Abstract

In the present paper, Non Equilibrium Molecular Dynamics (NE MD) simulation has been carried out to study the effect of interface wettability on the transport of water (assuming it to be a simple Lennard Jones fluid) in a nanochannel. In the said channel, the walls have been considered to be composed varying zones of hydrophilic and hydrophobic surfaces. In one design alternate patches exist along the channel length, whereas for the other design a checker box arrangement of hydrophilic and hydrophobic surfaces is considered. For the first case there is a prominent backflow at the near-wall locations, which is not present for the other case. Relative abundance of the patches of variable wettability at a selected zone in the channel is the primary cause for such variability. Other interesting variations regarding the number density distribution as a function of the proximity from the channel wall are also reported and explained for these two cases.

1. Introduction

In the past few years, studies of fluid flow at the nanoscale level have gained tremendous importance due to their diversified applications in nanofluidic devices, material sciences and biotechnological systems. A number of theoretical as well as experimental studies have revealed important understanding about the nanoscale flow physics. For example, nanochannels of different dimensions and materials have been fabricated [1-4], and investigations have been conducted to test the role of the material characteristics and the limiting dimensions on the transport behaviour. Regarding the theoretical studies, various simulation techniques have been practised, ranging from molecular level simulations to the usual continuum models [5-8].

The most important realization to have been established in the course of study of nanofluidics is that it cannot be treated as a limiting extension of the microscale studies. Nanoscale transport are characterized by large surface to volume ratios, which ensure that the fluid-wall interaction become extremely critical. Such interaction is rarely present in microflows, and requires inclusion of additional terms in the governing conservation equations, signifying the wall effects [9, 10]. In nanochannel water flows, if the channel dimension is of the order of 100 nm, the validity of continuum assumption is not questioned and application of these conservation equations with wall induced modifications is sufficient to describe the necessary flow physics. However for channels with dimension of the order of 10 nm and less, continuum hypothesis can no longer be assumed. Under such a strong confinement, the state variables like density can vary appreciably in the direction of the confinement, especially close to the walls. Thus under such circumstances continuum equations like the Navier-Stokes equations, which are
based on the assumptions that transport coefficients are position- and time-independent and state variables like temperature and density do not alter significantly on length and time scales comparable to the molecular mean free path and molecular relaxation time, remain no longer valid. Hence the usual continuum modeling methods should be avoided and the atomistic methods which account for the solvent-solvent and solvent-wall molecular level interactions must be adopted. In the present decade, Molecular Dynamics Simulation (MDS) has evolved as the most popular of the atomistic methods to study the molecular level physics of fluid flow in nanoconfinements [6-8]. In many cases the results obtained through MDS for the case of extreme confinement can show strong resemblance to the continuum case. For example, Poiseuille flow simulation of simple fluids in channels of height of only 10 molecular diameters show a quadratic velocity profile [11]. However, for many cases this strong confinement alters the physics so drastically that such resemblance is never observed. For example, the fact that the characteristic length scales for velocity variation approach the molecular scales close to the solid-liquid interface often gives rise to ‘apparent slip’ wall boundary conditions for narrow confinements, in order to relieve a stress singularity at the contact lines between multiple phases. Such slip phenomena are strong functions of the solid-fluid interaction energy or the wettability (hydrophobicity/hydrophilicity) of the surface [12-14]. Investigation of this dependence of the slip behaviour and hence the flow physics on interface wettability is best performed through the use of MDS [8, 15-17], since it directly captures the physics of molecular scales, which are otherwise not tractable through up-scaled mesoscopic or macroscopic simulations.

Nagayama and Cheng [18] were amongst the early researchers to use MDS to study the effect of interface wettability on pressure-driven transport of Lennard-Jones (LJ) fluid in a nanochannel. Among other noteworthy contributions in this area are the works of Priezjev et. al. [19], Yang and Fang [20], Yang [21] etc.

In almost all the existing studies on the effects of interfacial wettability in nanochannel flows, the researchers have assumed uniform surface characteristics (either entirely hydrophilic or entirely hydrophobic), for a given situation so as to compare the effect of variable wettability on the flow physics. However, there is rarely any work that discusses the details of molecular transport and the resultant flow features if patches with designed wettability conditions are simultaneously present on a nanochannel surface, although such studies have been executed with lower resolution physical models (the lattice Boltzmann model, for example). The repelling action of the hydrophobic surfaces and the attractive effect of the hydrophilic ones would be simultaneously operative in such a situation, leading to interesting behaviour at the molecular level.

In the present work, water flow in a nanochannel with surfaces having different designs composed of patches/boxes of alternate hydrophilic and hydrophobic zones is investigated. In one design there are alternate patches of hydrophilic and hydrophobic surfaces whereas in another design the hydrophilic and hydrophobic surfaces are arranged in a checker box pattern. The interactions between the water molecules among themselves and with the wall atoms are modeled through LJ potential, with necessary adjustments in the values of the LJ coefficients to account for the interface wettability. Results show that for the case with alternate patches along the channel length, there can be a strong backflow across the channel section bounded by hydrophilic walls. Presence of such backflow can be favourably exploited to devise a nano-mixer in a very low Reynolds number regime where mixing by conventional means is impossible. For a checker board pattern, however such backflow is absent primarily due to the mutually nullifying action of the hydrophilic and hydrophobic patches that are placed in extreme proximity of one another.

2. Modeling and Simulation

In the present study, we consider the transport of liquid water (assuming it to be a simple LJ fluid) through a nanoslit bounded by two solid walls in the z-direction (See fig 1a), whereas the other two dimensions are much larger. The distance between the inner layers of the solid atoms on the two walls is chosen as 10σ_f, where σ_f is a characteristic molecular length scale for the fluid phase. Apart from the case of channels with homogeneous surface conditions (i.e., either entirely hydrophobic or entirely hydrophilic), we also consider channels with surfaces having alternate patches of hydrophilic and hydrophobic zones.
(See fig 1b), and surfaces having checker board arrangement of hydrophobic and hydrophilic zones (See fig 1c).

For both the fluid and the wall atoms, the LJ potential is used to calculate the intermolecular interaction. The LJ potential for water-water interaction is given by

$$U(r_{ij}) = \begin{cases} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] & r_{ij} \leq r_c \\ 0 & r_{ij} \geq r_c \end{cases}$$  \hspace{1cm} (1)

where $r_{ij}$ is the distance between the water molecules $i$ and $j$, $\varepsilon_{ij}$ and $\sigma_{ij}$ are the energy and the length scales of the water phase respectively. $r_c$ is the cut-off radius beyond which the water-water LJ interaction is neglected. For the present problem we use $r_c = 2.5\sigma_f$, $\varepsilon_f = 1.67 \times 10^{-21}$ and $\sigma_f = 0.34 \text{nm}$.

The interaction potential between the liquid and the wall atoms is expressed through the modified LJ interaction given as

$$U(r_{fw}) = \begin{cases} 4\varepsilon_{fw} \left[ \left( \frac{\sigma_{fw}}{r_{fw}} \right)^{12} - c_{fw} \left( \frac{\sigma_{fw}}{r_{fw}} \right)^{6} \right] & r_{fw} \leq r_c \\ 0 & r_{fw} \geq r_c \end{cases}$$  \hspace{1cm} (2)

where $\sigma_{fw}$ and $\varepsilon_{fw}$ are the wall-fluid parameters identical to $\sigma_f$ and $\varepsilon_f$, respectively. The parameter $c_{fw}$ accounts for the surface wettability. In the present study, $c_{fw}$ is varied from 0.5 to 1.0, leading to the contact angle variation from $\theta = 140^\circ$ to $90^\circ$ at fluid-solid interface, the extremities being designated as hydrophobic and hydrophilic surfaces, respectively [15]. Thus, in the present simulations, depending on whether we are treating the interaction of the water molecule with a wall atom in the hydrophilic or hydrophobic patch/box, we choose the appropriate value of the parameter $c_{fw}$.

For the simulation purpose we choose a simulation cell of $z$-dimension equal to that of channel height ($10\sigma_f$), $x$-dimension of $10\sigma_f$ and $y$ dimension of $4\sigma_f$. A total of 400 water molecules is assumed to be present in the box. Water molecules are initially placed at the site of a simple cubic lattice. The two walls are made up of a single layer of atoms placed on a FCC lattice arrangement. From the interaction potentials (eqs. 1 and 2), one can calculate the total intermolecular force $\sum_{i,j} \vec{F}_{ij}$ on the $i^{\text{th}}$ water molecule due to the other moieties (other water molecules and wall atoms) present in the system. Hence the total force on the $i^{\text{th}}$ water molecule is given by:

$$\vec{F}_i = \sum_{i,j} \vec{F}_{ij} + \vec{F}_e$$  \hspace{1cm} (3)

where $\vec{F}_e$ is the external driving force applied in the x-direction due to the externally applied pressure gradient. The pressure is fixed at the inlet and exit of the simulation cell (thereby fixing the pressure gradient which is $1000 \text{ kN/m}^3$), and it is assumed that the pressure varies linearly between these two values. Thus, with a prior knowledge of the x-coordinate of a given water molecule at a given time instant in the simulation cell, one can ensure the value of $\vec{F}_e$ for that molecule at the said time instant. Eq. (3) gives the force equation at the time instant, say, $t$, which is now integrated by Velocity-Verlet algorithm to obtain the instantaneous position of the water molecules at the instant $t + \delta t$, where $\delta t$ is the simulation time step equal to $10^{-14} \text{s}$. These position values are modified through the application of periodic boundary conditions in $x$ and $z$ directions and the bounce-back (assuming elastic collision) boundary condition in $y$-
direction (wall bounded direction). Throughout the simulation, the temperature is kept constant using Velocity-scaling thermostat. After equilibration, average properties like the flow velocity and the number density distribution is calculated by a standard averaging technique popularly known as the binning method.

![Hydrophobic](Hydrophobic)  ![Hydrophilic](Hydrophilic)

**Fig 1c**: Channel surface with checker box arrangement

### 3. Results and Discussions

As a validation of the code developed for the present work, we first consider a well-documented case of transport of water through a purely hydrophobic surface [18], and investigate the resemblance of our results with the reported simulation data. Figure 2 plots the transverse variation (with z direction) of the axial component of the flow velocity for a channel with smooth hydrophobic walls for a dimensionless force value of $F_e=0.4$. The result is obtained by averaging over the other two directions. The MDS outcome here mimics the continuum flow situation under a constant externally applied pressure gradient. For the continuum case, the flow profile is parabolic with maxima at the channel centerline and zero velocity at the walls (no slip condition). The MDS result is compared with this as the reference. Like the continuum case, MDS result also gives maxima close to the channel centerline. However, at locations away from the centerline, relatively flatter plug-shaped profile exists. Physically this result is in strong agreement with the works of Nagayama and Cheng [18] (See fig 4d of Nagayama and Cheng [18]), which predict a plug shaped flow profile across the entire channel section for hydrophobic surfaces. For hydrophobic channels there is partial or even no wetting of the surfaces, depending on the value of the Lennard Jones wettability parameter $c_{fw}$. Smaller the value of $c_{fw}$, smaller is the force of attraction of the water molecules to the wall atoms (indicated by a larger obtuse angle value of the contact angle) and hence lesser is the surface wettability. Thus, one can expect a distinct reduction in the force of interaction of the wall atoms with the water molecules for hydrophobic surfaces. This would mean a significant lowering in the inter-particle (wall atoms-water molecules) shear stress, resulting in a much flatter velocity variations at locations intermediate to the near-wall regions and the channel centerline. Important information that can be extracted from fig. 3 is that if one extrapolates the velocity variations in the near-wall regions towards the solid boundary in the vicinity, then a non-zero slip velocity at the walls becomes apparent. Such microscopic slip is characteristic of hydrophobic surfaces. The reduced interaction of the water molecules with hydrophobic wall atoms creates a depletion zone in the wall-adjacent layers. This leads to nanobubble or depleted gas gap formation, which is the principle physical cause behind this slip [21]. In the existing literature, there is a strong controversy regarding the strength of this slip for hydrophobic surfaces. The extent to which slip occurs at the walls must be commensurate with the nature of the velocity profile existing across the channel. Thus, for a plug shaped velocity field where the near wall velocity would not be much reduced in comparison to the channel centerline velocity, a strong slip would exist at the walls, as can be observed from the present results. This is identical to the predictions of Nagayama and Cheng [18], who too obtained plug shaped velocity variations. Such a strong slip, however, is not manifested for the hydrophilic flow situations with nearly-parabolic velocity profiles obtained, as observed from the results of Yang [21] (See fig 3a of Yang [21]).
Figure 2: Axial velocity variation along with the channel height for a hydrophobic surface for $F_e = 0.4$. The units of velocity is in $\mu$m/sec and $z$ axis is in $\sigma_f$.

In the next part of the simulation, we consider that both the channel top and bottom walls have alternate patches of hydrophobic and hydrophilic surfaces (see fig 1b). Figure 3 gives the axial velocity variation across the channel height for a cross section bounded by the walls with hydrophilic patches on both sides. Existing literature [18, 21] suggests that for hydrophilic channels, the velocity profile falls to zero in the channel interior, indicating the absence of slip. In our MDS result also (fig 3), such a zero velocity is attained in the channel interior at particular locations from either of the channel walls. Beyond that location there exists a strong back current, which is in sharp contrast to the published results which suggest no further velocity variation once the zero velocity has been attained. Such a back flow can be attributed to the presence of hydrophobic patches that exist adjacent to the hydrophilic zone over which the velocity variation is plotted. Such alternate patches have not been considered in the existing literature on MDS for nanochannel flows. In the region of this backflow itself, the velocity first increases (in magnitude) and again decreases (in magnitude) as one move more and more towards the channel wall. Hydrophobic patches strongly repel the water molecules and thus they come in the zone of hydrophilic patches. The repelling action is strongest in proximity to the hydrophobic zones. Once repelled, the molecules would try to cluster over the nearest hydrophilic patches. At such locations, the molecules are primarily under the influence of the intermolecular forces of interaction exerted by the originally present water molecules and the hydrophilic wall atoms. The water molecules would exert a repelling thrust, which would create a component of velocity in the axially backward direction, ultimately resulting in the backflow.

Figure 3: Axial velocity variation along the channel height for $F_e = 0.4$ for cross section bounded by walls with hydrophilic patches in a channel with walls having alternate hydrophilic and hydrophobic patch. The units of velocity is in $\mu$m/sec and $z$ axis is in $\sigma_f$.

Figure 4: Velocity variation along with the channel height for $F_e = 0.4$ averaged over different cross sections for the channel with alternate hydrophilic and hydrophobic zones. The units of velocity is in $\mu$m/sec and $z$ axis is in $\sigma_f$.

From the device design point of view, one may be interested to know the overall volume flow rate in such a channel with alternate hydrophilic and hydrophobic patches. For this purpose we plot the axial velocity variations with channel height, averaged over different cross sections encompassing the alternate hydrophilic and hydrophobic patches, as depicted in fig.4. For either of the hydrophilic or the hydrophilic zones, there will always be a maximum in the velocity at the channel centerline. Thus, in the longitudinally-averaged velocity profile too, there exists a maximum at the channel mid plane. To be more precise, in the zone close to the channel mid plane, there exist alternate locations of maxima and minima. The effect of the backflow that existed in the hydrophilic zone is reflected in the presence of a strong minima (comparison of figs 3 and 4 suggest that the location of this minima coincides with the location of the maximum in the backflow for the flow at the cross section with the hydrophilic patch) from either walls in this averaged velocity
representation. At the walls, there will exist a
slip condition for the hydrophobic patch and a
no-slip condition for the hydrophilic patch. The
integrated effect of this (fig 3) shows a net slip at
the walls

In the final part of the simulation, we
consider a ‘checker box’ arrangement of the
hydrophilic and hydrophobic patches at the
channel walls (See fig 1c). Thus, at a given cross
section there will be alternate regions of
hydrophilic and hydrophobic surfaces. Figure 5
gives the density variation with the channel
height, at such a cross section averaged over the
width i.e., alternate boxes of hydrophilic and
hydrophobic surfaces. The large density peaks at
near wall locations represents the strong layer
formation of water molecules at the wall.
Attractive wall-fluid interaction, primarily
contributed by the hydrophilic boxes, is the
principal cause behind such layering effect.
Instead of a ‘checker box’ arrangement if one
had a homogeneous smooth hydrophilic surface,
then these high density fluid layers at near wall
locations will induce further layering. This
layering effect progressively weakens with
increasing distance from the wall [8]. As a result,
one will obtain more number of such density
peaks having gradually reducing strength with
increases in distance from the wall (See fig 2 of
Ref 8). For the present ‘checker box’
arrangement which represents a combined
physics of the flow in hydrophobic and
hydrophilic surfaces, contributions from the
molecules coming from the hydrophobic regions
are mostly absent at the near-wall locations,
since they are acted on by strong repulsions from
the walls. Hence close to the wall, layering
phenomena identical to that in a pure hydrophilic
surface starts to occur and one observe that the
density peak formed just next to the maximum at
the wall gets reduced in strength as compared to
the latter. At larger distances from the wall,
contribution of the molecules in the hydrophobic
region becomes important. These molecules are
repelled from the hydrophobic walls and cluster
at locations significantly away from the channel
wall. This will mean that at locations away from
the wall, the decreasing density value due to
progressively weakening layering effect,
characteristic of a pure hydrophilic surface, is
boosted up by the contribution of these
molecules coming from a hydrophobic surface.
Thus, the strength of the number density
maxima, even away from the walls, does not
reduce significantly in strength, unlike what
happens for a pure hydrophilic surface (See fig 2
of Ref 8).

Figure 6 gives the velocity variation
with the channel height for the same cross
section (and under identical averaging) as that of
fig 5. This velocity must give an averaged
representation of the involved physics in
alternate zones of hydrophobic and hydrophilic
surfaces. In this regard, it is qualitatively pretty
similar to the case depicted in fig 4. Thus,
similar to fig 4, in fig 6 also one observes a
number of velocity maxima in the zone
surrounding the channel centerline and a strong
reduction of the velocity value at near wall
locations. The justification for such variation is
already presented for that of fig 4, and hence is
not repeated here. The only difference lies in the
fact that the central velocity maximum for fig 6,
is much smaller as compared to the other
maxima. This is in sharp contrast to that of fig 4,
where all the velocity maxima are virtually
identical in strength. From the discussion of
density distribution (fig 5), it is clear that the
hydrophilic boxes are responsible in pushing the
molecules more and more towards the wall,
whereas the hydrophobic boxes push the
molecules towards the channel center line. There
are also chances that this repelling push from the
hydrophobic boxes becomes such that the
molecules actually cross-over to the hydrophilic
zone and subsequently represent the
characteristics of the hydrophilic surfaces. Effect
of this cross-over can be significantly large,
as we are dealing with the velocity profile only
within a small sectional zone of the channel
containing relatively small number of molecules.
This cross-over for fig 6 will mean that for the
cross section under study, the contribution of the
molecules from the hydrophilic zone is stronger
than that of the hydrophobic zone. The
hydrophilic zone molecules have a tendency to
be skewed towards the wall. This implies that the
velocity maxima that are slightly skewed
towards either of the canal walls are of much
larger strength as compared to the one that is
centrally located. For fig 4, where the entire
channel length was considered for averaging,
there were sufficiently large number of water
molecules that were considered for averaging
and hence the effect of this local cross-over from
hydrophobic to hydrophilic zones was small
even for any significant contribution,
thereby implying that all the velocity maxima
were virtually of equal strength.
A detailed investigation of the water transport in channels of the order of 5 nm with varying surface wettability has been conducted. The initial results validate the existing works [18, 21] of nanochannel transport in conduits of homogeneous wettability characteristics (hydrophilic/hydrophobic). Subsequently, flow physics is investigated in channels which have different geometrical combinations of these hydrophilic and hydrophobic patches. In channels with alternate hydrophobic and hydrophilic patches, the velocity variation across a hydrophilic patch shows a strong backflow at the near-wall locations. Such backflow can be explained by virtue of the entrance of the molecules into the hydrophilic zone after being repelled from the hydrophobic zone and the subsequent complex interplay of the interactions that operate between these newly entered molecules with the molecules of the hydrophilic zone and also the wall atoms. In channels with ‘checker box’ arrangement of hydrophilic and hydrophobic zones, a number density variation is obtained that characterizes a pure hydrophilic surface at near-wall locations [8], but deviates strongly at other location. The velocity distribution in such a ‘checker box’ arrangement is also represented as a weighted average of the contribution of the hydrophilic and hydrophobic patches, with the weights being functions of the varying nature of interaction of the molecules with patches of varying wettability.

4. Conclusions

A detailed investigation of the water transport in channels of the order of 5 nm with varying surface wettability has been conducted. The initial results validate the existing works [18, 21] of nanochannel transport in conduits of homogeneous wettability characteristics (hydrophilic/hydrophobic). Subsequently, flow physics is investigated in channels which have different geometrical combinations of these hydrophilic and hydrophobic patches. In channels with alternate hydrophobic and hydrophilic patches, the velocity variation across a hydrophilic patch shows a strong backflow at

References

molecular separation in nanoscale fluidic channels, Lab Chip 5, 1271-1276, 2005.