Coupling MD with Continuum through a Mesoscopic Model

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Concurrent Triple-Scale Simulation

Motivation:

to perform MD of open domains with relatively large molecules, either in the grand canonical ensemble or under non-equilibrium conditions.

Method: Triple-scale AdResS-HybridMD scheme

- Is a combination of two dual-scale models: a particle-based Adaptive Resolution Scheme (AdResS), which couples the atomic and mesoscopic scales, and a hybrid continuum-molecular dynamics scheme (HybridMD)
- covers the length-scales ranging from the micro- to macro-scale
- successfully sorts out the problem of large molecule insertion in the hybrid particle-continuum simulations of molecular liquids
- opens up the possibility to perform efficient grand-canonical molecular dynamics simulations of truly open molecular liquid systems

Results:

the structural and dynamical properties of the liquid are accurately captured

Triple-Scale Model



R. Delgado Buscalioni, K. Kremer, MP, J. Chem. Phys. 128, 114110 (2008).

Molecule Insertion

Motivation:

- Coupling MD with continuum requires molecule deletion or insertion into a dense liquid.
- **Method:** Usher, J. Chem. Phys. **121**, 12139 (2004)
 - Insertion of a molecule at a desired potential energy into a liquid.
 - Using a Newton-Raphson-like search in the potential energy surface.
- Problem:
 - Complex molecules cannot be easily inserted.
- Solution:
 - MD is coupled to continuum via a mesoscale regime using soft coarse-grained particles by AdResS.

Hybrid atomistic/mesoscopic liquid



MP, L. Delle Site, K. Kremer, J. Chem. Phys. **126**, 134902 (2007). MP, L. Delle Site, K. Kremer, Phys. Rev. E **73**, 066701 (2006).

Changing Number of Degrees of Freedom

A tetrahedral molecule has a defined spatial orientation and 3N = 12 DOFs:

- 3 translational
- 3 rotational
- 3N 6 = 6 vibrational
- One particle mesoscopic molecule has no defined spatial orientation and only 3 translational DOFs.



MP, L. Delle Site, K. Kremer, J. Chem. Phys. **123**, 224106 (2005). MP, L. Delle Site, K. Kremer, Annu. Rev. Phys. Chem. **59**, 545 (2008).

Geometrically induced phase transition

In thermodynamical equilibrium, boundary conditions analogous to to two-phase coexistence must be satisfied:

$$\mu_{ex} = \mu_{cg}, \quad p_{ex} = p_{cg}, \quad T_{ex} = T_{cg}.$$

The rotational and vibrational parts of the free energy can be viewed as the latent heat, which is supplied or taken by the thermostat, at this transition.

Transition region



- Molecules in A and B are physically identical but differently represented.
- **P** The number of DOFs is n = n(x) with: $n_A = const_A$; $n_B = const_B$; and $n_\Delta = n(x)$

The system is in equilibrium which implies:
$$\lim_{x \to d^{-}} \frac{\partial F_A(x)}{\partial x} = \lim_{x \to d^{+}} \frac{\partial F_B(x)}{\partial x} = 0 \Longrightarrow$$

$$\lim_{x \to d^{-}} \frac{\partial n_A(x)}{\partial x} = \lim_{x \to d^{+}} \frac{\partial n_B(x)}{\partial x} = 0$$

Weighting Function = Order Parameter



The values w = 1 and w = 0 correspond to the atomistic and coarse-grained regions, respectively, while the values 0 < w < 1 correspond to the transition (*hyb*) regime.



AdResS consists of two main steps:

- 1. Derive the effective pair potential U^{cm} between coarse-grained molecules on the basis of the reference all-atom system.
- 2. Couple the atomistic and mesoscopic scales:

$$\mathbf{F}_{\alpha\beta} = w(X_{\alpha})w(X_{\beta})\mathbf{F}_{\alpha\beta}^{atom} + [1 - w(X_{\alpha})w(X_{\beta})]\mathbf{F}_{\alpha\beta}^{cm},$$

where

$$\mathbf{F}^{atom}_{lphaeta} = \sum_{ilpha,jeta} \mathbf{F}^{atom}_{ilpha jeta}$$

is the sum of all pair interactions between explicit atoms of molecules α and β and

$$\begin{aligned} \mathbf{F}_{i\alpha j\beta}^{atom} &= -\frac{\partial U^{atom}}{\partial \mathbf{r}_{i\alpha j\beta}}, \\ \mathbf{F}_{\alpha\beta}^{cm} &= -\frac{\partial U^{cm}}{\partial \mathbf{R}_{\alpha\beta}}. \end{aligned}$$

May the Force be with you



One must interpolate the **forces** and not the interaction potentials if the **Newton's Third Law** is to be satisfied!

MP, K. Kremer, L. Delle Site, J. Phys. A: Math. Theor. 40, F281, 2007.

Mapping of structural properties

Effective pair potential that reproduces the structure of the all-atom system as closely as possible is determined using the RDF_{cm} of the reference all-atom system via the potential of mean force (*PMF*) as

 $U^{cm}(r) \approx PMF(r) = -k_B T \log g_{ex}^{cm}(r),$

 $g_{ex}^{cm}(r)$ is the all-atom RDF_{cm} and $U^{cm}(r)$ is the effective potential.

Effective potential is:

- in general temperature and density dependent
- **softer** than the interatomic potentials

Iterative Boltzmann inversion

In the limit $\rho = 0$:

$$U^{eff}(r) = F(r) = -k_B T \ln g(r).$$

For systems with $\rho > 0$ the above relation is used as an initial approximation in the iteration scheme:

$$U_{i+1}^{eff}(r) = U_i^{eff}(r) + k_B T \ln \frac{g_i(r)}{g_{target}(r)}$$

Ramp pressure correction:

$$\Delta U_{lin} = A(1 - \frac{r}{r_{cut}}).$$

D. Reith, M. Pütz, F. Müller-Plathe, J. Comput. Chem., 24, 1624, 2003.

Equation of state



The pressure tensor:

$$\mathbf{J} = p\,\mathbf{I} + \rho\mathbf{v}\mathbf{v} + \mathbf{\Pi}$$



Transverse DPD Thermostat



- The variation of the dissipative particle dynamics (DPD) thermostat includes the damping of the perpendicular components of the relative velocity, yet keeping the advantages of conserving Galilei invariance and within our error bar also hydrodynamics. It allows for controlling transport properties of molecular fluids.
- C. Junghans, MP, K. Kremer, Soft Matter 4, 156 (2008).

Liquid Water



- MP, S. Matysiak, L. Delle Site, K. Kremer, C. Clementi, J. Phys.: Condens. Matter 19, 292201 (2007).
- S. Matysiak, C. Clementi, MP, K. Kremer, L. Delle Site, J. Chem. Phys. 128, 024503 (2008).

Electrostatics: Reaction field method

The electrostatic forces interactions are described using the Reaction field (RF) method:

$$\mathbf{F}_{C_{i_{\alpha}j_{\beta}}}^{atom}(\mathbf{r}_{i_{\alpha}j_{\beta}}) = \frac{e_{i_{\alpha}}e_{j_{\beta}}}{4\pi\epsilon_0} \left[\frac{1}{r_{i_{\alpha}j_{\beta}}^3} - \frac{1}{R_c^3}\frac{2(\epsilon_{RF}-1)}{1+2\epsilon_{RF}}\right]\mathbf{r}_{i_{\alpha}j_{\beta}}.$$

The RF is suitable to be used with AdResS because:

- it is pairwise
- like AdResS it must also be applied with a thermostat

Interface effect of the cg water



The transition regime neutralizes the interface effect of the *c*g water \implies the structure of water in the explicit regime is the same as in the bulk.

Position dependent Langevin thermostat

The Langevin equation with a position dependent coefficient $\Gamma(x)$ can be written as:

$$m_i dv_i/dt = F_i - m_i \Gamma(x) v_i + R_i(x, t) \tag{1}$$

where $R_i(x,t)$ is:

$$\langle R_i(x,t) \rangle = 0, \tag{2}$$

$$\langle R_i(x,t_1)R_j(x,t_2)\rangle = 2\Gamma(x)m_ikT\delta(t_1-t_2)\delta_{ij}$$
(3)

$$\Gamma(w) = \begin{cases} \Gamma_{cg} & \text{if } w \le 0.6\\ \alpha w + \beta & \text{if } 0.6 < w \le 1.0 \end{cases}$$
(4)

This choice provides a simple interpolation between the two limit values of $\Gamma(0.6) = \Gamma(0) = \Gamma_{cg} = 15ps^{-1}$ and $\Gamma(1) = \Gamma_{all-atom} = 5ps^{-1}$. The parameters α and β are $-25ps^{-1}$ and $30ps^{-1}$, respectively.

Diffusion coefficient



S. Matysiak, C. Clementi, MP, K. Kremer, L. Delle Site, J. Chem. Phys 128, 024503, 2008.

Diffusion across the transition regime



HybridMD

- The hybrid particle-continuum scheme (HybridMD) is designed to connect the dynamics of a "molecular domain" with that obtained from a continuum description of the surrounding fluid flow.
- The method is based on flux-exchange.
- The system is divided in (at least) two domains, described via classical molecular dynamics (MD) and continuum fluid dynamics (CFD), i.e., solving the Navier-Stokes equations.
- The MD and CFD domains share one unique "hybrid interface", H: Flux balance implies the conservation of mass and momentum across H.

G. De Fabritiis, R. Delgado Buscalioni, P. Coveney, Phys. Rev. Lett 97, 134501 (2006).R. Delgado Buscalioni, G. De Fabritiis, Phys. Rev. E 76, 036709 (2007).

AdResS-HybridMD: Combined Scheme



Domain decomposition of the combined scheme. The top part of the figure shows the location of the fluid model layers (cg, hyb and ex) within the HybridMD setup. The bottom part of the figure shows the set of control cells used in the HybridMD setup.

R. Delgado Buscalioni, K. Kremer, MP, J. Chem. Phys. 128, 114110 (2008).

Molecular Density Profile



9 (a)
$$\rho_m = 0.1 \sigma^{-3}$$
. (b) $\rho_m = 0.175 \sigma^{-3}$

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RDFs: Equilibrium



RDF_{cm}s of the liquid in the atomistic and transition domains (ex + hyb) and in the total molecular region (ex + hyb + cg) of the triple-scale model together with the reference RDF_{cm} of the all-atom system (ex(PBC)) at $\rho = 0.175/\sigma^3$.

Couette Flow



Velocity profile at the particle region of an hybrid simulation of a Couette flow.



Stokes Flow



Velocity in the y-direction at some selected cells in a hybrid simulation of a Stokes flow.

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Two Possible Setups



R. Delgado Buscalioni, K. Kremer, MP, J. Chem. Phys. 128, 114110 (2008).

Buffer: Two Possible Setups

Homogeneous buffer:

- *pro*: Requires small buffer size.
- pro: Allows us to introduce CG molecular information into the explicit MD region (structure, diffusion rates, etc.)
- con: Requires fine tuning of CG model ,i.e., EOS, viscosity or diffusion coefficient: *Transversal DPD*; C. Junghans, MP, K. Kremer, Soft Matter 4, 156 (2008).

Heterogeneous buffer:

- *pro*: All-atom MD region: correct viscosity, EOS, fluctuations.
- *pro*: Does not requires fine tuning of CG and HYB models.
- *pro*: Enables energy exchange, as the MD region is fully explicit.
- *con*: Larger buffer size.

Triple-Scale Simulation: Liquid Water



R. Delgado Buscalioni, K. Kremer, MP, submitted.

Coarse-Grained Model



Center-of-mass RDF of the flexible TIP3P water model and the effective potential.



Couette Flow: Liquid Water



Density profile and velocity distribution across the particle domain.

Grand Canonical Ensemble

Mass fluctuations

Standard deviation of mass $Var[\rho] = \rho k_B T / (Vc_T^2)$, $c_T^2 = \left(\frac{\partial p}{\partial \rho}\right)_T$, $\beta_T = (c_T^2 \rho)^{-1}$

Flexible TIP3P: $c_T = 7.38 (\varepsilon_{OO}/m_O)^{1/2}$, $\rho = 1.20 m_O / \sigma_{OO}^3$

• $V = 3.50 \times 6.18 \times 11.12 \sigma_{OO}^3$: grand canonical: $Var[\rho] = 0.0187$, simulation: $Var[\rho] = 0.020 \pm 0.002$

V = $10.50 \times 6.18 \times 11.12 \sigma_{OO}^3$:
grand canonical: $Var[\rho] = 0.0108$, simulation: $Var[\rho] = 0.011 \pm 0.005$

Oscillatory Shear Flow



Time evolution of the velocity. For comparison, the deterministic Navier-Stokes solution is shown.

Conclusions

AdResS-HybridMD Scheme:

- We performed a triple-scale simulation of a molecular liquid.
- Length scales from the micro- to macro-scale are concurrently coupled.
- The triple-scale scheme is robust against the details of the mesoscopic model.
- The method allows us to perform efficient molecular dynamics simulations of molecular liquids in the grand canonical ensemble or under non-equilibrium flows.

Future work:

- Applications to study phenomena involving flow-matter interactions at multiple length scales.
- Grand canonical molecular simulations involving complex molecules.

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