Smooth capping of short-range repulsive forces in hybrid atomistic/coarse-grain molecular dynamics simulation

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ABSTRACT

In adaptive multiscale simulation, particles automatically adapt their resolution when they move from the atomistic region to the coarse-grained surrounding or vice versa. The latter process entails the smooth insertion of the extra atomistic degrees of freedom onto the coarse-grain particles, which is prone to problematic atom-atom overlaps. Here we show that this so-called reverse mapping problem is significantly reduced by smoothly capping the repulsive part of the atomistic pair-interactions to a maximum absolute force. Not surprisingly, capping the interactions at too low a force affects the properties of the system, firstly seen in the pressure and the diffusion coefficient. Good results are obtained for forces capped between 10^4 and 10^8 K/Å.

1. Introduction

Hybrid atomistic/coarse-grain molecular dynamics simulation [1,2,3], or hybrid MD for short, is a relatively new method to model soft matter systems that exhibit an intrinsic multiscale character. Examples of such systems are polymers and bio-molecular assemblies, such as lipid membranes and proteins. These materials display interesting phenomena that take place on time and length scales that are too large to model by brute force molecular dynamics simulation in full atomistic detail. Instead, mesoscopic coarse-grain models have been developed, in which each particle typically represents a chemical group of several atoms, to model systems of micrometer and microsecond length and time scales, however at the cost of losing the atomistic details [4,5,6]. Hybrid MD simulation aims to link the mesoscale phenomena to the underlying atomistic motions, by focusing locally in atomistic detail while treating the environment of the atomistic region at the computationally less demanding coarse-grain representation.

A key feature of a multiscale modeling method is its ability to bridge between the different molecular representations [7,8]. A hybrid MD simulation of a fluidic system requires, in the first place, a proper coupling between the particles in the atomistic region and those in the coarse-grained environment, and secondly, a mechanism to switch between the two representations of particles that diffuse from one region to the other. Especially the on-the-fly switching from a low-resolution coarse-grain representation to the high-resolution atomistic representation is fraught with difficulty. There is not a unique solution to re-insert the atoms into a coarse-grained particle, such that the inserted degrees of freedom are in thermal equilibrium with their surrounding.

We have recently developed a hybrid MD method that combines two so-called reverse mapping techniques to smoothly map the atoms onto a coarse-grained molecule when it enters the high-resolution region [9]. In the first place, a special "healing region" is introduced in between the high and low resolution regions, in which particles gradually adapt their representation by smoothly scaling their interaction potentials [2]. Although this approach was shown to work well

for relatively simple liquids that consist of molecules that can be represented by a single coarse-grained bead, such as liquid methane, a second reverse mapping technique is required to model molecules that consist of two or more connected coarse-grained beads. The problem with connected beads is that a proper orientation of the atomic fragments with respect to that of the molecular frame is essential to allow for a smooth insertion of the atoms when in the healing region. By preconditioning the orientations of the atomistic fragments through an auxiliary rigid body rotation dynamics in the low-resolution region, hybrid MD of interesting macromolecular soft matter systems has become possible[9].

In the present work, we investigate an additional technique to improve the reverse mapping in hybrid MD simulation: capping of the repulsive part of the atomistic pair-potentials. Typical pair-potentials, such as the Lennard-Jones potential or the Buckingham potential describe the repulsive interaction that two closed-shell atoms feel at short distance due to the electronic Pauli exchange repulsion with a steep inverse twelfth power function or an exponential function respectively. At inter-atomic distances very close to zero the forces on the atoms become extremely large (so-called atom overlaps), which can cause havoc for the molecular dynamics integrator. Under normal, not too extreme temperature and pressure, conditions this does not happen in practice in atomistic equilibrium simulations. However, reverse mapping atomistic details into a coarse-grained molecule is not an equilibrium process and very short inter-atomic distances may occur due to the relatively soft nature of the coarse-grain beads.

Especially when the level of coarse-graining is high, that is, when a coarse-grain bead represents many atoms, and also when the underlying atomistic fragment structure is highly anisotropic, catastrophic overlaps may occur when the atomistic details are inserted into coarse-grain particles that move through the healing region toward the high-resolution region. Enlarging the healing region so that particles move on a longer transition path and thus switch resolution more gradually reduces the probability of overlaps. It is however computationally advantageous to keep the healing region as thin as possible. As an alternative, we consider here to cap the repulsive part of the pair-potential at very short distances. Anticipating our results, we find that such capping improves the reverse mapping, as indicated by better total energy conservation in hybrid MD simulation of liquid hexane, and that the capping does not affect the structural and dynamical properties of the system, unless the capping is done at too low values of the forces.

2. Methods

2.1 Pair-potential capping

The purpose of capping the atomistic pair-interactions is to avoid too large forces at atom-atom distances close to zero, which configurations can occur when atoms are gradually inserted into the coarse-grained particles during a hybrid MD simulation. The capped potentials are constructed starting from the standard 12-6 Lennard-Jones pair-potential:

$$V^{\mathrm{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{1}$$

where r is the distance between the atoms, ϵ is the depth of the the potential well, and σ is the distance where the inter-particle potential is zero. At distances shorter than σ the first term dominates, which governs the steep r^{-12} repulsive wall.

In order to set a maximum allowed absolute force, F^{max}, at inter-particle distances shorter than
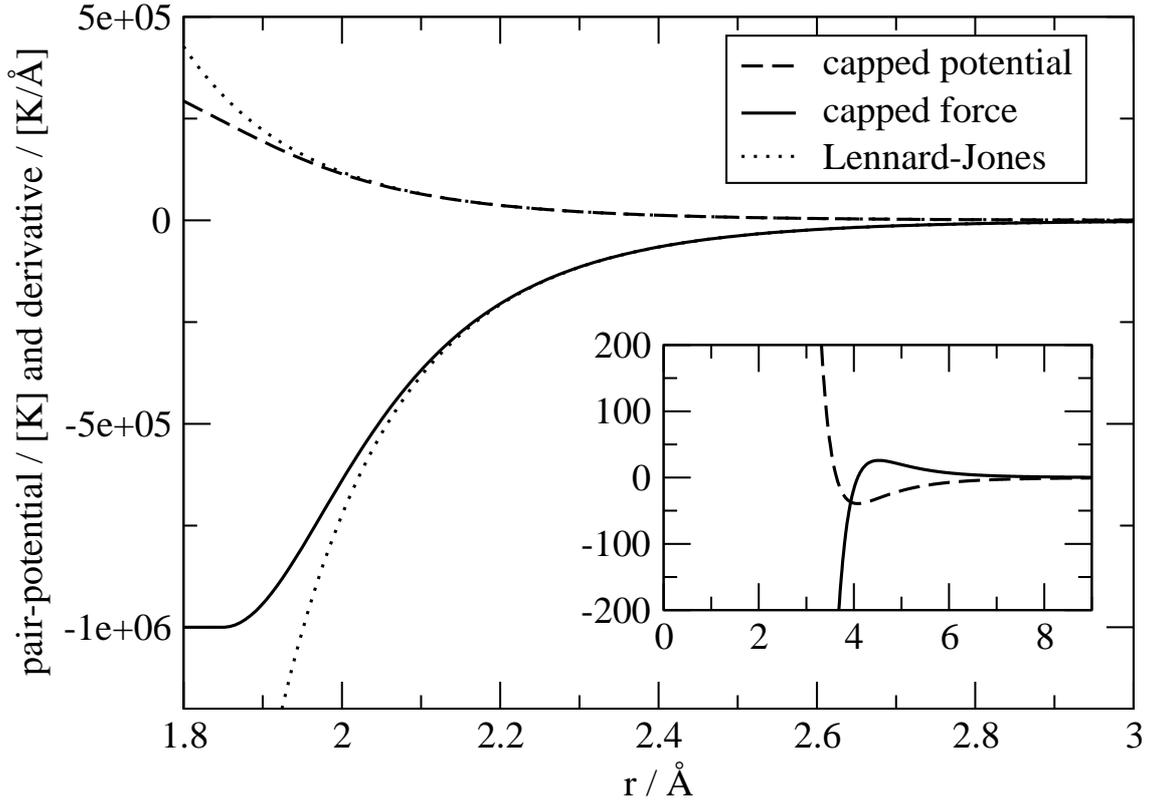
Figure 1: Comparison of the capped tabulated potential (dashed line) and force (solid line) with the original Lennard-Jones functions (dotted lines). The force is capped to -10^{-6} K/Å, which results in a linear potential at short distances. The inset zooms in on the potential well.

a cutoff r^{cut}, the force of the capped interaction is taken to be:

$$
F^{\mathrm{capped}} = \begin{cases} F^{\mathrm{max}} & \text{if } r < r^{\mathrm{cut}} \\ -w(r) * \frac{dV^{\mathrm{LJ}}(r)}{dr} & \text{if } r \geq r^{\mathrm{cut}} \end{cases} \tag{2}
$$

in which $w(r)$ is,

$$
w(r) = \frac{1 - \left(\frac{r^{\mathrm{switch}}}{r}\right)^{26}}{1 - \left(\frac{r^{\mathrm{switch}}}{r}\right)^{52}}, \tag{3}
$$

a function that switches smoothly from 0 to 1 in the neighborhood of the distance r^{switch}. The cutoff distance, r^{cut}, is found by moving the position of the switch function, r^{switch}, in an iterative procedure such that the target maximum absolute force, F^{max} is set at r^{cut}. The potential belonging to this function for the force is obtained by integration. The potentials and forces are input to the MD program as tabulated functions on a grid of 4000 points between $r = 0$ and the interaction cutoff distance of 10 Å. Fig. 1 shows an example capped force and potential compared to the original Lennard-Jones potential for a carbon-carbon interaction.

2.2 Hybrid molecular dynamics

The hybrid atomistic/coarse-grain molecular dynamics simulations are performed using the algorithm presented in Refs.[2,9]. In brief, the entire molecular system is simultaneously represented in both the atomistic and the coarse-grained detail. The system is spatially partitioned in a high-resolution region with a surrounding healing region in which the atoms are propagated

and a low-resolution region in which the coarse-grained particles are evolved. In both regions, the coordinates of the inactive representation are updated by matching the centers of mass of the particles every time step. In addition, in the low-resolution region the orientation of the inactive, frozen, atomistic fragments are evolved using an auxiliary rigid body rotation dynamics, governed by a reduced energy function of selected atomistic intra-molecular potentials[10].

The coupling between atoms and coarse-grain particles, as well as the switching between representations in the healing region is governed by a hybrid potential,

$$V^{\mathrm{A/CG}} = \sum_{\alpha\beta} \left(\lambda_{\alpha\beta} \Phi^{\mathrm{CG}}_{\alpha\beta} + (1 - \lambda_{\alpha\beta}) \sum_{\substack{i\in\alpha \\ j\in\beta}} \Phi^{\mathrm{A}}_{ij} \right), \tag{4}$$

which sums over all pairs of coarse-grain particles α and β and mixes the course-grain pair-interaction, Φ^{CG}, with the sum of atomistic pair-interactions, Φ^{A}, of atoms i grouped in α and atoms j grouped in β, using a scaling function $\lambda \in [0, 1]$ that depends on the particle positions. Further details on the hybrid MD method are found in Ref.[2].

3. Results

3.1 Effect of capping on structural and dynamical properties

To assess the effect of capped pair-interactions on the properties of the system, we performed a series of fully atomistic MD simulations of liquid hexane, in which the Lennard-Jones potentials were capped to maximum forces of 600, 10^3, 10^4, 10^6, 10^8, and ∞ K/Å. To this end, 250 hexane molecules were simulated in a cubic box subject to periodic boundary conditions in the NVT ensemble. A temperature of $T = 303.15$ K was maintained using the Nosé-Hoover chain thermostat. The CHARMM[11] force-field was used and adapted by capping the Vanderwaals interactions. The simulations were performed using our in house CM3D molecular dynamics program.

The following properties were computed: the average pressure, the carbon-carbon and carbon-hydrogen radial distribution functions, the carbon and hydrogen velocity auto-correlation functions (from which the infrared spectrum was computed), and the carbon mean-square displacement, from which the self-diffusion coefficient was obtained. In Fig. 2 is shown that the radial distribution functions (top panel) and vibration spectra (middle panel) are indistinguishable with respect to the different capped potentials. However, the capping has a noticeable effect on the mean square displacement (bottom panel), the diffusion, D, and the pressure P (see Tab. 1) for capping values lower than $F^{\mathrm{max}} = 10^4$ K/Å.

3.2 Effect of capping on reverse mapping in hybrid MD

To test the effect of using capped potentials on the reverse mapping in a hybrid MD simulation, we performed multiscale simulations of hexane using the previous series of capped atomistic pair-potentials. The hybrid system contained 1900 hexane molecules in a rectangular box with dimensions close to 60 x 60 x 120 Å using periodic boundary conditions. The atomistic region was chosen to be a 2D slab with a width of 24 Å flanked on both sides by a healing region with a width of 5 Å. At the coarse-grained level, hexane was modeled using the forcefield of Nielsen *et at*, in which each molecule is modeled by two beads (representing C_3H_7) bonded with

Table 1: The self-diffusion coefficient, D, obtained from the slope of the mean square displacement, and the average pressure, P, computed using interactions capped at different absolute maximum forces, F^{max}.

F^{max} [k/Å]	D [10^{-5} cm^2/s]	P [atm]
600	5.4	-0.38
10^3	4.7	0.27
10^4	3.9	1.7
10^6	4.0	1.7
10^8	3.7	1.6
∞	4.0	1.7
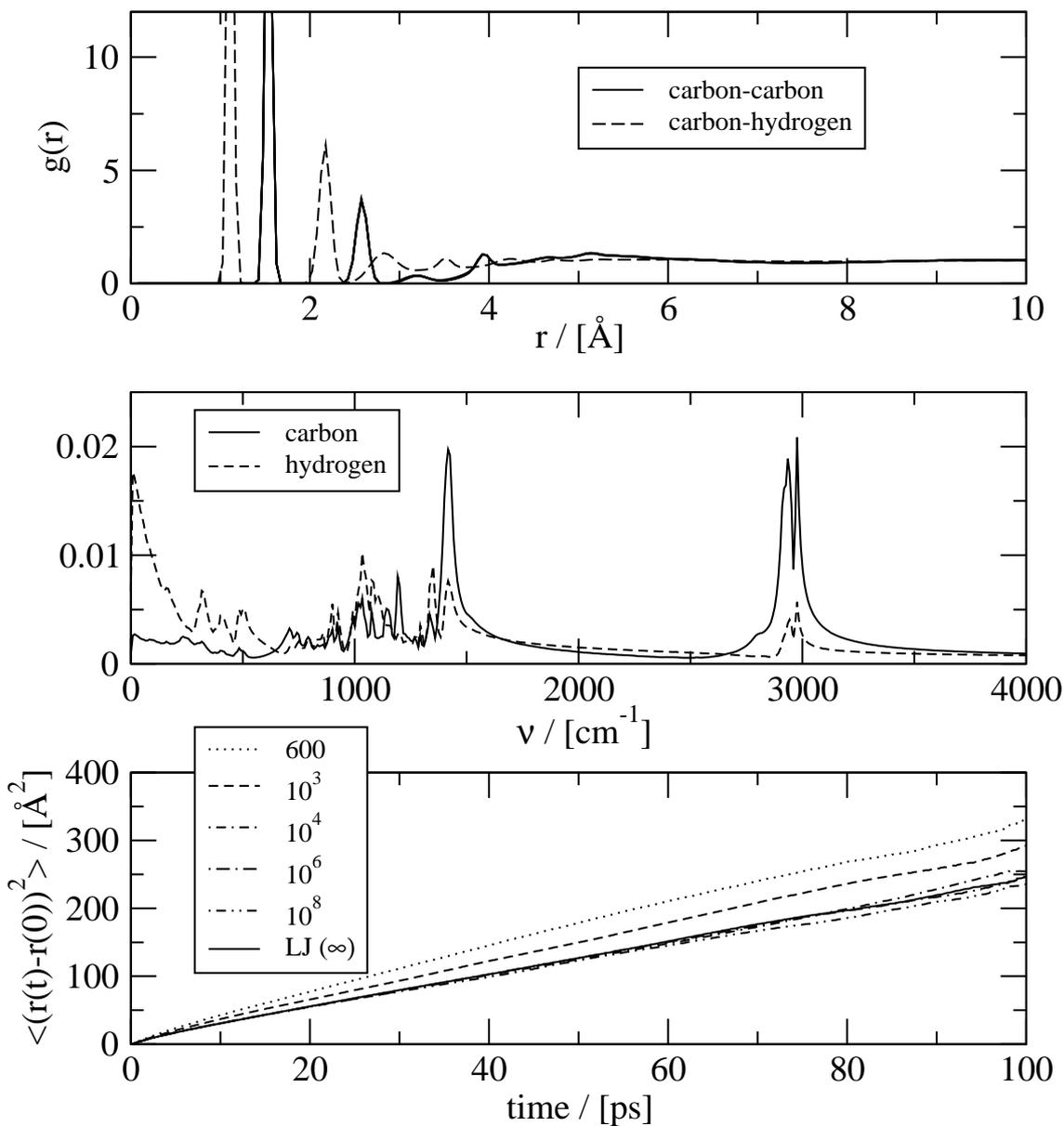
Figure 2: Structural and dynamical properties of liquid hexane modeled with Vanderwaals interactions capped at a maximum force of 600, 10^3, 10^4, 10^6, 10^8, and infinite (i.e. normal Lennard-Jones)

a harmonic spring and interacting through 9-6 Lennard-Jones pair-potentials[12]. To assess the performance of the reverse-mapping, we monitor the hybrid total energy, which is very sensitive to the accuracy of the integration of the equations of motion. This hybrid total energy is not a physical property, but rather an auxiliary conserved quantity that allows for quality control.

Fig. 3 shows this total energy for 200 ps hybrid MD simulations using the potentials capped at 10^6 and 10^8 K/Å respectively, as well as the original Lennard-Jones potentials. Clearly, the total energy is not properly conserved, and shows jumps due to atom-overlaps in the healing region using the (uncapped) Lennard-Jones potentials, and a healing region width of 5 Å. The simulations using the capped potentials show very good energy conservation, indicating a smooth switching of resolution of hexane molecules. Capping at 10^6 K/Å shows slightly better performance than capping at 10^8 K/Å, and further improvement may be reached by capping at even lower absolute forces, but that may affect the dynamics of the system as was shown above.
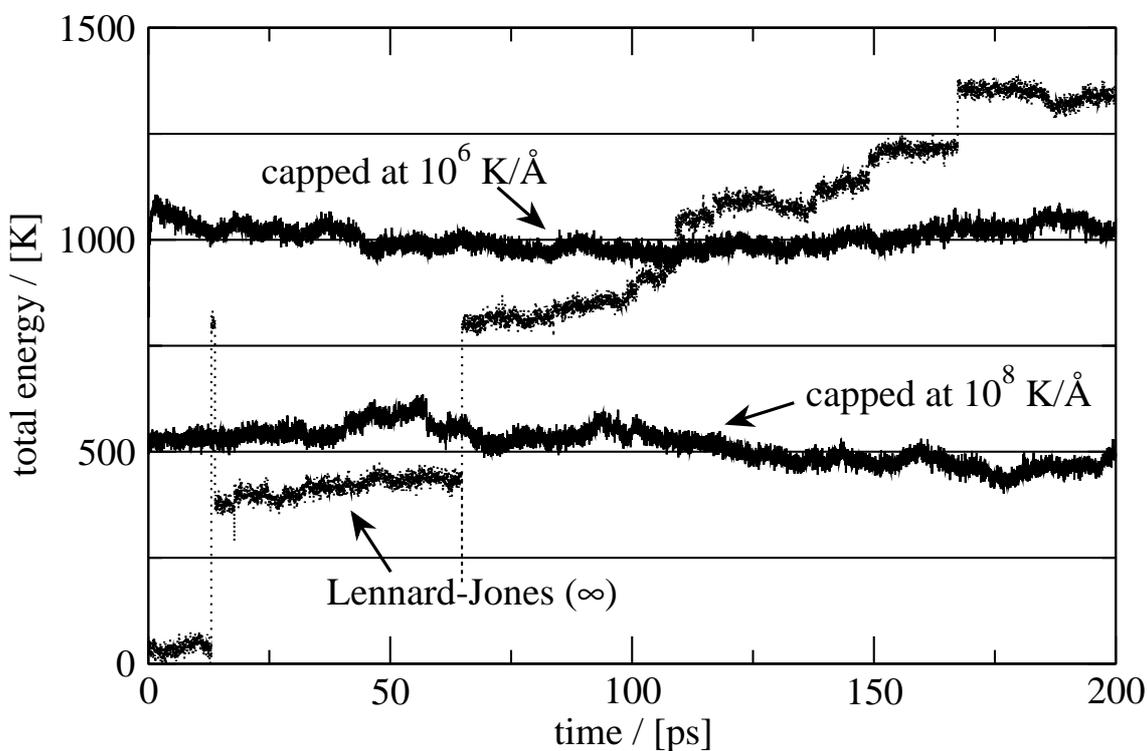
Figure 3: Hybrid total energy conservation from three different multiscale simulations of liquid hexane using pair-interaction capped at a maximum force of 10^6, 10^8, and infinite (i.e. normal Lennard-Jones).

Conclusion

We have investigated the effect of capping the repulsive part of the Lennard-Jones pair-potentials on structural and dynamical properties for the benefit of improving the reverse mapping of atomic fragments onto coarse-grained particles in hybrid MD simulation. Capping the interactions to a too small maximum absolute force (smaller than 10^4 K/Å in our bulk hexane calculations) is, perhaps not surprisingly, first seen to affect the pressure and the self-diffusion. Nevertheless, capping at larger values still has a positive effect on the reverse-mapping in hybrid atomistic/coarse-grain simulations, as seen from the conservation of the total energy. This is because accidental overlaps between atoms when they are inserted onto the coarse-grained particles do no longer cause extremely large repulsive forces that disrupt the MD integration.

Acknowledgments

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