How to Efficiently Deal with Electrostatic Interactions in Soft Matter Simulations: The Reaction-Field Approach

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Introduction

- Accurate treatment of electrostatic interactions in molecular dynamics (MD) simulations is crucial for a proper description of biologically relevant soft matter systems [1,2].
- At the same, to reach large systems and long time scales, one should employ electrostatic schemes that are as efficient as possible.
- The Particle-Mesh Ewald (PME) technique is currently the method of choice for incorporating electrostatics into the systems. However, besides being highly accurate, it is also computationally demanding.
- Here we show that the reaction-field (RF) approach provides a useful compromise between speed an accuracy for simulations of soft matter systems [3].

Model of DPPC bilayer

- DPPC (dipalmitoyl phosphatidylcholine) bilayer composed of 128 DPPC molecules fully hydrated by 3655 water molecules (SPC).
- United atom GROMACS force field
- $T = 323$ K, time scale 50 ns
- A full description of the system is given in Refs. [1,2].
- Electrostatics: Particle-Mesh Ewald (PME), or abrupt truncation at 1.8 nm, or truncation at 1.8 nm together with switching, or the Reaction-Field (RF) scheme.
- In the RF approach, all Coulombic interactions are fully accounted for up to some cutoff distance r_{RF}, beyond which electrostatics is treated through a reaction field ($V(r) \sim 1/\epsilon r$) whose main parameter is the dielectric constant $\epsilon = 80$.

Results

Results for the area per lipid molecule shown in Fig. 1 illustrate that truncation with and without switching leads to compressed bilayers with respect to the PME case. The PME results are consistent with experiments [3], i.e. $\langle A \rangle \approx 0.64 \, \text{nm}^2$. The RF with $r_{RF} \geq 1.8 \, \text{nm}$ is consistent with PME.

Figure 2 demonstrates that the truncation of electrostatics leads to serious artifacts in the pair correlation and phase behavior. Swiching reduces the artifacts, but does not remove them. The RF schemes perform considerably better (see Figures 2 and 3), and for large r_{RF} (of the order of 1.8 nm) the artifacts are essentially negligible as the phase behavior is then consistent with that found by PME (see Fig. 5).

Further results of other structural and dynamic quantities support these conclusions.

As for efficiency, for the present system the RF method with $r_{RF} = 1.8$ nm is faster than PME by a factor of 1.6.
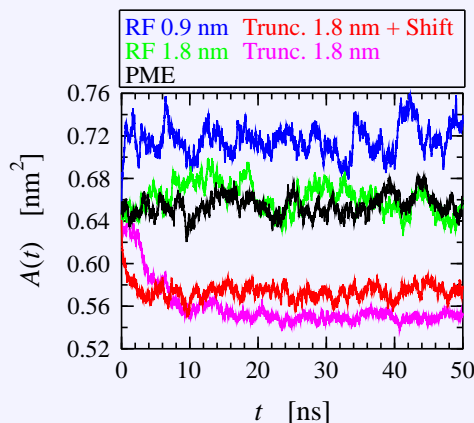

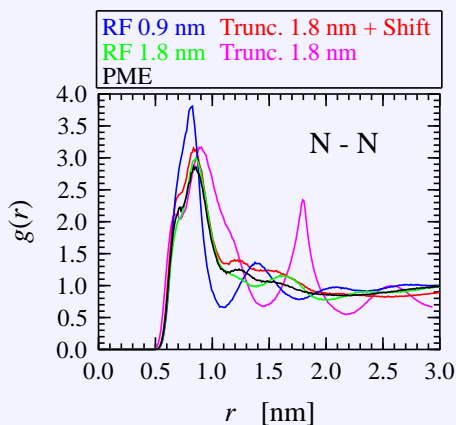
Fig. 1: Evolution of the area per molecule in time.

Fig. 2: The radial distribution function for pairs of intermolecular nitrogen atoms in the headgroups of DPPC molecules.
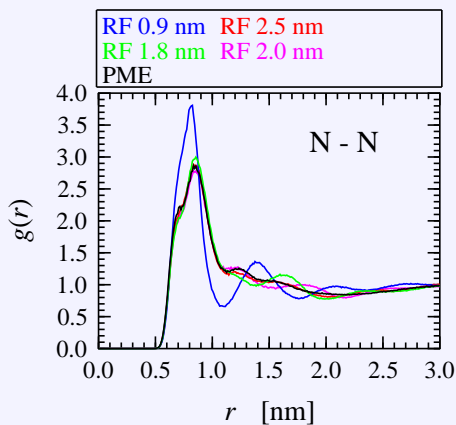

Fig. 3: RDFs as in Fig. 2 but for the Reaction-Field scheme with different truncation distances.
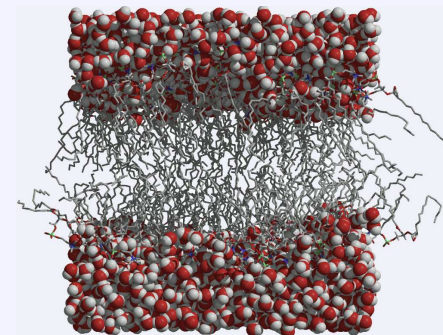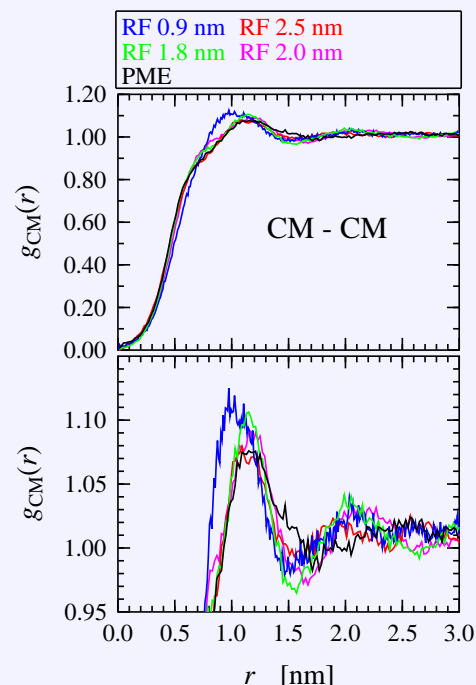

Fig. 4: DPPC bilayer.

Fig. 5: RDFs between center of mass positions of DPPC molecules: Comparison of RF schemes with PME.

Conclusions

If the computational load is not a limiting factor, use PME. Otherwise, for simulations of large systems over very long times, use the Reaction-Field approach instead of truncation.

References

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