Thermo-osmosis in silica nanochannels

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ABSTRACT

Thermo-osmosis is a coupled phenomenon describing the fluid flow induced by a thermal gradient. Recent studies on thermo-osmosis in clays and within the coupled thermal, hydraulic and mechanical analysis have revealed the importance of this physical processes in geo-energy and geo-environmental applications. This paper presents a series of molecular dynamics simulations of the interfacial water behaviour at the vicinity of silicate layers to quantify the nanochannel size effect on the thermo-osmotic coefficient and reveal some aspects of governing mechanisms of thermo-osmosis in nanoscale space. Our results show that the size effect emerges from the specific liquid structure controlled by the channel width. The overlapping and interfering boundary layers lead to the variations of thermo-osmotic response with the channel width. Our findings not only facilitate a basic knowledge of thermo-osmosis, but also contribute insights and methods to analyse a wider category of coupled heat and mass transfer problems in nanometric space.

Keywords: thermo-osmosis, coupled phenomena, mechanico-caloric, molecular dynamics, liquid structure, quartz

1 INTRODUCTION

Thermo-osmosis is a coupled heat and mass transport phenomenon, describing fluid flow due to thermal gradients. Thermo-osmosis is of great interest to a wide range of research areas including chemistry, biology, energy and environment, separation and membrane technologies, and energy geo-structures. Thermo-osmosis phenomenon has recently received attentions in geotechnical engineering in order to develop a more comprehensive assessment of thermally coupled hydromechanical processes in clays (e.g. Goncalves et al., 2012, Zagorscak et al., 2017, Goncalves et al., 2018). The recent developments on thermo-osmosis are mainly motivated by the need to assess the impact of elevated temperature on clay behaviour in geological disposal of high level radioactive waste and energy foundations. The focus of these studies have mainly been on the applications of macroscopic and phenomenological implementations of thermo-osmosis in coupled THM models. However, the developments in microscopic understanding of thermo-osmosis is rather insufficient. There is specifically a gap in the fundamental knowledge about the mechanisms controlling the thermo-osmosis in complex porous systems such as clays. Of particular interest is to understand what mechanisms and effects can affect the thermo-osmotic coefficient through which the macroscopic phenomenological description is commonly adopted in studying coupled problems. Moreover, the current descriptions of thermo-osmotic coefficient are mostly based on local continuum theories. Such continuum approximations may be sufficient for larger length scales. However, their applicability at the nanometric solid-fluid interface has not been fully validated.

Using molecular dynamics simulations, we aim to quantify the size effects on the thermo-osmotic response of nanometric channels and reveal the underlying molecular mechanisms. The system studied is the quartz-water interface in which a light hydrophilic interactions are anticipated. This system was selected to gain insights into the interfacial interactions between water and surfaces in the absence of a strong electrostatic interactions.

2 METHODOLOGY

With a pressure and temperature gradient applied in the x direction, according to nonequilibrium thermodynamics, the fluid flow \( j_1 \) and heat transport \( j_2 \) in the x direction are described by (Derjaguin et al., 1987, Farago, 2019):

\[
\begin{bmatrix}
  j_1 \\
  j_2 
\end{bmatrix} =
\begin{bmatrix}
  m_{11} & m_{12} \\
  m_{21} & m_{22}
\end{bmatrix}
\begin{bmatrix}
  -\nabla p \\
  -\nabla T / T
\end{bmatrix},
\]

where, \( \nabla p \) and \( \nabla T \) are pressure and temperature gradients along the x direction, respectively. And \( T \) is the fluid temperature.

\( m_{ij} \) are phenomenological coefficients: \( m_{11} \) is the hydraulic conductivity, \( m_{22} \) is the thermal conductivity,
2.2 Calculations of the fields and coefficients

According to Eq. (1), the off-diagonal phenomenological coefficient of the nano-sized system shown in Fig. 1 can be described as:

\[ m_{21} = m_{21} = -\frac{j_2}{\nabla p}, \]

where, \( j_2 \) is calculated by

\[ j_2 = \frac{1}{L_z} \int \delta h(z) v_x(z) dz, \]

where, \( v_x(z) \) is the water velocity along the x-direction, \( \delta h(z) \) is the excess specific enthalpy of water, and \( L_z \) is the channel width. \( \delta h(z) \) is calculated by:

\[ \delta h(z) = h(z) - h_b, \]

where \( h_b \) is the specific enthalpy of the bulk fluid, which can be obtained as the channel size is sufficiently wide.

The local specific enthalpy \( (h(z)) \) is calculated by (Ganti et al., 2017):

\[ h(z) = u(z) + p_{xx}(z), \]

where, \( u(z) \) and \( p_{xx}(z) \) are the specific internal energy and the pressure component along the x-direction of the interfacial water. The water velocity curve of the planar Poiseuille flow, induced by a pressure gradient \( \nabla p \) in the nanochannel is calculated by solving the Stokes equation:

\[ v_x(z) = -\frac{\nabla p}{2\eta} \left[ L_z b + \left( z + \frac{L_z}{2} \right) \left( \frac{L_z}{2} - z \right) \right], \]

where, \( b \) is the slip length and \( \eta \) is the interfacial water viscosity.

The velocity profiles of the interfacial water from MD simulations can be fitted with Eq. (6), yielding the hydrodynamic parameters \( \eta \) and \( b \). The pressure gradient \( -\nabla p \) in Eqsns. (2) and (6) is computed by (Corry, 2008, Azamat et al., 2015, Wang et al., 2017)

\[ -\nabla p = \frac{1}{V} \sum_{i=1}^{N} f_i, \]

where, \( N \) and \( V \) are the total number and volume of the interfacial water molecules.

3 RESULTS AND DISCUSSION

To investigate the nanochannel size effect on thermo-osmotic response, the MD model in Fig. 1 with different channel size is constructed. The system is firstly relaxed at 300 K for \( 1.2 \times 10^{-9} \) s. Then extra body forces are applied to every fluid particle to produce a Poiseuille flow. After 0.4 ns stabilization, the numerical data is saved every 0.001 ns for 0.8 ns.

The interfacial water’s liquid structure is quantified by its spatial distribution/orientation and the solvation
mode. For the spatial arrangement, the mass density profiles shown in Fig. 2a highlight the significant fluctuations in the vicinity the quartz surfaces and constant density in the nanochannel’s middle part, which is equal to the value of bulk water. The fluctuations indicate the tendency of water molecules to remain at fixed layers near the quartz surfaces. The peaks and valleys in the curves correspond to the higher and the lower distribution probability of water molecules.

The charge profiles are also shown in Fig. 2b, which present the spatial orientation of interfacial water molecules. The peaks in Fig. 2b describe the layers mainly composed of hydrogen (H) atoms, while the valleys indicate the layers mainly made up of oxygen (O) atoms because H carries positive charge and O carries negative charge in the adopted water molecule model (Cygan et al., 2004). The charge density is neutral in the middle part of the nanochannel when the channel width is sufficiently large, indicating a random and disordered spatial arrangement of the bulk water molecules (Chen et al., 2019). It is also found that the position of the valleys in Fig. 2b is consistent with those of the peaks in Fig. 2a.

Fig. 2. The distribution profiles of (a) mass density, (b) charge, (c) excess enthalpy, (d) number density, (e) velocity, and (f) SDF cloud visualizations of the interfacial water including a 3-D plot for the channel width $L_z = 3.0$ nm, and 2-D plots on clipping planes $z = 0$ and $x = 0$ for different channel widths, where I–V shows the typical interaction sites of surrounding water molecules relative to central one.
Fig. 2a–b show the formation of a “boundary layer” near the solid surfaces, where a layered liquid structure of the interfacial fluid is created and alternating peaks and valleys can be observed on the profiles. In contrast, the bulk water in the mid-section of a sufficiently large channel consists of randomly oriented and distributed water molecules and the fluctuation become negligible on the profiles. The depth of the boundary layer is therefore \( \approx 0.75 \text{nm} \) according to Fig. 2a–b. When \( L_z < 1.5 \text{nm} \), the two boundary layers from two quartz surfaces overlap and bulk water disappears.

Fig. 2c shows the excess enthalpy profiles, where the thickness of the boundary layer are consistent with that of Fig. 2a–b. The profiles fluctuate within the boundary layers and maintain constant in the bulk region. Similarly, when \( L_z < 1.5 \text{nm} \), the two boundary layers overlap and interfere with each other, leading to a complex excess enthalpy profile of the interfacial water.

Fig. 2d presents the number density distribution of hydrogen and oxygen atoms. The results show that the peaks in Fig. 2c appear between the peaks of oxygen and hydrogen profiles, roughly corresponding to the peaks of oxygen profiles. The valleys (apart from the first valley) in excess enthalpy profiles correspond to the peaks of hydrogen profiles.

The boundary layers also influence the hydrodynamic properties of the interfacial fluid. Fig. 2e presents the velocity profile in fluid. Fitting curves based on Eq. (6) agree well with the simulation scatter, evidencing that the induced flow can be well predicted by Poiseuille flow. The fitting results show that no slippage occurs between fluid and solid surface \((b \approx 0 \text{ nm})\). As for the water viscosity, for \( L_z \geq 1.5 \text{nm} \), \( \eta \) gradually decreases to a constant value, while for \( L_z < 1.5 \text{nm} \), the two overlapping and interfering boundary layers lead to complicated changes with channel width of water viscosity. It is found that with \( L_z \) increasing, \( \eta \) firstly rises and then reduces to a stable value.

The water solvation mode was studied by computing the spatial distribution function (SDF) of the interfacial water molecules (see details in the work of Chen et al., 2019), which quantifies the relative position relations between any central water molecule and its neighbouring water molecules (similar to the well-known radial distribution function, but more favourable for 3-D viewing). The clipping 2-D views of SDFs for different channel widths in Fig. 2f show that the water solvation mode for the case \( L_z = 1.0 \text{ nm} \) is different from that of other cases, indicating a unique liquid structure, which may lead to a unique thermo-osmotic coefficient. A constant water solvation mode is observed for \( L_z \geq 1.5 \text{ nm} \), showing that size effect gradually diminishes for larger channels.

The thermo-osmotic coefficient \( m_{12} \) is computed by Eq. (2). The variation of \( m_{12} \) with \( L_z \) in Fig. 3 shows that: (1) For \( L_z \geq 1.5 \text{ nm} \), \( m_{12} \) is approximately constant, while for \( L_z < 1.5 \text{nm} \), \( m_{12} \) varies with \( L_z \), which results from the overlap and interference of the boundary layers as explained above; (2) A unique value was found for \( L_z = 1.0 \text{ nm} \), related to the unique liquid structure as observed in Fig. 2f.

![Fig. 3. Evolution of the thermo-osmotic coefficient with the channel width.](image)

The MD simulations above have revealed that the nanochannel size effect emerges from the alterations of the interfacial water’s liquid structure due to the overlapping boundary layers with decreasing channel width, which changes both the excess enthalpy density and the hydrodynamic behaviour of the interfacial fluid. The comparisons of different profiles in Fig. 2a–d evidence that the excess enthalpy density is governed by the layer-by-layer liquid structure of interfacial fluid. Fig. 2e shows that the hydrodynamic behaviours of the interfacial water are greatly influenced by the varying liquid structure as well.

4 CONCLUSIONS

The size effect on the thermo-osmotic coefficient in nanochannels and their mechanisms were studied by tailored MD simulations. According to the results, the following conclusions are deduced:

1. The continuum hydrodynamics remains valid at the nanoscale;
2. The interfacial water’s liquid structure varies with decreasing channel width, because of the overlapping and interfering boundary layers forming near the quartz surface. This results in changes of the interfacial water’s excess enthalpy and hydrodynamic properties, leading to changes of the thermo-osmotic coefficient;

Our findings and modelling approach used in this investigation, lay a solid foundation for future studies on coupled transport phenomena at the nanoscale.

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