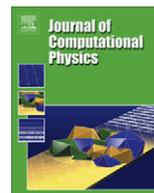




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Short note

Multiscale simulation of water flow past a C_{540} fullereneJens H. Walther^{a,b}, Matej Praprotnik^c, Evangelos M. Kotsalis^a, Petros Koumoutsakos^{a,*}^a Institute of Computational Science, ETH Zurich, CH-8092 Zurich, Switzerland^b Department of Mechanical Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark^c Laboratory for Molecular Modeling, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

ARTICLE INFO

Article history:

Received 6 June 2011

Received in revised form 14 October 2011

Accepted 15 December 2011

Available online 2 January 2012

Keywords:

Multiscale simulation

Fluid flow

Buckyball

Molecular dynamics

Lattice–Boltzmann

Domain decomposition

Flux-based algorithms

ABSTRACT

We present a novel, three-dimensional, multiscale algorithm for simulations of water flow past a fullerene. We employ the Schwarz alternating overlapping domain method to couple molecular dynamics (MD) of liquid water around the C_{540} buckyball with a Lattice–Boltzmann (LB) description for the Navier–Stokes equations. The proposed method links the MD and LB domains using a fully three-dimensional interface and coupling of velocity gradients. The present overlapping domain method implicitly preserves the flux of mass and momentum and bridges flux-based and Schwarz domain decomposition algorithms. We use this method to determine the slip length and hydrodynamic radius for water flow past a buckyball.

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The transport of nanoparticles through fluids is essential for applications ranging from gene delivery [1], to industrial coatings [2], and diagnosis and therapy in cancer [3]. Here, we propose the study of fullerenes in aqueous environments as a prototypical problem for such transport processes. Simulations can provide insight into such systems when they can access, both, the atomistic length scales associated with size of the fullerenes and the micro/macro scales characteristic of the carrier flow field. Simulations using molecular dynamics (MD) can capture the atomistic details of the fullerene–liquid interface [4,5] but due to their computational cost they cannot be extended, in the foreseeable future, to the macroscale regime of the full flow field. In turn continuum descriptions, using the Navier–Stokes (NS) equations may capture the macroscale behavior of the flow but they fail to represent accurately the flow field at the fullerene surface.

The interfacing of continuum and atomistic descriptions in a multiscale framework has attracted significant interest in recent years (see reviews [6–8] and references therein). Earlier works on multiscale modeling have addressed methodological developments on the exchange of information between monoatomic molecules and continuum descriptions in the context of flux-exchange and Schwarz domain decomposition algorithms [9–12]. In recent years, these approaches have been extended to systems with polyatomic and polar molecules, e.g., water [7,13,14]. A recent extension to include a coarse-grained molecular description in the model [15,16], has opened up the route to perform MD simulations of complex liquids in the grand-canonical ensemble or under non-equilibrium conditions [17]. In spite of substantial progress, hybrid schemes are yet to become a practical simulation tool for micro-nanoscale flow phenomena. One of the remaining challenges is that, to this date, all hybrid schemes have coupled the MD and continuum regimes only along one direction of the system, while periodic boundary conditions (BCs) have been employed in the other directions. The extension of these methodologies to fully three-dimensional (3D) interfaces would allow for a much wider spectrum of applications, e.g., studies of 3D fluid flows

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past 3D obstacles (with general flow BCs), which can differ significantly from 2D counterparts. Recently, a simulation of a 3D flow past a neutrally buoyant impermeable bead was presented using a hybrid scheme that couples an explicit fluctuating compressible NS solver with the isotropic Direct Simulation Monte Carlo method [18]. However, to date, a fully 3D coupling scheme of MD and NS solvers has not been reported.

In this Note, we present a multiscale simulation of liquid water flow with a freestream velocity $u_\infty = 0.05$ nm/ps past an immobile C_{540} fullerene molecule with a radius $R \approx 1.03$ nm, cf. Fig. 1. We extend the Schwarz domain decomposition scheme [19,20,14] and introduce the following algorithmic improvements:

1. Velocity gradient coupling between the atomistic and continuum descriptions, thus bridging flux based and Schwarz domain decomposition schemes.
2. A full 3D coupling between atomistic and continuum domains.
3. A DPD thermostat to ensure conservation of momentum.

The coupling is performed by embedding a spherical atomistic region inside a cubical continuum domain of size $L_{LB} = 16$ nm where the NS equations are solved by the Lattice-Boltzmann (LB) method. We deploy a L_{LB}^3 lattice covering the entire computational domain with lattice nodes centered in corresponding cubical MD sampling cells of size $a = 1$ nm. This spatial resolution enables us to capture the high velocity gradients of the flow. In the atomistic region we use MD simulations, solving Newton's equations of motion for each atom to describe the flow in the vicinity of the fullerene. The MD domain, which provides the LB method with the velocity and density BCs, is spherical with a diameter of $L_{MD} = 10$ nm. The fullerene molecule is at the center of the domain and is fixed during the simulation. To exert the correct mean virial pressure on the MD domain we impose non-periodic BCs in all three directions using a boundary force [14]. Due to symmetry, the force has only a radial component, normal to the interface. In addition, we use a specular boundary to impose the ideal kinetic part of the system pressure. We model liquid water using the rigid SPC/E water model [21]. The simulations are performed at $T = 300$ K and $\rho = 0.997$ g/cm³. We assume that the flow is incompressible, and hence perform the MD simulations using a constant volume ensemble. The parameters for the interaction between water molecules and carbon atoms in the rigid fullerene are taken from Refs. [22,23]. Long range electrostatic interactions are treated by the reaction field method with a cutoff of 0.8 nm [24]. The time step δt used for the MD integration is 2 fs. In order to correctly describe the hydrodynamics and account for the resolution change [17] we employ in this study the linear momentum preserving dissipative particle dynamics (DPD) thermostat [25] with a friction constant $\zeta = 1.0$ amu/ps. The latter is small compared to the intrinsic friction coefficient of water, so that the dynamics is not affected [25]. We use the Schwarz alternating method to compute the steady state solution. The details of the basic scheme are given in Refs. [19,14]. Here we present its extension to the fully 3D atomistic-continuum interface employing an improved coupling between the two regimes. The velocity BCs passed from the MD to the LB domain at the inner part of an overlap region (transparent grid cells in Fig. 2). We extract the velocity BC for the MD from the corresponding LB solution and impose it to all computational grid cells at the outer part of the overlap region [9]. These grid cells are depicted in Fig. 2 as blue grid cells. By matching the local MD and LB velocities in adjacent grid cells of the overlap domain we match in addition the velocity gradients in the two domains. Consequently, the momentum flux (on the continuum level) is implicitly conserved across the atomistic-continuum boundary [15]. The geometry mismatch

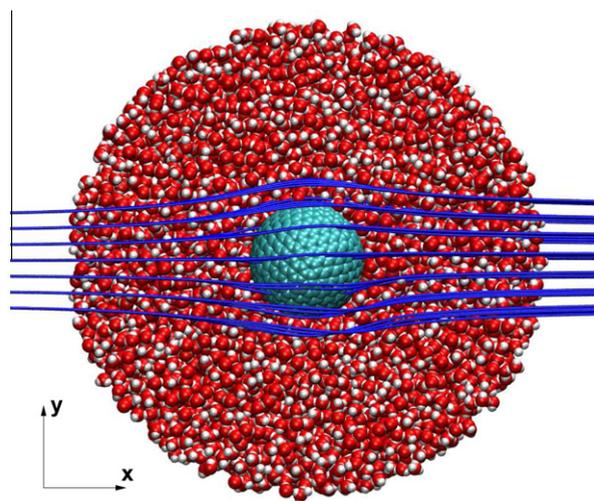


Fig. 1. Multiscale flow past the C_{540} fullerene molecule with the central atomistic domain embedded in a continuum model. The flow is from left to right and blue lines denote the streamlines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

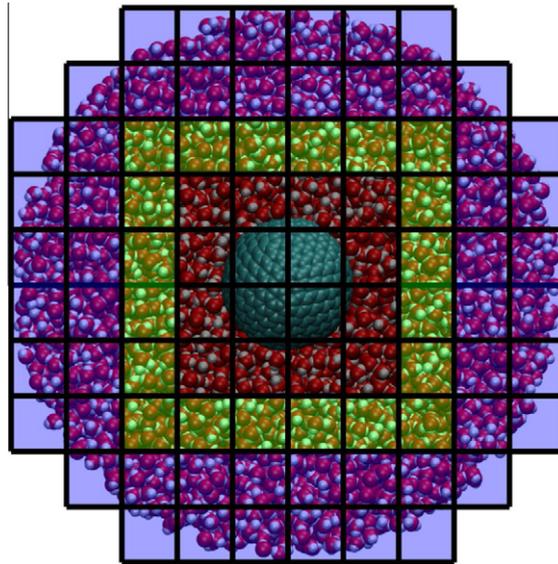


Fig. 2. Cross-section through the overlap region. The transparent grid cells around the fullerene serve to pass information from MD to LB. The blue cells are the outer part of the overlap region where the LB information is passed to MD. Both descriptions co-exist at the green layer, between the inner and outer parts. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

between the spherical MD boundary and cubically decomposed LB domain leads to overlap grid cells, which are only partially filled with MD particles (see grid cells close to the spherical boundary in Fig. 2). To circumvent this problem of corner singularities these grid cells are discarded from the MD to LB information passing. Note that we only consider the MD solution and discard the continuum one in the inner part of the overlap region for the computation of physical quantities. The opposite is done in the outer (blue) domain. In the intermediate, green domain, no BCs are imposed at any time. Here both solutions are valid and we report their average.

In the hybrid simulation, velocity BCs are exchanged between the MD and LB every 40,000 MD steps so that the MD averages are sufficiently sampled to ensure convergence. An $\mathcal{O}(10)$ iterations are needed to reach the steady solution depicted in Fig. 1. The streamlines display a weak asymmetry in the upstream and downstream of the buckyball, characteristic for flows at a finite, low Reynolds number [26]. The Reynolds number ($Re = \rho u_\infty 2R/\eta$, where η is the dynamic viscosity of the fluid [27]) for our flow is $Re \approx 0.13$.

We validate our multiscale technique against a reference (full-blown) atomistic MD simulation. In Fig. 3(a) we depict u_x , the x -component of the fluid velocity along the center line of the simulation domain passing through the fullerene in the x -direction, obtained from hybrid and reference atomistic MD simulations. The box size of the reference system is L_{LB}^3 . The system is subject to periodic BCs with the center of mass velocities of the molecules adjusted to satisfy the velocity BC of u_∞ in the flow direction. We adjust the velocities in cells located at the inlet of the computational domain. The velocity profile from the multiscale simulation is a time average of a steady-state system, i.e., we consider only iterations after the system has

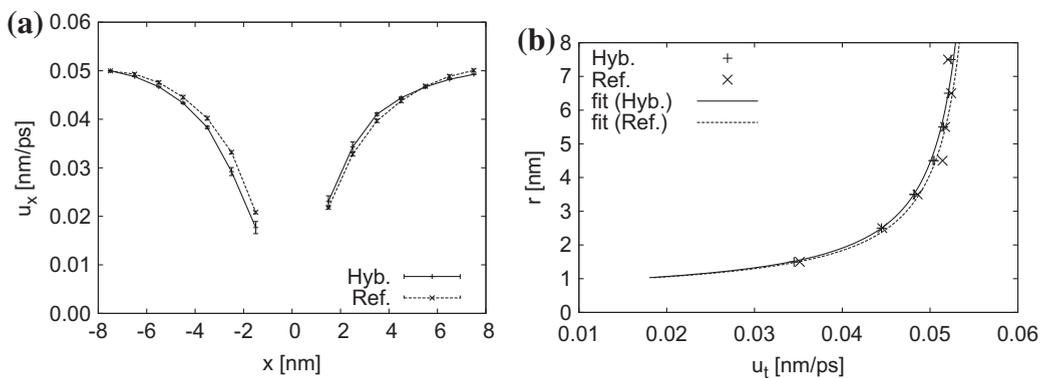


Fig. 3. (a) The x -component velocity profile along the line passing through the fullerene molecule in the x -direction. Both hybrid and reference all-atom solutions are shown. (b) The tangential velocity profile in the radial direction from the fullerene (sampled in the interval $|x| < 0.5$ nm).

reached the steady-state. The reference MD solution was sampled from an equilibrated system. The agreement between the results from multiscale and reference simulations is good. Nevertheless, it can be further improved by fine-tuning the relaxation strength parameter for imposing the velocity BCs from LB to MD [9] and a . As expected, u_x decreases from u_∞ far away from the fullerene to zero at its surface (here we do not present the actual values at the surface due to the chosen size of a) in both upstream and downstream sides.

Experimental studies show that the type of velocity BC on the buckyball surface depends on the solvent type [28]. Therefore, to determine the velocity BC we measure the drag force F_D acting on the buckyball. The F_D s from the hybrid and reference MD simulations are 431 ± 24 kJ/mol nm and 449 ± 46 kJ/mol nm, respectively. The drag force F_D is calculated by summing up the total forces on all carbon atoms of the fullerene in the direction of the flow. F_D is sampled over 40,000 MD steps and block-averaged using data blocks of 100 MD steps. To extract the hydrodynamics radius R_H we use $F_D = 6\pi \left(\frac{R_H + 2\lambda}{R_H + 3\lambda} \right) \eta R_H u_\infty$, where λ is the slip length, for the Stokes flow past a sphere with partial slip BCs [29]. Limits $\lambda = 0$ and $\lambda \rightarrow \infty$ yield standard $F_D = 6\pi\eta R_H u_\infty$ and $F_D = 4\pi\eta R_H u_\infty$, for the stick and perfect-slip BCs, respectively [30]. We determine the unknown λ by fitting the computed tangential velocity u_t radial profile presented in Fig. 3(b) with a function $u_t(r) = u_s + (u_\infty - u_s)(1 - 3R_H/4r - R_H^3/4r^3)$ [26]. We start with the initial guess $R_H = R$ and measure the slip velocity $u_s = u_t(R_H)$, and extract from $u_s = \lambda(\partial u_t / \partial r|_{r=R_H} - u_t/R_H)$ the slip length λ . We insert λ in the above expression for F_D and calculate a new estimate for R_H . With this value we repeat the fitting. After a few iterations the converged values are $u_s = 0.027 \pm 0.001$ nm/ps, $\lambda = 0.60 \pm 0.02$ nm, $R_H = 1.22 \pm 0.06$ nm and $u_s = 0.030 \pm 0.001$ nm/ps, $\lambda = 0.94 \pm 0.03$ nm, $R_H = 1.32 \pm 0.11$ nm for the hybrid and reference simulations, respectively. The respective fits are displayed in Fig. 3(b). These λ values are of the order of the characteristic length scale of the fluid–solid interaction, i.e., the Lennard–Jones interaction parameter $\sigma_{CO} = 0.34$ nm, consistent with our previous findings for nanotubes [31]. Also, R_H s are comparable with $R + \sigma_{OO}$ [32]. We note a $\approx 36\%$ difference on the slip length as computed by the hybrid and the reference computation. We attribute this discrepancy in the limited number of data available of the velocity fitting and the subsequent gradients used to obtain the slip length. Having calculated u_s , λ , and R_H we compare the diffusion constant D of the buckyball, computed from an equilibrium periodic BCs all-atom simulation using the finite size correction [33], with the one obtained from our multiscale flow simulations assuming Stokes–Einstein relationship $D = k_B T / \zeta = k_B T u_\infty / F_D$ [28]. Here ζ is the frictional coefficient of the buckyball. We find a reasonable agreement between $D \approx 3.2 \times 10^{-4}$ nm²/ps and $D \approx 2.8 \times 10^{-4}$ nm²/ps (approximately an order of magnitude lower than the self-diffusion constant of water) for the equilibrium and flow simulations, respectively. This is a further indication that the nanoscale flow characteristics are correctly determined by our multiscale approach.

In conclusion, we have presented a multiscale flow simulation of water past a C_{540} fullerene using, for the first time, a fully 3D interface between atomistic and continuum descriptions of the flow and an algorithm that conserves the mass and momentum flux. The atomistic region was limited to a sphere embedding the fullerene molecule, leading in this particular case to an approximate speedup of ≈ 15 compared to the full-blown MD simulation (note that the LB solver is $O(100)$ faster than MD). This is important because hydrodynamic interactions are long-ranged and we often need very large systems to eliminate finite size effects. Our results help demonstrate that the proper description of the BCs as obtained by MD and passed to the continuum play an essential role in the multiscale modeling of nanoscale flows. The present method enables the study of nanoscale flow phenomena that are beyond the reach of either pure atomistic or continuum simulations and paves the way for simulation based studies of nano-bio interfaces such as the use of fullerenes for targeted drug delivery.

Acknowledgements

JHW acknowledges additional financial support through the Grant 274-06-0465 from the Danish Research Council. MP acknowledges additional financial support through the Grants J1-2281, P1-0002, and BI-DK/11-12-002 from the Slovenian Research Agency.

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