 more pores are displaced by water due to swelling of thin water film. From Fig. 17b we
 544 can also find in the oil filled pores the water saturation increases as the average pore
 545 radius decreases. As a consequence, water saturation at the end of imbibition process

546 increases with decrease of average pore radius and leads to an increasement of water
 547 relative permeability especially when the average pore size is smaller than 100 nm (as
 548 Fig. 15 show).

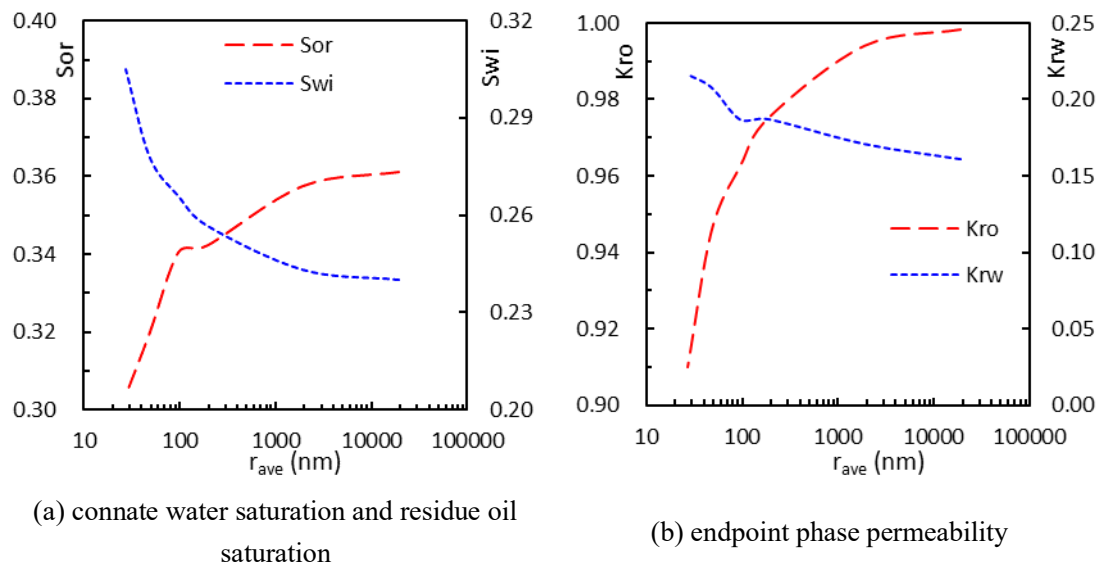


Fig. 15 Endpoint of relative permeability curves for different permeable core samples during imbibition process

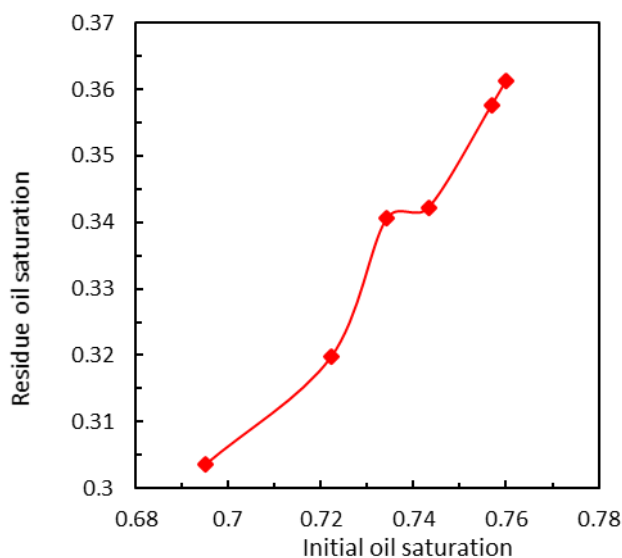
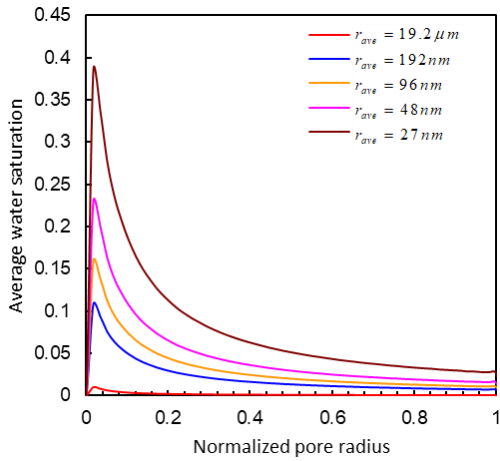
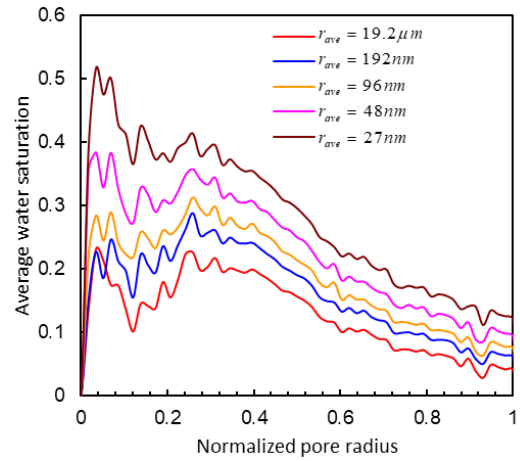


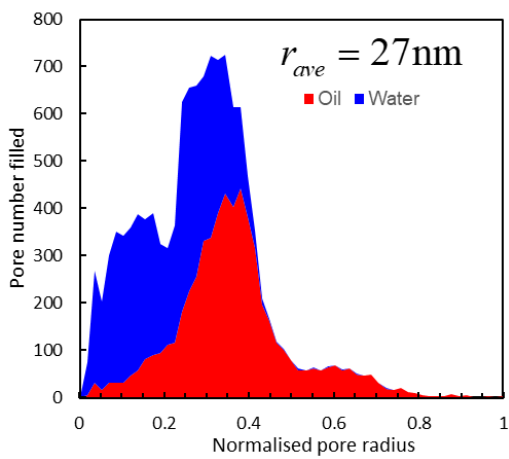
Fig. 16 Relationship between residual oil saturation and initial oil saturation



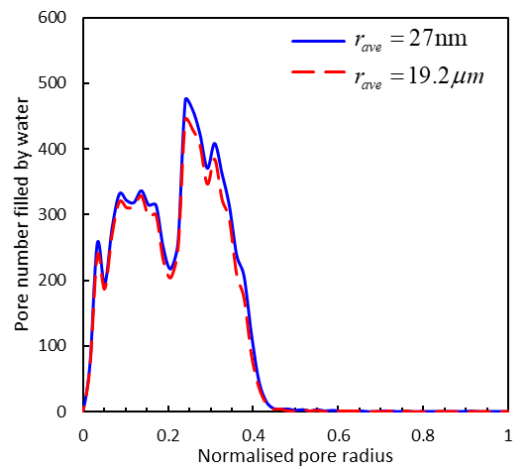
(a) water saturation distribution at connate water saturation



(b) water saturation distribution at residue oil saturation



(c) pore number occupied by oil and water in the scaled-down by 1/700th case at residue oil saturation



(d) pore number displaced by water under different average pore radius at residue oil saturation

Fig. 17 Effect of average pore size on fluid and water saturation distribution

3.4. The influence of pore shape on relative permeability

As discussed in previous Section 3.2, pore shape is one of the most important factors to determine the relative permeability. Here we use shape factor to characterize pore throat shape which is defined as the cross area divided by the perimeter squared. A low shape factor indicates a highly irregular pore. Normal distribution function is adopted to describe the distribution of pore throat shape factor. Assuming a constant standard deviation is 0.005, the mean shape factors are set to 0.03, 0.04, 0.05 and 0.06 respectively (as shown in Fig. 18). The networks are generated on the basis of Berea downscaled pore-network by 1/700th. In order to compare the flow characteristic on the same flow area, the radii of the downscaled pore-network are calculated according to

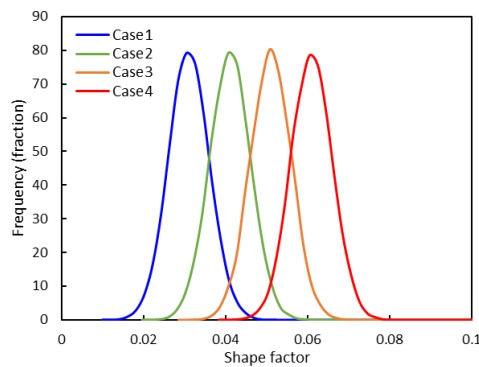
560 the shape factor. Thus, these networks have the same porosity as the Berea sandstone
 561 and have different absolute permeabilities as shown in Table 3.

562 Table 3 Fundament properties for the networks with various shape factor distribution

Properties	Mean shape factor (Dimensionless)	Porosity (Dimensionless)	Permeability (mD)
Case1	0.03	0.183	0.0052
Case2	0.04	0.183	0.0069
Case3	0.05	0.183	0.0076
Case4	0.06	0.183	0.0095

563

564 The relative permeability curves predicted by our extended pore network model
 565 are shown in Fig. 19. The result shows that the water relative permeability increases
 566 with the increase of pore irregularity. However, the oil relative permeability is enhanced
 567 slightly at a given saturation. This characteristic is mainly dominated by the existence
 568 of corner water and snap off event. As the shape factor decreases, the water saturation
 569 in a pore throat increases when snap off event happens [73] which results in a low
 570 residue oil saturation. On the other hand, snap-off is more likely to occur for more
 571 angular throats [98]. At a given water saturation, the proportion of bulk water increases
 572 with an increase of the shape factor. However, its connectivity is limited by existence
 573 of bulk oil phase. On the contrary, corner water is connected throughout the water-wet
 574 network and the increase of corner water proportion will enhance water phase
 575 permeability. Therefore, water relative permeability is enhanced with the increase of
 576 pore irregularity in networks.



577

578

Fig. 18 PSD with various mean shape factor with a constant peak frequency

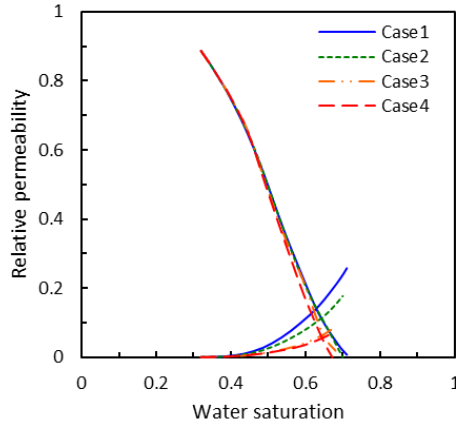


Fig. 19 The effect of shape factor on relative permeability

3.5. The influence of thin water film on relative permeability

It has been noted that the thin water film plays an important role in relative permeability curves of tight formations, while it is not well known how the thin water film affects relative permeability during imbibition process in water-wet rock sample. In this section, we investigate the influence of thin water film in the tight formation with pore size spans over tens of nano meters. The pore network is generated from reconstructed Berea sandstone [90] and then scaled-down by multiplying its physical size by $1/700^{\text{th}}$, and the average pore and throat radii are 27.4nm and 15.7nm, respectively. The fundamental properties of the pore network are presented in Table 2. The detailed pore throat geometry is presented in Table 4. As shown in this table, the majority of the pores and throats are triangular, and very limited pore and throat with circular.

Table 4 The proportion of each shape in scaled-down Berea sandstone

Shape	Triangle (%)	Square (%)	Circular (%)
Pore	0.909	0.089	0.002
Throat	0.835	0.148	0.017

In the simulation, we first simulate the primary drainage process until the capillary pressure reaches to 50MPa, and then reduce the capillary pressure stepwise until either of following conditions is satisfied (1) capillary pressure goes down to the preset minimum capillary pressure (here we set the minimum capillary pressure equal to -50MPa to enable a full imbibition cycle (spontaneous and forced imbibition); (2) water saturation equals 1.0; (3) no connected oil phase exists. The relative permeability and capillary pressure during the imbibition process are predicted in Fig. 20 and Fig. 21,

601 respectively. As shown in Fig. 20, the capillary entry pressure during drainage becomes
 602 larger when the thin water film is included. Compared to NF (no thin water film exists)
 603 case, in DFC (dynamic thin water film with conductance) case, capillary pressure starts
 604 to rise dramatically at higher water saturation which illustrates due to the existence of
 605 thin water film non-wetting phase invades the smaller pores earlier. And due to the
 606 space occupied by thin water film, irreducible water saturation in DFC case is higher
 607 than that in NF case. In imbibition process, water invasion ends when there no longer
 608 exists available oil to displace and at that time capillary pressure is still positive which
 609 suggests that forced imbibition doesn't occur. DFC case has a lower residue oil
 610 saturation than NF case. That's because the trapped pore throat elements which contain
 611 oil are almost the same for two cases, while thin water films occupy considerable
 612 amount of space in these elements and result in lower residue oil saturation. We also
 613 found neglecting thin water film in tight porous media will overestimate the
 614 displacement efficiency (53.8% for NF case and 46.5% for DFC case). This can be
 615 explained by the increased probability of snap off by thin water film swelling.

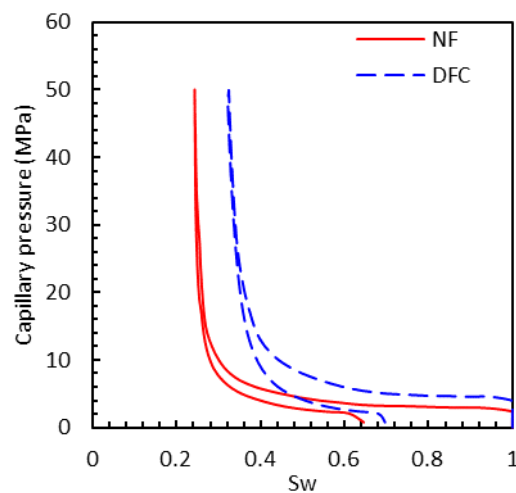


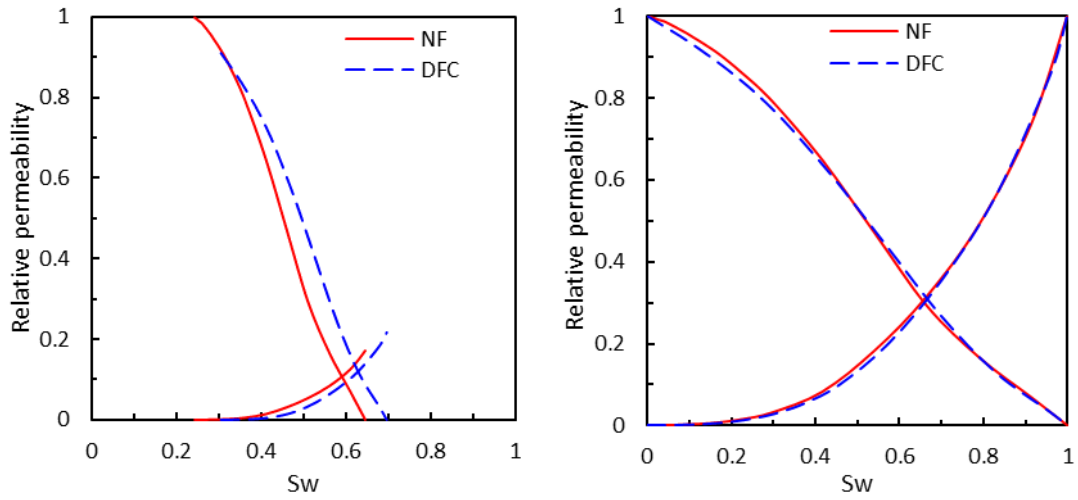
Fig. 20 Nanoscale effects on capillary pressure during imbibition. NF: no thin water film; DFC: dynamic thin water film with conductance

616 As shown in Fig. 21, for a given water saturation, the existence of thin water films
 617 attached to the water-wet rock surface reduces the water relative permeability and
 618 improves the oil phase relative permeability; this is due to the significant amount of

619 water contributes to water saturation existing in thin water films, while thin films have
620 very limited conductivity and oil phase occupying more central part has higher
621 conductivity as seen in Fig. 22. The existence of nano-scale thin water film also
622 increases the connate water saturation and reduces the oil phase permeability at connate
623 water saturation during primary drainage process; for example, the connate water
624 saturation increases from 0.22 to 0.42, and the associated oil relative permeability
625 reduces from 0.99 to 0.90 when the thin water film is considered. On the contrast, it
626 reduces the residual oil saturation and improves the associated water relative
627 permeability significantly. As shown in Fig. 21a, the residue oil saturation changes from
628 0.36 to 0.31 and the water relative permeability at residue oil saturation changes from
629 0.17 to 0.21 if the thin water film is considered. Fig. 21b presents the normalized
630 relative permeability predicted by two models. It is found that thin water film has almost
631 no effect on normalized relative permeability. This is because thin water film mainly
632 changes the conductivity and phase saturation and has limited effect on displacement
633 sequence.

634 Except for its contribution to saturation and conductivity, thin water film could
635 also increase connectivity of water phase especially in porous media consisting of
636 circular shaped pores and throats. Previous pore network models [38, 88, 99] assumed
637 circular shaped pores only contain one single fluid, however due to a considerable
638 amount of thin water film in tight formation its contribution to connectivity should be
639 included in circular shaped pores. Because reconstructed Berea sandstone only has few
640 circular shaped pores, we employ the stochastic method to generate the pore network
641 which only contains circular shaped pores and throats. As shown in Fig. 23, thin water
642 films enhance the water phase connectivity and thus resulting in higher water relative
643 permeability. At the same time, non-wetting phase displaces more wetting phase and
644 obtain higher relative permeability at connate water saturation.

645



(a) Relative permeability curves (b) Normalized relative permeability curves
 Fig. 21 The influence of thin water film on relative permeability during imbibition

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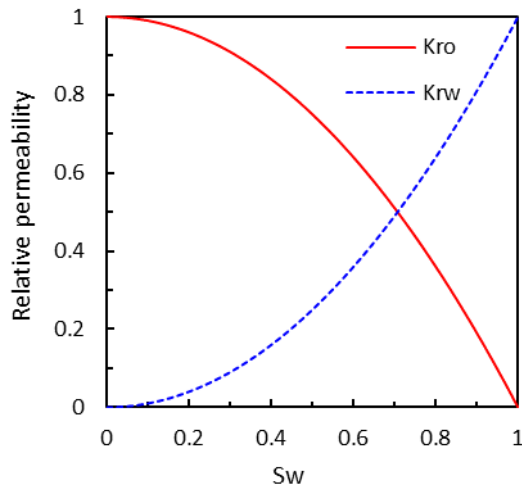
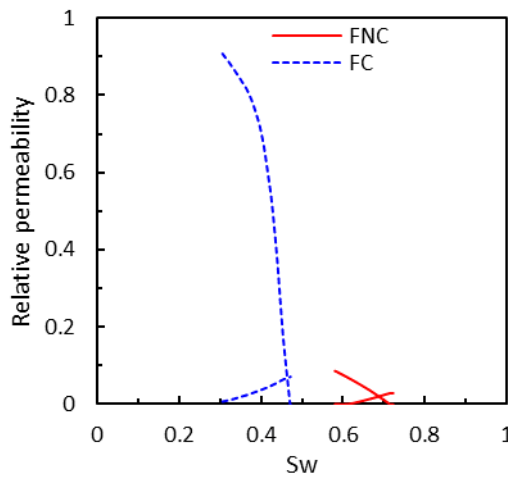


Fig. 22 Relative permeability curves in a tube

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Fig. 23 Relative permeability curves during imbibition in porous media of circular shaped pores

652 (FC – considering water film connectivity; FNC – without considering water film connectivity)

653 Previous relative permeability models also consider water film thickness as a
654 constant thickness [22, 31], thus here we also simulated the relative permeability using
655 pore network modeling cooperated with a thin water film whose thickness remains
656 constant. As shown in Fig. 24, the connate water saturation in the dynamic water film
657 (DFC) case is lower than static water film (FC) case due to the thinning of water film
658 that has been considered in the dynamic thin film model. In imbibition process, since
659 the critical thickness of water film is larger than initial state, the residue oil saturation
660 in DFC case has a lower value than that in FC case.

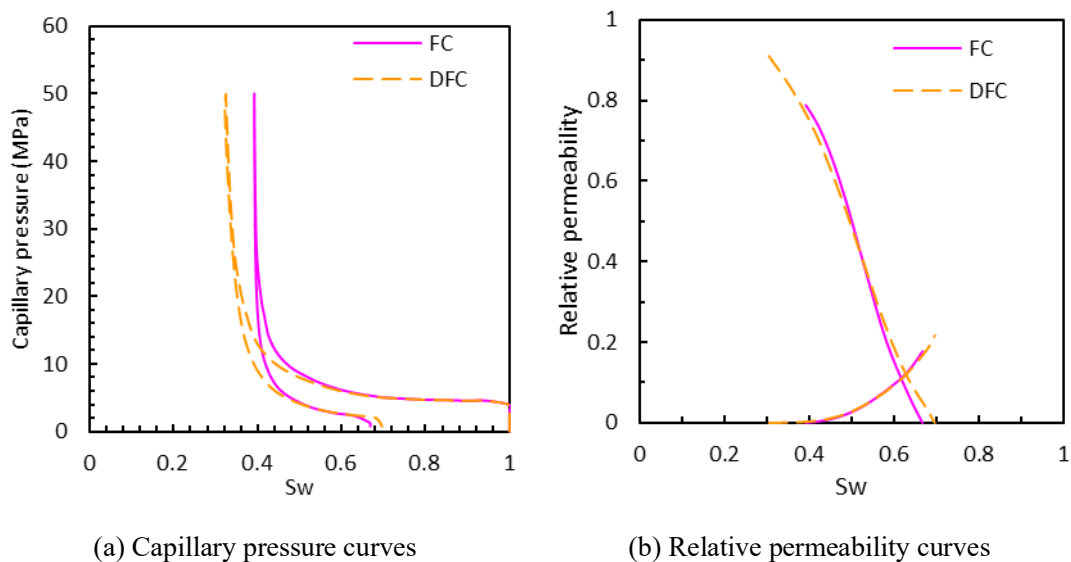


Fig. 24 Effect of water film thickness variation on capillary pressure curves and relative permeability curves (FC – constant water film thickness, DFC – dynamic water film thickness)

661 3.6. Discussion

662 Our present work has characterized the effect of thin water film on the relative
663 permeability in tight porous media, and it has also clarified at which scale the thin water
664 film should be considered.

665 However, it has to be noticed that out that our model is limited in water-wet porous
666 media where the thin water film exists. When the wettability changes (such as oil-wet
667 or mix-wet porous media) or thin water film ruptures due to the adsorption of polar
668 compounds, the deposition of organic matter and roughness of solid surface and so on
669 [17, 20], the oil will contact with solid surface directly and our model becomes invalid.

670 Zhou et al. [100] found that the water flooding performance depended strongly on initial

671 **water saturation at mixed-wet conditions**. Besides, since we mainly focus on the effect
672 of thin water film on relative permeability, a rather simple pore filling mechanism [85]
673 is employed in our model which controls the displacing sequence in imbibition process
674 and **pore throat cross-sections are assumed to be regular**. Ruspini et al. [57] proposed a
675 more realistic pore filling method which proves to have better agreement with
676 experimental fluid distribution. **Zhou et al [101, 102] investigated the capillary entry**
677 **pressure for pores whose cross-section is obtained directly from 2D SEM rock image**.
678 Furthermore, the effect of viscosity on multiphase flow behavior is not incorporated in
679 our model due to the lack of viscous coupling which need to be investigated further
680 [103].

681 Therefore, more simulation models are still required to reveal the two-phase flow
682 characteristics in tight formations under mix-wet or oil-wet condition. And more
683 accurate imbibition mechanism at nano-scale needs to be introduced into pore network
684 model.

685 **4. Conclusions**

686 In this paper, a quasi-static pore network model considering the effect of the thin
687 water film is developed to describe multiphase flow in tight formations. Berea
688 sandstone experiments and corresponding network generated from reconstructed Berea
689 sandstone are used to validate the accuracy and reliability of the model. Based on the
690 developed pore network model, pore-scale flow characteristics in nano porous media
691 and its effect on relative permeability are then studied. Furthermore, the critical size of
692 the average pore radius when the water film has a significant influence on relative
693 permeability is investigated. The main conclusions can be drawn as follows:

694 (1) The thin water film plays an important role in fluid flow behavior in nanoscale
695 pores. With a decrease in pore radius, the thickness of thin water film attached
696 to solid wall becomes thinner however its effect on water saturation becomes
697 more significant. The contribution of thin water films to water saturation can
698 be up to approximately 20% for angular pores and 30% for circular pores with
699 radius of 20 nm. Besides when the size of pore radius is below 20 nm,
700 considering no thin wetting film will underestimate the capillary entry

701 pressure. The relative water conductance increases with a decrease in pore
702 size while oil phase conductance decreases.

703 (2) Water film plays an important role in the prediction of relative permeability
704 when the average pore radius is smaller than 100 nm. When average pore size
705 reduces, the connate water saturation increases while residual oil saturation
706 and oil relative permeability at connate water saturation decrease. As porous
707 media has more irregular pores, water relative permeability increases.

708 (3) Thin water film influences relative permeability in nano porous media through
709 the variation in water saturation, the phase connectivity and the thin water film
710 swelling and thinning. In a tight formation dominated by angular pores, the
711 effect of thin water film on the connectivity is negligible as shown in our study.
712 On the contrary, in a tight formation dominated by the circular shaped pores,
713 the thin water film increases the connectivity of the water phase and results in
714 higher oil relative permeability at the connate water saturation.

715 **Nomenclature**

716 $\Pi(h)$ — the disjoining pressure between surfaces, Pa;

717 $\Pi_m(h)$ — the van der Waals force per unit area between surfaces, Pa;

718 $\Pi_{el}(h)$ — the electrostatic forces between charged surfaces per unit area, Pa;

719 $\Pi_{st}(h)$ — the structural force between charged surfaces per unit area, Pa;

720 h — the water film thickness, m;

721 A_{ows} — the Hamaker constant in an oil-water-solid system, J;

722 A_{oo} — the Hamaker constants of oil/oil via vacuum, Pa;

723 A_{ww} — the Hamaker constants of water/water via vacuum, Pa;

724 A_{ss} — the Hamaker constants of solid/solid via vacuum, Pa;

725 h — the water film thickness, m;

726 l — the London wavelength, m;

727 n_b — the ion density in bulk phase, M;

728 k_B — the Boltzman constant, J/K;

729 T — the temperature, K;

730 ζ_1 — the zeta potential at solid/water surface, V;

731 ζ_2 — the zeta potential at water/oil interface, V;

732 A_k — the coefficient for the structural force, Pa;

733 λ — the decay length, m;

734 κ — the Deby-Huckel reciprocal length, m^{-1} ;

735 e — the electron charge, C;

736 ϵ_0 — the dielectric permittivity of vacuum, F/m;

737 ϵ — the relative permittivity of water, Dimensionless;

738 z — the ion valence, Dimensionless;

739 P_o — the oil phase pressure, Pa;

740 P_w — the water phase pressure, Pa;

741 $S_{w,t}$ — the water saturation of the network, Dimensionless;

742 $S_{w,i}$ — the water saturation of a pore throat, Dimensionless;

743 V_i — the volume of a pore throat, m^3 ;

744 N — the total number of pores and throats, Dimensionless;

745 V_t — the total volume of the network, m^3 ;

746 q_{ij} — the flow rate between pore i and pore j , m^3/s ;

747 g_{ij} — the flow conductance between pore i and pore j , $\text{m}^2/(\text{Pa}\cdot\text{s})$;

748 P_i — the pressure of pore i , Pa;

749 P_j — the pressure of pore j , Pa;

750 L_t — the length of the throat connecting pore i and pore j , m;

751 L_i, L_j — the lengths from the pore-throat interface to the pore center, m;

752 σ — the oil/water interfacial tension, N/m;

753 R — the radius of the tube, m;

754 r_{ow} — the capillary radius of arc meniscus, m;

755 θ_{ow} — the water-oil contact angle, degree;

756 G — the shape factor of pore throat cross-section, Dimensionless;

757 A — the area of pore throat cross-section, m^2 ;

758 L — the perimeter of pore throat cross-section, m;

759 r_a — the oil maximum inscribed radius, m;

760 n — the corner number of the pore throat, Dimensionless;

761 α_k — the corner half angle, degree;
762 A_o — the area occupied by oil in a pore throat, m^2 ;
763 L_{ow} — the length of the oil-water interface, m;
764 L_{os} — the length of the solid-water interface, m;
765 L_{of} — the length of the thin water film, m;
766 $\theta_{h,k}$ — the hinging contact in a corner, degree;
767 θ_a — the advancing contact angle, degree;
768 m — the number of adjacent non-wetting phase filled throats, Dimensionless;
769 x_i — the random weight coefficient number ranging from zero to one,
770 Dimensionless;
771 K — the permeability, m^2 ;
772 μ_p — the fluid viscosity, Pa·s;
773 μ_w — the viscosity of water phase, Pa·s;
774 μ_o — the viscosity of oil phase, Pa·s;
775 G_c^* — the shape factor with zero curvature on the oil-water interface,
776 Dimensionless;
777 A_c — the corner water area, m^2 ;
778 A_f — the film water area, m^2 ;

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786 **Appendix: Calculation of capillary entry pressure in angular pores**

787 In order to account for the thin water film, we have modified the inscribe
788 maximum circle $r_a=R-h$ to calculate the capillary entry pressure.

789 Oil invasion scenario for polygon-shaped duct is sketched in Fig. A 1. Taken
790 remaining thin water film into consideration, the oil phase doesn't contact solid surface

791 directly.

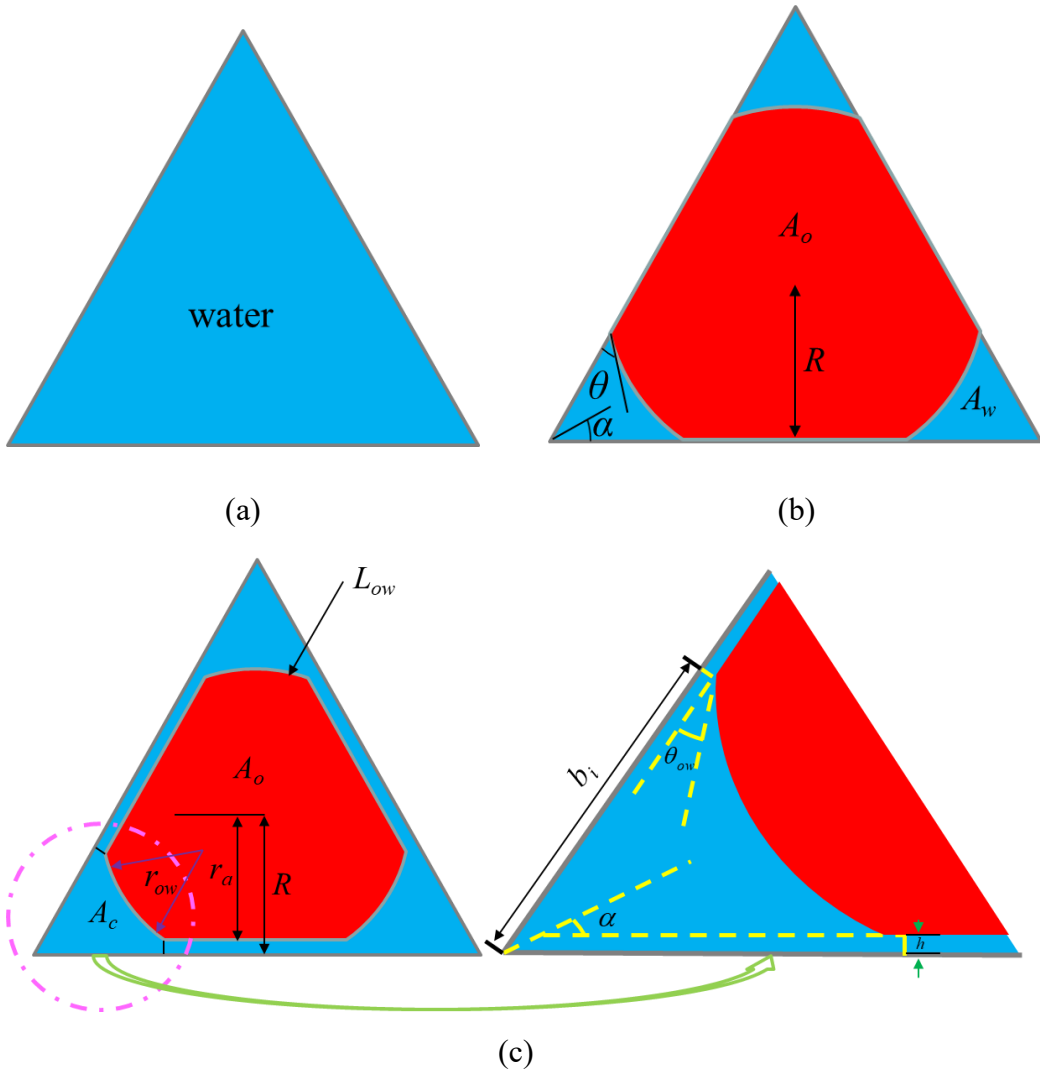


Fig. A 1 Three fluid configurations (a) initial state (b) drainage process without water films (c) drainage process with water films. Blue-water phase, red-oil phase.

792 Based on MS-P method [104], the entry capillary pressure for polygon shaped
793 elements can be found from:

$$794 \quad -\frac{\Delta A_o}{r_{ow}} + \cos \theta_{ow} \Delta L_{os} + \Delta L_{ow} = 0 \quad (A1)$$

795 where A_o is the oil phase area, θ_{ow} is the contact angle, r_{ow} is the capillary radius
796 of arc meniscus, L_{os} is the length of oil-solid interface and L_{ow} is the length of oil-water
797 interface. For convenience we define $r_a = R - h$, the interface lengths and oil phase area
798 can be calculated from elementary geometry as follows:

$$799 \quad A_o = \frac{r_a^2}{4G} - \sum_{k=1}^n r_{ow}^2 \left\{ \theta_{ow} + \alpha_k - \frac{\pi}{2} + \cos(\theta_{ow}) \frac{\cos(\theta_{ow} + \alpha_k)}{\cos(\alpha_k)} \right\} = \frac{r_a^2}{4G} - r_{ow}^2 S_1 \quad (A2)$$

$$800 \quad L_{ow} = 2r_{ow} \sum_{k=1}^n \left\{ \frac{\pi}{2} - \theta_{ow} - \alpha_k \right\} + \frac{r_a}{2G} - 2r_{ow} \sum_{k=1}^n \frac{\cos(\theta_{ow} + \alpha_k)}{\sin(\alpha_k)} = r_{ow} S_3 + \frac{r_a}{2G} - 2r_{ow} S_2 \quad (A3)$$

801
$$L_{os} = 0 \tag{A4}$$

802 where n is the total number of corners containing arc meniscus, α_k is half corner
803 angle at corner k and G is the shape factor. The entry capillary pressure is then given by
804 Eq. (A5).

805
$$P_c = \frac{\sigma(\sqrt{1+4GD}+1)}{r_a} \tag{A5}$$

806 where

807
$$D = \sum_{k=1}^n \left\{ \frac{\pi}{2} - \theta_{ow} - \alpha_k \right\} + \cos \theta_{ow} \sum_{k=1}^n \frac{\cos(\theta_{ow} + \alpha_k)}{\sin(\alpha_k)} \tag{A6}$$

808

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