Multiscale Simulation of Flow past Nanotubes

XUEYU ZHU

KTH Computer Science and Communication

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Multiscale Simulation of Flow past Nanotubes

XUEYU ZHU

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Supervisor at CSC was Anders Szepessy
Examiner was Axel Ruhe

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Royal Institute of Technology
School of Computer Science and Communication

KTH CSC
SE-100 44 Stockholm, Sweden

URL: www.csc.kth.se
Abstract

An existing hybrid atomistic-continuum coupling scheme is used for multiscale simulation of flow through nano-channels functionalized by the nanotubes. Molecular dynamics (MD) simulation is used to provide the atomistic information near the solid/fluid interface; the region far from the interface is handled by Navier-Stokes equations solved by finite element methods. The hybrid solution reproduced the basic flow pattern of 2D and 3D flow configurations of the MD reference solution qualitatively. In addition, we also did a systematic study of the dependence of the convergence and accuracy on the different parameters in the hybrid scheme.
Multiskalsimulering av flöde förbi nanorör

Sammanfattning

En hybridmetod har studerats för flödesberäkning i nanokanaler med nanotuber, där molekyldynamik används i området kring de fasta kropparnas ränder medan området långt därifrån modelleras med Navier-Stokes ekvationer för inkompressibel strömning. Hybridmetoden reproducerade flädesbilden kvalitativt riktigt jämfört med en referensberäkning med molekyldynamik i hela området. En systematisk studie av konvergens och noggrannhet med avseende på hybridmetodens parametrar redovisas.
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Chapter 1

Introduction

Flow through microscale and nanoscale channels is of fundamental interest for many biological and engineering devices and systems. However, due to the limited knowledge of fluid behavior at the nanoscale, many interesting phenomena that puzzled people for a long time are still not unraveled. Numerical simulation of such a physical system is a preferable approach for many applications, which does not only validate the experiments but also provides the information which is beyond the limits of the experimental observation. In many nano-devices, the molecules are not far from the surface of channel walls. The fluids can not move freely due to the interaction between fluid and solid. In addition, many physical quantities, such as density and viscosity, would deviate from the bulk properties; surface effects dominate in this regime, which leads to a main problem: the continuum hypothesis breaks down at the nanoscale and the simple no-slip boundary condition treatment is not applicable anymore for many cases. Although molecular dynamics simulation (MD) is enough to provide accurate information in that region, it would be computationally prohibitive for those problems with realistic sizes. In fact, full MD simulation is not computationally necessary for the whole domain; only the region near the boundary is needed. The rest of the domain can be handled less costly by the continuum description. In this way, we can not only gain the accurate description from MD, but also utilize the efficiency from the continuum description.

Although several hybrid methods for these multiscale problems have been proposed in the past ten years, no fully satisfactory scheme has been developed. In this project, we summarize the various aspects of a common hybrid solver and focus on one hybrid scheme, which is useful for the steady state solution, based on the alternating Schwarz method. The aim of this project is to examine the performance of the algorithm proposed by Werder
Figure 1.1: Schematic of biosensors based on nanotube arrays [1]

via simulating the flow confined in nanochannels with various surface patterns. The surface is functionalized by carbon nanotubes (CNTs) in order to mimic the realistic system: flow past the nano-biosensors shown Fig.1.1. A nanotube has great biocompatibility and electronic conductivity, which is more sensitive than many metal based electrodes. If we can functionalize biomolecules on the nanotubes, we can build the sensor to detect and qualify the presence of virus and bacterial that would be very useful for many lab-on-chip systems. It would be very important to know how the nanotubes interact with different molecules at various kinds of flow configurations. This leads to another objective utilize the hybrid scheme to further understanding of how the interaction between liquid and CNTs affects the flow pattern in nanochannels in order to improve the design of biosensors.
Chapter 2

Numerical Methods

In this chapter, we discuss the numerical methods for simulating the flow of dense fluids at atomistic level and continuum level. The atomistic description (molecular dynamics) is required to explore the microscopic details in nano- and micro- systems; The continuum description (Navier-Stokes description), is useful to extend systems beyond the size restriction of MD systems. In the meantime, we focus on how to bridge scales between the continuum and atomic description by the alternating Schwarz method, and discuss various aspects for designing a hybrid scheme in detail.

2.1 Molecular dynamics

2.1.1 Formulation

In the classical theory, the properties of complex systems, such as dilute gas, can be predicted if we know the coordinates and velocities of the particles in the system. In MD, we track the coordinates $r_{ij}$ and velocities $v_{ij}$ of the particles based on Newton’s law:

$$\frac{\partial}{\partial t} r_i = v_i(t),$$

$$m_i \frac{\partial}{\partial t} v_i = F_i = - \sum_{j \neq i} \nabla U(r_{ij}),$$

where $i$ is the index of particles, $F_i$ is the total force exerted on particle $i$, $m_i$ is the mass of particle $i$ and $r_{ij}$ is the distance vector between particle $i$ and $j$. $U(r_{ij})$ is the interaction potential between particles and other subjects in the system, which is originated from the physics of the system. For a Lennard-Jones fluid, the interaction potential can be described as follows:
The function $U_m(r_w; \rho, T)$ models the interaction between the atomic region and the surrounding environment, which depends on the distance $r_w$ of each atom to the MD boundary and the local state variables ($\rho, T$). Since the analytical form of $U_m(r_w; \rho, T)$ is usually unknown, numerical approximation is always precomputed in an separate simulation. In addition, the function $U_{12-6}^{AB}$ is a pair-wise interaction potential between particle A and B:

$$U_{12-6}^{AB}(r_{ij}) = 4\varepsilon_{AB}\left[\left(\frac{\sigma_{AB}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{AB}}{r_{ij}}\right)^6\right].$$

(2.4)

The form of this potential shows that it is dominated by the attractive term at large $r$ due to the term $\sim \frac{1}{r^6}$ and becomes repulsive at short distance due to the term $\sim \frac{1}{r^{12}}$. The length parameter $\sigma$ and the energy parameter $\varepsilon$ are chosen to fit the physical properties of the material under investigation. The detailed information of these parameters used in this project will be given later. In practice, we don’t have to evaluate the potential of the infinite distance, it is customary to introduce a cut-off radius ($r_c$) and ignore the contribution from the particles, which is separated by more than $r_c$, in order to reduce the computation time.

### 2.1.2 Integration scheme

In order to evolve the system, a numerical scheme is needed to integrate the governing equations : Eq.(2.1) and (2.2). Popular intergration schemes are Verlet scheme, Velocity-Verlet scheme and leap-frog scheme. In this case, we choose the leap-frog scheme, since it is stable and accurate, but simple:

$$r_i^{n+1} = r_i^n + \Delta t_{MD}v_i^{n+1/2},$$

(2.5)

$$v_i^{n+1/2} = v_i^{n-1/2} + \Delta t_{MD}f_i^n/m_i,$$

(2.6)

where $\Delta t_{MD}$ is the time step, $r_i$, $v_i$, $f_i$ is the position, velocity, force for the corresponding particle $i$ with mass $m_i$ at time $n\Delta t_{MD}$. The local truncation errors introduced at each time are of the order $O(\Delta t_{MD}^3)$, but the velocity $v_i^n$ is only accurate to $O(\Delta t_{MD}^2)$. The details about the selection of time step $\Delta t_{MD}$ will be specified later.

### 2.1.3 Berendsen thermostat

In the previous section, the formulation of MD simulation is for microcanonical ensemble (NVE), which has a fixed number of atoms N, a fixed volume
2.2 Continuum description

V and a constant energy E. In order to study a dissipative non-equilibrium system, we need to impose external constraints to keep the temperature $T$ constant for the system, in order to approximate a canonical system (NVT). Rescaling velocity is a common approach to maintain a target temperature for the system. In this project, Berendsen thermostat is chosen to achieve this goal. At each time step, a proportional scaling of the velocity from $v$ to $\lambda v$ is done with the scaling factor $\lambda$ as follows:

$$\lambda = [1 + \frac{\Delta t_{MD} (T_0 / T) - 1}{\tau_T}]^{1/2},$$

(2.7)

where $\tau_T$ is a time constant to control the strength of the coupling. In order to minimize the disturbance to system introduced by the coupling, a optimal value $\tau_T = 0.1 \Delta t_{MD}$ is chosen in this project, which can be varied to meet requirements for different applications.

In addition, we will carry out the MD simulation at certain states of the fluids and report the result in term of reduced units: $T^* = k_B T / \epsilon$, $\rho^* = \rho \sigma^3$, $P^* = P \sigma^3 / \epsilon$.

2.2 Continuum description

In the continuum part of the hybrid method, we consider a two/three dimensional flow of an incompressible, viscous, isothermal fluid which can be described by the Navier-Stokes (N-S) equations as follows [12]:

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} - \nu \Delta \mathbf{u} + \frac{1}{\rho} \nabla p = 0,$$

(2.8)

$$\nabla \cdot \mathbf{u} = 0,$$

(2.9)

where $\mathbf{u}$, $p$ are the velocity and pressure fields, $\rho$ is the density of the fluid, and $\nu$ is the kinetic viscosity of the fluid. Dirichlet boundary condition, which will be extracted from the atomic region as described later, is needed to solve the N-S equation in this project. The above equations are solved numerically by a free finite element solver FreeFEM++ [12] in 2D and a commercial finite element solver COMSOL Physics in 3D [13].

For a two dimensional flow, the Navier-Stokes equation is solved on a mesh with mesh sizes $\Delta x$ and $\Delta y$. In order to get a stable solution, the Courant-Friedrich-Lewy(CFL) condition must be fulfilled as follows [5]:

$$\Delta t_{FEM} \leq \Delta x \Delta y / 2\nu.$$

(2.10)
2.3 Hybrid formulation

In the meantime, in order to minimize the thermal noise induced by the boundary condition provided by the MD subdomain, the continuum step $\Delta t_{FEM}$ is required to be larger than the auto-correlation time $\tau_{uu}$ of the particle velocity $u$. With these two restrictions in mind, we will specify $\Delta t_{FEM}$ later.

The Reynolds number based on the characteristic length $L$ of geometry and kinetic viscosity $\nu$ is $Re = u_{max}L/\nu$. In this project, Re is around order of 10.

2.3 Hybrid formulation

2.3.1 Formulation

In the hybrid approach, we coupled the two methods: the finite element method and molecular dynamics described in the previous sections through the alternating Schwarz method presented in [2]. Figure 2.1 illustrates the alternating Schwarz method with two subdomains: the continuum region $\Omega_C$ and the atomic region: $\Omega_A$. The two subdomain overlap over the region between $\Gamma_C$ and $\Gamma_A$. 

![Figure 2.1: Schematic of the hybrid method for a 2D problem.](image)
2.3 Hybrid formulation

2.3.2 Molecular fluctuations

Before focusing on the hybrid method, we need to discuss one important consideration: Molecular fluctuations. In the hybrid scheme, the atomistic region is not only an essential part to lead to the correct and interesting phenomena, but also an important source of considerable statistical noises for low speed flow problems that may influence the accuracy, stability and efficiency of the hybrid method [7].

Hadjiconstantinou [6] pointed out that the relative statistical error \( E_q \) of a typical quantity \( q \) (e.g., velocity, pressure, density) in low speed flows depends on the number of samples \( N_q \) in order to get the average \( \bar{q} \):

\[
E_q = \frac{\sigma(\bar{q})}{\bar{q}} = \frac{\sigma(q)}{\sqrt{N_q \bar{q}}},
\]

where \( \sigma(q) \) is the standard deviation of \( q \). Under the assumption that the deviation of the low speed flows is not far from the equilibrium, he also gave an a priori estimate of the number of samples \( N_u, N_\rho, N_p \) required to measure the averages of velocity, density and pressure in a MD cell of volume \( V \):

\[
\begin{align*}
N_u &= \frac{k_B T_0}{u_0^2} \frac{1}{\rho V E_u^2}, \\
N_\rho &= \kappa_T k_B T_0 \frac{\rho V E_\rho^2}{V E^2}, \\
N_P &= \gamma k_B T_0 \frac{1}{P_0^2 \kappa_T \rho V E_p^2},
\end{align*}
\]

(2.12)

where \( u_0, \rho_0, T_0, P_0 \) denote the average velocity, density, temperature and pressure. The constant \( k_B \) is the Boltzmann constant, \( \gamma \) is the ratio of the specific heats and \( \kappa_T \) is the isothermal compressibility of the fluid. He [7] also showed that the associated statistical error of a hydrodynamic flux \( E_f \) (e.g., pressure) scale as:

\[
E_f \sim E_s / Kn,
\]

(2.13)

where \( E_s \) denotes the associated statistical error of a state hydrodynamic quantity (e.g., density, temperature) and \( Kn \) is the Knudsen number (defined as the ratio of the molecular mean free path to the characteristic flow length-scale). This indicates that in the case of the low speed flow, if \( Kn \ll 1 \) (where the coupling between atomic region and continuum domain is usually needed), to achieve the same statistical error for an average quantity \( q \), a hydrodynamic flux needs much more samples than a state hydrodynamic quantity needs. With this in mind, we can turn to the choice of coupling strategy.

2.3.3 Coupling scheme

The coupling scheme refers to the exchange the information between the atomic domain and the continuum domain. Two strategies are typically used to handle this process:
2.3 Hybrid formulation

1. **flux-based coupling**
   involves the transfer of the flux of mass, momentum and energy.

2. **state-based coupling**
   involves the transfer of state variables (e.g. density, temperature).

The choice of coupling scheme is inherently linked with flow physics (flow speed). For a low speed flow, a state-based coupling scheme is preferred, since less samples are needed than that required in the flux-based coupling; whereas for a high speed (compressible) flow, a flux-based coupling appears to be appropriate and convenient, since high speeds means a smaller statistical error according to Eq.(2.12). Werder [2] validated the above statement by a simple calculation in a low speed uniform flow. He showed that the flow density-based scheme is the best to obtain a modest accuracy in terms of number of samples; the pressure-based scheme is computational prohibitive; the velocity-based scheme is computationally acceptable. In the mean time, velocity field is appropriate to be the Dirichlet boundary condition for the continuum region without additional calculation compared with the case in pressure-based scheme. Based on these considerations, velocity-based scheme is preferred here, since we are considering low-speed flows in this project.

The above discussion leads to another important aspect of coupling choice: **time coupling**, which refers to the frequency of coupling in time and can be categorized as follows:

1. **explicit time coupling scheme**
   involves the transfer of information at certain frequency. The simplest scheme [5] is to exchange the information at every time step, which shares the same time step for the atomic and the continuum regions. Nie [3] proposed a modified scheme, which coupled time scale at a lower frequency (a continuum step corresponds certain steps of MD step). Although it is somehow ad hoc, it did reproduce the flow pattern of certain two-dimensional flows.

2. **implicit time coupling/time decoupling scheme**
   This scheme is appropriate for the steady state interest problem that is proposed by Hadjiconstantinou [6] based on the alternating Schwarz method. The general framework says that in a hybrid cycle, we iterate both continuum solution and atomic solution to its steady or quasi-steady state with the boundary condition exchanged at previous iteration, then repeat the hybrid cycles until the solution reaches the steady state. In other words, the time scale has been already decoupled
in this problem. Recent works [2],[4] showed that this approach leads a considerable computational saving in time.

Since we are more interested in a steady state solution in this project, the implicit time coupling strategy is preferred.

2.3.4 Boundary condition imposition

Imposing boundary condition is always a challenging problem. The major difficulties are

1. how to extract the information from the atomic domain for the boundary condition with less thermal noise?

2. how to impose the boundary condition provided by the continuum domain to the atomic domain with less perturbation to the correlation of the particle dynamics?

Many recent works are aiming at these two problems. Since traditional MD is often developed for homogenous systems. Periodic boundary conditions are sufficient to reproduce the right bulk properties for the systems. However, in the context of hybrid methods, it is essential to impose a non-periodic boundary condition provided by the continuum domain. For simplicity, a two-dimensional formulation is illustrated in Fig. 2.1, 1D and 3D problems can follow the same principles. Here Ω_C, Ω_A denote the continuum domain and MD domain respectively; Γ_C, Γ_A refer to the boundary of the continuum domain and MD domain in hybrid methods. In this case, the artificial boundary Γ_A precludes the continuity of bulk properties (the density and temperature). The region between Γ_C and Γ_A is the overlap region, which is designed for screening the termination effect by Connell [5]. He also observed that a normal (to Γ_A) effective boundary force can induce a smaller oscillation to particle density (layering effect) near the artificial boundary (Γ_A), which in turn resolves the solution with a smaller overlap region.

Effective boundary force

Based on the Connell’s idea, a number of boundary effective force models have been developed. Recently, Werder recognized that the particles near the artificial boundary experience forces from two sources: first, the forces from the particles inside the homogenous MD domain within a cutoff distance; second, the forces from the surrounding media outside MD domain
within a cutoff distance. By taking account of the local structure (radial distribution function $g(r)$), he proposed an effective boundary force model based on the equilibrium local structure, which significantly reduced the density oscillation near the boundary force. Kotsalis [4] observed that the density oscillation depends on the state point $(\rho^*, T^*)$ of the fluid and the oscillation is significantly large at certain state points, even when the effective boundary force is applied. Therefore, he proposed that a modified version of Werder’s boundary force model: using a dynamic control theory to improve the effective boundary force based on the error measured in the local fluid density. Simulation tests showed that the amplitude of the density oscillation is significantly reduced for fluids at rest at different state points.

In addition, it is important to realize that the particles may escape from $\Omega_A$, even when an effective boundary force is exerted. Therefore, Werder proposed a specular wall to reflect the particles which has a potential to leave the MD domain. For the particles that already escaped from the MD domain, they will be reinserted into the MD domain, whose position and velocity after reinsertion are determined by USHER algorithm [2].

**Boundary condition consideration**

Imposing the boundary condition to the continuum domain is a straightforward process. A temporal average based on a volume $V$ is a common choice for most hybrid schemes. It is the estimate of the number of samples that represents the difficulty, which might influence the convergence of a hybrid solver based on the discussion in section 2.3.2.

In this section, we will focus on the issue about the imposition of the boundary condition on the MD domain. Several approaches have been developed:

1. **particle reservoir**: Hadjiconstantinou [8] employed a particle reservoir to impose the target boundary condition (e.g., velocity, temperature) based on biased Maxwellian distributions. He claimed that this technique would not only constrain the required local state fields of molecular flow to the continuum flow, but also provide the information of local state field gradients.

2. **constraint dynamics**: Werder [2] developed a method to impose the boundary condition on the MD domain through applying body forces. A body force is applied to meet the requirement to instantaneous
center-of-mass velocity in a cell \( k \):

\[
\bar{v}_k = \frac{1}{N_k} \sum_{i \in k} v_i, \quad (2.14)
\]

where \( i \) is the index of the particle. At each time step, the body force \( b_k \) is adjusted so that the center-of-mass velocity \( \bar{v}^{n+1/2}_k \) at next time step can be prescribed by the continuum velocity field \( u^n_k \). The body force \( b^n_k \) in cell \( k \) can be calculated through the following formula based on the velocity update scheme Eq.2.6:

\[
b^n_k = \frac{N_k m}{\Delta t_{MD}} (u^n_k - \bar{v}^{n-1/2}_k) - f^n_k, \quad (2.15)
\]

and then the body force is equally distributed to the individual particle in cell \( k \).

\[
\bar{v}^{n+1/2}_k = \bar{v}^{n-1/2}_k + \frac{\Delta t_{MD}}{N_k m} (f^n_k + b^n_k), \quad (2.16)
\]

where \( f^n_k \) is the total physical force exerted on the center of mass of cell \( k \) at time \( n \Delta t_{MD} \). This driving mechanism is similar to the constrain dynamics proposed by Connell [5]. They use a parameter \( \xi \) to control the relax rate of the average MD velocity to the corresponding local continuum velocity. Arbitrary relaxation rate can be introduced, but they emphasized that only an appropriate value of \( \xi \), which usually should fulfill the condition: \( \Delta t_{MD}/\xi > t_{uu} \), can resolve the correlations of the particles. For Werder’s case, Eq.(2.15) means a direct imposition of the boundary condition without relaxation. In this project, we adopt the constrain dynamics algorithms and investigate the dependence of the convergence of hybrid solution on the coupling strength between the continuum region and the atomic region by adjusting the relaxation parameter.
Chapter 3

2D nanoscale Couette flow

In this chapter, we present the hybrid scheme in detail by illustrating a 2D pure Couette flow confined between two graphite plates.

The convergence behavior of a hybrid scheme is a crucial criteria to evaluate its performance, therefore it is important to understand how the various parameters affect the convergence of the hybrid approach. Here, we investigated the dependence of the convergence behavior on the overlap size \(d_{\text{olp}}\), the number of samples \(N_s\) for the MD subdomain in each hybrid cycle, the coupling strength \(\tau_f\) between the continuum subdomain and the MD subdomain.

3.1 Formulation

Now we apply the hybrid scheme discussed in last chapter to the case of the Couette flow of liquid argon. Fig. 3.1 illustrates the sketch of the Couette flow of liquid argon confined between two graphite plates. The regions \(\Omega_A\) (MD1, MD2) near the upper and lower boundary are described by molecular dynamics; the other region \(\Omega_C\) is described by finite element methods (FEM). The areas below the dash line 2 and above the dash line 3 are described by MD; the region between dash line 1 and 4 is described by FEM; The overlap regions are the area between 1 and 2 and the area between 3 and 4.

In each iteration \(i\), MD and FEM will exchange information within the overlap region: the continuum velocity field \(\mathbf{u}_C^i\) is computed in FEM region with the natural boundary condition \(\mathbf{u}_A^{i-1}\) at dashlines 1, 4 from the previous iteration of molecular dynamics; the velocity field \(\mathbf{u}_A^i\) is obtained by iterating MD solver with the boundary condition \(\mathbf{u}_C^i\) at dashlines 2, 3 and provides
3.1 Formulation

Figure 3.1: Schematic of the hybrid method of Couette flow problem, the area filled with circle is described by molecular dynamics; the area without circle is described by finite element method; the area between the two dash lines is the overlap region.

the boundary condition for the continuum solver at this iteration. This is a full iteration. The exchanged boundary data is problem-dependent. In the case of Couette flow, only the flow velocity field is needed to exchange. This can be summarized as follows:

Start $u_{0C}|_{\Gamma C} = u_{0A}$

For $i = 1, n$

- solve N-S equation $L_C u_{iC}^i = f_c$ in $\Omega_C$ with BC: $u_{iC}^i = u_{iA}^{i-1}$ on $\Gamma_C$;
- solve MD equation $L_A u_{iA}^i = f_A$ in $\Omega_A$ with BC: $u_{iA}^i = u_{iC}^i$ on $\Gamma_A$;

end

where $L_i$ is the differential operator in domain $\Omega_i$; $f_i$ is the forcing term in domain $\Omega_i$. 

13
3.2 Simulation details

Here, we consider a setup of 2D Couette flow similar with Nie’s [3]. The flow is confined in a computational domain: \(30.0 \times 4.3 \times 4.9\) nm\(^3\). Each of two MD subdomain with 4250 atoms has a region with size of \(10.0 \times 4.3 \times 4.9\) nm\(^3\), which is subdivided into \(10 \times 4 \times 1\) MD cells; the FEM subdomain with a size of \(16.0 \times 4.3 \times 4.9\) nm\(^3\) that corresponds to \(16 \times 4 \times 1\) FEM cells. Therefore, the overlap region between each MD and the FEM subdomain is chosen to 3 nm in \(x\) direction, which corresponds to 3 MD cells. The criteria for selecting the overlap region will be discussed in the later chapters.

The equations of motions (2.1) and (2.2) are integrated through a leap-frog scheme with a time step \(\Delta t_{MD} = 0.01\) ps. The parameters for Lennard-Jones potential are presented as follows:

- Unit length: \(\sigma, \sigma_{Ar} = 0.34\) nm
- Unit energy: \(\epsilon, \epsilon_{Ar,Ar} = 0.996\) kJ mol\(^{-1}\)
- Unit mass: \(m\) (the mass of the atoms), \(m_{Ar} = 39.95\) a.m.u\(^1\)

The simulation are performed at the state point \((T^*, \rho^*) = (1.1, 0.81)\). For the MD reference solution, a system of 12767 argon atoms starts to relax from its initial configuration for 10 ns, and then we sample the data over next 20 ns. During the simulation, a cell-wise Berendsen thermostat is imposed in \(z\) direction with a time constant \(0.1 \Delta t_{MD}\) to keep the temperature constant. In the hybrid case, the thermostat is coupled with the boundary cells \(^2\) in 3 dimensions whereas the rest part of MD subdomain should be only thermostated in \(z\) direction that is perpendicular to the shear plane in order to avoid the perturbation from the thermostat.

3.3 Numerical results

In order to qualify the convergence and the accuracy of hybrid method, several numerical tests are carried out in this project. The root mean square of the error is defined as follows:

\[
e = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \frac{(u_i - u_{i,MD})^2}{u_{max}^2}},
\]

\(1\) a.m.u denotes the atomic mass unit, which is defined as one twelfth of the mass of an unbound atom of the carbon-12 nuclide

\(^2\) the boundary cell denotes the cell next to the artificial boundary in the MD subdomain.
where $N$ is the number of cells in the computational domain, $i$ is the index of the cell and $u_{\text{max}}$ is the maximal velocity in the Couette flow.

### 3.3.1 The size of overlap regions

In this case, we apply the hybrid scheme with different sizes $d_{\text{olp}}$ of overlap regions: 3 nm, 5 nm, 6 nm in $x$ direction, which corresponds to 3, 4, 5 cells. Fig.3.2 reveals the similar linear velocity profile with the MD reference solution. It is clear that the no-slip boundary condition breaks down near the graphite surface and velocity slips occurs. To quality the velocity slip, a slip length $L_s$ is defined as follows [10]:

$$L_s = \frac{u_{\text{fluid}} - u_{\text{wall}}}{\frac{\partial u(x)}{\partial x} \big|_w},$$

(3.2)

where $\frac{\partial u(x)}{\partial x} \big|_w$ is the local shear rate at the wall. The slip length means the length the fluid need to travel to reach the same velocity with that of the wall surface [10]. Based on this definition, the slip length of the upper region and the lower MD region in this case is symmetric and around 10 nm.

As shown in Table.3.1, to increase the size of the overlap region, the error $e$ doesn’t decrease as expected, there is no general trend: the solution with $d_{\text{olp}} = 3$ nm is best and the solution with $d_{\text{olp}} = 5$ nm is the worst. In addition, we present the evolution of error in Fig. 3.3. It can be seen that three cases are run for at most 50 cycles to achieve the steady-state state, then the solutions oscillate around the steady state. The solution with a overlap size of $d_{\text{olp}} = 6$ nm reaches to the steady state faster, but the solution is noisier than that with small overlap regions shown in Fig. 3.3. It suggests that a larger overlap region leads to a faster convergence, but does not guarantee better accuracy in this example. The reason could be that the density perturbation near the artificial boundary, in which the external effective boundary force proposed by Werder [2] is deterministic in nature and can not reproduce the correlations of the forces that atoms experience as time evolves.
3.3 Numerical results

Table 3.1: Convergence analysis of hybrid solution with different sizes $d_{olp}$ of overlap regions

<table>
<thead>
<tr>
<th>$d_{olp}$</th>
<th>$N_s$</th>
<th>$\tau_f$</th>
<th>$e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>10000</td>
<td>1</td>
<td>1.29</td>
</tr>
<tr>
<td>5</td>
<td>10000</td>
<td>1</td>
<td>2.12</td>
</tr>
<tr>
<td>6</td>
<td>10000</td>
<td>1</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Figure 3.2: Comparison of the velocity profiles of Couette flow between MD and hybrid solutions with different sizes of overlap region $d_{olp} = 3, 5, 6$ nm in x direction.
3.3 Numerical results

![Figure 3.3: Comparison of the evolution of global error $e_k$ between hybrid solutions with different sizes of overlap region $d_{olp} = 3, 5, 6$ nm in x direction.](image)

3.3.2 The number of samples

In the classical molecular dynamics, increasing samples is supposed to effectively reduce the noise introduced by the MD domain. Here, we investigated how the number of samples $N_s$ in each cycle affects the convergence and accuracy in hybrid simulation. Fig. 3.4 shows that the comparison of the hybrid solutions with an overlap size of 6 nm in x direction with different number of samples $N_s = 1500, 5000, 10000$ at each iteration. We observe that the solution with more samples has a better agreement with the MD reference solution.

Fig.3.5 depicts that the time evolution of global error $e_k$ for different number of samples $N_s$ at each cycle. In those cases, the general trend is that the error $e_k$ decays fast in the first 50 cycles, then oscillates around a mean value. In the meantime, it can be seen that the decay rate at first depends on the numbers of samples $N_s$ at each cycle. $N_s = 10000$ decays fastest, $N_s = 1500$ is the slowest. In addition, we also observed that for cases $N_s = 10000, 5000$, they decay at first, then reach a plateau after 50 cycles, whereas for $N_s = 1500$, it first reaches a plateau after 50 cycles, BS then oscillates around the second plateau after 100 cycles. We also measure the average error between cycle 100 and cycle 300 with a value of 0.4% for $N_s = 10000$, 0.8% for $N_s = 5000$.
Table 3.2: Convergence analysis of hybrid solution with different number of sample $N_s$ in each cycle

<table>
<thead>
<tr>
<th>$d_{olp}$</th>
<th>$N_s$</th>
<th>$\tau_f$</th>
<th>$e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1500</td>
<td>0.1</td>
<td>1.3</td>
</tr>
<tr>
<td>6</td>
<td>5000</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>6</td>
<td>10000</td>
<td>0.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Figure 3.4: the comparison of the evolution of the global error $e^k$ of the velocity profiles of Couette flow between hybrid solutions with the overlap region ($d_{olp} = 6$ nm) and $\tau_f = 0.1$ but different $N_s = 1500, 5000, 10000$.

and 1.3% for $N_s = 1500$. It indicates that less samples will lead to a large fluctuation, but more samples will sacrifice certain computational efficiency. As we stated, more samples $N_s = 20000$ didn’t further reduce the error. In general, it can be seen that increasing the number of samples in each cycle does lead to better accuracy and faster convergence, but if we collect more samples (20000 samples), the accuracy and convergence are not further improved. Therefore, an optimal $N_s$ could be chose as $N_s = 10000$ in this case.
3.3 Numerical results

![Graph of time evolution of residual of hybrid velocity profile for Couette flow](image)

Figure 3.5: the comparison of the evolution of the global error $e^k$ of the velocity profiles of Couette flow between hybrid solutions with the overlap region ($d_{olp} = 6$ nm) and $\tau_f = 0.1$ but different $N_s = 1500, 5000, 10000$.

<table>
<thead>
<tr>
<th>$d_{olp}$</th>
<th>$N_s$</th>
<th>$\tau_f$</th>
<th>$e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>10000</td>
<td>1</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>10000</td>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>impose3</td>
<td>10000</td>
<td>1</td>
<td>4.2</td>
</tr>
</tbody>
</table>

### 3.3.3 Control test

Based on this hybrid scheme, we use an artifical hard wall and sophisticated particle insertion mechanism to keep the atoms stay inside the MD submain [2]. However, it would lead to an undesirable effect: density fluctuations near the artificial MD boundary. If the density deviation is too large, the material behaviors in the continuum domain and the MD subdomain will not be matched. Therefore, we use the control method proposed by E.M.Kotsalis in [4]. We didn’t see better result for the solution with the overlap size $d_{olp} = 3$ nm after control depicted in Fig.3.6 and Table.3.3; The accuracy is roughly the same before and after control. As shown in Fig.3.8, the evolution of global error $e^k$ with control is almost as smooth as the solution without control and the converge rate is also roughly the same that indicates that although the
Figure 3.6: Comparison of the velocity profiles of Couette flow between MD and hybrid solutions with controller, which has an overlap region $d_{olp} = 3$ nm.

density perturbation near the artificial hard wall has been minimized by the controller, the way of boundary condition imposition in our hybrid scheme didn’t give the right correlations of the particle dynamics.

To support this idea, we designed a new test: in a hybrid simulation with a overlap region $d_{olp} = 6$ nm, we imposed velocities within an imposition area with a size of 3 nm in x direction next to the MD artificial boundary instead of imposition in 1 nm. If the imposition of velocity reproduced the right physics, the solution should lead to a faster convergence and better accuracy. If the imposition of velocity will play an important role on the correlations of particle dynamics in a wrong way, the result should be even worse than the solution with a smaller imposition region. Fig. 3.9 and Table. 3.3 shows that the solution with a smaller imposition region (1 nm) shows not only faster convergence, but also better accuracy that indicates that the second guess, the imposition of the velocity from the continuum domain to the MD domain does arise a deviation from the correct correlations of particles.
3.3 Numerical results

Figure 3.7: Comparison of the velocity profiles of Couette flow between MD and hybrid solutions with controller, which has a overlap region $d_{olp} = 6$ nm.

Figure 3.8: Comparison of the evolution of global error $e^k$ between hybrid solutions with controller and a overlap region of $d_{olp} = 6$ nm in x direction.
3.3 Numerical results

Figure 3.9: Comparison of the velocity profiles of Couette flow between MD and hybrid solutions without control, which has a overlap region $d_{\text{overlap}} = 6$ nm, 3 nm of which is used for imposing velocity boundary condition from the continuum domain to MD domain.

Figure 3.10: Comparison of evolution of global error $e^k$ between hybrid solutions with different sizes of imposition region (1 nm, 3 nm).
3.3 Numerical results

Table 3.4: Convergence analysis of hybrid solutions with different resolution for the same size of MD region

<table>
<thead>
<tr>
<th>$d_{olp}$ (nm)</th>
<th>$N_s$</th>
<th>$\tau_f$</th>
<th>$\epsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3(higher resolution)</td>
<td>10000</td>
<td>1</td>
<td>1.53</td>
</tr>
<tr>
<td>6(higher resolution)</td>
<td>10000</td>
<td>1</td>
<td>1.29</td>
</tr>
</tbody>
</table>

3.3.4 Resolution test

As many grid-based numerical methods suggest, increasing the spatial resolution will improve the overall accuracy. Here, we double the resolution in x direction but keep the same size of overlap region ($d_{olp} = 3, 6$ nm) to see if we can improve the accuracy. As shown in Fig. 3.13 and Fig. 3.12, we observed that for the same overlap region, in the case of $d_{olp} = 6$ nm, the higher resolution give a better accuracy (1.3% for higher solution, $0.5 \times 1 \times 4.3$ nm$^3$, 1.6% for lower resolution, $1 \times 1 \times 4.3$ nm$^3$) but not faster convergence; for $d_{olp} = 3$ nm, higher resolution ($0.5 \times 1 \times 4.3$ nm$^3$) achieves the overall accuracy of 1.3% that is better than the case in lower resolution (1.5 %). This indicates that the accuracy is weakly dependent on the spatial solution for this example, which is probably because the shrink of cell volume will lead to larger fluctuation that beat the improved accuracy induced by the increase of the spatial resolution.
3.3 Numerical results

Figure 3.11: Comparison of the velocity profiles of Couette flow between MD reference and hybrid solutions with the same overlap region ($d_{\text{olp}} = 3$ nm in x direction) but different resolutions (1 nm, 0.5 nm in x direction).

Figure 3.12: Comparison of the velocity profiles of Couette flow between hybrid solutions with the same overlap region ($d_{\text{olp}} = 6$ nm in x direction) but different resolutions (1 nm, 0.5 nm in x direction).
3.3 Numerical results

Figure 3.13: Comparison of evolution of global error $e^k$ between hybrid solutions with the same overlap region ($d_{olp} = 6$ nm in x direction) but different resolutions (1 nm, 0.5 nm in x direction).

3.3.5 Relaxation test

In this case, we investigated the dependence of the convergence on the coupling strength between the MD subdomain and the continuum subdomain by applying a relaxation method similar with Connell [5] as follows:

$$\vec{v}_k^{n+1/2} = \vec{v}_k^{n-1/2} + \frac{\delta t}{N_{km}} (f_k^n + \tau_f b_k^n) \quad (3.3)$$

This is similar with Eq.(2.16) but with the body force term multiplied by a coupling strength factor $\tau_f \ll 1$. O’Connell indicated that if $\Delta t_{MD}/\tau_f < \tau_{uu}$, the solution would relax to a steady-state solution. The difference between

<table>
<thead>
<tr>
<th>$d_{olp}$ (nm)</th>
<th>$N_s$</th>
<th>$\tau_f$</th>
<th>$\epsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>10000</td>
<td>0.01</td>
<td>0.4</td>
</tr>
<tr>
<td>6</td>
<td>10000</td>
<td>0.1</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>10000</td>
<td>0.01</td>
<td>1.9</td>
</tr>
<tr>
<td>6</td>
<td>10000</td>
<td>0.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>
3.3 Numerical results

this case and O’Connell’s is that he chose an unsteady coupling strategy, while our case is steady/quasi-steady coupling.

In this case, four tests are run as listed in Table 3.5. As shown in Fig. 3.14 and Fig. 3.15, the best results (the global error is below 1.0%) are got at \( \tau_f = 0.01 \) for 3 nm overlap region and at \( \tau_f = 0.1 \) for 6 nm overlap region. Compared with the experiments we stated in the previous sections (eg. enlarge the overlap regions), it seems that the relaxation approach is more effective to achieve a moderate accuracy. Although Nie [3] argued that it would induce a lag between particle velocities and the prescribed continuum velocities, the delay might be essential to resolve the intrinsic thermal fluctuations for the time scales less than the autocorrelation time \( \tau_{uu} \). In addition, many references suggested to enlarge the overlap region, because a large gradient of velocity field can die off within the overlap region. However, it might be effective for a uniform flow case. For a Couette flow, increasing the overlap region means that we have to collect more samples in order to achieve the same accuracy according to Hadjiconstantinou’s theory:

\[
N_u = \frac{k_B T_0}{u_0^2} \frac{1}{\rho V E_u^2}. \tag{3.4}
\]

The formula shows that to obtain the same relative error \( E_u \), the number of samples of a larger overlap region needs to be \( N_u^* u_S^2 \) (where \( N_u^* \) is the number of samples for small overlap regions, \( u_S^2 \) and \( u_L^2 \) are the corresponding average velocity fields for small and large overlap regions), which requires more computational resources. Therefore, the relaxation approach is preferred in this case. We observed that with the optimal \( \tau_f \), it is possible to get a qualitative match with the reference solution with a moderate accuracy. This reminds us that in the case, in which it is not desirable to increase the overlap region, the relaxation approach will be a good candidate to fix the problem.

Actually, we also employed another relaxation scheme similar to the DSMC (direct simulation Monte Carlo)-continuum scheme [9]. They showed that the subrelaxation technique successfully reduced the scatterness of the boundary condition for the continuum domain. Basically, when we impose the boundary condition to the MD region, the cumulative history is included with a weight factor or relaxation factor \( \theta \). The subrelaxation formula can be expressed as follows:

\[
u_{MD}^{n+1} = \theta u_{MD}^n + (1 - \theta)u_C^n. \tag{3.5}\]

we noticed that if \( \theta = 0 \), it turned out to be the alternating Schwarz method without relaxation. In this case, we set \( \theta = 0.1 \) to compare with the case
3.3 Numerical results

Figure 3.14: Comparison of the velocity profiles of Couette flow between hybrid solutions with the overlap region \((d_{\text{olp}} = 3 \text{ nm})\) but different relaxation factors \(\tau_f = 0.01, 0.1, 1\).

\(\theta = 0\). As shown in Fig. 3.15, the subrelaxation approach \((\theta = 0.01, 0.1)\) shows a better agreement with the reference solution, which suggests that it is better to include the relaxation feature in the hybrid scheme to achieve the better accuracy.

In conclusion, a multiscale simulation of a Couette flow confined between two graphite sheets is studied in this chapter. The hybrid solution has a qualitative match with the MD reference solution, whose global error is within 4%. The dependence of the convergence and accuracy of the hybrid solution on different parameters is also investigated. In general, we found that

- larger overlap size leads to a faster convergence but does not guarantee better accuracy.

- more samples in each hybrid cycle leads to a faster convergence and better accuracy. However, beyond the certain number of samples, the convergence and accuracy is not sensitive to this parameter anymore.

- higher solution didn’t give a better accuracy. This might be because the extra error due to the shrink of MD cell volume beats the improved accuracy in continuum region.
3.3 Numerical results

Figure 3.15: Comparison of the velocity profiles of Couette flow between hybrid solutions with the overlap region ($d_{olp} = 6$ nm) but different relaxation factors $\tau_f = 0.01, 0.1, 1$.

- adjusting the coupling strength between the MD and the continuum region by tuning the relaxation parameter $\tau_f$ can effectively improve the accuracy, though this approach is somehow ad hoc.
Chapter 4

2D Couette flow past an array of nanotubes

In the last chapter, we have investigated a pure Couette flow. In this chapter, we consider a more complex 2D shear-driven flow: 2D Couette-like flow past nanotube array parallel to the channel wall, as sketched in the Fig. 4.1.

In the following section, we concentrate on how the existence of nanotubes will influence the interaction of liquids and walls, and then affect the steady state fluidic behavior in the whole domain. In particular, we present the details of simulation, error analysis and convergence analysis.

4.1 Problem setup

Now we are considering a flow of liquid argon confined between two graphite plates with a domain size of $14 \times 4.254 \times 4.912$ nm$^3$ as shown in Fig. 4.1, which is similar with that in the last chapter. In this case, a constant velocity $u_y = 100$ ms$^{-1}$ is imposed at the upper graphite plate ($x = 15$ nm) and the lower graphite plate ($x = 1$ nm) is kept stationary. The carbon nanotube with a length of 4.912 nm and chirality (8,8) corresponding to a radius of $r = 0.54$ nm is set parallel to the lower graphite surface and the centerline of the nanotube is set at $z = 2.127$ nm.
4.1 Problem setup

Figure 4.1: Schematic of the setup of the hybrid method of couette flow in a confined channel, in which the centerlines of nanotube arrays are parallel to the lower graphite plate.

Figure 4.2: Density profile of liquid argon in the MD reference, the upper MD subdomain and the lower MD subdomain in equilibrium state.
4.1 Problem setup

To validate the hybrid simulation, we compare it with the MD reference solution. For MD simulation, 5840 argon atoms start to relax from their initial configuration for 5 ns, and then we sample the data from 5 ns to 15 ns. During the simulation, a cell-wise Berendsen thermostat is imposed in z direction with a time constant $0.1 \Delta t_{MD}$.

For the hybrid simulation, the whole computational domain is divided into 3 subdomains. The upper MD subdomain with 2550 argon atoms has a size of $6.0 \times 4.3 \times 4.9$ nm$^3$, which is subdivided into $6 \times 4 \times 4$ MD cells; The lower MD region with 2450 argon atoms (the volume occupied by nanotube has been taken into account) has a size of $6.0 \times 4.3 \times 4.9$ nm$^3$; FEM subdomain has a size of $8.0 \times 4.3 \times 4.9$ nm$^3$.

In addition to the size of overlap region, since we want to match the velocity between the atomic and the continuum region, the density at the FEM boundary cell should be equal to the density in that MD cell, which should be equal to the bulk density. To this end, we plot the density profiles of the MD reference, the upper MD subdomain and the lower MD subdomain. It is clear that the density in the MD subdomain is consistent in the whole computational domain except the cells close the artificial boundary; the density oscillation is restricted within a distance of 1 nm to its corresponding artificial boundary; the layer effect vanishes around $x = 7$ nm in the lower MD region due to the interaction between the liquid and the nanotube and the counterpart in the upper MD subdomain recovers the bulk density around $x = 12$ nm. With this in mind, the MD subdomain and the FEM subdomain is chosen to overlap over a strip with a width of 3 nm in x direction, which corresponds to 3 MD cells. The cell-wise thermostat is imposed in 3 directions of the boundary cells with a coupling time constant $1 \Delta t_{MD}$ in order to prevent the cooling effect by the deterministic boundary force imposed there; the rest of cells are only thermostated in z direction with a coupling time constant $0.1 \Delta t_{MD}$. Each hybrid cycle consists of one FEM iteration and 10000 MD time steps (0.1 ns MD sampling time). This procedure is slightly different from Weders’s [2], in which the system equilibrates for extra time before sampling in each cycle.
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

Table 4.1: 2D Simulation of flow confined between two graphite plates, in which nanotubes are parallel to the lower graphite surface. $\tau_f$ denotes the relaxation parameter when we pass the information from the continuum region to MD region.

<table>
<thead>
<tr>
<th>$\tau_f$</th>
<th>sample</th>
<th>resolution</th>
<th>global error(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybrid1</td>
<td>1</td>
<td>10000</td>
<td>7x4 x 1</td>
</tr>
<tr>
<td>hybrid2</td>
<td>1</td>
<td>40000</td>
<td>7x4 x 1</td>
</tr>
<tr>
<td>hybrid3</td>
<td>1</td>
<td>40000</td>
<td>14x8 x 1</td>
</tr>
</tbody>
</table>

4.2 Flow past an array of nanotubes aligning parallel to graphite surface

To characterize the quality of hybrid solution, we first averaged the solution in y direction as if there are no nanotubes. Fig.4.3 presents the comparison of the velocity profile of the MD reference and hybrid solutions that are averaged by neglecting the atomistic details in y direction. We observed that the hybrid solutions are in good agreement with the MD reference. In addition, we observed that velocity slip occurs in the upper graphite surface as we have seen in the pure couette flow; the velocity vanishes near the lower graphite surface due to the existence of the nanotube.

Fig. 4.4 and 4.7 shows the comparison of hybrid solutions (hybrid 1,2,3) with different parameters described in Table. 4.1 and the MD reference solution at the shear plane. All of the results are sampled over 10 ns. It is clear that the velocity profile of the hybrid simulation shows good agreement with the MD reference solution and the basic 2D flow pattern is reproduced.

We present the point-wise error normalized by each point between the hybrid simulation (hybrid 1) and MD reference solution at different x-y planes in Fig. 4.5. It can be seen that the error in the region close to the nanotube is extremely large, above 20%; the error at the rest region is hardly above 5%. However, this large deviation is not what it looks like, because the flow field near the nanotube is too weak and even a small deviation in this region leads to a significantly large relative error. In another point of view, the signal-to-noise ratio is smaller than other regions and it is noisier than other places in the computational...
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

domain. However, this deviation in the lower MD domain seems not to influence the good agreement of the hybrid solution with the MD reference solution in the whole domain shown in Fig.4.3. In the mean time, we also plot another point-wise error normalized by the maximum velocity shown in Fig.4.6. It can be seen that the point-wise error is within 4%. We can see neither of the point-wise error maps can display the information in a reasonable way, therefore it is better to combine two plots when we want to gather the error distribution in the whole computational domain.

Fig. 4.13 shows the evolution of global error $e_k$ and the rate of change of the velocity field $d_k$. We monitored the error for 10 ns, which corresponds to 100 cycles for hybrid1 with 10000 samples in each cycle; 25 cycles for hybrid2 with 40000 samples in each cycle. It can be seen that the error with 10000 samples in each cycle runs for 20 cycles before the solution reaches the steady state and then fluctuates around 5%; the error with 40000 samples in each cycle doesn’t get to the steady state faster, but level off around a value of 2%. In addition, we also measure the averaged error 1.3% for hybrid1 and hybrid2 over 10 ns. The result reveals that the global accuracy and the convergence rate is weakly dependent on the number of iterations in each cycle for this example. Furthermore, the rate of the change $d_k$ reduces faster in the first 20 cycles, and then keeps constant, wherever the error $e_k$ is not further reduced.

Resolution test: The dependence of hybrid simulation on the spatial resolution (the volume of the MD cell) is investigated by considering a finer resolution with a cell volume: $0.5 \times 0.5 \times 4.912 \text{ nm}^3$ (hybrid3), which is 4 times smaller than those in hybrid1, hybrid2. Since the cell volume is reduced, it is better to increase the samples in each cycle to compensate the larger fluctuation due to the decrease of cell volume. Fig. 4.10 shows that the velocity profile has a qualitative match with the MD reference solution and a more detailed flow pattern near the nanotube than that in lower spatial resolution. However, higher resolution doesn’t result in a better accuracy and the global error is still around 1.3%, which is roughly the same level with that in lower resolution. The conventional idea of grid-based numerical methods that the accuracy increases as the mesh is refined, is not applicable here. In other words, the extra noise induced by the shrink of cell volume beats the improved accuracy due to the refinement of the mesh in this
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

![Graph showing velocity profiles](image)

Figure 4.3: Comparison between velocity profiles of MD reference and hybrid solutions that averaged in y direction.

In conclusion, we simulated a flow of liquid argon confined between two graphite sheets, in which nanotubes are parallel to the lower graphite surface. We found that although we has a large deviation in the lower MD region, the results still agree well with the MD reference solution, which indicates that the continuum solver seems to screen out the noise from the MD subdomain. In addition, we found that the accuracy and the convergence of hybrid solution are weakly dependent on the number of samples in each cycle in this case. Furthermore, higher resolution roughly achieves the same accuracy compared with the case in lower resolution.
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

Figure 4.4: Comparison between MD reference and hybrid solution (hybrid1). The colorscale and contour lines described the norm of velocity in the unit of ms$^{-1}$.

Figure 4.5: Point-wise error map between MD reference and hybrid solution (hybrid1) normalized by each point.
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

Figure 4.6: Point-wise error map between MD reference and hybrid solution (hybrid1) normalized by the maximal velocity.

Figure 4.7: Comparison between MD reference and hybrid solution (hybrid2). The colorscale and contour lines described the norm of velocity in the unit of ms$^{-1}$.
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

Figure 4.8: Point-wise error map between MD reference and hybrid solution (hybrid2) normalized by each point.

Figure 4.9: Point-wise error map between MD reference and hybrid solution (hybrid2) normalized by the maximal velocity.
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

Figure 4.10: Comparison between velocity profile of MD reference and hybrid solution (hybrid3). The colorscale and contour lines described the norm of velocity in the unit of ms\(^{-1}\).

Figure 4.11: Point-wise error map between MD reference and hybrid solution (hybrid3) normalized by each point.
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

Figure 4.12: Point-wise error map between MD reference and hybrid solution (hybrid3) normalized by the maximal velocity.
4.2 Flow past an array of nanotubes aligning parallel to graphite surface

Figure 4.13: the evolution of the global error $e^k$ and residual $d^k$ between MD reference solution and hybrid solutions ($\text{hybrid1}$, $\text{hybrid2}$, $\text{hybrid3}$) averaged over 10 ns.
Chapter 5

3D flow past an array of nanotubes

In this chapter, we consider a flow of liquid argon encounters into a channel with a more complicated geometry: flow past an array of nanotubes perpendicular to the channel wall. This gives us a chance to investigate how an array of carbon nanotubes will tune the surface properties of the channel and then lead to different fluidic behaviors, which is of fundamental interest for many bio- and nano-systems. Since the interface of such systems ranges from micrometers to nanometers, this is the exact place where multiscale simulation can exert its strength.

In particular, we present details of the hybrid simulation, including the practical problems we met during the simulation. The 3D simulations are chosen to carried out in a Couette flow like configuration at a state point of density $\rho = 1360$ kg m$^{-3}$ and temperature $T = 131$ K, which corresponds to the dimensionless state point $(T^*, \rho^*) = (1.1, 0.81).

5.1 Density oscillation revisited

In the order to improve understanding of the artifact imposed by the non-periodic boundary condition, we first consider the liquid argon in equilibrium in a computational domain with a size of $6.0 \times 4.3 \times 4.9$ nm$^3$ and $10.0 \times 4.3 \times 4.9$ nm$^3$, which correspond to the systems of 2550 and 4240 argon atoms respectively. y and z direction are treated periodically. The upper boundary in x direction is treated as an artificial
5.1 Density oscillation revisited

Figure 5.1: Schematic of the setup of the hybrid method of Couette flow confined between two graphite plates, in which the nanotube is perpendicular to the lower graphite plate.
5.1 Density oscillation revisited

Figure 5.2: top: 3D view of schematic of the setup; middle: the side view of the setup of the hybrid method of Couette-like flow on the rough surface, bottom: the top view of the setup of the hybrid method of Couette-like flow on the rough surface.

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5.1 Density oscillation revisited

Figure 5.3: Top: the schematic of the setup for non-periodic boundary condition test; Bottom: Density profile of liquid argon in equilibrium (×) and nonequilibrium states. In nonequilibrium state, the artificial boundary is treated by a specular wall (⋆), or by effective force and a specular wall (□).
5.1 Density oscillation revisited

Figure 5.4: a closer window of Fig.5.3.

Figure 5.5: Density profile of liquid argon in equilibrium state with different sizes in x direction (x=7 nm, 10 nm). The artificial boundary is treated by effective boundary force and a specular wall (□).
Figure 5.6: Density profile of liquid argon in MD reference domain, upper MD subdomain and lower MD subdomain in equilibrium state.

As we expected from [2], the artificial wall will induce a density oscillation near the boundary and the density will recover to the bulk density within a cutoff distance. It can be seen that the maximum amplitude of the density oscillation in a system with a size of 10 nm in x direction is 10% higher than the bulk density; we also measure an increase of 20% of the maximum amplitude in the system with a size of 7 nm in x direction. It suggests that the size of the system affects the maximum amplitude of density oscillation shown in Fig. 5.5.

At the same time, we use the same setup in the previous section, but impose a constant velocity \( u_y = 100 \text{ ms}^{-1} \) in the upper graphite plate in y direction. The computational domain is subdivided in \( 6 \times 4 \times 4 \) cells and each cell corresponds to a box with a volume of \( 1 \times 1 \times 1 \) nm\(^3\). The corresponding mean potential energy for particle insertions
5.2 Flow past an array of nanotubes aligning vertically in graphite surface

Table 5.1: 3D Simulation of flow confined between two graphite plates, in which nanotubes are perpendicular to the lower graphite surface. \( \tau_f \) denotes the relaxation parameter when we pass the information from the continuum region to the MD region.

<table>
<thead>
<tr>
<th></th>
<th>( \tau_f )</th>
<th>sample resolution</th>
<th>global error(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybrid1</td>
<td>0.1</td>
<td>10000</td>
<td>7 × 4 × 4</td>
</tr>
<tr>
<td>hybrid2</td>
<td>0.1</td>
<td>40000</td>
<td>7 × 4 × 4</td>
</tr>
<tr>
<td>hybrid3</td>
<td>1</td>
<td>10000</td>
<td>7 × 4 × 4</td>
</tr>
</tbody>
</table>

in USHER algorithm [2] is \( \epsilon_0 = -5.4 \text{ kJ mol}^{-1} \), which is precomputed in a fully periodic simulation.

Two different treatments at the artificial boundary in x direction are considered, while y and z directions are again set to be periodic. The first treatment sets a specular wall with reinsertion of particles that leave the computational domain; The second treatment includes in addition the effective boundary force and potential. Fig.5.3 and Fig.5.4 show that the density profiles along the flow perpendicular direction. It can be seen that the effective force reduced the density oscillation significantly as expected; it should be noticed that density oscillation in non-equilibrium is stronger than that in equilibrium state, which indicates that the density oscillation is not only state point dependent [4], but also flow-configuration dependent (probably because particle will be reinserted into the computational domain, which will cause extra perturbations to the system).

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Now we are considering a 3D Couette flow of argon in a domain of size 18 × 4.254 × 4.912 nm³ as shown in Fig. 5.1. In this case, a constant velocity \( u_y = 100 \text{ m s}^{-1} \) is imposed at the upper graphite plate \( x = 19 \text{ nm} \) and the lower graphite plate \( x = 1 \text{ nm} \) is kept stationary. The carbon nanotube is perpendicular to the surface and centered in the x-y plane of the lower graphite plate with a length of 5 nm and chirality (8,8) with a radius of \( r = 0.54 \text{ nm} \).
For the reference solution, 7560 argon atoms are initially equilibrated for 5 ns, and then we gather the samples from 5 ns to 15 ns. During the simulation, $z$ direction is weakly coupled with a Berendsen thermostat at 131 K with a time constant $0.1 \triangle t_{MD}$.

For the hybrid simulation, we split the computational domain into 3 subdomains. The upper MD subdomain with 2550 argon atoms has a size of $6.0 \times 4.3 \times 4.9$ nm$^3$, which is subdivided into $6 \times 4 \times 4$ MD cells; the lower MD region with 4120 argon atoms has a size of $10.0 \times 4.3 \times 4.9$ nm$^3$; FEM subdomain with 7232 tetrahedral elements has a size of $8.0 \times 4.3 \times 4.9$ nm$^3$.

Fig.5.6 depicts the density profiles of the MD reference, the upper MD subdomain and the lower MD subdomain. It can be seen that the density fluctuation near the nanotube in the lower MD region vanishes at around 7 nm; the layering effect near the upper graphite plate ends up around 16 nm; the density oscillation near the two artificial boundary is approximately limited within a distance of 1 nm to the corresponding artificial boundaries ($x=10$ nm for the lower MD subdomain, $x=14$ nm for upper MD subdomain). In order to avoid extra perturbation from the layer effect to pollute velocity boundary condition extracted from MD subdomain, it is better to choose the overlap region so that the density in the cell, in which we extract the boundary condition for the continuum domain, is close to the bulk density. Based on the density profile in Fig.5.6, the size of the overlap region between each MD and the FEM subdomain is chosen to 3 nm in $x$ direction, which corresponds to 3 MD cells. The cell-wise thermostat is applied in 3 directions of the boundary cells with a coupling time constant $1 \triangle t_{MD}$ in order to prevent the cooling effect by the deterministic boundary force imposed there; the rest of cells are only thermostated by rescaling the $z$-component of the velocity with a coupling time constant $0.1 \triangle t_{MD}$. Each hybrid cycle consists of one FEM iteration and 10000 MD time steps (0.1 ns MD sampling time) to extract the velocity boundary condition for the continuum region.

In order to get an overview of how good the hybrid solution is, we compared the MD reference solution and hybrid solutions that neglect the atomistic details near the lower graphite surface by averaging the solutions in $y$-$z$ planes shown in Fig.5.7. In general, the difference between averaged MD and hybrid solutions are almost indistinguishable,
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except the small deviations near the upper graphite plates. Fig.5.8 and 5.9 depicts the comparison of hybrid solution (hybrid 1,2,3) with different parameters described in Table.5.1 and the MD reference solution at different x-y planes. All of the results are sampled over 10 ns. It can be seen that the velocity in the main stream (y direction) are generally close to the MD reference solution. We observed that the velocity vanishes near the nanotube and velocity slip occurs in the upper graphite surface as we showed in pure Couette flow. However, the hybrid velocity profile shows deviations in wall-perpendicular direction (x direction), atoms seem not to experience a drift due to the existence of nanotube, though the velocity profile is in good agreement with the MD reference solution. There are several reasons for this problem:

1. we chose a Couette flow near the graphite surface, which is more challenging problem than the high-speed flow of flow past nanotube [2]. Even we impose a reasonable large velocity \( u_y = 100 \text{ m s}^{-1} \) in the upper graphite surface, the maximum velocity in the profile is only \( 50 \text{ m s}^{-1} \) due to the velocity slip in the upper graphite surface. The atoms will experience a low-speed flow in the lower MD subdomain, especially no-slip boundary condition is reproduced near the surface of the nanotube. Due to the weak flow field there, we would get a smaller signal-to-noise ratio near the nanotube.

2. the spatial resolution with a cell volume of \( (1 \text{ nm}^3) \) might not resolve the velocity profile near the nanotube. However, to increase the solution, we will meet new problems, which will be discussed later.

3. Since one end of the nanotube is open, some of atoms of argon fall off into the nanotube, which causes a slight decrease of the density near the outlet of the nanotube. How this density discrepancy will influence the result is still unclear.

The point-wise error between hybrid simulation (hybrid 1) and the MD reference solution at different x-y planes normalized by each point are shown in Fig.5.11. It can be seen that the lower MD region (close to the nanotube) leads to the significant large error above 20%; while the upper MD region and the continuum region deviate further from the MD reference solution up to 5%. As shown in Fig.5.15 and Fig.5.19, hybrid 2,3 show the similar pattern. This is understandable: in the low speed region (smaller signal-noise ratio), even a small deviation would cause a large relative error. An large relative error doesn’t indicate a
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bad performance in the lower MD subdomain, which can be verified by the averaged solutions shown in Fig.5.7.

Fig.5.20 shows the evolution of the global error $e^k$ and the rate of change of the velocity field $d^k$. We monitored the error for 10 ns, which corresponds to 100 cycles for hybrid1, hybrid2 with 10000 samples in each cycle; 25 cycles for hybrid3 with 40000 samples in each cycle. It can be seen the error with 10000 samples in each cycle reaches the steady state around 20 cycles, and then fluctuates around 10%; The error with 40000 samples in each cycle gets to the steady state faster, and then level off around a value of 5%. In addition, we also measure the averaged error 2.65% for hybrid1, 1.93% for hybrid2, 2.68% for hybrid3 over 10 ns. The result indicates that more samples in each cycle will lead to a faster convergence with smaller noise but the global accuracy is weakly dependent on the number of samples in each cycle. Furthermore, the rate of the change $d^k$ reduce faster in the first 20 cycles and then reaches a plateau, wherever the error is not further reduced. In the mean time, we investigated the dependence of the simulation results on the strength of passing information from the continuum domain to the MD domain by adjusting the relaxation parameter $\tau_f$. As shown in Table.5.1 and Fig.5.20, the overall accuracy is roughly the same, which suggests that the result is not sensitive to the coupling strength between the MD domain the continuum domain for this example.

In the meantime, we also try to increase the spatial resolution to improve the convergence and accuracy. However, two problems comes out:

1. Thermostat problem: the thermostat used here is based on the cell-wise fluctuation of particle velocities during every MD time step. In the coarser grid, there are around 20 atoms in each cell. Now, if I try to double the resolution, there will be only 10 atoms in each cell, which might not be enough to get the accurate fluctuation. Therefore, it is hard to control the temperature, especially for the cells near the artificial boundary.

2. Convergence problem: since the velocity information passed from the MD domain to the continuum region is also averaged in cell-wise. In the higher spatial resolution, it leads to nosier data from the MD domain, which will cause a convergence problem in the continuum solver.
In conclusion, we show that hybrid solution of 3D nonlinear Couette flow has a good agreement with the MD reference solution, though larger deviations appear in the lower MD subdomain. In the meantime, the resolution seems not enough to resolve the details of flow pattern near the nanotube. In addition, more samples in each cycle leads to a better accuracy, but not a faster convergence. The relaxation approach by adjusting coupling strength parameter $\tau_f$ doesn’t improve the overall accuracy in this example.
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Figure 5.8: Comparison between MD reference and hybrid solution (hybrid1) in x-y plane of $z=0.614, 1.84$ nm. The colorscale and contour lines described the norm of velocity in the unit of $\text{ms}^{-1}$. 
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Figure 5.9: Comparison between MD reference and hybrid solution (hybrid1) in x-y plane of z=3.07, 4.298 nm. The colorscale and contour lines described the norm of velocity in the unit of ms\(^{-1}\).
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Figure 5.10: Point-wise error map between MD reference and hybrid solution (hybrid1) in x-y plane of z=0.614, 1.84, 3.07, 4.298 nm normalized by each point.

Figure 5.11: Point-wise error map between MD reference and hybrid solution (hybrid1) in x-y plane of z=0.614, 1.84, 3.07, 4.298 nm normalized by maximal velocity.
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Figure 5.12: Comparison between MD reference and hybrid solution (hybrid2) in x-y plane of z=0.614, 1.84 nm). The colorscale and contour lines described the norm of velocity in the unit of ms$^{-1}$. 
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Figure 5.13: Comparison between MD reference and hybrid solution (hybrid2) in x-y plane of z=3.07, 4.298 nm. The colorscale and contour lines described the norm of velocity in the unit of ms$^{-1}$. 
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Figure 5.14: Point-wise error map between MD reference and hybrid solution (hybrid2) in x-y plane of z=0.614, 1.84, 3.07, 4.298 nm normalized by each point.
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Figure 5.15: Point-wise error map between MD reference and hybrid solution (hybrid2) in x-y plane of z=0.614, 1.84, 3.07, 4.298 nm normalized by the maximal velocity.
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Figure 5.16: Comparison between MD reference and hybrid solution (hybrid3) in x-y plane of z=0.614, 1.84 nm. The colorscale and contour lines described the norm of velocity in the unit of ms$^{-1}$. 
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Figure 5.17: Comparison between MD reference and hybrid solution (hybrid3) in x-y plane of z=3.07, 4.298 nm. The colorscale and contour lines described the norm of velocity in the unit of ms$^{-1}$.
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Figure 5.18: Point-wise error map between MD reference and hybrid solution (hybrid3) in x-y plane of z=0.614, 1.84, 3.07, 4.298 nm normalized by each point.
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Figure 5.19: Point-wise error map between MD reference and hybrid solution (hybrid3) in x-y plane of z=0.614, 1.84, 3.07, 4.298 nm normalized by the maximal velocity.
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Figure 5.20: the evolution of the global error $e^k$ and residual $d^k$ between MD reference solution and hybrid solutions (hybrid1, hybrid2, hybrid3) averaged over 10 ns.
Chapter 6

Conclusion and Future work

6.1 Conclusion

We have presented a systematic study of a hybrid scheme by coupling continuum solution of Navier-Stokes equation with an atomic solution of molecular dynamics simulation via an alternating Schwarz method. The capability of the algorithm is examined by performing three numerical tests: a pure Couette flow confined between graphite plates, a Couette-like flow through a nanochannel with nanotubes parallel to the channel wall and a Couette-like flow through a nanochannel with nanotubes perpendicular to the channel wall.

We demonstrated that the hybrid scheme successfully reproduced the basic flow pattern of the MD reference solution under various flow configurations. We showed that the no-slip boundary condition breaks down near the graphite surface, velocity slip occurs in this length scale; the velocity around CNTs vanishes.

We also investigated the dependence of the convergence characteristics on different parameters involved in the hybrid scheme. The general results are summarized as follows:

- Increasing the size of the overlap region $d_{olp}$ leads to a faster convergence of the hybrid solution to the MD reference solution. However, the global error averaged over a certain time interval is weakly dependent on the overlap size.
6.2 Future work

- Increasing the number of samples $N_s$ in each hybrid cycle not only leads to a faster convergence, but also leads to a better accuracy in pure couette flow case. However, beyond the certain samples, the accuracy is not sensitive to this parameter anymore.

- Including relaxation feature by adjusting the coupling strength parameter $\tau_f$ effectively improves the overall accuracy in the simple Couette flow configuration, but it is not pronounced in the other two cases.

- Increasing spatial solution provides a more specific information of the flow pattern in nanoscale. However, it doesn’t result in a faster convergence; more samples in each hybrid cycle are usually required in order to compensate the extra noise due to the shrink of the cell volume.

6.2 Future work

So far, we have presented the simulation results of Couette-like flow through nanochannels with various surface patterns or constructions. Several interesting issues on the physics and algorithm level as follows are still worthwhile to try in the future in order to improve the understanding and performance of the hybrid scheme:

- On a physics level:
  1. different flow configurations other than shear-driven flow, such as pressure-driven flow and surface tension-driven flow (droplet spreading, nanowicking [11]), might be interesting to consider, which is of fundamental interest for many biological and engineering applications. In the meantime, other flow configurations could be easier to examine the performance of the hybrid scheme and a stronger velocity field near the nanotubes might be needed in order to compensate the large thermal fluctuations at the corresponding state point.
  2. In this project, since the system might be small, the resolution may be not enough to resolve the details near the nanotubes. Therefore, it would be good to use a larger system and a higher resolution to test the hybrid scheme in the future work.
  3. In this project, we only considered an isothermal system. Actually, it is also useful to include the thermal effects in the hybrid model to see how the temperature gradient with other
parameters, such pressure and surface tension, jointly affects the flow pattern that would be more exciting for the design of the prototype of micro- and nano-systems.

- On an algorithm level:
  1. Since many features, such as temperature control, the extraction of velocity boundary condition, in this hybrid scheme are based on a cell averaged value, it is better to design certain function to effectively distinguish the signal and noises, eg, add a filter before exchanged the information at the boundary.
  2. Improve the algorithm for the boundary condition imposition from the continuum domain to the MD domain. In this scheme, we impose the boundary condition in a deterministic approach, which will kill the correlations of atoms experience and prevent the hybrid solution from fully converging to the MD reference solution. Therefore, it is better to modify the boundary condition imposition routine with stochastic nature (adding more fluctuations) in order to reproduce the correct physics behind the phenomena.
  3. The convergence analysis should be further developed. The existing way to qualify the accuracy is not effective. For example, if one component of velocity is much larger than other components, the ways of calculating the point-wise error in which absolute error is normalized by each point and the maximal velocity can neither express the accurate information of the error in a reasonable way. The error information in different directions with low speeds could be screened out. Therefore, it might be useful to characterize the error in component-wise.
Bibliography


