

Reply to comments by R. Klein on “Open boundary molecular dynamics”

R. Delgado-Buscalioni^{1,a}, J. Sablić², and M. Praprotnik^{2,b}

¹ Departamento Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain

² Laboratory for Molecular Modeling, National Institute of Chemistry, Hajdrihova 19, 1001 Ljubljana, Slovenia

Received 16 June 2015 / Received in final form 15 July 2015

Published online 21 September 2015

1 Replies to comments and suggestions

Open Boundary MD vs. AdResS

We agree with prof. Klein [1] that there are some similarities between our method [2] and the one presented in Ref. [3] (see also Ref. [4]). There are, however, several relevant differences we would like to outline.

Firstly, both approaches aim to simulate fluids in a grand-canonical ensemble by molecular dynamics (MD) simulation. However, the number of molecules in the approach from Ref. [3] varies only in the atomistic domain by exchanging molecules with the coarse-grained domain whereas one imposes a periodic boundary condition at the boundaries of simulation box in all three directions. Thus, the *total* number of molecules in the system remains constant. In our approach, on the other hand, the simulation box is open in at least one direction, enabling the exchange of molecules with the surroundings. As a result, the *total* number of molecules in the open system is a fluctuating quantity whose variance increases linearly with the system's volume in agreement with the grand canonical ensemble [5]. In our setup, we were able to seamlessly connect the compressibility (mass fluctuations) and other properties across both sides of the hybrid interface (which defines the interest region), by using a heterogeneous buffer, which contains a portion of the atomistic slice.

Secondly, the methodology presented in our contribution [2] is a way to generalize boundary conditions in molecular simulations. Ideally, the dynamics of the atomistic system remains *free of computational artifacts*, and resembles the case of experiments, where driving forces are applied through the system's boundaries. The Open Boundary Molecular Dynamics (OBMD) setup allows then to model non-equilibrium states under quite general conditions, with an arbitrary external pressure tensor and

^a e-mail: rafael.delgado@uam.es

^b e-mail: praprot@cmm.ki.si

more generally, external heat flux. In this context, rather than using AdResS to connect to subsystems with different resolution, the main purpose of AdResS [6] in OBMD simulations is to facilitate the insertion of molecules into the dense atomistic system. We also show that another interesting application of AdResS is to speed up the equilibration step in “delicate” systems, such as polymer melts [2].

Thirdly, for this same reason, our method allows to couple an MD sub-system with a larger domain described by a continuum fluid solver. This hybridMD scenario, which can include hydrodynamic fluctuations [7,8] allows to consider how the larger hydrodynamic scales affect molecular domains and vice-versa [9,10].

Flux coupling

Concerning the reason why the microscopic fluxes should be averaged over volume fluid cells [1], it should be noted that the source of fluctuations in the momentum density (hydrodynamic) field arises in the form of the divergence of a fluctuating pressure tensor. This is indeed the main hypothesis of the Landau-Lifshitz description of fluctuating hydrodynamics, and this form can be also derived *ab initio* by following the Mori-Zwanzig route, starting from the Liouville’s equation for the atomic degrees of freedom (see e.g. [11]). This means that the real source of momentum (and mass) fluctuations is the fluctuating stress; a volume averaged quantity whose covariance should decay like the inverse of the averaging volume [5]. The extent of this small “volume of fluid” is one of the bricks of the coarser hydrodynamic level of description which one aims to recover or couple with the atomistic scales. The fact that fluxes are not measured as averages over areas (“across a surface”) does not mean that there is not a clear separation between the domains that are to be coupled. Following Gauss’s theorem, the flux across the dividing surface can be expressed in terms of those measured from the two adjacent volumes. Usually a linear combination is accurate enough for most purposes. For more information on this issue, the reader is referred to Refs. [7,8] where an atomistic domain (MD) is coupled with fluctuating hydrodynamics using a similar hybridMD setup.

Coupling to fluctuating hydrodynamics

About the last comment by prof. Klein on statistics of fluctuations [1], it has first to be said that the intention of fluctuating hydrodynamics is to describe the evolution of hydrodynamic fields up to second order statistics, i.e. up to their covariances. Covariances determine the curvature of the hydrodynamic free energy functional near the equilibrium state. The statistics of the fluctuations of the MD model might surely differ from a Gaussian, depending on the system’s size, the thermodynamic state and the property considered (mass, energy, momentum densities). However, if departures from equilibrium are small (and densities not so dilute), the Gaussian approximation is excellent, even for relatively small systems used in simulations. This is precisely why computer simulations of molecular systems were able to survive as a scientific tool. Near equilibrium, fluctuations are determined by susceptibilities (second order derivatives of the free energy) and some of these can be altered by simulation artifacts as thermostats. The role of OBMD is precisely to avoid using these artifacts inside the *sacred* atomistic domain. In an hybridMD setup, these “coupling” artifacts are placed in the buffer, and so it is the coarse-grained description, as it is obviously a simplified model. Fluctuations are only relevant in the interest domain (which using a heterogeneous buffer) only contains the atomistic description. Finally, full compatibility

(at level of fluctuations) with the fluctuating hydrodynamic (coarser) description requires a priori matching of the susceptibilities involved (e.g. compressibility for sound or heat capacities for energy transport).

J. S. and M. P. acknowledge financial support through grants P1-0002 and J1-4134 from the Slovenian Research Agency. R.D-B acknowledges support from Spanish MINECO projects FIS2010-22047-C05 and FIS2013-47350-C5-1-R.

References

1. R. Klein, *Eur. Phys. J. Special Topics* **224**(12), 2509 (2015)
2. R. Delgado-Buscalioni, J. Sablić, M. Praprotnik, *Eur. Phys. J. Special Topics* **224**(12), 2331 (2015)
3. H. Wang, A. Agarwal, *Eur. Phys. J. Special Topics* **224**(12), 2269 (2015)
4. K. Kreis, A.C. Fogarty, K. Kremer, R. Potestio, *Eur. Phys. J. Special Topics* **224**(12), 2289 (2015)
5. G. De Fabritiis, M. Serrano, R. Delgado-Buscalioni, P.V. Coveney, *Phys. Rev. E* **75**, 026307 (2007)
6. M. Praprotnik, L. Delle Site, K. Kremer, *J. Chem. Phys.* **123**, 224106 (2005)
7. G.D. Fabritiis, R. Delgado-Buscalioni, P.V. Coveney, *Phys. Rev. Lett.* **97**, 134501 (2006)
8. R. Delgado-Buscalioni, G. De Fabritiis, *Phys. Rev. E* **76**, 036709 (2007)
9. R. Delgado-Buscalioni, K. Kremer, M. Praprotnik, *J. Chem. Phys.* **128**, 114110 (2008)
10. R. Delgado-Buscalioni, K. Kremer, M. Praprotnik, *J. Chem. Phys.* **131**, 244107 (2009)
11. P. Español, J.G. Anero, I. Zuñiga, *J. Chem. Phys.* **131**, 244117 (2009)