

Tools for Multiscale Simulation of Liquids Using Open Molecular Dynamics

Rafael Delgado-Buscalioni

Abstract This work presents a review of recent tools for multiscale simulations of liquids, ranging from simple Newtonian fluids to polymer melts. Particular attention is given to the problem of imposing the desired macro state into *open* microscopic systems, allowing for mass, momentum and energy exchanges with the environmental state, usually provided by a continuum fluid dynamics (CFD) solver. This review intends to highlight that most of the different methods developed so far in the literature can be joined together in a general tool, which I call OPEN MD. The development of OPEN MD should be seen as an ongoing research program. A link between the micro and macro methods is the imposition of the external conditions prescribed by the macro-solver at or across the boundaries of a microscopic domain. The common methodology is the use of external particle forces within the so called particle buffer. Under this frame, OPEN MD requires minor modifications to perform state-coupling (i.e. imposing velocity and/or temperature) or flux exchange, or even any clever combination of both. This tool can be used either in molecular or mesoscopic-based research or in CFD based problems, which focus on mean flow effects arising from the underlying molecular nature. In this latter case an important goal is to allow for a general description of Non-Newtonian liquids, involving not only transfer of momentum in incompressible situations, but also mass and energy transfers between the micro and macro models.

1 Introduction

During this last decade the prefix *multi* has spread over many different disciplines, ranging from sociology to physics. In part, this is a consequence of dealing with new

R. Delgado-Buscalioni (✉)

Dpto. Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, Campus de Cantoblanco, Madrid E-28049, Spain

e-mail: rafael.delgado@uam.es

problems resulting from non-trivial interactions between entities of quite different nature. A natural approach to tackle these problems has been to design new methods from combinations of well-established theories. In this scenario *multiscale* has emerged as a new theoretical and computational paradigm in natural sciences. In particular, this work presents some tools for multiscale treatment of the liquid state. The general purpose is to connect the (classical) dynamics of an atomistic description of the liquid state (microscale) with other less involved descriptions, like the so called coarse-grained level, based on effective molecules (mesoscale) and with hydrodynamic and thermodynamic descriptions (macroscale). One can understand the different types of *multiscale* methods for fluids and soft condensed matter by dissecting the very term multiscale. First (abusing the latin root “multus”) multi means at least two models which, might be solved concurrently (at the same time) or in a sequential (hierarchical) fashion (i.e. solve the fine description to extract information for the coarser level). The hierarchical strategy is in fact part of the coarse-graining methodology, which has usually been based on reproducing the essential microscopic structural (static) information. A recent challenge of coarse-graining is to incorporate dynamical information from the microscopic level [30]. On the other hand, concurrent coupling schemes deserve to qualify as *hybrids*. These hybrids can be divided in two types depending on how the space is decomposed. One can let the coupled models evolve in the same spatial domain or within different sub-domains. The first option is usually designed to treat solute-solvent flows: the solute (polymer, colloid, etc.) is solved with a particle approach while the solvent is treated using any preferred scheme (lattice Boltzmann [54], finite volume [9, 27], multiparticle collision dynamics [33], etc.). Depending on the flow regime, the solute-solvent coupling might be based on the Stokes friction force (low Reynolds number) or using more involved boundary conditions. By contrast, hybrids based on domain decomposition are required for many other types of problems which could depend on the interaction between a microscopic region and the outside hydrodynamic (or thermodynamic) state, or on how the stress is released by a microscopic model in a macroscopic flow (examples will be given later). Several types of domain decomposition strategies can be designed depending on the aspects of the multiscale research under study. In brief, there are two important issues (or categories) to be considered: first, the research might be focused either on the micro-dynamics or on the macroscopic level and second, the ratio of time scales for the *evolution* of the relevant micro and macroscopic process might be large $\tau_{mic}/\tau_{mac} \geq O(1)$ or small $\tau_{mic}/\tau_{mac} \ll 1$. I highlight “evolution” to warn about the fact that in a steady state $\tau_{mac} \rightarrow \infty$, so in practical terms, steady states can be grouped in the category of problems with *separation of time scales*. In liquids, the first category mentioned above separates continuum fluid dynamics (CFD) problems (such as polymeric fluid flow [5, 20, 38, 41, 56] or mean flow effects of singularities or defects in boundaries of micro or nano-fluidics [20, 29, 43]) from molecular based research (external flow effects on single molecules [2, 57], on membranes, melting or condensation [53] processes, wetting or sound-soft matter interaction [7, 11]). Logically, any macro-scale based research should be concerned about any possible gain in computational time from the separation of time and length scales, while if

the molecular dynamics are the main concern this separation is irrelevant and the time-gap can only be reduced by molecular coarse-graining [30].

Most of the multiscale tools in this article originally come from molecular research but they can be quite useful in multiscale CFD programs because both share an important problem: how to impose the desired macro state on the micro domain. To frame this statement, let me briefly review some recent advances in CFD based multiscale research. An important class of domain decomposition hybrids is based on performing non-equilibrium microscopic simulations (using stochastic models, Brownian dynamics, molecular dynamics) at every (or some selected) nodes of a continuum solver grid. The local velocity gradient is imposed at each micro-solver box in order to measure the local stress used then to update the velocity field in the macro-solver. In the field of polymeric fluids this idea was probably introduced by Laso and Öttinger's CONFESSIT approach [38] and in recent years it has been continuously reappearing in the literature under many different flavours [5,41,52,56]. Two groups have set this multiscale approach in general mathematical frameworks, leading to the heterogeneous multiscale modeling (HMM) [21] or equation free models [34]. The HMM or equation-free formalism exploits time scale separation between micro and macro processes and gain computational time by sampling the micro-solver boxes over short temporal windows. However, the micro and macro clocks are the same so, after the macro solver is updated in time, the new dynamical state has to be imposed in the microscopic box. This operation (usually called lifting or reconstruction) might be a challenge in molecular simulation of liquids (see [39]). A clever asynchronous (multi-time) alternative, which avoids lifting, was recently proposed by E et al. [20] but indeed it also exploits time scale separation. Unfortunately, the interesting phenomena in complex liquids arise when the ratio τ_{mic}/τ_{mac} (i.e., Weissenberg or Deborah number, etc.) exceeds one. So in practise, gain in time can only be expected for flows of Newtonian liquids or probably to reach the steady state of a complex liquid flow at a faster pace. Spatio-temporal memory effects are essential in complex fluid dynamics, a relevant example being flow of polymer melts. Recent works have shown that the macro-solver is able to transmit spatial correlations between (otherwise independent) MD boxes [5,56] (i.e. gain in length) but, indeed, one needs to synchronize the micro and macro time updates (i.e. no gain in time). In polymers, local ordering effects induced by the trajectory of fluid packages can be important and difficult to implement. A possible solution is to use a Lagrangian-CFD solver [41] to feed the local state (velocity gradient) at each MD node.

A common feature of all these methods is that the microscopic domain is an open system which receives/sends information from/to the outside world. Most of the CFD multiscale research have dealt with incompressible flows and thus the MD domains only need to receive momentum through their boundaries. However density and energy variations might be important in many kind of problems (e.g. thermal effects in sheared polymers) and as mentioned in recent works on the subject, some general and flexible formalism for "grand-canonical" molecular dynamics would be of great value [41]. In the same way, slip-stick motion at physical boundaries can only be described at molecular level and the tools described hereby could be deployed in a

multiscale CFD scheme to solve this task (for instance, in unsteady polymeric flow under oscillatory walls [56]).

In what follows I will first describe a general formalism called OPEN MD, which enables to *open up* a molecular dynamic (MD) box so that it might exchange mass, momentum and energy with the outside world. Section 3 describes an adaptive resolution scheme acting as a coarse-grained particle interface model around the (atomistic) MD domain. This mesoscale interface makes feasible mass and momentum transfer in simulations of liquids made of large molecules. Section 4 discusses how to connect the molecular box with a continuum dynamics solver, including thermal fluctuations. Conclusions and perspectives are given in Sect. 5.

2 OPEN MD: Molecular Dynamics for Open Systems

The most delicate part of any hybrid scheme is the transmission of the state of the coarser description into the fine resolution model. The reason being that, in doing so, one needs to reconstruct microscopic degrees of freedom which should be consistent with the prescribed macroscopic state imposed. This task is sometimes called *one-way coupling*, lifting or reconstructing in the HMM and Equation-Free communities. The state of a solid is essentially given by the imposed stresses (forces) because the average velocity of a solid molecule is zero. By contrast, the thermo-hydrodynamic state of a gas require control over molecules velocity, as interaction forces are absent. An inherent complication in liquids is that their energy contains equal amount of kinetic and potential contributions and thus, control over both stresses and velocities is required. Of course, the stress and velocity fields are not independent and two strategies are possible: one can either choose to impose the average state variables (mean velocity, temperature) [40] or the fluxes of conserved variables (pressure tensor, energy flux) [7, 24]. In any case one is restricted to play with the set of microscopic mechanical quantities, namely, velocities and forces of the individual molecules of the system. As an aside, there are several popular methods to impose shear in *closed* MD boxes with periodic boundary conditions (BC), such as Lee-Edwards type BC or SLLOD dynamics used by many CFD multiscale works [20, 56]. Although they shall be not be reviewed here, a recent comparison between SLLOD and the type of boundary-driven imposition described hereby [31] showed some problems in SLLOD temperature homogenisation under shear. Also, alternatives based on Monte Carlo steps might also be possible [42], although the Metropolis algorithm does not preserves the system's dynamics and these will be not considered here either. Another relevant feature of liquids (and gases) is that they can be compressed, or when working with mixtures, vary in concentration. Compression effects may indeed arise from many different sources, such as sound transmission, or even shear rate pressure dependence in Non-Newtonian liquids. This means that, in general, one needs to devise some way to work with open molecular systems, i.e., with a variable number of molecules. A solution to this computational problem was proposed by Flekkøy *et al.* [24] some years ago and

the idea, which I call OPEN MD, is still being generalised [17, 18]. In the original formulation of the OPEN MD scheme it is possible to impose the exact amount of work and heat into an open (variable density) molecular domain. OPEN MD has been used as the core of several particle-continuum hydrodynamic hybrids [7, 18, 37] but its range of applications is wider. In fact, by controlling the amount of work and heat introduced into an open system, one can study processes with different kinds of thermodynamic constraints. This makes OPEN MD a flexible method for many different fields ranging from confined systems [23] (where thermodynamic forces are driven by chemical potential gradients) to the rheology of Non-Newtonian liquids (where the normal pressure is known to depend on the imposed shear and constant volume measurements are not equivalent to constant pressure measures).

2.1 Open MD Setup

Figure 1 depicts a simple set-up of OPEN MD. A molecular system resolved by MD is extended with a buffer domain B, where the state of the outer domain is imposed. Particles are free to cross the hybrid interface but once inside B they will feel a certain external force \mathbf{F}_i which should be prescribed to carry the desired information of the outside domain into the MD system. The objective of the original OPEN MD formulation [24] is to impose the desired momentum and heat flux (\mathbf{P} and \mathbf{J}_e) across the so called *hybrid* interface H, i.e., it is based on flux-exchange. However the computational setup can be easily modified so as to impose the desired (external) velocity field \mathbf{V} via constraint dynamics [43, 44] and in this paper I will unify both (flux and state coupling) approaches in the same framework.

The OPEN MD scheme can be divided in two main tasks:

1. Imposition of the desired macro-state via external forces and,
2. Control of mass and density profile at the buffer region.

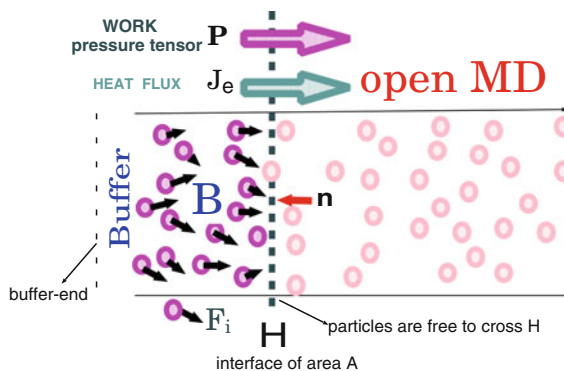


Fig. 1 Open molecular dynamics (OPEN MD) setup. A molecular dynamics box is extended using a buffer domain B where the state of the outer domain is imposed. In the flux-based scheme the external forces \mathbf{F}_i^{ext} imposed to the buffer particles are prescribed so as to yield the desired momentum flux (stress tensor) \mathbf{P} and heat flux \mathbf{J}_e across the system interface H

2.2 Imposition of the Macro-State

As stated above the information prescribed at the buffer might either be a set of state variables (i.e. velocity, temperature) or the fluxes of conserved variables across H. A type of scheme based on variable coupling introduced by Patera and Hadjiconstantinou [28] use Maxwell daemons to modify the velocities of the buffer particles according to the local equilibrium distribution. This method is usually implemented in hybrids based on the Schwartz method, which alternatively imposes the local velocity of the adjacent domain at the overlapping layer until the steady state is reached. This is a good way to drive the (total particle+continuum) system towards a steady state (probably faster than its natural convergence rate) but it significantly alters the local dynamics (molecule diffusion, velocity time correlations) and it is restricted to closed systems (constant number of particles). Starting from the pioneer work of Thompson and O'Connell [44] several alternatives based on the imposition of external forces [12, 24, 43] were then developed. It is important to stress that external force imposition at the buffer allows for the implementation of either state and flux coupling. We shall now briefly discuss both approaches.

2.2.1 State-Coupling Based on Constrained Dynamics

The state-coupling approach comes from the continuum fluid dynamics community whose priority is to ensure that the external flow and convective forces are imposed into the molecular region. In this sense, the philosophy behind state-coupling is to treat the coarse (hydrodynamic) exterior domain as the *master* model and the microscopic dynamics as *slaved* one. Let us begin with the momentum transfer, which is carried out by imposing the desired (external) average velocity \mathbf{V} at the particle buffer, i.e.

$$\frac{1}{N_B} \sum_{i \in B} \mathbf{v}_i = \mathbf{V}. \quad (1)$$

This might be seen as a constraint in the particle equations of motion $\ddot{\mathbf{r}}_i = \mathbf{f}_i/m$,¹ which can be written in terms of an external force \mathbf{F}_i added to \mathbf{f}_i . An example is the Langevin type force used by O'Connell and Thompson [44] $\mathbf{F}_i = -\gamma (\mathbf{v}_i - \mathbf{V}) + \tilde{\mathbf{F}}$, with $\langle \tilde{\mathbf{F}}(t) \tilde{\mathbf{F}}(0) \rangle = 2k_B T \gamma \delta(t)$. Nie et al. modified this approach and proposed the following constrained dynamics at the buffer,

$$\ddot{\mathbf{r}}_i = \frac{1}{m} (\mathbf{f}_i - \langle \mathbf{f} \rangle) - \xi (\langle \mathbf{v} \rangle - \mathbf{V}), \quad (2)$$

where I have introduced the local microscopic average $\langle \mathbf{f} \rangle = \sum_i^{N_B} \mathbf{f}_i / N_B$ and the relaxation parameter ξ which, in principle, can be freely tuned. The idea underlying this approach is to substitute (at each time step) the average microscopic force $\langle \mathbf{f} \rangle$ at

¹ In what follows upper case letters indicate externally imposed quantities (\mathbf{V}, \mathbf{F}) while lower case ($\mathbf{v}_i, \mathbf{f}_i$) stands for microscopic variables.

the coupling domain for its macroscopic counterpart $MD\mathbf{V}/Dt$. In other words, by summing (2) over $i \in B$ one gets the total external force at the buffer $\xi M (\mathbf{V} - \langle \mathbf{v} \rangle)$, where $M = mN_B$ is the buffer mass. Thus, by choosing $\xi = \frac{1}{\Delta t_{MD}}$, as Nie *et al* [43] did, it is easy to show that the average microscopic velocity instantaneous relaxes to the imposed value, i.e., $\langle \mathbf{v} \rangle(t + \Delta t_{MD}) = \mathbf{V}(t + \Delta t_{MD})$. Instantaneous relaxation destroys the microscopic dynamics (altering the velocity time correlation) and this can be alleviated by increasing ξ (as originally proposed in [44]). If the imposed velocity changes (fast) in time, the price to pay is some lag (time delay) between the input $\mathbf{V}(t)$ and output $\langle \mathbf{v} \rangle(t)$ values.

Mass and energy transfer

In state-coupling methods the mass flux arising from the microscopic dynamics is in fact destroyed once the average local velocity at the system boundaries is *imposed*. In order to ensure mass continuity at the interface one thus needs to take the information from the coarser level (usually the Navier-Stokes equation), and modify the number of particles on the molecular system to an amount given by the continuum expression for the mass flow across H, $A\rho\mathbf{V} \cdot \mathbf{n}\Delta t/m$. Energy transfer might also be introduced in a state-coupling fashion by imposing the local temperature gradient at the buffer domain [12]. Particle-continuum hybrids can also impose heat transfer via temperature coupling by using a larger buffer (overlapping domain) with two parts: the local “continuum” temperature is imposed at the microscopic buffer, while the local microscopic temperature is imposed at the (adjacent) boundary of the continuum macro-solver [40]. In general, the use of unphysical artifacts (such as pure velocity rescaling [40] to impose a local temperature) introduces several drawbacks: for instance, transport coefficients (viscosity, thermal conductivity) need to be finely calibrated to control the amount of heat transferred via velocity and temperature gradients. Also, the length of the buffer (or the overlapping domain) will need to be increased so as to avoid error propagation into the MD domain, thus paying a larger computational price for the hybrid coupling.

2.2.2 The Flux-Based Scheme

The flux-coupling approach tries to reduce the number of unphysical artifacts at the buffer by retaining all possible information from the microscopic domain (e.g. fluctuations). In fact, hybrid models using flux exchange consider the coarse (hydrodynamic exterior) domain as the *slave* model while the microscopic dynamics stand the *master* model (see e.g. [1]). This approach permits, for instance, coupling of molecular dynamics and fluctuating hydrodynamics (FH) [7]. It should be the preferred one when dealing with problems where thermal fluctuations or molecular transport are relevant and they usually are at these nanoscopic scales and low or moderate Reynold numbers. The flux boundary conditions imposed at the buffer domain are specified by the normal component of the energy flux $j_\epsilon = \mathbf{J}_e \cdot \mathbf{n}$ and

the normal component of the momentum flux $\mathbf{j}_p = \mathbf{P} \cdot \mathbf{n}$, where \mathbf{P} is the pressure tensor and \mathbf{n} the unit normal shown in Fig. 1. Both fluxes will in general include advective terms. In an open system, energy and momentum enters into the particle system both through the force \mathbf{F}_i and via particle addition/removal. The prescribed momentum and energy fluxes need to take into account both effects i.e.

$$\mathbf{j}_p A dt = \sum_i \mathbf{F}_i dt + \sum_{i'} \Delta(m\mathbf{v}_{i'}), \quad (3)$$

$$j_\epsilon A dt = \sum_i \mathbf{F}_i \cdot \mathbf{v}_i dt + \sum_{i'} \Delta\epsilon_{i'}, \quad (4)$$

where i' runs only over the particles that have been added or removed during the last time step dt , and A is the buffer–bulk interface area. The momentum change is $\Delta(m\mathbf{v}_{i'}) = \pm m\mathbf{v}_{i'}$, where (+) corresponds to inserted particles and (-) to removed ones (similarly for the energy change $\Delta\epsilon_{i'}$). The sums $\sum_i \mathbf{F}_i dt$ and $\sum_i \mathbf{F}_i \cdot \mathbf{v}_i dt$ are the momentum and energy inputs due to \mathbf{F}_i during the time dt . In order to simplify (3) and (4) it is useful to define $\tilde{\mathbf{j}}_p$ and \tilde{j}_ϵ through the relations

$$A dt \tilde{\mathbf{j}}_p = A dt \mathbf{j}_p - \sum_{i'} \Delta(m\mathbf{v}_{i'}) = \sum_i \mathbf{F}_i dt, \quad (5)$$

$$A dt \tilde{j}_\epsilon = A dt j_\epsilon - \sum_{i'} \Delta\epsilon_{i'} = \sum_i \mathbf{F}_i \cdot \mathbf{v}_i dt. \quad (6)$$

Provided that the force \mathbf{F}_i satisfies these conditions the correct energy and momentum fluxes into the particle system will result. To solve these set of equations the external force is decomposed into its average and fluctuating parts, $\mathbf{F}_i = \langle \mathbf{F} \rangle + \mathbf{F}'_i$. Momentum is introduced by the average component of \mathbf{F}_i and thus,

$$\langle \mathbf{F} \rangle = \frac{A}{N_B} \tilde{\mathbf{j}}_p, \quad (7)$$

where $N_B(t)$ is the total number of particles receiving the external force at a given time t and A is the area of the interface H . On the other hand, the fluctuating part of the external force ($\sum_i \mathbf{F}'_i = 0$) introduces the desired heat via dissipation, i.e.,

$$\mathbf{F}'_i = \frac{A \mathbf{v}'_i}{\sum_{i=1}^{N_B} \mathbf{v}'_i} \left[\tilde{j}_\epsilon - \tilde{\mathbf{j}}_p \cdot \langle \mathbf{v} \rangle \right], \quad (8)$$

where we have used the fact that the total energy input by external forces is $\sum_{i=1}^{N_B} \mathbf{F}_i \cdot \mathbf{v}_i = N_B \mathbf{F} \cdot \langle \mathbf{v} \rangle + \sum_{i=1}^{N_B} \mathbf{F}'_i \cdot \mathbf{v}'_i$.

As shown in [24], by *exactly* controlling the amount of work and heat introduced into the particle system, one can implement several sorts of thermodynamic constraints. For instance, constant chemical potential (grand canonical ensemble), constant enthalpy, constant pressure. Also, steady (or unsteady) non-equilibrium states, such as constant heat flux or shear stress can be imposed. An interesting aspect of this OPEN MD method is that all these constraints occur at the particle

boundaries (in fact, as it happens in any real system), so the dynamics of the molecular core are not unphysically modified *whatsoever*.

Mass flux

In the OPEN MD flux-based scheme, the mass flux across H naturally arises as a consequence of the pressure (or chemical potential) differences between the inner and outer domains. In other words, mass flux is not imposed. In a hybrid configuration, the microscopic domain will dictate the mass flux across H, which can be simply measured by counting the number of particles crossing the interface. Indeed, many problems crucially depends on the molecular transport (such as confined systems driven by the chemical potential difference between the interior and exterior) and the natural approach of the flux-based scheme permits one to retain this sort of microscopic information (e.g. fluctuations).

2.3 Mass and Density Profile at the Buffer

In a molecular simulation of an open fluid system one necessarily needs to decide what to do at the edges of the simulation box. The essential problem is to control the density profile normal to the interface H. Thus, two variables needs to be monitored: *i*) the shape of the density profile and *ii*) the total number of particles at the buffer.

2.3.1 Distribution of the External Force

The density profile depends on how the external force \mathbf{F} is distributed at the buffer. For an interface of area A, pointing in the negative x direction, $\mathbf{n} = -\mathbf{i}$ (see Fig. 1), the force along the α direction on a buffer particle can, in general, be set as,

$$F_{i,\alpha} = \frac{g^\alpha(x_i)}{\sum_{i \in B} g_\alpha(x_i)} AP_{x\alpha} \quad \alpha = \{x, y, z\}, \quad (9)$$

where $P_{x\alpha}$ is the $x\alpha$ component of the pressure tensor (or any other total external force such as the one used in state-coupling). Although, most of the works done so far use a single distribution $g(x)$ for all directions, one is free to use different distributions $g_\alpha(x)$. In fact, depending on the problem, it might be useful to choose different shapes of g for tangent (shear) and normal forces (pressure).

Most of the concern in the literature on this subject logically corresponds to the shape of g_x (normal to the interface) because it directly determines the shape of the density profile $\rho(x)$. Figure 2 shows a qualitative picture on the relationship between $g(x)(= g_x(x))$ and $\rho(x)$.

Several values of g_i have been proposed in the literature. For instance, Flekkøy *et al.* [25] initially proposed a distribution $g(x)$ which tends to zero at H and diverges at the end of the particle buffer thus preventing particle to leave the system. Werder and Koutmoutsakos [55], showed that an evaluation of $g(x)$ from a previous calculation of the particle distribution function in the normal x coordinate, enables to maintain a constant density profile across the whole buffer (a comparison between several choices of g_i was also provided). Recently the group of Koutmoutsakos [36] introduced a feedback (relaxation) procedure to self-adapt a binned distribution according to the local density gradients, in such way that the fixed solution were the constant density profile. In some situations, such as the state-coupling approach, it is important to have a constant density profile at the buffer [36]. However, in flux-based schemes the most important aspect is to have a flat profile locally *across the interface* H [14] to avoid any spurious current.

Energy transfer and $g(x)$

It is important to note that flux based schemes implement the energy transfer via the power dissipated by the external force $\sum_{i \in B} \mathbf{F}_i \cdot \mathbf{v}_i$. Therefore, in this case, one is not free to choose $g(x)$ because heat will be produced in an uncontrolled way, at a rate $\sum_{\alpha} \sum_i g_{\alpha}(x_i) P_{x\alpha} v_{i,\alpha} / \sum_{\alpha} \sum_i g_{\alpha}(x_i)$. In fact when using any $g(x)$ with sharp gradients, strong thermostatting will be required to remove all this spurious heat. This is probably be the case of the state-coupling schemes based on temperature

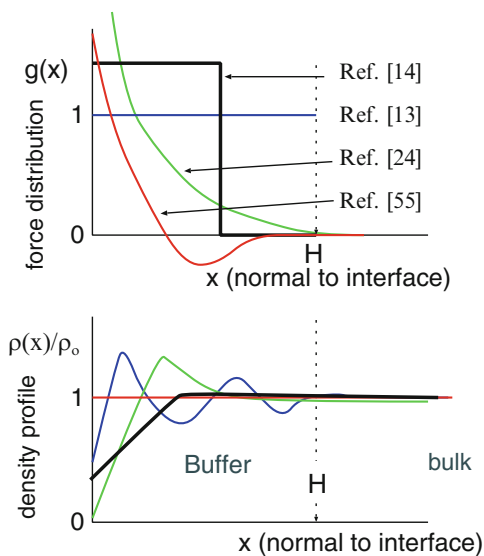


Fig. 2 Qualitative diagrams illustrating some types of external force distribution $g(x)$ used in open molecular dynamics (*top*) and the resulting density profile at the buffer (*bottom*)

imposition [40]. In order to keep control of the average energy dissipated by the external force, a pioneer work on energy transfer in hybrids [12] used $g(x) = 1$ and placed a couple of adjacent thermostats to transfer heat. The need of thermostats was finally avoided by the flux boundary condition method of [24], leading to (7) and (8) above. Note that (7) uses $g(x) = 1$ (or at least a step function, see Fig. 2) to distribute the mean external force. In this way the energy contribution of the mean external force is precisely the rate of reversible work done by the external forces $P_{xx}\langle v_x \rangle$, plus the rate of heat dissipation by shear forces $\sum_{\alpha} P_{x\alpha}\langle v_{\alpha} \rangle$, with $\alpha \neq x$. The entropic heat production is separately furnished by the fluctuating part of the external force.

2.3.2 The Buffer Mass: Particle Insertion and Deletion

The buffer domain can be understood as a *reservoir* which represents the outside world. This means that the number of particles at the buffer should be large enough to avoid important momentum and temperature fluctuations, which will certainly lead to numerical instabilities. In a typical flux-based method this means that, in average, the buffer should contain at least $\langle N_B \rangle \sim O(10^2)$ particles; which is not much considering that a typical MD simulation may contain $O(10^{4-5})$ or more. A simple way to keep the average $\langle N_B \rangle$ under control is to use a relaxation equation

$$\dot{N}_B = \frac{1}{\tau_B} (\langle N_B \rangle - N_B), \quad (10)$$

where $\tau_B \sim 10^2 \Delta t_{MD}$. As times goes on a number $\mathcal{N} = \text{INT}[\Delta N_B]$ of particle insertions (or deletions) should be performed as soon as $\Delta N_B = \sum_i \dot{N}_B(t_i) \Delta t_{MD}$ becomes a positive (or negative) number with absolute value larger than one. Basic bookkeeping should then be performed to update N_B accordingly. Several possible tricks might be done with those particles reaching the buffer-end: one can just delete them randomize or reverse their velocity. In a conservative (flux-based) scheme the resulting momentum exchange should be accounted for in (3) (e.g. the later case would yield $-2\Delta m \mathbf{v}'_i \cdot \mathbf{n}$ per reversed particle). To minimise perturbations, particle deletions and insertions are usually done at the dilute region of the buffer (see Fig. 2), whenever it exists. A particularly delicate issue when dealing with open MD simulations of dense liquids is to avoid overlapping upon insertion (which results in extremely high energy jumps). In a pioneer work on open MD simulations we introduced a fast and efficient particle insertion method called USHER, now used in many hybrid particle-continuum simulations [35, 37]. It was initially designed for spherical (Lennard-Jones) particles [13] and then extended to polar molecules, such as water [8]. USHER is based on a Newton-Raphson algorithm with adaptable length step, which search some location within the complex multiparticle energy landscape where potential energy of the inserted particle equals the desired value. USHER solves this problem in a very efficient way (partly because it reboots any search once some increase in potential energy is performed) and can also explore

low energy domains in the search for (however biased) chemical potential evaluation [49]. In open MD simulations it usually represents less than 5% of the computational task. The main limitation of USHER is that it is not suitable to insert big (or I should rather say complex) molecules. Typical examples could be star polymers in a melt. This limitation was sorted out recently [18] by introducing an adaptive coarse-grained layer at the buffer, whereby a coarse-grained version of the molecule is gradually and nicely decorated with its atomistic complexity as it enters into the MD core from the buffer corner, and vice versa. Implemented in a particle-continuum hybrid, this suggestive idea permits a macro-meso-micro zoom along the spatial coordinates, and has been called *triple-scale* method. Let us now comment on this approach.

3 Using Adaptive Resolution: The Mesoscopic Interface

The adaptive resolution scheme (AdResS) proposed by Praprotnik et al. [47, 48] is a type of domain decomposition based on coupling particle sub-domains with different resolution: from coarse-grained *cg* to explicit (i.e. atomistic) *ex* description. Figure 3 illustrates this idea in an open MD setup. The number of degrees of freedom of a molecules is modified (reduced/increased) as it crosses the “transition” layer, where a hybrid model (*hyb*) is deployed. In particular, the force $\mathbf{f}_{\alpha\beta}$ acting between centres of mass of molecules α and β is expressed as,

$$\mathbf{f}_{\alpha\beta} = w(x_\alpha)w(x_\beta)\mathbf{f}_{\alpha\beta}^{ex} + [1 - w(x_\alpha)w(x_\beta)]\mathbf{f}_{\alpha\beta}^{cg}, \quad (11)$$

where x_α and x_β are the molecule’s position along the coupling coordinate. Pairwise atomic forces are \mathbf{f}_{ij} and $\mathbf{f}_{\alpha\beta}^{ex} = \sum_{i \in \alpha, j \in \beta} \mathbf{f}_{ij}$ is the sum of all atomic interactions between molecules α and β . Finally $\mathbf{f}_{\alpha\beta}^{cg} = -\nabla_{\alpha\beta} U^{cg}$ results from the coarse-grained intermolecular potential. These interactions are weighted by a function $w(x)$ which switches from $w = 1$ at the *ex* region to $w = 0$ at the *cg* layer. Intermediate values $0 < w < 1$ might be understood as hybrid (*hyb*) model. With a few restrictions, one is rather free to choose the explicit form of $w(x)$, see e.g. [17, 47]. The great benefit of this sort of *on-the-fly* transition from coarse-grained to atomistic models is that molecule insertions can be quite easily performed at the *cg* end of the buffer because there, intermolecular interactions are soft. The whole set of hard-core atomic potentials is thus avoided in the open MD setup.

The key ingredient of AdResS is that (11) conserves momentum. Thus, it can be used in combination with any momentum conserving (flux-based) scheme [17, 18], and of course, it could be also combined in any state-coupling method. However, energy is not conserved by (11) and in fact, as a molecule moves towards the coarse-grained layer it loses all the kinetic energy associated with its internal degrees of freedom (sum of squared velocities w.r.t. centre-of-mass). This energy is lost forever and to maintain an equilibrium state (a flat free energy profile [46, 48]) it needs to be furnished by a thermostat, which usually is set to act along the whole simulation box

(or at least within the buffer). A modification of AdResS solving this problem would certainly be an important contribution. Meanwhile, it might be still possible to allow for (averaged) energy exchange with the MD core, using some thermostating tricks, although this idea is not still published.

Other issues which deserved some attention in the literature [17, 32] are related to how the change in resolution introduces differences in mass diffusion coefficient and viscosity in the *cg*, *hyb* and *ex* fluid models. This is a problem in a “pure” (i.e. closed) AdResS simulation and also if, for some reason, one is interested in placing the hybrid interface *H* of the open MD setup within the *cg* layer (note that Fig. 3 places *H* within the *ex* domain). In these cases one needs to take care to calibrate all the *cg*, *hyb* and *ex* viscosities and diffusion coefficients. This is, in general, not possible: in fact, either diffusivities or viscosities can possibly be matched at once [17] using either position dependent Langevin thermostats or DPD thermostat with variable tangential friction [32]. Liquid equilibrium structures (radial distribution functions $g(r)$) of the *cg* model can also be tuned to fit the *ex* one, using the standard tools [50]. This adds an extra pre-computational price to pay. However, as shown in [18] all this calibration burden (which needs to be repeated each time the thermodynamic state is changed) can be greatly alleviated by using the sort of setup illustrated in Fig. 3. In summary, variations in transport coefficient and fluid structure of the different fluid models within the buffer do not affect the proper transfer of momentum across *H* (which is guaranteed by fulfillment of the third Newton Law across all layers).

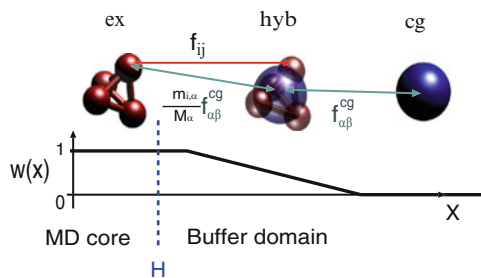


Fig. 3 Schematic setup of the adaptive resolution scheme (AdResS) being used within the buffer domain of an open MD simulation of a tetrahedral liquid. Molecules gradually transform from a coarse-grained *cg* to an explicit *ex* (atomistic) representation, as they cross the transition layer, *hyb*. The pairwise forces between atoms \mathbf{f}_{ij} and molecules centre-of-mass $\mathbf{f}_{\alpha\beta}^{cg}$ are weighted by $w(x)$

4 HybridMD: Particle-Continuum Hybrid Scheme

This section discusses the most important details about the implementation of a particle-continuum hybrid based on domain decomposition. For a more complete view of each different method the reader is referred to the original papers cited hereby and references therein. There are (at least) three types of approaches to this

problem: state coupling [43,44], flux coupling [14,25] and velocity-stress coupling [52,56]. How to couple time marching algorithms of macro and micro solvers is a common problem for all kind of hybrids. The following is a brief discussion on this subject (see [20] for recent developments).

4.1 Time Coupling

In general, the time steps of the micro and macro solver (respectively δt and Δt) satisfy $\delta t \leq \Delta t$. However, the ratio of both quantities depends on the type of models to be coupled. For instance in hybrids of deterministic CFD and MD one can choose $\Delta t \gg \delta t$ but, solving fluctuating hydrodynamics (FH) requires much smaller time steps and Δt is only few time larger than δt [7]. On the other hand, communications between models occur after a certain time coupling interval Δt_c , which in general $\Delta t_c \geq \Delta t$ (an example of $\Delta t_c > \Delta t$ is discussed in [14]). Figure 4 illustrates some time coupling protocols. Concurrent algorithms (Fig. 4a) permit parallelization (tasks 1a and 1b) and might be quite useful if the computational load of micro and macro solvers is balanced by the implemented architecture (for instance use a fast GPU solver [6] for the MD domain and a slow CPU solver for a vast CFD region). Indeed, parallelization is most easily achieved if the need for performing averages in the micro domain are completely or substantially avoided. Examples are FH-MD hybrids [7] where the exchanged quantities are the actual MD and FH fluctuating variables at each coupling time (see Fig. 4a). Another example is the asynchronous time coupling devised by Weinman et al. which (if the signal-to-noise ratio is large enough) can work without explicit averaging because it is indirectly implemented in the deterministic macro-solver updates. Fluctuations are usually considered a nuisance in mean flow CFD problems [20,39] and microscopic averages might become necessary. Deterministic CFD-MD hybrids thus need to consider time synchronisation errors arising from performing MD averages lagging behind the coupling time (see Fig. 4b). These are $O(\Delta t_c)$ errors which might be significant if Δt_c is large compared with some relevant microscopic relaxation time. A possible solution, shown in Fig. 4c, consists on shifting the discretised time mesh of both models. The scheme of Fig. 4d is an example of the synchronous coupling used in HMM-type schemes where the micro-solver is sampled during small time intervals, compared with the coupling time, and then lifted or reconstructed towards the updated state. This lifting operation might be a problem in MD of liquids so the new recent seamless multiscale asynchronous scheme, which avoids the MD reconstruction step [20], is particularly suited for solving flows where time separation applies, $\tau_{mic} \ll \tau_{mac}$.

4.2 Hybrids Based on State Coupling

State coupling relies on Dirichlet boundary conditions. This statement is valid either for hybrids based on the Schwartz scheme [28, 37] or for constraint dynamics [43]. I will focus on the constraint dynamics approach, whose typical setup is shown in Fig. 5a. The MD and CFD (finite differences in Fig. 5a) domains are connected in an overlapping region, sometimes called *handshaking* domain. The state variables of each model are mutually imposed at two different cells $P - C$ and $C - P$. At the $P - C$ cells the local average microscopic velocity (v_{PC}) is imposed to the continuum as a Dirichlet BC, while at the $C - P$ cell the continuum velocity V_{CP} is imposed to the particle system, using the scheme explained in Sect. 2.2.1. The same strategy is for the imposition of local temperatures, so as to simulate an energy exchange between both models (see [40] for details). It is important to note that the $P - C$ and $C - P$ cells are some cells apart in order to let the particle system relax from all the dynamic constraints imposed at the $C - P$ cell (instantaneous velocity jumps of (2) and rescaling of peculiar velocity towards the desired temperature [40]). As an example in [40] the (linear) length of the overlapping domain is 4 cells of $\Delta x = 6.25\sigma$, thus a total of 25σ (where σ is the particle radius). When dealing with two or three dimensional flows, this is a relatively large computational load for the handshaking region. Molecular dynamics

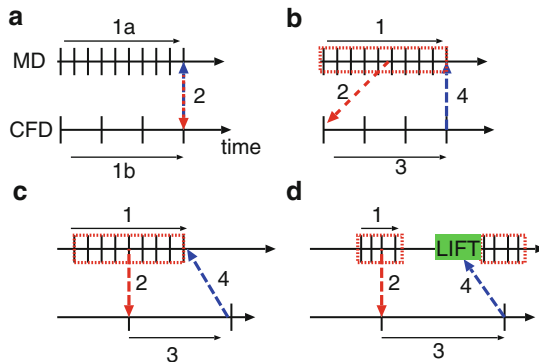


Fig. 4 Some possible (synchronous) time coupling schemes in hybrids. Horizontal arrows indicate time axis of each model (here molecular and continuum fluid dynamics, MD and CFD) and vertical lines their time steps. A dashed square means a time average operation and dashed arrows communications between models. Tasks are numbered in chronological order. (a) Concurrent coupling allowing parallelization. (b) Sequential coupling. (c) Sequential scheme avoiding time lag in MD averages. (d) HMM-type sequential coupling with a lifting step (4) to set the advanced state into the MD system

is by far the most expensive part of the hybrid algorithm and being able to reduce the length of the overlapping domain is a benefit one should take into account.

4.3 Hybrids Based on Flux Exchange

If our hybrid is going to be based on flux exchange, the most natural choice for continuum solver is one based on an integral conservative scheme, such as the finite volume method (see Patankar for an excellent textbook [45]). From the continuum solver perspective communications between continuum and molecular cells are essentially the same as those among continuum cells; i.e. there are only little modifications to do. Following the standard procedure of the finite volume method, the *whole* domain is divided into computational cells (see Fig 5c) which could be either w =boundary cells (walls) or f =fluid cells. The hybrid scheme introduces two more cell types, the m = molecular cells and the C cells. A conservative scheme simply calculates and sum up the amount of any conserved variable crossing the interface between every pair of adjacent cells. In particular $\Delta\Phi_H$ is the amount of Φ crossing the hybrid interface H over the coupling time Δt_c . The interface H separates cells C and the border molecular cells, sometimes called P (see Fig. 5b). If the flux across H is $J_H = \mathbf{J}_H \cdot \mathbf{n}$ then $\Delta\Phi_H = A J_H \Delta t_c$. Thus the central quantity is J_H : it will be imposed at the particle buffer following Sect. 2.2.2 and used to update the C cell, in the standard finite volume fashion. The interface flux J_H might be evaluated in different ways: one can perform a linear piecewise interpolation $J_H = (J_C + J_P)/2$ and evaluate J_P from microscopic expressions (Irving-Kirwood) or pass via the fluid constitutive relations using the hydrodynamic variables at the surrounding (fluid and molecular) cells into the selected type of discretised gradient.

Molecular-continuum hybrids are explicit in time and the time marching protocol is usually simple. Typically (Fig. 4a) the macro-solver updates all types of cells during a number $n_{FH} \Delta t_c / \Delta t$ of time steps² and at each coupling time it receives the hydrodynamic variables at the molecular m cells. The only modifications required on a standard code are set to ensure the mass conservation and momentum continuity at the C cells . The continuum solver structure is,

$$\Delta\Phi_i = \Delta t \text{NS} [\{\Phi_j\}] + \delta_{fC} \Delta\phi^{MD}, \quad (12)$$

where Φ are the set of conserved variables (mass, momenta and energy), NS is a discretised Navier-Stokes operator (which may include hydrodynamic fluctuations [9, 19]) and the delta Kronecker δ_{fC} symbol is used to input the molecular flux corrections $\Delta\phi^{MD}$ into the C cells, as explained below.

² This number should not be large $1 \leq n_{FH} < O(10)$ [14].

4.4 Mass Transfer and Continuity in Flux Based Schemes

As stated above, the flux scheme permits one to minimise the number of unphysical artifacts imposed on the particle system by using the molecular system as the fundamental (or master) model which determines the mass flux and velocity at the interface. This philosophy was first proposed by Garcia *et al.* in an elegant hybrid model for gases [26]. Mass conservation is ensured by evaluating the molecular mass flux across H, ΔM_H^{MD} and releasing this mass to the C cell. A relaxation equation can be used for this sake, providing the following mass correction which needs to be added at C, according to (12),

$$\Delta M^{MD} = \frac{\Delta t_c}{\tau_M} (\Delta M_H^{MD} - \Delta M_H^{NS}). \tag{13}$$

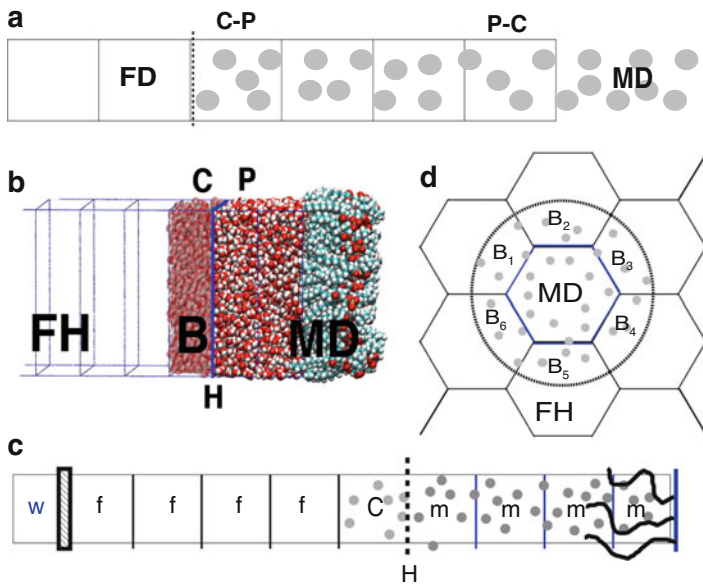


Fig. 5 (a) Typical setup used in state-coupling hybrids with a molecular dynamics (MD) and a deterministic Navier-Stokes finite difference (FD) solver domain. The overlapping domain contains $C - P$ cells where the local FD velocity is imposed to MD and $P - C$ cells where the average particle velocity is used as Dirichlet B.C. for the FD scheme. (b) Set-up of a flux based coupling MD (water wetting a lipid monolayer) and finite volume fluctuating hydrodynamics (FH). Exchange of fluxes between cells $P \in MD$ and $C \in FH$ are made through their interface H (no overlapping domain). (c) Arrangement of finite volume cells in a hybrid flux scheme (see text) (d) A possible 2D MD-FH flux-based coupling in a hexagonal lattice. Local pressure tensors and heat fluxes at each neighbour FH cell are imposed to MD from each sub-buffer B_i , flux exchange take place across each H_i interface

Here, τ_M is a relaxation time which usually can be set equal to the C-solver time step (instantaneous mass transfer and exact conservation) and $\Delta M_H^{NS} = -A\rho_H \mathbf{V}_H \cdot \mathbf{n} \Delta t$ is the mass crossing towards C according to the local hydrodynamic prediction (the NS solver).

On the other hand, a pure flux scheme does not impose velocity continuity and it has been shown to suffer from numerical instability, leading to velocity jumps at the interface [16, 51]. A simple solution to this problem, proposed in [16], is to add an extra relaxation term $M_C \Delta \mathbf{V}_C$ into the C cell momentum equation, where

$$\Delta \mathbf{V}^{MD} = \frac{\Delta t_c}{\tau_v} ((\mathbf{v}_C^{MD})_{[\delta t, \tau]} - \langle \mathbf{V}_C \rangle_{[\Delta t, \tau]}). \quad (14)$$

The relaxation time can usually be set to be rather fast $\tau_v \sim O(100)$ fs and \mathbf{v}_C^{MD} is obtained from linear extrapolation of adjacent m cells (i.e. not from the buffer). Note that (14) is essentially the same idea used in the constrained molecular dynamics of the state-coupling hybrid, but here, it is the continuum velocity at the boundary C cells which is “constrained” to follow the molecular counterpart. A comparative study of continuity in several hybrids performed by Ren [51] confirmed the robustness of this approach. The averages used in (14) take into account the possibility of coupling two models with intrinsic fluctuations (such as FH and MD). I have defined $\langle \cdot \rangle_{[\delta t, \tau]}$ as a time average over τ sampling each δt steps. In a FH-MD hybrid τ is usually the coupling time Δt_c while Δt and δt are FH and MD time steps.

Exact momentum conservation

From the standpoint of momentum conservation, it is important to note that the particle buffer B is not part of the system. According to the OPEN MD procedure of Sect. 2.2.2, imposing the pressure tensor \mathbf{P}_H at the buffer B will inject $A\mathbf{P} \cdot \mathbf{n} \Delta t_c$ momentum into MD+B, but one does not know how much of it will be transferred into MD across H. This source of momentum error is bounded by the mass of B (and was shown to be quite small in 1D coupling geometries [7]); however a slight modification of the scheme allows for exact momentum conservation. This might be necessary when dealing with two and three dimensional geometries (see e.g. Fig. 4d). The idea is to adjust the transfer towards each C cell so as to ensure global conservation along the interface contour. Consider Fig. 4b, the MD model is the first to move so $\Delta \phi^{MD} = \phi_{MD}(t_1) - \phi_{MD}(t_0)$ is known before the FH field is updated (in the concurrent scheme of Fig. 4a, the MD correction will be just transferred at the next time step). Local conservation means that $-\Delta \phi^{MD}$ crosses towards the C cell. In a general setup (see e.g. Fig. 5d), the interface H is divided in $h = \{1, \dots, \mathcal{N}_H\}$ surface portions, each one h , facing a different C_h cell. We require conservation over the whole contour of the hybrid interface,

$$\sum_{h \in H} \Delta \Phi_h = -\Delta \phi^{MD}, \quad (15)$$

where $\Delta\Phi_h$ is the amount crossing the portion h of the interface H towards the corresponding C_h cell. The corresponding hydrodynamic prediction is $\Delta\Phi_h^{\text{pred}} = -A_h \mathbf{J}_h \cdot \mathbf{n} \Delta t_c$ where \mathbf{J}_h the local flux, \mathbf{n} points outwards C and A_h is the area of the h portion of H . The overall disagreement with respect to the molecular value is just,

$$E[\Phi^{\text{pred}}] = \left[(-\Delta\phi^{\text{MD}}) - \sum_{h \in H} \Delta\Phi_h^{\text{pred}} \right], \quad (16)$$

and in order to fulfill the conservation constraint (15) the transfer across each portion h of the H interface is corrected with,

$$\Delta\Phi_h = \Delta\Phi_h^{\text{pred}} + \frac{1}{\mathcal{N}_H} E[\Phi^{\text{pred}}]. \quad (17)$$

5 Conclusions and Perspectives

In writing this review I realised that the number of papers including the prefix *multi* has boomed in recent years. It might well be that like in many other disciplines (art is an example), the stamp “multi” is able to promote some works with no real significance. For instance, in many processes continuum liquid hydrodynamics are known to remain valid up to quite small length scales [10, 12], thus making useless an hybrid particle-continuum, CFD based, approach (this is not the case for rarefied gases [1]). However, after the initial phase of “topic heating” the main relevant ideas and application fields will soon settle down. In my opinion, multiscale techniques for molecular liquid modeling will become a standard tool in commercial or open source packages (see [3] for recent work in this direction). The state of the art will soon benefit from modern faster parallel computing in cheaper architectures, which may also be grid-distributed [4]. To this end, the multiscale algorithms should allow for maximum flexibility with minimum computing modifications. It is easy to imagine that a farm of parallel MD simulations talking with a single macro-solver in a velocity-stress coupling scheme will soon permit to solve unsteady flow of non-Newtonian liquids with the desired molecular structure and (molecular) boundaries. For certain applications these MD simulations will necessarily need to describe open systems of nanoscopic size, evolving with the minimum amount of unphysical artifacts. The present review intends to highlight that a single computing framework should be able to allow for a flexible formulation of this sort of open molecular dynamics, which for instance, can combine state and flux coupling in the same hybrid scheme (see e.g. [19]).

This review is clearly not complete and some issues have been omitted for the sake of space. Other recent reviews can be found in [35, 37]. Some comments should have been made on the tests required at each level of description [14, 18] (molecular structure, radial distributions transport coefficients, fluctuations, hydrodynamics and thermodynamics) or how to couple fluctuations in hybrids of fluctuating

hydrodynamic and MD [7, 14] or variants of Direct Simulation Monte Carlo [19]. As stated in the abstract, OPEN MD is an ongoing research program. Some interesting research lines are the molecular implementation of the open boundary conditions for fluctuating hydrodynamics [15], mass transfer involving multiple species [46] or polymer melts flow under constant external pressure (i.e. in open domains) using an OPEN MD-AdResS combined strategy [18]. Finally important challenges remain to be solved, such as a first-principle generalisation of the adaptive resolution scheme to allow for energy conservation (maybe based on the Mori-Zwanzig formalism [22]) or the extension of OPEN MD to nematic or ionic liquids.

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