

# Atomistic-Continuum Simulations of Liquids

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## ABSTRACT

We present a novel algorithm for the coupling of atomistic and continuum solvers for the simulation of liquids. The algorithm is based on the coupling of Lattice Boltzmann (LB) and Molecular Dynamics (MD) using an iterative Schwarz domain decomposition algorithm. The MD and LB formulations communicate via the exchange of velocities and velocity gradients at the interface. The lack of periodic boundary conditions in the molecular dynamics simulations, hinders the proper accounting for the virial pressure and leads to spurious density fluctuations at the continuum-atomistic interface. We present a novel control algorithm that eliminates such spurious density fluctuations. The present LB-MD model is validated on benchmark problems and it is used for the simulation of flows of liquid argon past a carbon nanotube.

**Keywords:** hybrid, atomistic, continuum, liquids, control

## 1 ATOMISTIC-CONTINUUM COUPLING

Multiscale computational modeling is required in order to describe effectively nanoscale phenomena that influence the behaviour of micro and macroscale flows. Examples include drag reduction phenomena for flows over nanopatterned surfaces and the motion of droplets as influenced by the structure of the contact line. Atomistic descriptions, such as Molecular Dynamics, are suitable for simulating the behavior of nanoscale systems while computational solutions of the Navier Stokes equations account effectively for continuum hydrodynamics. The need for efficient computations dictates a hybrid approach to integrate atomistic simulations with finite volume approximations and Lattice Boltzmann models

of the Navier Stokes equations, for simulations of flows at larger scales [5]. A number of hybrid models [1], [2],[3] coupling atomistic to continuum descriptions of dense fluids have been proposed. A recent work [4] has identified several computational difficulties in coupling atomistic and continuum descriptions that are mostly attributed to the elimination of periodicity in the MD description. A boundary force, based on the physics of the fluid being simulated [4], has been proposed in order to compensate for the density variations often observed in these couplings. Here we report on the extension of the model proposed in [4] by coupling the MD simulations with a Lattice Boltzmann (LB) method [6] of the incompressible NS equations, enhancing the exchange between atomistic and continuum domains by communicating velocity gradients in addition to velocities. In addition here we propose a novel control algorithm in order to circumvent the difficulties associated with this coupling.

We consider flow of a liquid past a Carbon Nanotube (CNT). An MD model describes the flow in the vicinity of a carbon nanotube (CNT) while a LB approach is used to simulate the behaviour of the continuum system away from the CNT.

The atomistic region is described by MD simulations where the positions  $\mathbf{r}_i = (x_i, y_i, z_i)$  and velocities  $\mathbf{u}_i = (u_{x,i}, u_{y,i}, u_{z,i})$  of the particles evolve according to Newton's equations of motion

$$\frac{d}{dt}\mathbf{r}_i = \mathbf{u}_i \text{ and } m_i \frac{d}{dt}\mathbf{u}_i = \mathbf{F}_i = - \sum_{j \neq i} \nabla U(r_{ij})$$

where  $\mathbf{F}_i$  and  $m_i$  are the force and mass of particle  $i$ , and  $r_{ij}$  is the distance between the particle  $i$  and  $j$ . Here we consider Lennard-Jones (LJ) model of argon interacting with

CNTs. The potential  $U(r_{ij})$  is defined as

$$U(r_{ij}) = 4\epsilon_{AB} \left[ \left( \frac{\sigma_{AB}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{AB}}{r_{ij}} \right)^6 \right] + U_b(r_w, \rho, T)$$

where  $\epsilon_{AB}$  and  $\sigma_{AB}$  are energy and length parameters,  $A$  and  $B$  denote species. The LJ interaction parameters for argon-argon and argon-carbon interactions are respectively  $\epsilon_{ArAr} = 0.9960$  kJmol<sup>-1</sup>,  $\sigma_{ArAr} = 0.3405$  nm,  $\epsilon_{ArC} = 0.5697$  kJmol<sup>-1</sup>,  $\sigma_{ArC} = 0.3395$  nm. The term  $U_b$  is the boundary potential and accounts for the interaction of the boundary region with the surrounding medium. The CNT is modeled as a rigid structure to and all interaction potentials are truncated for distances beyond a cutoff radius  $r_c = 1.0$  nm. The equations of motion are integrated using a leapfrog scheme with a time step  $\delta t = 10$  fs.

The continuum hydrodynamics are described by the incompressible Navier-Stokes equations

$$\begin{aligned} \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} &= -\nabla p / \rho + \nu \nabla^2 \mathbf{u} + \mathbf{g}, \\ \nabla \cdot \mathbf{u} &= 0 \end{aligned}$$

where  $\mathbf{u}$  is the fluid velocity,  $p$  the pressure,  $\rho$  the density and  $\mathbf{g}$  a body force. We use  $\mathbf{g}$  to enforce Dirichlet boundary conditions. We solve the Navier-Stokes equations by using a Lattice Boltzmann algorithm [6]. The atomistic and continuum descriptions are coupled in a hybrid approach based on a Schwarz domain decomposition technique, originally proposed in [1]. The key assumption of this hybrid approach is that the decomposition of the system is valid and that the two descriptions match in the overlap domain (see Fig. 1).

A Schwarz iteration  $t_c$  consists of computing the continuum velocity field  $\mathbf{u}_c(t_c)$  with boundary conditions set by the previous atomistic cycle  $\mathbf{u}_a(t_c - 1)$  and an external boundary condition that depends on the system considered. Then,  $\mathbf{u}_c(t_c)$  is used to set the boundary condition for computing  $\mathbf{u}_a(t_c)$ .

MD velocities are sampled in cells of same size as in the LB domain and are enforced on the continuum according to two coupling methods. The first approach corresponds to the one used by Werder *et al.* and is to impose MD velocities within a one cell wide strip located at a distance  $\delta_s$  of the MD subdomain, see Fig. 1. This velocity coupling (VC) approach does not enforce velocity gradients implying that the geometry of the system and

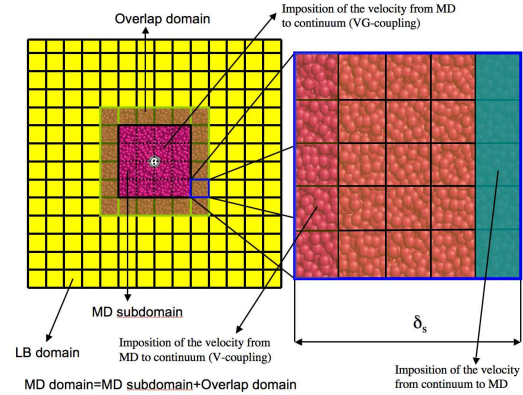


Figure 1: Domain decomposition. The converged solution is obtained by alternating iterations in the LB and MD domains. We consider two ways for imposing the velocity boundary condition from the MD to the continuum. In the case of V-coupling we pass the velocities within a one-cell wide strip located at distance  $\delta_s$  from the end of the MD domain. In the case of the VG-coupling we impose MD velocities on every common cell except within a strip of width  $\delta_s$  close to the boundary.

the external boundary conditions dictate whether the hybrid solution evolve into a good approximation of the reference solution. To alleviate this issue we propose an enriched coupling method which enforces velocities, and implicitly velocity gradients (VGC) by imposing MD velocities on every common cell except within a strip of width  $\delta_s$  close to the boundary (see Fig. 1). Our results indicate that the VGC approach leads to a closer match with MD reference solutions than the VC method.

We present hybrid simulations of the flow past a CNT [6] embedded normal to the flow direction in order to compare our results with [4]. The hybrid model is run for 100 cycles which consists of running the LB simulation for 7 ns (15000 iterations) followed by an MD step equilibrating for 0.2 ns (20000 iterations) and sampling for  $t_s = 0.4$  ns. We quantify the convergence towards the reference MD solution by defining an error  $e^j$  between the hybrid solution at cycle  $j$  and the reference MD solution as

$$e^j = \frac{1}{N} \sum_{k \in \Omega} \frac{|\mathbf{u}_k^j - \mathbf{u}_{k,MD}|}{u_\infty} \quad (1)$$

where  $N$  is the number of cells in  $\Omega$ ,  $\mathbf{u}_k^j$  and

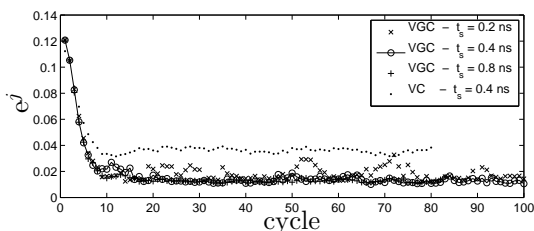


Figure 2: Evolution of the error  $e^j$  between the hybrid solution and the reference MD solution. Different sampling time  $t_s$  and coupling techniques are considered. In the case of VGC the error reaches a plateau (top) three times smaller than in the VC approach.

$\mathbf{u}_{k,MD}$  are respectively the hybrid and reference MD velocities at cycle  $j$  in the cell  $k$ .

Fig. 2 shows the time evolution of the error which rapidly decays during the first 10 cycles. The error then fluctuates around an average value which is a function of the sampling time  $t_s$ . Considering the VGC approach we observe in Fig. 2 that considering short  $t_s$  leads to undesirable fluctuations whereas long  $t_s$  decreases the computational efficiency of the model. An optimum is found to be  $t_s = 0.4$  with an average error of 1.3% approximately 3 times smaller than the one found considering the VC method.

## 2 DYNAMIC CONTROL OF DENSITY FLUCTUATIONS

Werder *et al.* [4] combined a hard wall with boundary potentials based on the radial distribution function of the system that is being simulated in order to impose the local system pressure. This scheme was found to significantly reduce the density perturbations in the molecular system compared to existing algorithms at the supercritical state point ( $T^* = 1.8, \rho^* = 0.6$ ). However in [7] we demonstrate that even this approach cannot fully eliminate density oscillations whose amplitude depends on the state point of the liquid. We examine the validity of this method in an additional state point in the liquid regime ( $T^* = 0.7, \rho^* = 0.89$ ). The method is found to encounter difficulties when lowering the temperature, while increasing the density, at constant pressure, leading to density oscillations close to the boundary. The amplitude of these oscillations amounts to 15% and is well below

previously reported values in hybrid simulations [4] but they may still cause unnecessary disturbances to the atomistic system.

We develop a mean external boundary force using a control algorithm to minimise the density perturbations in the MD system. An iteration progresses as follows: we start by applying the external boundary force as proposed in [4]. We conduct the MD simulation sufficiently long so as to measure the density with an uncertainty less than 2%. The density profile is measured with a spatial resolution of 0.0164 nm. We then evaluate the error as:

$$e(r_w) = \rho^t - \rho^m(r_w), \quad (2)$$

where  $r_w$  is the distance to the boundary,  $\rho^t$  the desired constant target density and  $\rho^m$  the measured value. We compute the gradient of this error as  $\epsilon(r_w) = \nabla e(r_w) = -\nabla \rho^m(r_w)$  and amplify this with a factor  $K_P$ . We filter the resulting signal to avoid spurious oscillations during the iteration process to obtain the changes  $\Delta F$  in the boundary force. The boundary force is finally computed as:

$$F_i^{new} = F_i^{old} + \Delta F_i,$$

We test this approach for the state point ( $T^* = 0.7, \rho^* = 0.89$ ) where the mean force algorithm of Werder *et al.* [4] failed to eliminate fluctuations. The results shown in Fig. 3 demonstrate that the method converges and eliminates the density oscillations. When compared with the initial force, we observe a decrease of the magnitude of the force close to the boundary and a shift for the location of the minimum. At larger distances from the wall ( $r_w > 0.6$  nm) the shape of the force is not altered. We find a value of  $K_P = 0.4 \frac{\text{nm}^3 \text{mol}}{\text{amu kJ}}$  to guarantee good stability properties and fast convergence.

In addition, we examine the performance of the control algorithm in the case of parallel flow at the state point ( $T^* = 0.7, \rho^* = 0.89$ ). The periodicity is broken in the flow direction ( $x$ ). As described in [4] atoms at the non-periodic boundary of the computational domain bounce with hard walls, which move with the local fluid velocity. At the end of each time step these walls are reset to their initial positions to maintain a fixed frame of reference. As a consequence some particles may remain outside the computational domain and are reinserted in regions

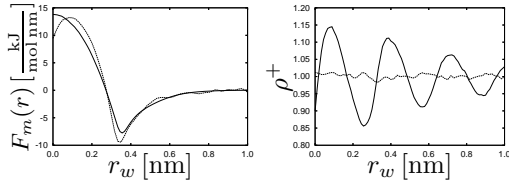


Figure 3: Left: The initial external boundary force computed taking the fluid structure into account and the resulting one after applying dynamic control theory at the state point ( $T^* = 0.7, \rho^* = 0.89$ ). Right: The corresponding uncontrolled (—) and controlled reduced density values (---).

of inflow. This removal and insertion of particles is not symmetric and therefore we control the forces at the inlet and outlet of the computational domain separately. In Fig. 4 we show the external boundary force in the controlled and uncontrolled cases and the resulting reduced density profiles. The perturbed density in the uncontrolled case also leads to oscillations in the streaming velocity ( $u$ ) of the atoms (see Fig. 4). The controller successfully eliminates the deviations from the target value for both quantities at both the inlet and outlet boundaries.

## Conclusions

We introduce hybrid, LB-MD simulations of dense fluids using a Schwarz domain decomposition technique. The two descriptions are coupled by velocities or velocity gradients. The improvement through the latter approach is attributed to the exchange of shear forces. In addition, we propose a control algorithm to eliminate spurious density fluctuations in continuum-MD couplings. The validity of the algorithms is shown in a number of benchmark problems and in three-dimensional simulations of liquid flows past carbon nanotubes.

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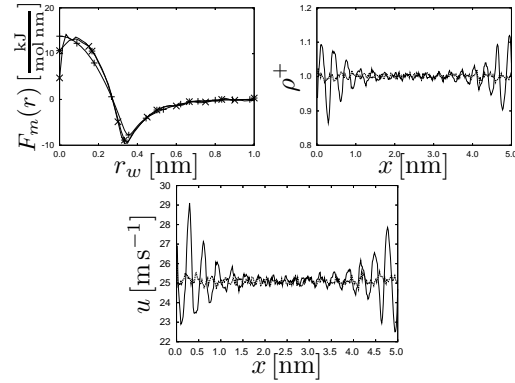


Figure 4: Top Left: The external boundary forces at the state point ( $T^* = 0.7, \rho^* = 0.89$ ) in the case of parallel flow: (—+—) uncontrolled case, (—×—) controlled case (inflow), (—\*—) controlled case (outflow). Top Right: The resulting reduced density ( $\rho^+$ ) profiles in the  $x$ -direction: (—) uncontrolled case, (---) controlled case. Bottom: Resulting velocity profiles in the  $x$ -direction at the state point ( $T^* = 0.7, \rho^* = 0.89$ ) in the case of parallel flow: (—) uncontrolled case, (---) controlled case.

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