Capillary dynamic under nanoconfinement: Coupling the energy dissipation of contact line and confined water

Dong Feng [a,b,*], Xiangfang Li [a], Keliu Wu [a,b,c], Jing Li [a,c], Wen Zhao [a]

[a] MOE Key Laboratory of Petroleum Engineering, China University of Petroleum (Beijing), Beijing 102249, PR China
[b] State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum (Beijing), Beijing 102249, PR China
[c] Chemical and Petroleum Engineering, University of Calgary, Calgary, Alberta T2N1N4, Canada

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ABSTRACT

Understanding the dynamic imbibition behaviors through nanopores is a subject of great interest in many fields. Recent molecular dynamics (MD) simulations and pressure-driven experiments demonstrated the increased flow resistance of nanoconfined water, which proposed a challenge to the classical molecular kinetic theory (MKT) that the friction dissipation mainly occurs at the three-phase contact line (TPCL) during the dynamic imbibition process. To address this issue, a unified model that combines the friction of moving contact line and confined water behind the meniscus is proposed to capture the dynamic imbibition behaviors at the nanoscale. The model is successfully validated against the published literatures. The results demonstrate that (1) the friction of confined water in hydrophilic silica nanopores (<10 nm) is several times larger than that of bulk water, and the magnitude will increase as the pore dimension and contact angle decrease. (2) The increased resistance of confined water is on account of solid-liquid two-phase interaction, the friction at the TPCL is the result of three-phase interaction (liquid/air/solid). The liquid-gas interface will give rise to the higher friction at the TPCL. (3) Compared with the energy dissipation at the TPCL, the role of friction induced by nanoconfined water strongly depends on the pore size and wettability. In our work, when the silica nanopore is smaller than 12 nm, the friction of confined water behind the meniscus always plays an important role on the spontaneous imbibition; when the pore size is larger than 200 nm, the energy dissipation mainly occurs at the vicinity of TPCL, which is consistent with the classical theory.

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1. Introduction

Understanding the dynamic imbibition behaviors through nanopores is a subject of great interest, which has significant applications in many industries, such as energy conversion/storage, ultrafine filtration process, oil recovery in unconventional reservoirs, etc [1–3]. Traditionally, Lucas-Washburn (LW) equation is the most common model to describe such flow process, since this theory was carried out by Bell and Cameron and later by Washburn and Lucas [4–6]; many aspects (inertia force, roughness, precursor films and dynamic contact angle, etc.) have been further discussed to make this theory more perfect [7–9]. Moreover, when the pore dimension is down to nanoscale, the extremely large surface to volume ratio would lead remarkable surface effects, presenting other challenges to the application of longstanding classical theory of capillary filling [10,11]. The theoretical research for dynamic imbibition behaviors at the nanoscale is urgently desired.

Under the horizontal condition, the classical LW equation is established based on the assumption that the flow is purely viscous [6]. However, this model fails in predicting the capillary filling at the early stage because it ignores the inertial force related to the accelerating mass of fluid [8,12,13]. At the beginning of liquid uptake, inertial drag dominates the liquid flow. Based on the assumption that the capillary force is only balanced by the inertial force, Quere et al. [14] suggested a capillary rise with constant velocity at the early stage. Bosanquet et al. [7] found a solution to feature the inertial and viscous force and gave a good description for the entire imbibition process. Moreover, Kornev and Neimark [15] pointed out that the imbibition is affected by the solid-liquid interactions and outside hydrodynamic effects. In a word, many experiments and molecular dynamics (MD) simulations suggested that capillary filling process is purely dominated by inertial forces at the very first stage, subsequently transforming towards the fully developed viscous flow regimes [7,12].

Nomenclature

λ	jump length of water molecule, m	ΔG_v	viscous interactions between the liquid molecules, J
k_b	Boltzmann constant, J/K	ΔG_{sl}	activation energy induced by pore wall, J
Wa	reversible work of adhesion, N/m	ΔG_w	Van der waals interaction, J
μ_0	the viscosity of bulk water, Pa·s	ΔG_e	electrostatic interaction, J
N_A	the Avogadro constant, mol^{-1}	ΔG_s	hydrophobic interaction, J
h_p	the Planck constant, J·s	ρ_w	bulk water density, kg/m^3
v_m	molar volume of liquid, L/mol	A_{ss}	the Hamaker constant of solid surface, J
T	temperature, K	A_{ll}	the Hamaker constant of liquid, J
μ_1	the viscosity considering water-wall interactions, Pa·s	ε_0	permittivity in vacuum, F/m
M_w	the molar mass, kg/mol	ε_r	relative permittivity of media, dimensionless
ρ_{bulk}	density of bulk water, kg/m^3	$\triangle r$	effective radius of water molecule, m
D	the nanopore diameter, m	r^*	'cut-off' distance, m
γ	the surface tension, N/m	φ_0	surface potential, V
λ_0	decay length, m	κ	reciprocal of Debye length, m
n	the number of molecules per unit area, m^{-2}	e	electron charge, C
$\mu(D)$	the effective viscosity in nanotubes, Pa·s	PH_0	isoelectric point of silica surface, dimensionless
θ_e	the equilibrium contact angle, °	Z	cation valence, dimensionless
θ_d	the dynamic contact angle, °	ζ	the friction coefficient at the TPCL, Pa·s
ΔG	the total activation energy of kinetic unit, J		

Another feature of the classical LW model is that the wettability of pore surface is constant during the imbibition process, however, it is not always correct because the dynamic contact angle θ_d corresponding to the moving three-phase contact line (TPCL) is often observed with a reasonable reproducibility in many experiments and simulations, and its value strongly depends on the meniscus velocity [6,16]. Under the dynamic wetting conditions, the energy dissipation mechanisms must be identified to model the capillary filling process. Hydrodynamic model thought that the dynamic filling process is dominated by the viscous dissipation in the triangular liquid wedge [16,17]. However, this model does not take account of the effects of solid surface from the molecular view, which plays a remarkable role in dynamic capillary filling process. In contrast to the hydrodynamic loss, molecular-kinetic theory (MKT) considered that the friction dissipation mainly occurs at the TPCL [18–20]. This theory explains the macroscopic behaviors of the contact line from a microscopic point of view, that is, the motion of meniscus strongly depends on the overall statistics of the individual molecular jump near the three-phase zone. Subsequently, the application of the two models were widely discussed. During the wetting process, many investigations suggested that the kinetics can be dominated by molecular energy dissipation for larger contact angle (higher speed) and viscous dissipation for small contact angle (lower speed) [19,21]; Martic et al. [22,23] used MD simulation to investigate the energy dissipation in the dynamics of pore imbibition and found that the MKT theory is sufficient to describe the capillary filling process because the meniscus always moves with a certain speed with the effect of capillary force, the hydrodynamic regimes may play a dominant role after a very long time. Moreover, when the pore scale is down to nanometer, the surface effects play a significant role for the nanoscale conduits. Many investigations have shown the drastically change of liquid properties in nanopores [3,10,11]. The high density layer is widely acknowledged, resulting in a different flow resistance near the solid surface, as well as in the pore center [24]. Koklu et al. [25] presented an experiment to focus on the pressure-driven water flow through hydrophilic nanomenbranes with 5 nm, 10 nm and 20 nm pore radii, the obviously slower flow rates were observed compared with the classical Hagen-Poiseuille model; the hydraulic characteristics of clay nanopores demonstrated high liquid density (3 g/cm³) and viscosity (6 mPa·s) [26]; the MD simulation carried out by Haria et al. [27] indicated the water viscosity

near kaolinite surface could be one order of magnitude discrepancies with the bulk water. Vo et al. [24] employed the MD simulations to study the water viscosity in 2 nm copper and aurum nanopores, the magnitude is far larger than that of bulk water and will increase with the decrease of contact angle. All the mentioned above proposed a doubt that whether the energy dissipation induced by the confined water is still very small compared with that of TPCL.

Considering these challenges, how the energy dissipation of TPCL and the confined water behind the moving meniscus affect the dynamic imbibition behaviors in nanopores is needed to be investigated. Therefore, a better model and prediction will be performed in this paper. our work is structured as follows: (1) firstly, the friction coefficient of TPCL and nanoconfined water are modelled; (2) secondly, a unified model, taking the friction of contact line and confined water into account, is developed for an imbibition calculation; (3) thirdly, the comparison of friction induced by contact line and confined water are conducted, the mechanism and exact control are discussed in detail; (4) finally, the results are made. In addition, some basic assumptions are listed as follows:

(1) The continuum theory is still valid for the nanopore with the dimension larger than 2 nm, which has been discussed in the work of Bocquet et al. [28].
(2) The slip effect is ignored because the spontaneous filling driven by the capillarity only occurs in hydrophilic nanopores.

2. Model establishment

2.1. Friction at the TPCL

Under dynamic condition, the MKT theory builds the relationship of macroscopic behavior and microscopic movement (Fig. 1). According to this theory, the macroscopic contact angle θ_D is equal to the nanoscopic local angle θ_m by ignoring the bending effect (Fig. 1(b)), the macroscopic moving of the wetting line is the result of overall statistics of the individual molecular displacements that occur near the TPCL (Fig. 1(a) and (c)), depending on the jump length λ and frequency of molecular displacements κ^0. During the capillary filling process, the interfacial curvature changes, resulting in the dynamic contact angle θ_d larger than the equilibrium one θ_e, the contact line movement is driven by unbalanced