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MD boundary conditions for pressure gradient flows: nano-mixing, and nano-droplet deformation in extensional flows

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ABSTRACT

We present new algorithms for simulating pressure-gradient flows in molecular dynamics (MD) simulations. Nano-channel inlet and outlet non-periodic boundary conditions are implemented using hydrodynamic state-reservoirs and flux boundary models at arbitrary boundaries of the domain geometry. We demonstrate the new method in a complex nano-mixer configuration and for droplet deformation in extensional flow channels. The technique which we propose is applicable to any complex nano-channel configuration, and may serve as a useful tool in engineering design of nano-scale applications.

Keywords: Nanofluidics, Molecular Dynamics, Hybrid Continuum-Molecular, Boundary Conditions

1 INTRODUCTION

Periodic boundary conditions (PBCs) [1], [2] are by far the most frequently used boundary condition in molecular dynamics (MD) simulations, since they are easy to implement numerically and they conserve mass, momentum and energy at the boundaries. Despite these advantages, PBCs have geometry and periodicity constraints — only simple (typically cubic), symmetric systems close to equilibrium may be simulated. In more realistic engineering problems, however, it is necessary to simulate non-equilibrium MD within arbitrary geometries [3], [4] entailing non-periodic boundary conditions (NPBCs) [5], [6]. An important fluid mechanics problem for the development of nanoelectromechanical systems (NEMS) using MD as the simulation tool, is pressure gradient flows in nano-channels that encompass complex three-dimensional geometrical features, such as bends, constrictions, and multi-inlet and outlet regions of different sizes. The application of the gravitational method [7] concomitant with periodic boundary conditions is ambiguous for simulating these cases, and generally inapplicable for applying pressure gradients, mainly owing to the streamwise pressure and density homogeneities which the method imposes. Another fluid mechanics problem in which development of NPBCs are important is in the implementation of multi-scale hybrid methods, for example, at the coupling interface between the continuum and MD sub-domains.

2 METHOD

We consider a domain of arbitrary geometry, defined by an unstructured polyhedral mesh, as typically used in finite-volume Computational Fluid Dynamics (CFD). The MD fluid occupies the domain geometry and consists of "molecules" that interact through a pair-wise potential $U(r_{ij})$, where $r_{ij} = |\mathbf{r}_{ij}|$ and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the separation vector between a pair of molecules (i, j). The standard shifted Lennard-Jones (LJ) 12-6 potential and the Weeks Chandler Anderson (WCA) potential [2] are used in this paper. The positions $\mathbf{r}_i$ and velocities $\mathbf{v}_i$ of molecules evolve according to standard Newtonian dynamics, using a molecular time-integration step $\Delta t_m = 10$ fs.
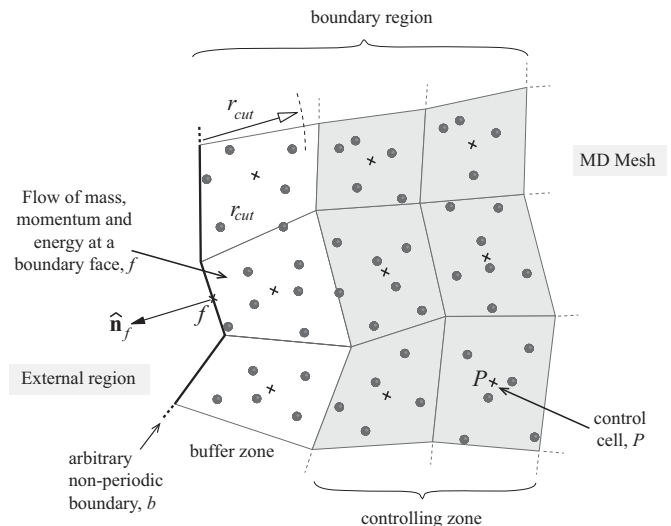

Figure 1: Schematic showing the implementation of our non-periodic boundary conditions at the inlet of a nano-channel using MD. Boundary conditions consist of imposing flow of molecular properties in a buffer region next to an arbitrary boundary b, in addition to feedback-loop control of macroscopic (continuum) properties in the adjacent controlling zone.

An arbitrary non-periodic boundary of the MD domain may be defined as an "inlet" or "outlet". At an inlet, we construct small controlling regions, defined by a group of cells on the mesh (see Figure 1). Con-

trol of hydrodynamic and thermodynamic state properties is established by directly applying perturbations to molecules residing within an arbitrary control cell. This process is facilitated by the 'cell-occupancy' data structure [3], in which each cell on the MD mesh stores an inexpensive link to occupant molecules. Fields of target continuum properties (typically, velocity, density and temperature) are prescribed to the state controller. Control is then performed using a simple feedback loop control system, in which the sampled property (averaged over the preceding time interval $\Delta t \sim 1$ ps) in an arbitrary control cell is first compared with its target property, and then the 'error' is imposed within the same cell over the subsequent Δt.

To manipulate mass density in an arbitrary control cell P, the number of molecules is controlled uniformly over $t \to t_n = t + \Delta t$:

$$\Delta N_P(t \to t_n) = \text{NINT}\left(\left[\rho_P^{\text{t}}(t_n) - \langle \rho_P(t) \rangle \right] \frac{V_P}{m_i} \right), \quad (1)$$

where V_P is the volume of cell P, m_i is the mass of the molecule being inserted, $\rho_P^{\text{t}}(t_n)$ is the target mass density and $\langle \rho_P(t) \rangle$ is the time- and cell-averaged density. The $\text{NINT}(x)$ function is required to apply the nearest integer, since only whole molecules may be introduced ($\Delta N_P > 0$) or removed ($\Delta N_P < 0$). An arbitrary molecule is inserted within the cell using the USHER algorithm [8] so that its initial potential energy is close to the average potential energy of the cell $\langle U_P \rangle$, while an existing molecule is deleted based on its closest potential energy to $\langle U_P \rangle$.[1]

Continuum velocity is controlled by applying an external force to all molecules i within the control cell at uniform control steps within $t \to t_n$

$$\mathbf{f}_i^{ext}(t_k) = \frac{\Delta \mathbf{u}_P(t \to t_n)}{n_{\text{cont}} \Delta t_m} m_i, \quad (2)$$

where $t \le t_k < t_n$, $\{k = 1, 2, \ldots, n_{\text{cont}}\}$, n_{cont} are the number of control steps and

$$\Delta \mathbf{u}_P(t \to t_n) = \lambda \left(\mathbf{u}_P^{\text{t}}(t_n) - \langle \mathbf{u}_P(t) \rangle \right). \quad (3)$$

In Equation (3), $\lambda \sim 0.8$ is a modifiable parameter that defines the rate at which the velocities of molecules occupying cell P are accelerated towards the target value.

Control of temperature involves an adaptation of the velocity-rescaling thermostat [2]. The method scales the velocities of molecules within the control cell P using a scaling factor

$$\chi_P(t_k) = \left(\frac{T_P^{\text{t}}(t_n)}{\langle T_P(t) \rangle} \right)^{1/(2n_{\text{cont}})}. \quad (4)$$

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[1] The potential energy of one molecule is given by $U_i = \frac{1}{2} \sum_{j=1(\ne i)}^{N_{\text{mol}}} U(r_{ij})$, where N_{mol} is the number of molecules within interaction range.

To complete the notion of non-periodic boundary conditions, inlets include also the flow of mass, momentum and energy at the termination edge of the boundary. For mass and momentum flow, molecules are inserted/deleted (using a similar procedure to the density controller) at an arbitrary face f of the boundary to match the target mass flux, $\dot{m}_f = (\rho^t \mathbf{u}^t)_f \cdot \mathbf{A}_f$, where $\mathbf{A}_f = A_f \hat{\mathbf{n}}_f$ is the face-normal surface area vector and $(\rho^t \mathbf{u}^t)_f$ is the face interpolated target mass flux density. Energy flux is implemented by applying external forces on molecules residing within interaction distance ($r_{\text{cut}} = 0.85$ nm) of the boundary so as to include the effect of the missing molecules beyond the boundary [9], [5], [6].

An outlet of a nano-channel is modelled to control the flux exiting the system that contributes to a pressure gradient across the domain. A vacuum boundary condition [10], that is, a boundary model that removes instantaneously the molecules colliding with the boundary, has been shown to produce highly non-linear pressure gradients, as well as uncontrollable (typically, very low) pressure values at the outlet. In our method, the boundary is instead modelled by a diffuse thermal wall, in which colliding molecules are reflected back into the domain with a velocity resampled from a Maxwell-Boltzmann distribution [11]. The mass flux at the same boundary is then controlled at uniform control steps using the relationship:

$$\dot{m}_f(t) = -\frac{V_Z}{n_{\text{faces}} \Delta t} \left(\rho_Z^{\text{t}}(t) - \langle \rho_Z(t) \rangle \right), \quad (5)$$

where Z denotes a large spatial zone, placed adjacent to the boundary, typically covering the entire domain size, and n_{faces} are the number of faces on the outlet boundary; $\rho_Z^{\text{t}}(t)$ is a phenomenological parameter which determines the pressure/density gradient occurring within the target zone. Additionally to this, an energy flux boundary model is applied at the outlet.

3 RESULTS

In order to test these models, we investigate flows of liquid argon molecules, which have a characteristic length scale of $\sigma = 0.34$ nm, a characteristic energy of $\epsilon = 120 k_b = 1.65678 \times 10^{-21}$ J, where k_b is the Boltzmann constant, and a mass $m = 6.69 \times 10^{-26}$ kg. A cutoff radius of $r_{cut} = 2.5\sigma = 0.85$ nm is used. We present our results in reduced units: time, $t^* = t\sqrt{\epsilon/m\sigma^2}$, number density $\rho^* = \rho\sigma^3$, temperature $T^* = T(k_b/\epsilon)$ and velocity $\mathbf{u}^* = \mathbf{u}\sqrt{m/\epsilon}$.

3.1 Simple 2D Poiseuille flow

We verify the new inlet and outlet boundary conditions by applying them to a simple two-dimensional isothermal MD flow channel. The nano-channel of dimensions ($L_x = 175\sigma$, $L_y = 30\sigma$, $L_z = 20\sigma$), consists of

a top and bottom MD face-centre cubic wall of thickness 5σ, and periodic boundary conditions in the cross-channel direction. The inlet region is set to control properties uniformly at values of $\rho^* = 0.6$, $T^* = 2.4$ and $\mathbf{u}^* = (0.5, 0, 0)$, while at the outlet we choose a target density of $\rho_Z^* = 0.5$. Results show a linear pressure and density gradient along the channel, as seen in Figure 2.
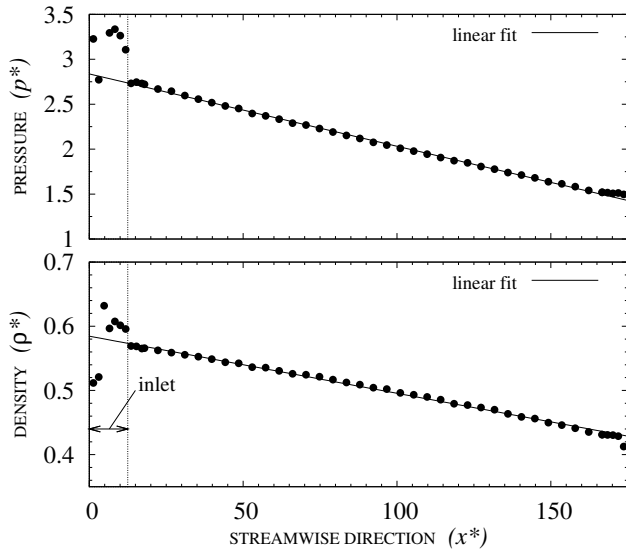

Figure 2: Centre-line profiles of pressure p^* and density ρ^* measured from the Poiseuille flow MD simulation.

3.2 3D complex mixing channel

We now consider a micro-scale mixing channel of three-inlet one-outlet design, taken from Hertzog *et al.* [12], and reduce its scale to nanometers so that reasonable mixing time-scales may be simulated using molecular dynamics. Our modified nano-mixer geometry is constructed using the following route, which we generally adopt for other complex geometry cases. Initially the part is drawn in Pro/ENGINEER®, a commercial computer-aided design (CAD) drawing application, and exported in STEP format (.stp) to GAMBIT® (a meshing utility normally used for FLUENT® CFD). The geometry is meshed using hexahedral cells, and subsequently exported in mesh format (.msh) into Open-FOAM [2], where it is filled with molecules of two species, Fluid I and Fluid II, as shown in Figure 3.

The two fluids are essentially isotopes of argon; the Lennard-Jones potential is used for all I-I, II-I and II-II fluid interactions. Both fluids have identical properties

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[2]OpenFOAM is an open-source toolbox of C++ libraries for computational physics in which our MD code is implemented. It may be downloaded freely from [13].

but different identification (id) numbers, so that mixing can be observed and measured. The non-periodic boundary conditions at the inlet A (Fig 3), supply molecules of Fluid I at a constant rate, $\mathbf{u}_A^* = (0, 0, 0.25)$, while inlets B1, B2 supply molecules of Fluid II at the same rate: $\mathbf{u}_{B1}^* = (0.07, 0, 0)$, $\mathbf{u}_{B2}^* = (-0.07, 0, 0)$. The NPBCs at the inlets are of the same description as in the previous case for Poiseuille flow, with target density and temperature set to $\rho^* = 0.6$ and $T^* = 2.4$ respectively. At the outlet C, the mass flux boundary model removes molecules of Fluid I and II equally, based on the total zonal density $\rho_Z^* = 0.55$. A Berendsen thermostat is applied in the whole domain to keep the local temperature close to $T^* = 2.4$. The values for inlet velocities and the zonal density were selected using a trial and error procedure until satisfactory mixing was observed at the outlet of the channel (see Figure 4).
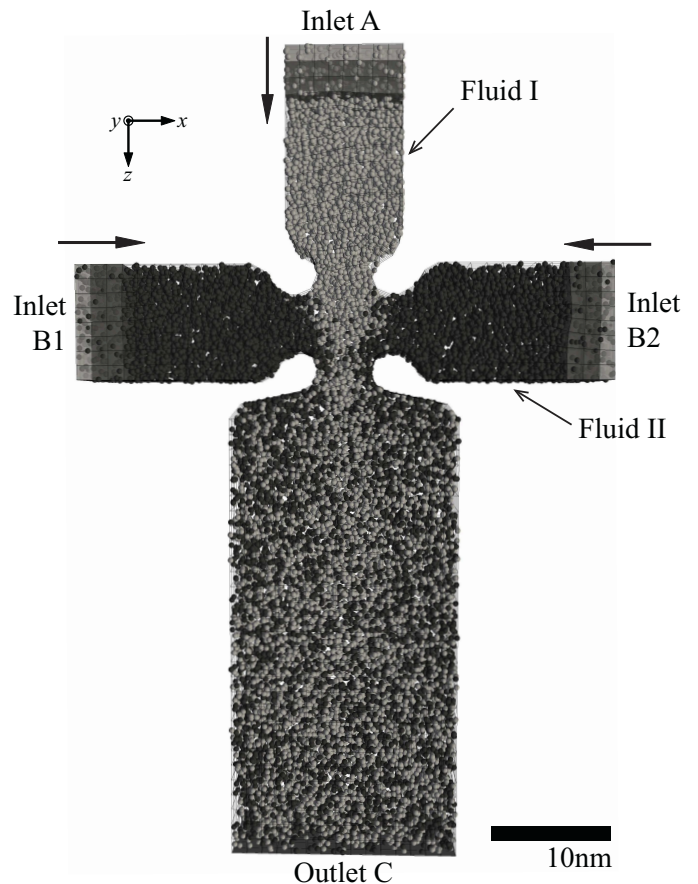

Figure 3: The nano-mixer MD case shown in its mixed state, i.e., after time $t^* = 2000$. Inlet NPBCs are applied at A,B1,B2 boundaries, depicted by the shaded regions, while an outlet NPBC is applied at boundary C. Note: only 30,000 random molecules are shown out of the $\sim$200,000 molecules that occupy the simulation domain.
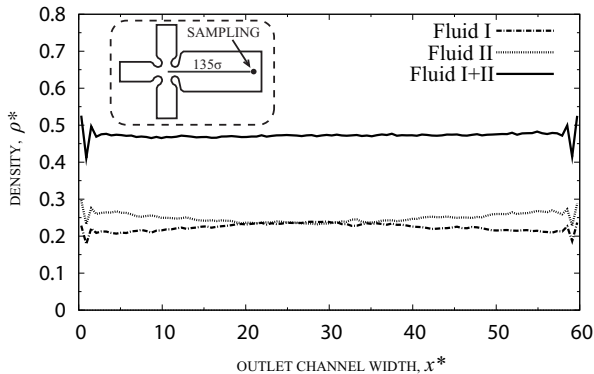
Figure 4: The partial-density cross-channel distribution for both fluids, sampled at the outlet of the mixer.

3.3 Nano-droplet deformation in extensional flow channels

We demonstrate the application of our non-periodic boundary conditions to extensional-type flow geometries in order to investigate emulsion droplet deformation and breakup. Such studies are important in nanofluidic and microfluidic technologies such as heat-exchange devices, lab-on-a-chip components and ink-jet printing.

The domain geometry consists of a cross-shaped nano-channel similar to the mixing channel above. Inlet NPBCs are applied at opposing boundaries (A1,A2), including control of density at $\rho^* = 0.6$, temperature at $T^* = 2.4$, and velocity constrained to point inwards to the domain, i.e. $\mathbf{u}_{A1}^* = (0, -0.25, 0)$ and $\mathbf{u}_{A2}^* = (0, 0.25, 0)$. At the outlets (B1,B2), two independent mass flux boundary models are applied at a value of density $\rho_Z^* = 0.57$, where Z is their respective outlet channel zone. These boundary conditions are imposed in order to create an extensional shear flow at the throat of the channel which acts to elongate, deform and breakup the three-dimensional viscous droplets that will pass through the channel.

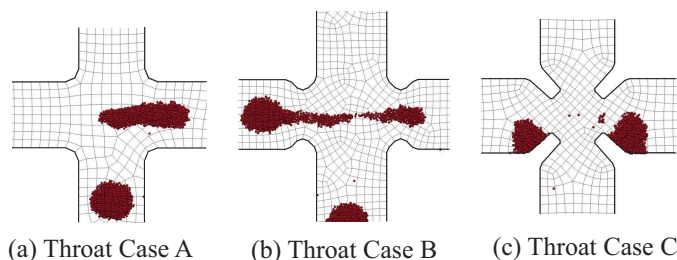(a) Throat Case A   (b) Throat Case B   (c) Throat Case C

Figure 5: The three trial throat geometries used for the extensional droplet flow cases. Solvent molecules are excluded from the snapshots for clarity.

Droplets of 6nm diameter are inserted close to the inlet boundary A1 at a rate of 2.314×10^9 s^{-1}, so that multiple droplets do not interact during their motion

through the channel. The interaction potentials are purposely chosen to prevent the molecules in the droplet (d) from diffusing into the solvent (s). A simple method to implement this is to use the repulsive WCA potential for the droplet-solvent pair-interactions with the following modified characteristics $\sigma_{sd}^* = 1.4$ and $\epsilon_{sd}^* = 0.8$. The droplet-droplet and solvent-solvent interactions are chosen to be the common shifted LJ potential with standard characteristics $\sigma_{dd}^* = \sigma_{ss}^* = 1.0$ and $\epsilon_{dd}^* = \epsilon_{ss}^* = 1.0$.

Deformation and breakup characteristics are generally dependent on a number of factors, such as droplet size, boundary conditions and geometry of the throat. Here we investigate droplet deformation caused by the geometry of the throats and examine the three cases in Figure 5.

The results show that breakup into two smaller droplets occurs more repeatedly in the throat case C, in which the throat geometry at the exit is narrower than the two other cases. In this case, however, all droplets that exit the throat tend to stick to the boundary of the channel due to the attraction characteristics of the wall and low speeds which are present close to the wall. In the other cases, droplets sticking to the wall are rare, due to the larger exit throat sizes.

4 CONCLUSIONS

We have presented new algorithms for applying inlet and outlet non-periodic boundary conditions (NPBCs) in molecular dynamics simulations, in order to set up pressure gradient flows in arbitrary domain geometries. In other work we show how the NPBCs may also be applied to couple a continuum solver with MD, in a hybrid simulation. The boundary conditions are tested in a simple Poiseuille flow channel, in a complex 3D mixing-channel and in a cross-shaped extensional flow nano-channel (to investigate nano-droplet deformation at the throat). The boundary method we propose is parallelised and generally applicable to any complex nano-channel configuration, and so may serve as a useful tool in engineering design and simulation for nano-scale applications.

5 ACKNOWLEDGMENTS

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