Hybrid molecular dynamics - hydrodynamics framework for modelling liquids

Dmitry Nerukh, Arturs Scukins, Evgen Pavlov, Sergey Karabasov, Anton Markesteijn
Department of Mathematics, Aston University, Birmingham, UK
School of Engineering & Materials Science, Queen Mary, University of London, UK
`D.Nerukh@aston.ac.uk`

A multiscale Molecular Dynamics / Hydrodynamics method is developed for simultaneous modelling liquid systems at atomistic and fluctuating hydrodynamics levels. The method is implemented for a 2D Mercedes Benz (MB or BN2D) water model. The concept and the governing equations of multiscale coupling together with the results of successful implementation are reported. It is demonstrated that the standard deviations of velocity fluctuations, the radial distribution of molecules, and their velocity autocorrelation functions are consistent with the structure and dynamics of the liquid at the limits of pure Molecular Dynamics and pure hydrodynamics descriptions and at all intermediate values of the coupled implementation.

Motivation

In molecular modelling the focus is increasingly shifting towards large molecular systems such as biological macromolecules, the aggregates of molecules (for example various kinds of membranes, including biological), or even entire living cell organelles with all their molecular complexities (the so called 'crowded' biomolecular systems). Necessarily approximations have to be used to make large scale representation of the system computationally feasible. These include various coarse graining techniques, continuum modelling, combinations of the two, and other approaches.

In the hydrodynamic limit the number of particles in atomistic molecular dynamics simulations makes critical difference in terms of computational efforts. Here 2D models can offer a reasonable compromise between the accuracy and the computationally efficiency. For water the 2D Mercedes Benz (MB) model reproduces many important aspects of experimentally observed behaviour, while it is significantly faster in comparison with high-fidelity 3D water models such as TIP4P.

Methodology

Following the standard approach in two-phase modelling, we consider a mixture of two completely miscible liquids in the system. One phase corresponds to the Lagrangian phase (MD particles) and the other is the Eulerian phase (FH continuum).

Coupling between the phases is introduced by allowing the exchange of mass and momentum between the phases. The parameter that quantifies the distribution of mass and momentum between the phases is denoted as s and mathematically it is represented by a smoothly changing function of space (and possibly time) describing the concentration of each phase. The value of s varies from 0 to 1, for example, in the centre of the system we could have mostly MD description ($s \approx 0$) and on the edges it is mostly FH ($s \approx 1$).

We use the following definitions. The MD phase is described by particles, the properties of which (density and velocity) are calculated as averages over the cell on the regular grid, and forms an MD 'liquid' with the density $\sum_p \rho_p$ and momentum $\sum_p \rho_p u_{ip}$, where $\rho_p = \frac{m_p}{V}$, u_{ip} are the MD particle's density and velocity of i^{th} spatial component respectively, m_p is the particle's mass, and V is the cell volume.

The Eulerian phase (FH), that corresponds to the cell averages on the regular grid, forms the FH 'liquid' with the density ρ and the momentum ρu_i, one value of each per grid cell.

The mixture of these two liquids has the density

$$\tilde{\rho} = s\rho + (1-s)\sum_p \rho_p$$

and the momentum

$$\tilde{u}_j\tilde{\rho} = s u_j \rho + (1-s)\sum_p \rho_p u_{jp}.$$

We require mass and momentum conservation of the mixture of FH and MD 'liquids' at all concentration values s.

Mass conservation

The conservation laws of mass of each phase are given by:

$$\frac{\partial}{\partial t} s\rho + \frac{\partial}{\partial x_i}\tilde{u}_i s\rho = J^\rho,$$
$$\frac{\partial}{\partial t}(1-s)\sum_p \rho_p + \frac{\partial}{\partial x_i}(1-s)\sum_p u_{ip}\rho_p = -J^\rho,$$

where J^ρ is a sink/source that transfers mass between the phases.

Momentum conservation

The FH phase is modelled using a generalisation of the deterministic Navier-Stokes equations for microscopic flows, Landau Lifshitz - Fluctuating Hydrodynamics equations (LL-FH), that account for fluctuating stochastic sources originating from microscopic molecular motion.

The momentum conservation equation for the FH 'liquid' can be written as

$$\frac{\partial}{\partial t} s\rho u_j + \frac{\partial}{\partial x_i}\tilde{u}_i u_j s\rho = sF_j + J^u$$

and for the MD 'liquid' it is

$$\frac{\partial}{\partial t}(1-s)\sum_p \rho_p u_{jp} + \frac{\partial}{\partial x_i}(1-s)\sum_p u_{ip}u_{jp}\rho_p =$$
$$= (1-s)\sum_p F_{jp} - J^u,$$

where J^u is the momentum exchange rate,

$$F_j = \nabla_j\left(\Pi_{ij} + \tilde{\Pi}_{ij}\right),$$

F_j is the hydrodynamic force, and F_{jp} is the intermolecular force that acts on each particle in the MD 'liquid'.

The deterministic hydrodynamic stress tensor is calculated as

$$\Pi_{ij} = -\left(P - \xi\nabla\cdot\vec{u}\right)\delta_{ij} +$$
$$+\eta\left(\partial_i u_j + \partial_j u_i - 2D^{-1}\nabla\vec{u}\cdot\delta_{ij}\right),$$

where ξ and η are shear and bulk viscosities, D is the dimensionality of the system, P is pressure.

The stochastic stress tensor is calculated as

$$\tilde{\Pi}_{ij} = \sqrt{\frac{2k_BT}{\delta t\delta V}}\left(\sqrt{2}\sqrt{\eta}\cdot G^s_{ij} + \sqrt{D}\sqrt{\xi}\frac{tr[G]}{D}E_{ij}\right),$$

where k_B is the Boltzmann constant, δV is the cell volume, δt is the time scale (equal to the time step in numerical implementations), T is temperature, G is the Gaussian matrix, and $G^s_{ij} = \frac{G_{ij}+G^T_{ij}}{2} - \frac{tr[G]}{D}E_{ij}$, where $tr[\mathbf{G}]$ is the trace.

Implementation

In order to maintain the conservation of mass we introduce the following dynamical law:

$$\frac{D}{Dt_0}\left(\tilde{\rho} - \sum_p \rho_p\right) = \frac{\partial}{\partial x_i}\left[s\left(1-s\right)\alpha\frac{\partial}{\partial x_i}\left(\tilde{\rho} - \sum_p \rho_p\right)\right],$$

controlled by a parameter $\alpha > 0$, where $\frac{D}{Dt_0} = \frac{\partial}{\partial t}\cdot + \frac{\partial}{\partial x_i}\tilde{u}_i\cdot$. This drives the deviation of the average density $\tilde{\rho}$ to the correct value $\sum_p \rho_p$ within the zone where $0 < s < 1$ and equals zero at the limits $s = 0$ and $s = 1$.

Using similar approach for momentum conservation leads to the following modified equations of motion for the atoms:

$$\frac{dx_{ip}}{dt} = u_{ip} + s(\tilde{u}_i - u_{ip}) +$$
$$+s(1-s)\alpha(x)\frac{1}{\rho_p N(t)}\frac{\partial}{\partial x_i}\left(\tilde{\rho} - \sum_p \rho_p\right),$$

$$\frac{du^N_{jp}}{dt} = (1-s)F_{jp}/\rho_p +$$
$$+\frac{1}{\rho_p N(t)}\frac{\partial}{\partial x_i}\left[s(1-s)\alpha(x)\frac{\partial}{\partial x_i}\left(\tilde{\rho} - \sum_p \rho_p\right)\frac{\sum_p u_{jp}}{N(t)}\right]$$
$$-\frac{1}{\rho_p N(t)}\frac{\partial}{\partial x_i}\left[s(1-s)\beta(x)\frac{\partial}{\partial x_i}\left(\tilde{u_j}\tilde{\rho} - \sum_p \rho_p u_{jp}\right)\right].$$

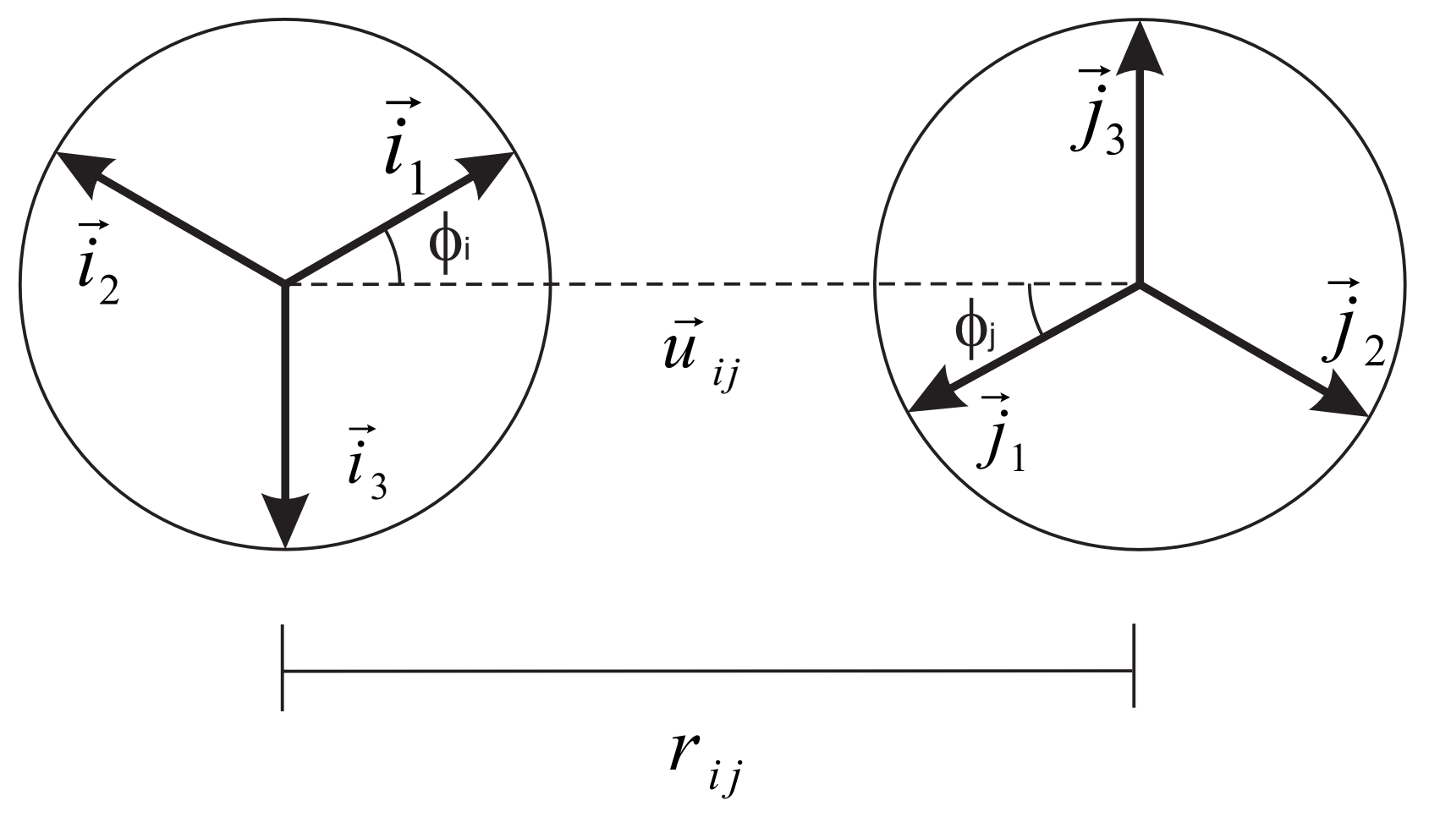
where $N(t)$ is the number of particles in the cell.

For the FH liquid the following conservation equation is used:

$$\frac{\partial}{\partial t}\tilde{\rho}\tilde{u}_j + \frac{\partial}{\partial x_i}\tilde{u}_i\tilde{\rho}\tilde{u}_j = \frac{\partial}{\partial t}\sum_p \rho_p u_{jp} + \frac{\partial}{\partial x_i}\tilde{u}_i\sum_p \rho_p u_{jp}$$
$$+sF_j + \frac{\partial}{\partial x_i}\left[s(1-s)\beta\frac{\partial}{\partial x_i}\left(\tilde{u_j}\tilde{\rho} - \sum_p \rho_p u_{jp}\right)\right].$$

Mercedes-Benz water model

Molecules interact pairwise through the Lennard-Jones term and an explicit hydrogen bounding term (which depends on the respective orientation of the arms).



The total potential is

$$\Phi = \Phi_{LJ} + \Phi_{HB},$$

where the Lennard-Jonnes potential Φ_{LJ}

$$\Phi_{LJ} = \sum_{ij}^{N} 4\,\epsilon_{LJ}\left(\left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{6}\right),$$

and Φ_{HB} is the explicit hydrogen bonding term defined as

$$\Phi_{HB} = \sum_{ij}^{N}\epsilon_{HB}\cdot G\left[(r_{ij} - r_{HB}), \sigma_r\right]\times$$
$$\times\sum_{k,l=1}^{3} G\left[(\vec{i}_k\cdot\vec{u}_{ij} - 1), \sigma_\phi\right] G\left[(\vec{j}_l\cdot\vec{u}_{ij} + 1), \sigma_\phi\right],$$

where G is the Gaussian function

$$G\left[(x), \sigma\right] = e^{\frac{-x^2}{2\sigma^2}}.$$

Results

The fluctuations of the velocities and densities of hydrodynamics and atomistic phases can be smoothly enforced on each other, thus constituting the macro- and micro- scale coupling. The structural properties, the radial distribution function for MB particles, are not affected by the coupling.

We are currently implementing the proposed coupling method for 3D systems, including common water models, such as TIP3P, TIP4P, etc., with biomolecules. We also plan to simulate large systems using the described 2D model for detailed analysis of various hydrodynamic processes, such as flows in microfluidic devices or water flows around large biomolecular aggregates.