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BOUNDARY CONDITIONS FOR MOLECULAR DYNAMICS SIMULATION OF WATER TRANSPORT THROUGH CARBON NANOTUBES

Docherty S.Y.*, Nicholls W.D., Borg M.K., and Reese J.M.
*Author for correspondence
Department of Mechanical and Aerospace Engineering,
University of Strathclyde, Glasgow G1 1XJ, UK
E-mail: stephanie.docherty@strath.ac.uk

ABSTRACT

We compare both new and commonly-used boundary conditions for generating pressure-driven flows through carbon nanotubes (CNTs) in molecular dynamics (MD) simulation. Three systems are considered: a finite CNT membrane with streamwise periodicity and gravity forcing; a non-periodic finite CNT membrane with reservoir pressure control; and an infinite CNT with periodicity and gravity forcing. The first system is simple to implement in common MD codes, while the second system is more complex to implement, and the selection of control parameters is less straightforward. The required level of user-input for such a system was found to be largely dependent on selection of state controllers used in the reservoirs. A large pressure difference is required across the realistic membrane system reservoirs to compensate for large pressure losses at the entrance and exit of the nanotube. Despite a dramatic increase in computational efficiency, an infinite length CNT does not account for these significant inlet and outlet effects, suggesting that a much lower pressure gradient is required to achieve a specified mass flow rate. Use of an infinite channel also restricts natural flow development through the CNT due to explicit control of the fluid. Observation of radial density profiles suggest that this results in over-constraint of the water molecules in the channel.

INTRODUCTION

Efficient desalination of salt water is an increasingly important issue, as the World Health Organization estimates that four billion people in 48 countries will not have access to sufficient fresh water by the year 2050. Aligned carbon nanotubes (CNTs) as part of a membrane have been found to possess properties that are potentially of use in filtration and desalination applications. Key characteristics observed are very fast mass flow rates (much faster than is predicted from the Hagen-Poiseuille equation), along with excellent salt rejection capabilities [1]. Although advances are being made in nano-fluid experimental work, there is still significant difficulty in experimental measurements for devices at this scale [2].

Although computationally intensive, non-equilibrium molecular dynamics (MD) simulation has recently been adopted as the numerical procedure of choice for nanoscale fluid dynamics due to its high level of detail and accuracy. Simulation of fluid transport through a CNT in MD requires generation of quasi-steady pressure-driven flow, which can be achieved by application of boundary conditions to the flow domain. Various boundary condition configurations exist, each with advantages and disadvantages, and selection often depends on the desired balance between computational efficiency and accurate representation of physical experiment.

There are two common approaches to CNT simulation in MD. The first is to model the CNT as part of a finite membrane in which the CNT is placed between two reservoirs that are set at different hydrostatic pressures. When using this approach, either periodic or non-periodic boundaries can be implemented in the streamwise direction. An existing technique, which uses streamwise periodicity and numerical permeability to generate a streamwise pressure difference across the CNT, is the "reflective particle membrane" (RPM) [3]. This RPM, located at the inlet of the system, controls the number of molecules crossing the inlet boundary in the negative streamwise direction probabilistically, hence adjusting the upstream reservoir density. It is however very difficult to control the pressures in both reservoirs and so extensive trial and error is required to achieve the desired pressure difference. A more common technique which uses streamwise periodicity, is to apply an external uniform streamwise force to molecules in a specific region in the upstream reservoir [4].

Despite increased computational efficiency and simplicity, periodic boundary conditions carry limitations and so non-periodic streamwise boundaries are often applied. One example is the method of self-adjusting plates [5] in which external forcing is applied to plates located at the outside boundaries of the system to achieve the desired pressure in each reservoir. However, as the number of molecules in the simulation is fixed, all molecules will eventually be forced out of the upstream reservoir, effectively ending the simulation. Another fairly new technique [6] which implements non-periodic boundaries is one in which the upstream system boundary is a specular-reflective wall, while the downstream boundary deletes molecules upon contact. Upstream pressure control is performed by use of a proportional-integral-derivative (PID) control feedback loop algorithm, along with adaptive mass-flux control at the inlet to replenish the system, while downstream pressure is controlled using a pressure flux controller.

The second approach to CNT simulation in MD involves modelling only a section of the nanotube and applying

streamwise periodicity to create a CNT of infinite length. Although this significantly reduces computational expense, there are concerns that significant inlet and outlet effects are not accounted for [7–9]. The most popular method for producing fluid flow for this configuration is to apply an external uniform force to all molecules in the CNT, known as the gravitational field method [10].

The aim of this paper is to compare several of these techniques in terms of flow behaviour, computational efficiency, and required level of user input. Three systems will be simulated: a finite CNT membrane with streamwise periodicity and gravity forcing; a non-periodic finite CNT membrane with reservoir pressure control; and an infinite CNT with periodicity and gravity forcing.

NOMENCLATURE

A_{cs}	[m^2]	Cross-sectional area of CNT
dp/dx	[MPa/nm]	Pressure gradient along CNT
f_g	[N]	Force applied to each molecule
$f(x)$	[N]	Streamwise forcing function
L	[nm]	Length of CNT
n	[m^{-3}]	Number density
N_{cnt}	[-]	Number of molecules inside CNT
ΔP	[MPa]	Pressure difference across system
t_f	[m]	Length over which forcing is applied
$T_{\Delta t}$	[s]	Execution time for one MD time-step
U	[m/s]	Streaming velocity through CNT
Δt	[s]	Time-step

SIMULATION METHODOLOGY

All simulations are performed using OpenFOAM [11]. This incorporates a parallelised non-equilibrium MD solver, mdFoam [12–14], written in the research group of the authors. In MD simulation, molecular motion is determined by Newton's second law. Integration of the equations of motion is implemented using the Verlet leapfrog scheme with a time step of 1×10^{-15} seconds. The water model chosen is the 4-site rigid TIP4P water model. This consists of a neutral oxygen atom site (O); positive electrostatic point charges of +0.4238e at the two hydrogen sites (H); and a negative electrostatic point charge of -0.8476e at a site M, just above O along the bisector of the HOH angle. Potential interaction between water molecules is represented by Lennard Jones (LJ) interaction between oxygen atoms only using the following parameters: σ_{OO} = 3.154$\mathring{A}$ and ϵ_{OO} = 0.6502 kJ mol^{-1}. Similarly, the carbon-water interaction is based only on the carbon-oxygen LJ potential using the following parameters: σ_{CO} = 3.19 $\mathring{A}$ and ϵ_{CO} = 0.392 kJ mol^{-1} [15]. Both electrostatic and LJ interactions are smoothly truncated at 1.0 nm.

The type of CNT used in this work is a (7,7) single-wall CNT with a diameter of 0.96 nm, which has been identified as possessing optimum attributes for desalination; it removes 95% of salt while transporting water at a suitably high flow rate [1]. To construct a model CNT membrane in MD, the CNT is placed between two perpendicular graphene sheets. To speed up the simulations, both the CNT and graphene sheets are modelled as rigid structures as previous studies have indicated that this is a fair assumption [9]. The CNT has a length of 2.5 nm while the fluid reservoirs have dimensions of 4.4 $\times$ 4.4 $\times$ 4.4 nm^3. In all simulations, periodic boundary conditions are implemented perpendicular to the streamwise direction.

When using a membrane configuration, fluid is controlled inside the fluid reservoirs in such a way that the flow dynamics inside the CNT are not disturbed. A Berendsen thermostat [16] is applied to both reservoirs to maintain a constant temperature of 298 K, removing any effects of temperature gradients on the fluid flow. To ensure fair comparison, a pressure difference of 200 MPa is imposed across all of the CNT membranes with the downstream reservoir maintained at atmospheric conditions. Such a significant pressure difference is essential to resolve the flow dynamics over the small time scales accessible in MD. In reality, industrial filtration processes use pressure differences of 5-7 MPa however resulting flow rates are too low for resolving a signal in MD due to high molecular noise. In both membrane simulations the reservoirs are initialised with water molecules, after which the CNT is opened and allowed to fill naturally. On reaching steady state conditions with a constant fluid velocity through the CNT, averaging of properties is then performed over a period of 4 ns.

System 1: Finite CNT membrane with streamwise periodicity and gravity forcing

Fully periodic boundaries are often employed in MD [17, 18] as they allow for representation of a large system with simulation of only a small volume. This can significantly reduce the computational expense of MD and hence increase achievable problem time scales with the same computational resources.

The combination of a fixed membrane, streamwise periodicity, and streamwise external forcing generates a pressure difference across the CNT. Regardless of the chosen form of forcing, use of this technique alone can produce the correct streamwise pressure difference across the CNT, however negative pressures can be observed in the downstream reservoir [19]. Such conditions are not an accurate representation of reality, and so density control is implemented in the bulk regions of both reservoirs to achieve atmospheric conditions in the downstream reservoir while maintaining the desired pressure difference.

Figure 1 shows a schematic of the simulation domain where "gaussian forcing" is distributed across both reservoirs. The variation of this gaussian forcing as a function of the streamwise coordinate is given by,

$$f(x) = \frac{\Delta P}{n\sigma\sqrt{2\pi}} e^{\frac{-x^2}{2\sigma^2}}, \tag{1}$$

where ΔP is the desired pressure difference across the reservoirs, n is the number density in the upstream reservoir, $\sigma = t_f/4$, and t_f is the streamwise length over which the force is applied. This forcing curve, shown in Fig. 2, produces a much smoother force variation in comparison with that of uniform forcing [4].

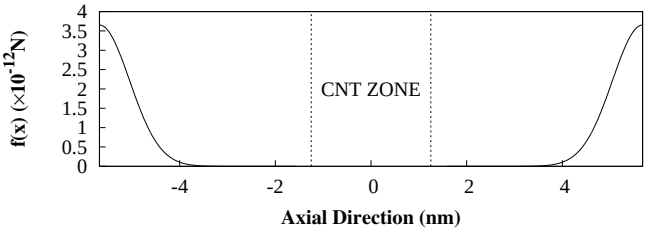

Figure 2: Gaussian distribution of streamwise forcing across the domain.

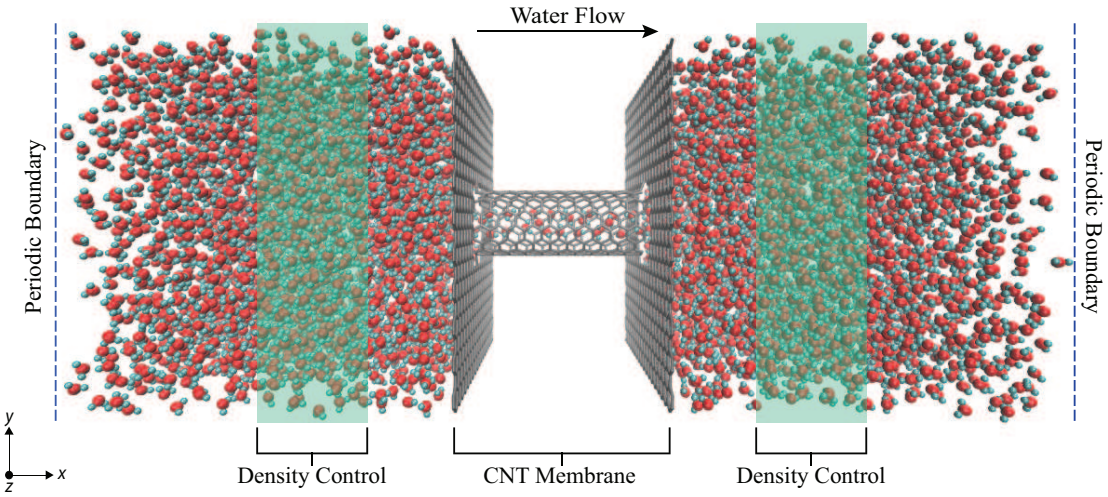

Figure 1: System 1 simulation domain, with streamwise periodicity and gaussian forcing.

This increases continuity of properties across the reservoirs, which can be observed by considering the resulting pressure profile across the system, shown in Fig. 3. Variation of pressure at the periodic boundaries of the system is gradual and smooth, levelling out to the bulk pressure value closer to the membrane.

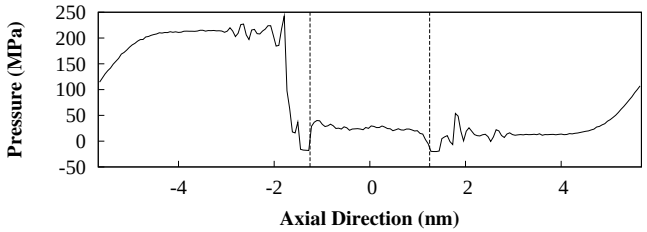

Figure 3: Axial pressure distribution across System 1.

System 2: Finite CNT membrane with streamwise non-periodicity and reservoir pressure control

Although more computationally intensive than periodic boundaries, non-periodic boundary conditions are necessary to simulate many engineering applications, for example in systems which require different inlet and outlet conditions/geometries. Hybrid MD-continuum simulations also require application of non-periodic boundaries to achieve continuum-like boundary conditions prescribed from the continuum solution at the coupling interface.

Implicit pressure control can be achieved through control of density and temperature at fixed values in both reservoirs [20] and use of specular-reflective walls at both boundaries. Although this method is effective, it is sometimes more practical to control pressure directly. This can be achieved using a new boundary condition configuration [6]. Upstream pressure is controlled explicitly by use of a PID feedback loop algorithm which exerts an external force over all molecules in a user defined control region. Three separate components of force are summed to create this external force: a proportional term, derivative term, and an integral term. Adaptive control of the mass-flux is implemented at the inlet to compensate for the molecules leaving the system. Downstream pressure control is performed using a pressure flux technique [21] such that flow can develop through the nanotube without over-constraint. Non-periodic boundaries are implemented in the form of a specular-reflective wall upstream while the downstream boundary deletes molecules upon contact, creating an open system [22]. This in turn regulates the pressure flux forcing automatically. While the pressure flux technique is suitable for control at low pressures, the PID control method is more effective at high pressures. This boundary condition configuration, summarised in Fig. 4, is a fair representation of a physical experimental setup. The corresponding pressure profile across the system is displayed in Fig. 5. A drop in pressure occurs towards the downstream boundary due to deletion of molecules, however this is not important as it occurs far from the membrane.

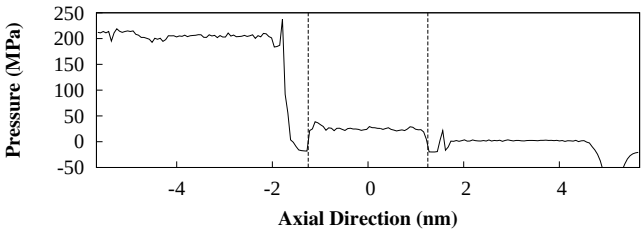

Figure 5: Axial pressure distribution across System 2.

System 3: Infinite CNT with streamwise periodicity and gravity forcing

Modelling a finite length of nanotube and applying streamwise periodicity is equivalent to simulation of flow through an infinitely long CNT. While it reduces computational effort, this technique does not account for the entrance and exit effects that are present in realistic flow through a finite length CNT. A previous study [5] considered the flow of liquid argon through a nanotube and indicated that the influence of these entrance and exit effects on the mass flow rate through the tube can be significant.

In order to imitate a pressure gradient along the CNT, an external force is applied directly to each molecule. To ensure that the behaviour of such a system is comparable to that of a finite membrane system, the number of molecules inside the tube N_{cnt} remains the same. The magnitude of the external force applied to each molecule, f_g, is chosen to produce an average streaming velocity and mass flow rate approximately

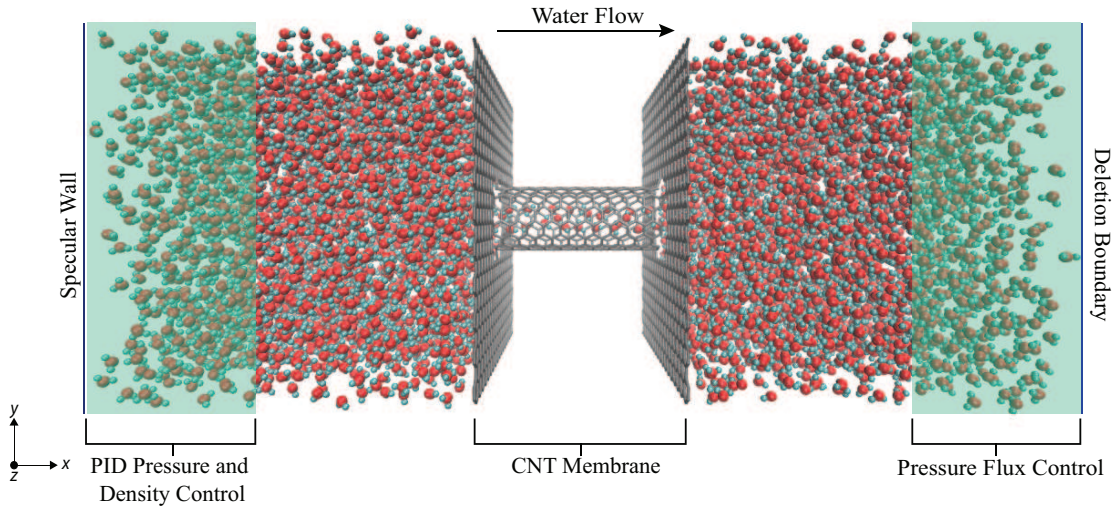

Figure 4: System 2 simulation domain, with non-periodic boundaries and pressure control.

equal to that produced in Systems 1 and 2. From this value of f_g, the equivalent pressure gradient along the tube $\frac{dp}{dx}$, can then be calculated using the following equation and compared with the pressure difference across the membrane systems to quantify entrance and exit pressure losses,

$$\frac{dp}{dx} = \frac{\Delta P}{L} = \frac{f_g N_{cnt}}{A_{cs} L}, \tag{2}$$

where ΔP is the streamwise pressure difference across the CNT, and L and A_{cs} are the length and cross-sectional area of the nanotube, respectively. It is important to note that for smaller CNT diameters, such as the 0.96nm diameter nanotube used in this work, there is difficulty in the definition of A_{cs} due to the structure of the water molecules flowing along the CNT, with no consistency in the literature [23]. The equivalent pressure gradient is dependent on the assumed area, in this case we take it equal to the full cross-sectional area of the tube, and hence there is uncertainty regarding its actual value.

The simulation domain is constructed of only a 2.5 nm length of nanotube, filled with water molecules as shown in Fig. 6. Periodic boundaries are applied in the streamwise direction, and a Berendsen thermostat is used directly on the water molecules inside the tube to control the temperature to 298 K.

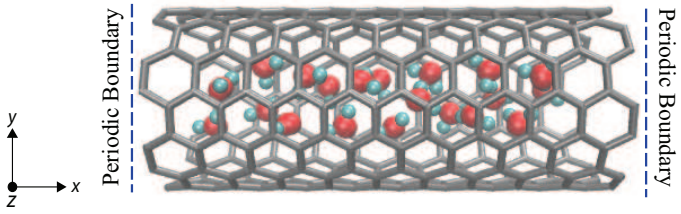

Figure 6: System 3 simulation domain, an infinite CNT with streamwise periodicity.

RESULTS AND DISCUSSION

Inlet and outlet effects

The average streaming velocities U and mass flow rates $\dot{m}$ through the channel over a period of 4 ns are displayed in Table 1 for Systems 1 and 2. As the flow through the CNT is non-continuum, this mass flow rate is measured by averaging the number of molecules which cross a plane located at the midpoint of the tube over a specified period of time. The flow behaviour in Systems 1 and 2 is shown to be very similar, as is expected given that both systems are essentially simulating the same conditions of flow through a membrane.

System	U (m/s)	$\dot{m}$ (kg/s)	N_{cnt}
1	14.51	3.36×10^{-15}	19.43
2	15.07	3.02×10^{-15}	17.98

Table 1: Average values of flow parameters in Systems 1 and 2.

In order to set up the third system, the number of molecules N_{cnt} inside the CNT must be defined explicitly as it is not possible to fill the CNT naturally. To produce a realistic estimate, simulation of a naturally filled CNT of the same length is required. The average number of molecules inside the channel in Systems 1 and 2, both of which allow the CNT to be filled naturally, are given in Table 1. From these values, the number of molecules inside the channel in System 3 was set equal to 19.

By trial and error it was determined that, to obtain approximately the same steady-state streaming velocity and mass flow rate as Systems 1 and 2, the force applied to each molecule in System 3, f_g, must be 2.39×10^{-14} N. The equivalent pressure gradient along the channel is then calculated using equation (2), giving a value of 0.63 MPa over a length of 2.5 nm, or 0.252 MPa/nm. This is significantly smaller than the pressure gradients across the membrane systems which, from Fig. 3 and Fig. 5, are around 200 MPa over a length of approximately 4 nm, or 50 MPa/nm. Thus, to obtain a specified flow rate along a CNT in a realistic finite membrane system, a much larger pressure difference is required across the reservoirs than is suggested by the required pressure gradient in simulation of an infinite system. This higher pressure difference is neccesary to compensate for significant inlet and outlet effects, which result in large pressure losses at the entrance and exit of the CNT, as observed in Fig. 3 and Fig. 5. This produces a considerably lower actual pressure difference across the nanotube for both membrane systems. Entrance and exit effects also manifest themselves as changes

in fluid properties at the inlet/outlet. Figure 7 displays axial pressure distributions along the nanotube for both membrane systems, measured using the same number of axial bins over a period of 4 ns.

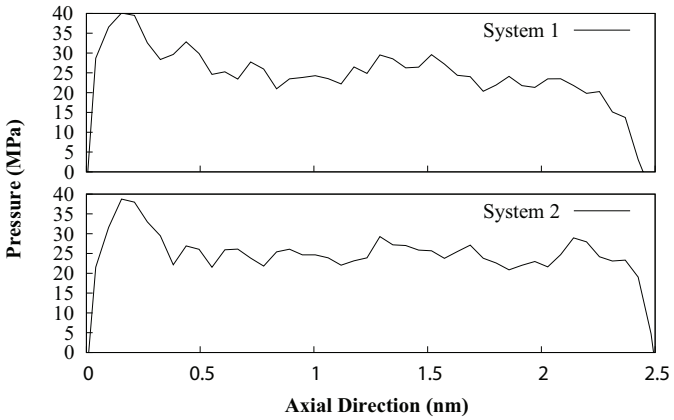

Figure 7: Axial pressure distribution along the nanotube for Systems 1 and 2.

Viscous losses are present at the inlet and outlet of these systems, with a central "developed" region where frictional losses are low. If we ignore these inlet and outlet effects, as the infinite CNT does, and consider only this central region of "developed" flow, we can approximate the pressure gradients in these regions. It should be noted however that, due to noise, these pressure gradients are subject to considerable error. Table 2 displays the pressure gradients along these central "developed" regions, from an axial position of 0.5 nm along to 2 nm, for both membrane systems. Also shown is the equivalent pressure gradient across System 3, in which flow along the entire length of the nanotube can be considered "developed". Very low frictional losses in this system result in the mass flow rate along the tube being very sensitive to changes in the magnitude of f_g.

System	dp/dx (MPa/nm)
1	0.962
2	0.485
3	0.252

Table 2: Pressure gradients in the regions of "developed" flow for all nanotube systems.

As expected, the pressure gradients in the central regions of Systems 1 and 2 are in much better agreement with the equivalent pressure gradient along the infinite CNT. Thus, to produce specified flow rates through a CNT in a realistic finite system, a considerably larger pressure difference is required across the reservoirs than that suggested by simulation of an infinite system, in order to compensate for significant inlet and outlet losses. It is possible that inlet and outlet losses could be less significant in longer CNTs as these central regions of "developed" flow have been found to extend proportionally with the length of the CNT in a membrane system [6].

Radial profiles inside the CNT

The structure of the water molecules flowing along the nanotube can be examined by considering the radial distribution of density in each system, as displayed in Fig. 8. Measurement of radial density is performed along an axial distance of 1 nm in the centre of the CNT, dividing the cross-section of the nanotube into 100 cylindrical bins of equal volume. The mass density in each bin can then be obtained by averaging the mass of water molecules in the bin over time and dividing by its volume.

The single-peak structure shown in Fig. 8 indicates that the average density profile is annular; the water molecules form one circular layer inside the CNT. This is consistent with previous results [6, 23]. Each of these profiles is normalised using the density of the downstream reservoir in the membrane systems. There is difficulty in expressing the total mass density in the channel due to the uncertainty in definition of the occupied fluid volume. It is clear from Fig. 8 that the peak density occurs at the same radius for all systems and hence the variation in boundary conditions does not alter the effective radius of the fluid ring. The peak density of System 3 is however significantly greater than in Systems 1 and 2. It is possible that this is caused by the external forcing placed directly onto the molecules in the tube, resulting in over-constraint of their radial movement. The application of temperature control inside the nanotube could also contribute to this behaviour. Another cause could be the explicit specification of the number of molcules inside the CNT. Use of System 3 therefore may not allow for natural development of the flow structure. Radial profiles of pressure and velocity are not considered as they would not provide useful insight into the flow properties because of the single ring structure of the water molecules.

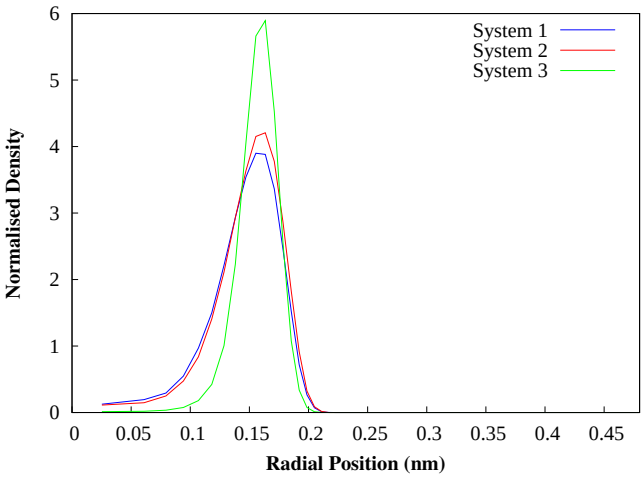

Figure 8: Radial density distributions normalised with downstream reservoir density.

Computational efficiency and ease of set-up

Table 3 shows, for each system, the average execution time for one MD time-step $T_{\Delta t}$, using a time-step of 1 fs, during an averaging period of 4 ns. Each system was simulated using 8 processors (Intel X5570 2.93 GHz CPU).

System	$T_{\Delta t}$ (s)
1	0.358
2	0.427
3	0.015

Table 3: Average execution time for one MD time-step.

Set-up of CNT simulations using molecular dynamics can require various levels of user-input depending on the complexity of the system. Use of membrane configurations, such as that in Systems 1 and 2, involves obtaining the desired conditions in both the upstream and downstream reservoirs. For both periodic and non-periodic boundaries, this can be a time-consuming process depending on the state controllers being used. For example, use of density control to produce a pressure difference across the system can require considerable iteration to achieve the desired pressure values.

Use of forcing with streamwise periodic boundaries as in System 1 requires relatively little input to achieve the desired pressure difference; perhaps some iteration of the forcing values is needed. Additional density control is however required to overcome the negative pressures which appear in the downstream reservoir, hence increasing set-up time and user-input. Use of gaussian forcing requires no additional user input above that of uniform forcing. As indicated in Table 3, implementation of periodic boundaries across a finite membrane system results in lower simulation times than non-periodic boundaries.

Use of feedback PID pressure control as in System 2 drastically reduces user-input, in comparison with density control, as this allows pressure to be defined explicitly. This method is, however, only suitable for high pressures. Due to the high level of control in this system, it is possible that it could be less stable than other configurations. Although this approach is the most computationally demanding of the three systems, it is fairly representative of an actual experimental set-up.

Simulation of an infinite nanotube, such as System 3, requires considerably less user-input than a membrane system if the aim is to specify a forcing value and monitor the resultant flow behaviour. Aside from temperature control, the user must only specify a value of force to be applied to each molecule. It should be noted however that, if the aim is to achieve a desired mass flow rate through the system, time-consuming iteration of forcing values is required. As discussed previously, the flow behaviour is very sensitive to the magnitude of the driving force applied due to the very low level of frictional losses in the system. Due to this, it can take a considerably long time for this type of system to achieve steady-state conditions. There is also difficulty with setting the number of molecules inside the CNT to an appropriate value. Simulation of a naturally-filled CNT of the same length may be required to obtain an accurate estimate. As expected, Table 3 indicates that simulation of an infinite CNT significantly increases computational efficiency. This is however at the expense of inlet and outlet effects, as discussed previously.

CONCLUSIONS

Various boundary condition configurations for the MD simulation of water transport through CNTs have been compared in terms of the resultant flow behaviour and computational efficiency. In modelling the CNT as part of a finite membrane system, flow behaviour was found to be independent of streamwise periodicity. While user-input is largely dependent on the state controllers used, streamwise periodic boundaries are slightly less computationally demanding than non-periodic boundaries. It should be noted that a combination of periodic boundaries and external forcing can lead to negative pressure in the downstream reservoir which requires additional density control, hence increasing simulation time and user-input. Use of PID pressure control allows explicit definition of pressure and hence a low level of user input. Despite a significant improvement in computational efficiency, modelling of an infinite length CNT by use of streamwise periodicity does not account for the important entrance and exit effects that are accounted for in a more realistic membrane system. To produce specified flow rates through a CNT in a realistic finite system, a considerably larger pressure difference is required between the system reservoirs than that suggested by simulation of an infinite system. This is to compensate for relatively large head losses at the inlet and outlet of the nanotube, significantly lowering the pressure difference across the channel. Observation of radial density profiles suggest that explicit control of the fluid inside the infinite nanotube may over-constrain the water molecules. Use of a finite membrane system, however, allows for control to be performed in the reservoirs only, resulting in natural flow development throughout the CNT.

Although this work has focused on boundary conditions for water transport along CNTs, these boundary conditions could be applicable to a variety of scenarios which involve transport of matter through a length of nanotube, for example protein translocation through nanochannels. Future work might involve combination of the techniques described in this paper to produce a "multiscale hybrid" algorithm for simulating longer realistic CNT membrane systems.

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