Non-Newtonian flow in microporous structures under the electroviscous effect

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1. Introduction

Electrokinetic phenomena in microporous structures have recently attracted intensive attention in various fields such as capillary electrophorography and high-performance micropumps due to the large surface of porous materials, the charged whole frit surface, and the less dispersion to an analyte, which motivates research toward a better understanding of microscale fluidic transport phenomena to optimize the device design and operation [1].

One of the well-known electrokinetic phenomena, the electroviscous effect, results from the combined action of the charged solid surface and the ions in the flowing liquid. It is known that electrostatic charges carried on the solid surface attract counterions in the liquid when the liquid contains a certain amount of ions. The rearrangement of charges on the solid surface and balancing charges in the liquid produce a so-called electrical double layer (EDL) [2,3], composed of the imobile compact layer and the mobile diffuse layer. The nonzero electrical charges in the mobile part of the EDL in the liquid produce a so-called electrical double layer (EDL) [2,3], composed of the immobile compact layer and the mobile diffuse layer. The nonzero electrical charges in the mobile part of the EDL are carried downstream by the liquid flow under a hydrostatic pressure, which builds a balance between the streaming current flowing in the streamwise direction and the conductance current flowing back in the opposite direction. The moved ions in the diffuse layer will pull the liquid along with them in the opposite direction to the pressure-driven flow, leading to a reduced flow rate. Such electrokinetic effect of the presence of the EDL on the flow behavior is usually referred to the electroviscous effect [2].

Tang et al. [4] conducted experiments for deionized water flowing in four smooth fuse silica microtubes (diameter $D = 50.55, 74.36, 102.74,$ and $530.3\,\mu m$ with the measured inner surface relative roughness far less than 1%) and two rough stainless steel microtubes (diameter $D = 119.09,$ and $172.0\,\mu m$ with the relative roughness 4.1% and 5.9%, respectively). The experimental results show that friction factors are in good agreement with the classical predictions for convectionalized channels and the flow resistance due to the electroviscous effect is not significant. The corresponding numerical simulation considering the electroviscous force term verifies the experimental results. Though the flow resistance was observed to increase significantly in the rough stainless steel microtubes, it is mainly attributed to the large surface roughness. Particularly, the non-Newtonian flow in smooth parallel microchannels taking into account the electroviscous force term is numerically studied and the results show that the shear thinning fluid is more sensitive to the electroviscosity effect [5]. Davidson and his colleagues also investigated the electroviscous effect in micro contractions using the finite volume method for Newtonian fluid [6,7] and non-Newtonian fluid [8,9].

However, to the author’s best knowledge, the existing investigations on electroviscous effect of Newtonian or non-Newtonian fluids are all focused on the simple channel flow. The flow behavior of non-Newtonian fluid in microporous structures is of high interest in practical applications such as sample collection, dispensing, reaction, detection, mixing, and separation of various biological and chemical species in capillary electrophorography [10] and high-performance micropumps [11–13]. The fluid rheological behavior combined with microscale effects in complicated geometry usually plays a more important role. Fundamental understanding of the non-Newtonian role in liquid transport through microporous structures is significant to correctly predict and control characteristics and performances of such microfluidic devices.
Recently the lattice Boltzmann method (LBM) has been developed as a new tool for simulating the fluid flow and heat transfer. Compared with traditional computational fluid dynamics methods, the lattice Boltzmann method is a micro- and meso-scale modeling method based on the kinetic theory. Its inherent advantages, such as simple coding, easy implementation of boundary conditions and full parallelism, make it especially suitable for complicated transport phenomena in complicated geometries [14–16]. The lattice Boltzmann simulation of pore-scale approach enables us to model explicitly, in the complex geometry of a porous network, the influence of fluid–fluid and fluid–solid interactions on bulk flow parameters. The detailed flow information in porous structures can be obtained with very high efficiency. In addition, the kinetic essence makes it capable of calculating local components of the stress tensor without estimating velocity gradients when computing the non-Newtonian fluid viscosity, while the Navier–Stokes stress tensor is often employed as a new tool for simulating the fluid flow and heat transfer.

In the next section, the lattice Boltzmann equations for the velocity field of power-law non-Newtonian fluid and for the electric potential distribution are presented. In Section 3, the flow fields for non-Newtonian fluid are computed with several different microporous structures under external pressure and obtained by considering the electroviscous effect. A brief conclusion is presented in Section 4.

2. Numerical methodology

The standard discrete lattice Boltzmann evolution equation with the Bhatnagar–Gross–Krook (BGK) collision approximation is [20]

\[
f_i(r + c_i \delta t, t + \delta t) = f_i(r, t) - \frac{\delta t}{\tau_c} \left[ f_i(r, t) - f^eq_i(r, t) \right] + \delta t \frac{F_i}{R T} \left( \frac{c_i - u}{R} \right) f^eq_i(r, t),
\]

(1)

where \( f_i \) is density distribution functions, \( F_i \) is an external force term, \( \tau_c \) is the relaxation time, \( c_i \) is the particle discrete velocity. In the D2Q9 square lattice, \( c_0 = 0, \) \( c_i = (\cos[(i-1) \pi/2], \sin[(i-1) \pi/2], c) \) for \( i = 1, 2, 3, 4 \) and \( c_i = (\cos[(i-5) \pi/2 + \pi/4], \sin[(i-5) \pi/2 + \pi/4]) \sqrt{2}/c \) for \( i = 5, 6, 7, 8 \), where \( c = \delta_x/\delta t \) is the particle streaming speed (\( \delta_x, \delta t \) is the lattice spacing and time step, respectively). The equilibrium density distribution function, \( f^eq_i(q = 0, 1, \ldots, 8) \) in the D2Q9 lattice [21]:

\[
f^eq_i = \rho_0 \alpha_c \left[ 1 + \frac{3(c_i \cdot u)^2}{c^2} + \frac{9(c_i \cdot u)^2}{2c^2} - \frac{3(u \cdot u)}{2c^2} \right],
\]

(2)

where \( \alpha_0 = 4/9, \rho_0 = 1/9 \) for \( i = 1, 2, 3, 4 \) and \( \alpha_0 = 1/36 \) for \( i = 5, 6, 7, 8 \). The relaxation time \( \tau_c \) is linked to the kinematic viscosity \( \nu \) via

\[
\tau_c = 3\nu \frac{\delta^2}{\delta x^2} + 0.5 \delta t.
\]

(3)

The mass density and momentum density are calculated by

\[
\rho = \sum_i f_i \quad \text{and} \quad \rho u = \sum_i f_i c_i.
\]

(4)

One knows that the stress tensor for an incompressible fluid with pressure \( p \) is given by

\[
\sigma_{xy} = -p\delta_{xy} + \eta \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right) = -p\delta_{xy} + 2\eta S_{xy},
\]

(5)

where \( \delta_{xy} \) is the Kronecker delta, \( \eta \) is the dynamic viscosity, and \( S_{xy} = (\partial u_x/\partial y + \partial u_y/\partial x) \) is the shear strain rate tensor. \( S_{xy} \) can be calculated at each node in the LBM as [22]

\[
S_{xy} = -\frac{3}{2\rho c^2 \tau_p} \sum_{i=0}^{f(1)} c_i \cdot c_p,
\]

(6)

where \( f^{(1)} \) is the non-equilibrium part of the distribution function and \( f^{(1)} c_i c_p \) in Eq. (6) is usually computed with second-order accuracy during the collision process in the LBM evolution. In the commonly used power-law model for non-Newtonian fluid, the viscosity is given by

\[
\eta = \eta_0 n^{-1} = \eta_0 (2S_{xy} S_{xy})^{1/2},
\]

(7)

where the shear rate-related \( \gamma \) is \( \gamma = \sqrt{2S_{xy} S_{xy}} \) and the parameter \( n \) is the power-law exponent which determines the response of the fluid to changes in shear rate. The fluid is classified into shear thinning for \( n < 1 \), and shear thickening for \( n > 1 \). The Newtonian behavior is recovered with shear-independent viscosity \( \eta_0 \) at \( n = 1 \). Note that the truncated power-law model was employed in the LBM to improve the numerical stability [23], however, without loss of generality, we still employed the general power-law non-Newtonian model in this paper.

Coupling Eqs. (3), (6), and (7), together with \( \eta = \rho \nu \), we can derive a shear-dependent relaxation time \( \tau_c \) at each node in the lattice Boltzmann evolution Eq. (1). Eq. (1) can recover the Navier–Stokes equation if using the Chapman–Enskog approximation,

\[
\rho \left( \frac{\partial u}{\partial t} + (u \cdot \nabla) u \right) = \nu \nabla^2 u + \rho F,
\]

(8)

The force term under external pressure gradient \( \nabla p \) can be expressed as

\[
\rho F = -\nabla p - \rho_e E,
\]

(9)

where \( \rho_e \) is the net charge density per unit volume at any location in the liquid, \( E \) is the stream electric field caused by the ion movement in the solution, and \( \rho_e E \) presents the electroviscosity term. Note that the stream electric field, \( E_0 \) generated by the streaming current due to the carried downstream counter-ions, is different from the usual electrostatic field, which is caused by the electrostatic charges carried by the solid surfaces. The stream electric field can be obtained through a balance between the streaming current and electrical conductance current at steady state,

\[
E = -\frac{\rho_e \nabla \psi}{\epsilon_0}.
\]

(10)

Here the net charge density per unit volume, \( \rho_e \), is linked with the electric potential in the liquid, \( \psi \), by the Poisson equation:

\[
\nabla^2 \psi = -\frac{\rho_e}{\epsilon_0}.
\]

(11)

and the net charge density distribution can be expressed as the sum of all the ions in the solution:

\[
\rho_e = \sum_z n_z e z \nabla \psi \exp \left( -\frac{z e \psi}{k T} \right).
\]

(11b)

where \( \epsilon_0 \) is the permittivity of free space, \( \epsilon \) is the relative dielectric constant of the solution, \( z_e \) and \( n_{z_0} \) are the valence of type \( z \) ions and the bulk ionic concentration, respectively. The bulk ionic concentration, \( n_0 \), can be expressed as the product of the ionic molar concentration, \( c_0 \), and Avogadro’s number, \( N_A \). The constant, \( e \), is the charge of a proton, \( k_B \) is the Boltzmann’s constant and \( T \) is the absolute temperature. To be in the same framework of the lattice Boltzmann method as solving the velocity field, the following discrete lattice Boltzmann evolution equation is employed to solve the electric potential in Eq. (11) [4,24]:
The power-law index is 0.75 and the imported pressure difference is 100 Pa. The simulated domain is extended in the entrance and exit of the porous region to improve the numerical stability and accuracy. The dark region represents the pores and the light represents the porous blocks. We can observe that the fluid flow avoids the blocks and goes through open spaces. Fig. 3 presents velocity vectors and viscosity distributions close to the exit of shear thinning fluid of \( n = 0.75 \).

\[
g_i(r + c_0 \delta t + \delta t) = g_i(r, t) - \frac{\delta t}{\tau_0} \left[ g_i^0(r, t) - g_i^\text{eq}(r, t) \right] \\
+ \frac{(\tau_0 - 0.5\delta t/\tau_0)}{\delta t} \left( \frac{1}{\tau_0} \sum_z z_3 e_n a_0 \exp \left( -\frac{z_3 e_n}{k_B T} \right) \right),
\]

where \( g \) is the distribution function, and \( g_i^\text{eq} \) is the corresponding equilibrium distribution function on the D2Q9 lattice, with \( g_i^\text{eq} = 0, g_i^\text{eq} = \psi/6, \) and \( g_i^\text{eq} = \psi/12 \). The potential diffusivity, \( \chi \), which is equal to unity in the simulations, is defined as

\[
\chi = \frac{2(\tau_0 - 0.5\delta t)}{3} \frac{\partial^2}{\partial t^2}
\]

The macroscopic electric potential in the liquid is calculated from

\[
\psi = \sum_i g_i + \frac{\delta t}{2} \sum_i \left( \frac{1}{\tau_0} \sum_z z_3 e_n a_0 \exp \left( -\frac{z_3 e_n}{k_B T} \right) \right) \omega_i.
\]

Thus one can eventually attain \( \rho_e \) in Eqs. (9) and (10) via Eq. (11b) when \( \psi \) is obtained from Eq. (14). The electrical conductivity of the liquid layer, \( \lambda \) in Eq. (10) can be calculated as [25]

\[
\lambda = n_c \Lambda_c + n_a \Lambda_a,
\]

where \( \Lambda_c \) is the molar conductivity of the cation, and \( \Lambda_a \) is the molar conductivity of the anion. The concentrations of cations, \( n_c \), and anions \( n_a \) are calculated with

\[
n_e = n_0 \exp \left( -\frac{z e \psi}{k_B T} \right).
\]

With regard to the boundary conditions for the lattice Boltzmann equations, the LBM is of good ability to handle general boundary conditions due to its kinetic nature and essential character of microscopic physics. When solving the electric potential, the zeta potentials, \( \zeta \), at all solid surfaces are fixed and the Dirichlet boundary conditions are employed [26]. The periodic boundary conditions are employed for the electric potentials at the channel inlet and outlet. For the velocity field, the nonslip boundary conditions at all the solid surfaces are treated with bounce-back, and the pressure is fixed at the channel inlet and outlet and the pressure boundary conditions are applied [27].

3. Results and discussion

3.1. Non-Newtonian flow in the porous structure without electroviscous effect

Firstly, the non-Newtonian single phase porous flow without considering the electroviscous effect is studied. The simulated porous structure is shown in Fig. 1, where the blue (dark) represents the skeleton of the porous structure while the red (light) represents the pore. To generate the data needed to calculate the porous structure, we first take the SEM images of a real porous sample, the sandstone rock sample. Then by the processing of contrast, brightness and filtering with technology of the imagine analysis in mat lab, the obtained image is transformed into a binary matrix with only two gray values and thus the porous structure is reconstructed.

Fig. 2 shows the velocity vectors and streamlines for the flow in the square porous structure with \( H \) (height) = \( L \) (length) = 0.1 mm. The power-law index is \( n = 0.75 \) and the imported pressure difference is 100 Pa. The simulated domain is extended in the entrance and exit of the porous region to improve the numerical stability and accuracy. The dark region represents the pores and the light represents the porous blocks. We can observe that the fluid flow avoids the blocks and goes through open spaces. Fig. 3 presents velocity vectors and viscosity distributions close to the exit of shear thinning fluid of \( n = 0.75 \).
porous region for shear thinning fluid flow of \( n = 0.75 \). We can see that the velocity gradient is quite large at the outlet of porous region and the local viscosity is relatively low (yellow zone), which corresponds well with the relationship between the viscosity of power-law fluid and shear rate, i.e. the higher shear rate, the lower viscosity. The velocity vectors and viscosity distributions in Fig. 4 for shear thickening fluid flow of \( n = 1.25 \) also confirm the relationship between the viscosity of power-law fluid and shear rate. We can see that at the exit of the porous region, the larger velocity gradient results in a larger local viscosity (green and yellow zone). These pictures of Figs. 2, 3 and 4 illustrate that, regardless of the complexity of the porous structure, the details of the flow are well captured.

Darcy’s law has been generalized to single phase power-law fluids by Larson [28] and for a power-law fluid, a generalized form of Darcy’s law holds in which the pressure drop is proportional to the flow rate raised to the power-law exponent. Specifically, Sorbie et al. [29] described that the Darcy velocity is given by the expression

\[
\frac{Q}{\rho A} = C \left( \frac{\Delta P}{\eta L} \right)^{1/n},
\]

where \( Q \) is the total mass flow rate, \( A \) is the cross-sectional area, \( \Delta P \) is the pressure drop between the porous region, \( L \) is the length of the porous region, and \( n \) is the Power-law exponent. The constant \( C \) is dependent on the porous permeability, porous structure parameters, and power-law index \( n \). From Eq. (17) we can see that there exists a linear relationship between the flow rate and pressure drop in logarthmic coordinates with a slope of \( 1/n \). The mass flow rates against pressure drops are presented in Fig. 5 which demonstrates that the simulated results are in good agreement with the linear fit of \( 1/n \) for Newtonian, shear thinning and shear thickening fluids.

3.2. Non-Newtonian flow in porous structures with electroviscous effect

To study the electroviscous effect on the non-Newtonian flow in microporous structures, we simulate three constructed microporous structures schematic as Fig. 6 (marked as P1, P2, and P3) under various electrokinetic conditions, where the blue (dark) represents the skeleton of the porous structure while red (light) of the pore. The corresponding porous parameters of P1, P2, and P3 are as follows: the porosities are 0.47, 0.58, 0.55, respectively, and the pore surface area ratios are 7.39, 14.1, and 26.8, respectively. The pore surface area ratio is calculated as: the sum of all the block-pore interface areas divided by the areas of top and bottom walls.

In the simulation, we set the non-Newtonian fluid to be moderate KCl solution with a fixed molar concentration of \( 10^{-2} \) mol/l. And we choose \( T = 293 \) K, \( z = 1 \), \( e = 1.6 \times 10^{-19} \) C, \( \varepsilon_0 = 7.79 \times 10^{-10} \) C^2/(J m), \( N_A = 6.02 \times 10^{23} \) mol^{-1}, \( k_B = 1.38 \times 10^{-23} \) J/K, \( \rho = 997.94 \) kg/m^3, \( \eta_0 = 983.75 \times 10^{-6} (\sqrt[1/2]{0.5})^{n-1} \) kg/(ms), \( \Delta \tau_C = 73.52 \times 10^{-4} \) Sm^2/mol, and \( \Delta \tau_T = 76.34 \times 10^{-4} \) Sm^2/mol. The surface zeta potentials at all porous blocks keep the same and the magnitude changes at \( \zeta = 0 - 25 \) mV, and \(-50 \) mV.

The flow rates against pressure drops are presented in Fig. 7 by fixing the surface zeta potential. For \( \zeta = 0 \) shown in Fig. 7a, which denotes that the electroviscous effect is not considered, we can see that the flow rate is linear proportional to the pressure drop in logarithmic coordinates for the simulated three power-law exponents, just as in Fig. 5. However, for nonzero surface zeta potential, the electroviscous effect becomes important, especially for the shear thinning fluid. The flow rate deviates from the linear fit of \( 1/n \) to the lower side obviously for \( n = 0.75 \). The deviations get larger as the surface zeta potential increases from \( \zeta = -25 \) (Fig. 7b) to \(-50 \) mV (Fig. 7c). For the Newtonian and shear thickening fluids shown in Fig. 7, the linear relationship still nearly holds. In the case of a shear thinning fluid \( n < 1 \), the shear rate closer to the pore surface is higher than that for a Newtonian fluid \( n = 1 \) or a shear thickening fluid \( n > 1 \) and therefore a lower viscosity near the pore surface. As discussed in the author’s previous work [5], a plug like velocity profile is formed in the high shear rate regions, therefore the resistance force close to the pore surface is much larger than the driving force as seen from Eq. (10), especially at lower power-law exponents and larger zeta potentials, which results in an evident reduced flow rate.

By fixing the power-law exponent we plot the data in Fig. 8 to compare the differences among different surface zeta potentials. We can see that for \( n = 0.75 \) (in Fig. 8a), the flow rate difference among different surface zeta potentials is very large. The flow rate of \( \zeta = 0 \) is the highest and the flow rate of \( \zeta = -50 \) mV is the lowest, while the flow rate of \( \zeta = -25 \) mV is intermediate within the presented pressure range. In addition, the gap increases as the applied pressure difference gets larger since the electroviscous force is proportional to the flow velocity as seen in Eq. (10). However, for the Newtonian fluid (in Fig. 8b) and shear thickening fluid (in Fig. 8c), though the decrease in flow rate from \( \zeta = 0 \) to \( \zeta = -50 \) mV can still be observed, it is not quite evident.
Fig. 6. The constructed three porous structures marked as P1, P2, and P3 from left to right.

Fig. 7. The flow rate versus pressure difference for non-Newtonian fluid flow in porous structure P1 at fixed surface zeta potential. (a) $\zeta = 0$, (b) $\zeta = -25$ mV, (c) $\zeta = -50$ mV.

Fig. 8. The flow rate versus pressure difference for non-Newtonian fluid flow in porous structure P1 at fixed power-law exponent. (a) $n = 0.75$, (b) $n = 1$, (c) $n = 1.25$. 
Similarly, the flow rates against pressure drops in more complicated geometries of P2 and P3 are presented in Figs. 9 and 10. For $f = 0$ shown in Fig. 9a without the electroviscous effect, we can see that the flow rate through both porous structures of P2 and P3 against pressure drop in logarithmic coordinates corresponds well with the linear relationship of $1/n$ slope for the simulated three power-law exponents. Compared to P1 and P2, P3 has the highest pore surface area ratio so that the flow resistance due to the electroviscosity is also the largest, resulting in the lowest flow rate. For surface zeta potential $f = /C_0 25$ mV (in Fig. 9b) and $f = /C_0 50$ mV (in Fig. 9c), the relation between flow rate and pressure drop departs from the linearity significantly to a lower slope. Compared to P1 (in Figs. 7a and b) and P2, the reduction for P3 is more evident, and compared to $f = -25$ mV, the reduction for $f = -50$ mV is more evident, which are mainly attributed to the larger pore surface area ratio for P3, and higher net charge density for $f = -50$ mV, respectively. The more pore surface causes more interface interaction between the charged surface wall and the fluid electric potentials, which induces a larger viscous drag force.

The flow rates in P2 and P3 are plotted in Fig. 10 by fixing the power-law exponent and thus the difference among the three types of rheological fluids can be observed more clearly. For the shear thinning fluid of $n = 0.75$ presented in Fig. 10a, the flow rate reduces significantly from $f = 0$ to $f = /C_0 50$ mV due to the increasing electroviscous effect. Compared to the flow rate through P1 presented in Fig. 8a, the reduction in P2 and P3 is larger due to their higher pore surface area ratio. The flow rate reduction from $f = 0$ to $f = -50$ mV for Newtonian fluid (in Fig. 10b) and shear
thickening fluid (in Fig. 10c) can still be observed. However, these two fluids do not behave so evident as the shear thinning fluid does. Nevertheless, compared to P1 shown in Fig. 8b and c, the electroviscous effect on Newtonian and shear thickening fluid is more significant due to higher pore surface area ratio in P2 and P3. In addition, we can also conclude that the electroviscous effect is not directly associated with the porosity if comparing the porosities of the three porous structures, which are 0.47, 0.58, and 0.55 for P1, P2, and P3, respectively.

4. Conclusions

Motivated by the growing applications for complex fluids in complicated microgeometries, in this paper we have numerically studied the power-law non-Newtonian fluid flow in combination with the electroviscous effect in microporous structures from the microscopic point of view. We have solved both the pore-scale electric potential field and the pore-scale velocity field in complicated geometries in the same framework of the lattice Boltzmann method. The obtained local viscosity distribution in microporous structures agrees qualitatively with the non-Newtonian rheological properties. The flow rate through the porous structure is linearly proportional to the applied pressure difference in a logarithmic coordinates with a slope of the inverse power-law without considering the electroviscous effect, which is in consistence with the theory of the modified Darcy flow.

It is found that the electroviscous effect on the flow characteristics in microporous structures is highly dependent on the fluid rheological property and the porous structure. Both the power-law exponent n and the pore surface area ratio play important roles while the porosity is less associated. For the shear thinning fluid with power-law exponent less than unity, the electroviscous force term takes a large part in the total force, which causes an evident resistance to the flow rate; the higher surface zeta potential, the larger flow resistance. In contrast, for the Newtonian fluid and shear thickening fluid, the electroviscous effect generally contributes little to the flow. However, for large pore surface area ratio, the resistance to the flow also becomes evident. For shear thinning fluid flow in microporous structures, the linear relationship with a slope of 1/n breaks down to a lower slope due to the electroviscous effect while it is not so evident for Newtonian and shear thickening fluids.

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