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Communication: Truncated Non-Bonded Potentials Can Yield Unphysical Behavior in Molecular Dynamics Simulations of Interfaces

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Non-bonded potentials are included in most force fields and therefore widely used in classical molecular dynamics (MD) simulations of materials and interfacial phenomena. It is commonplace to truncate these potentials for computational efficiency based on the assumption that errors are negligible for reasonable cutoffs or compensated for by adjusting other interaction parameters. Arising from a metadynamics study of the wetting transition of water on a solid substrate we find that the influence of the cutoff is unexpectedly strong and can change the character of the wetting transition from continuous to first order by creating artificial metastable wetting states. Common cutoff corrections such as the use of a force switching function, a shifted potential or a shifted force do not avoid this. Such a qualitative difference urges caution and suggests that using truncated non-bonded potentials can induce unphysical behavior that cannot be fully accounted for by adjusting other interaction parameters.

Keywords: Molecular Dynamics, Interfaces, Force Fields, Free Energy

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Short- to medium-range potentials such as the Lennard-Jones¹ or the Buckingham² potential are the backbone of classical MD simulations. They represent Pauli repulsion as well as non-directional dispersion attraction and there exist multiple flavors implemented in most MD codes under the term of non-bonded interactions. In practice there is a need to truncate these potentials since the number of neighbors that have to be considered for each entity grows enormously, drastically increasing the computational cost for the force calculation. Truncating between $r_c = 2.5$ and 3.5σ , where σ is the characteristic interaction range, is a very common practice in MD studies³ and has become the minimum standard, assuming that errors arising from this are small enough. Several studies have reported that with these settings significant problems can arise. For instance the truncation can alter the phase diagram of the Lennard-Jones system^{4,5} or yield different values for interfacial free energies⁶⁻¹⁰. These effects are quantitative in nature, meaning that they can in certain circumstances be analytically corrected for¹¹⁻¹³ or compensated for by other interaction parameters such as interaction strength or interaction range. The latter is important for the development of force fields where non-bonded potentials are often included and the cutoff can be seen as another fitting parameter. Naturally, a parametrization with a small cutoff would be preferred to another one if they deliver equal accuracy. This however is only true in the assumption that the underlying physical characteristics that are created by truncated and longer ranging potentials are the same.

In this work we investigated the influence of the cutoff for the interfacial phenomenon of water-wetting on a solid substrate. We found that the effect of the cutoff of the water-substrate interaction was not only unexpectedly strong, but also changed the fundamental physics of the wetting transition in an unprecedented way by creating metastable wetting states that have also never been seen in experiments. We show that proposed cutoff corrections such as the use of a force switching function, a shifted potential or a shifted force did not fix this and could even worsen the effect. This finding shows that atomistic simulations of interfaces need to be treated with great care since unphysical behavior could occur and easily remain undetected. This is particularly relevant since a large number of MD studies using truncated potentials are reported each year. Our results suggest the use of much larger-than-common cutoffs or long-range versions of non-bonded potentials in MD studies of wetting and interfacial phenomena.

We investigated two droplets comprised of 3000 and 18000 water molecules which were

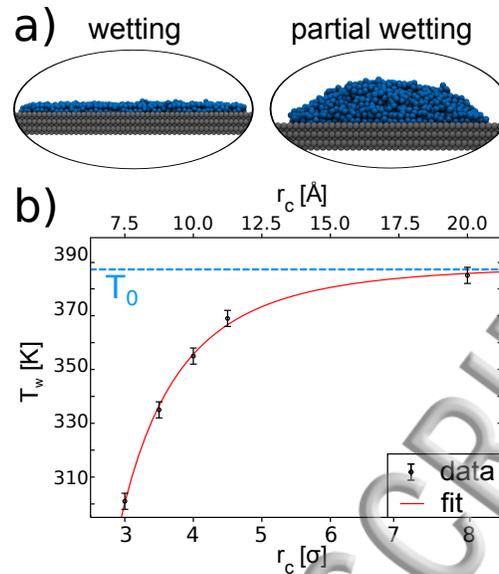


FIG. 1. a) Side view of the two wetting states for the small droplet. Water is blue and surface atoms are gray. b) Temperature of the wetting transition T_w (points) versus cutoff radius r_c and fit (red line). The T_w were obtained from the free energy profiles (see text) and we estimate errors to be ± 3 K. T_0 is the converged wetting temperature.

49 represented by the coarse-grained mW model¹⁴, on top of a rigid, pristine fcc(100) surface
 50 (lattice parameter 4.15 Å). Whilst this substrate does not aim at representing any partic-
 51 ular material, similar systems have been used to study ice nucleation¹⁵⁻¹⁸ or water-metal
 52 interfaces^{19,20}. The simulation cell had dimensions $17 \times 17 \times 11$ nm³ which is enough to
 53 avoid interaction of the water molecules with their periodic images for all wetting states.
 54 Even though the liquid is rather non-volatile even at the highest temperature considered,
 55 we employed a reflective wall at the top of the cell to avoid evaporation and mimic experi-
 56 mental conditions. Our simulations were performed with the LAMMPS code²¹, integrating
 57 the equations of motion with a timestep of 10 fs. This rather large timestep is commonly
 58 used in combination with the mW model and is acceptable for our system since during NVE
 59 simulations the total energy drift was found to be only about 2×10^{-9} eV per water molecule
 60 per ps. In addition, we verified that we obtain the same results using standard protocols for
 61 updating the neighbor lists compared with unconditionally updating them every timestep.
 62 All production simulations were performed in the NVT ensemble with constant tempera-
 63 ture maintained by a ten-fold Nosé-Hoover chain²² with a relaxation time of 1 ps. The

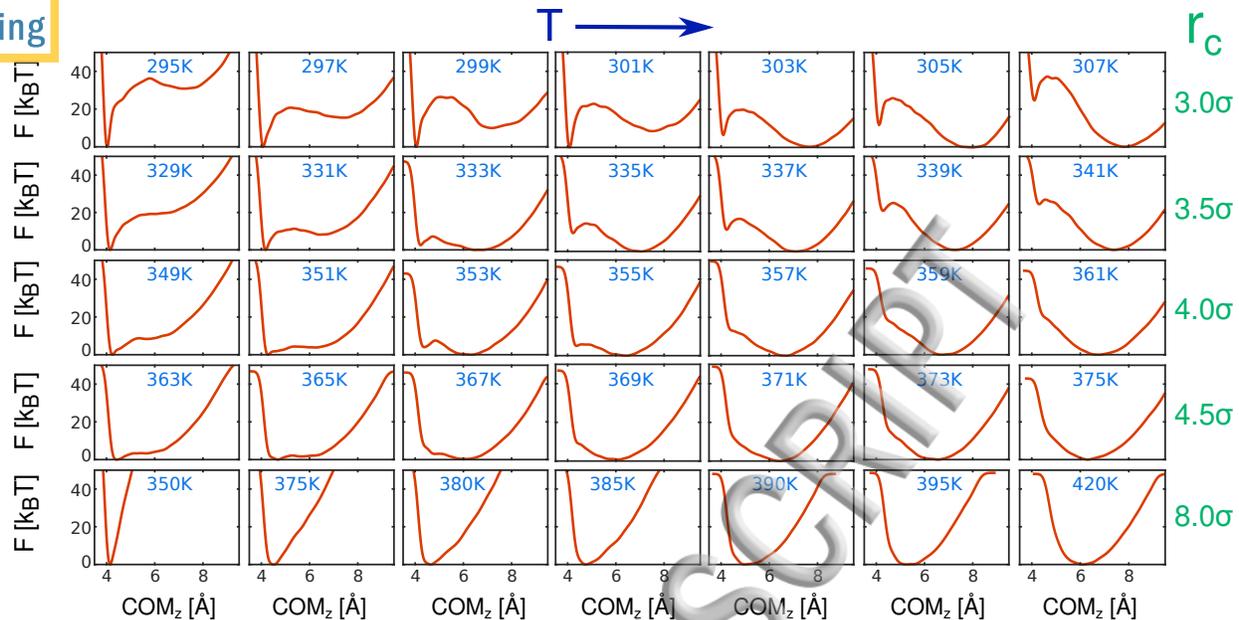


FIG. 2. Free energy profiles of wetting for different cutoffs in a small temperature range around the respective transition temperature T_w (generally at or near the central column for each system). As collective variable we chose the center of mass of the water droplet (COM_z , substrate at $z = 0$). We note that for the largest cutoff of 8σ the temperature range is slightly larger to highlight the shape of the free energy profile for complete and partial wetting.

64 substrate-water interaction was given by a distance (r) dependent Lennard-Jones potential

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (1)$$

65 with $\epsilon = 29.5$ meV, $\sigma = 2.5$ Å truncated at a cutoff r_c . This resulted in a maximum
 66 interaction energy of 154 meV for an adsorbed water monomer (weakly depending on the
 67 cutoff). Additionally we performed well-tempered metadynamics simulations^{23,24} for the
 68 smaller droplet with the PLUMED2 code²⁵. In these simulations the Gaussian height,
 69 width, bias-factor and deposition stride were 2.16 meV, 0.15 Å, 20 and 20 ps respectively.
 70 Metadynamics is usually applied to drive rare events such as nucleation^{26–29} or protein
 71 folding^{30,31}. In our systems, this method helped to uncover the underlying free energy
 72 profile of wetting.

73 We studied the wetting behavior of the larger droplet by performing standard MD runs
 74 at different temperatures first. As starting configurations we chose either a flat water film
 75 in direct contact or a spherical droplet placed above the substrate. Within at most 5 ns

simulation was equilibrated and a seemingly stable configuration was reached, where
77 the water is either wetting (contact angle $\theta = 0^\circ$) or partially wetting ($0^\circ < \theta < 180^\circ$).
78 An illustration of the two wetting states can be found in figure 1a. Initially we employed
79 a radial cutoff at $r_c = 3.0\sigma$ for the water-substrate interaction. With this setting we found
80 that interestingly a wetting transition happened at finite angle $\theta_0 \approx 23^\circ$, i.e. a smaller
81 non-zero contact angle was not possible. This behavior cannot be explained by the standard
82 Young's equation.

83 However, upon increasing the cutoff we found that the wetting behavior drastically
84 changed. First, the wetting temperature T_w at which the wetting transition took place
85 increased as we increased the cutoff (figure 1b). Whilst T_w shows a clear convergence behav-
86 ior with r_c , it is unexpectedly slow. A reasonably converged wetting temperature T_0 is only
87 reached for $r_c > 7\sigma$. Second, we noticed that for an increasing cutoff the minimum possible
88 contact angle θ_0 got smaller and eventually vanished. Most importantly, we also found that
89 for temperatures around T_w the stable configuration that was reached after the 5 ns could
90 depend on the starting configuration for smaller cutoffs, while for larger r_c it always reached
91 the same state. This suggests that for small r_c we actually found metastable wetting states
92 that are absent for large r_c . This also means that T_w cannot naively be defined through
93 visual analysis of trajectories at different temperatures but needs to be defined by the free
94 energy of wetting. For a first order phase transition we define T_w to be the temperature
95 where the two basins (corresponding to wetting and partial wetting) have the same free
96 energy. For a continuous phase transition T_w is the temperature where the single basin
97 represents a contact angle of $\theta = 0^\circ$ for $T < T_w$ and $\theta > 0^\circ$ for $T > T_w$.

98 Understanding the character of these wetting states with standard MD can prove difficult
99 as the dependence on the starting configuration always leaves doubt on the outcome of
100 the equilibrated configuration obtained from it. To clarify, we show the results from the
101 metadynamics simulations in figure 2. As a collective variable we chose the z-component of
102 the center of mass of the water droplet (COM_z), where z is the surface normal direction.
103 While this choice is not equivalent to the contact angle (as they are related in a non-linear
104 manner) it is clear that significantly different values for COM_z correspond to different contact
105 angles and can therefore distinguish the different wetting states. For the smallest cutoff at
106 T_w and around we found that two basins coexist, one being the flat film ($\text{COM}_z \approx 4 \text{ \AA}$)
107 and the other being a droplet with certain contact angle ($\text{COM}_z \gtrsim 5 \text{ \AA}$). These two states

109 being separated by a significant barrier larger than $20 k_B T$, which explains why we observed
 110 metastable states in the unbiased simulations for small r_c . This corresponds to a first-
 111 order phase transition between the wetting states. The occurrence of a minimum possible
 112 contact angle θ_0 is explained by the existence of the second basin, which does not approach
 113 the wetting basin, but rather becomes less stable as temperature changes. However, this
 114 character faded as we increased r_c . The barrier became smaller and the distance between
 115 the basins got smaller. For the largest cutoff investigated (8σ) we clearly see that only a
 116 single basin exists that changes its position with temperature. As a result no metastable
 117 wetting states exist and the phase transition is continuous. We note that in this case the
 118 estimate of T_w is more difficult than for the first order transitions, however in this work we
 119 aim at presenting qualitative results and from figure 2 it is clear that T_w is higher than for
 the smaller cutoffs.

120 Only the results for the largest cutoff are in agreement with the fact that water wetting
 121 transitions are generally continuous when probed in experiments^{32,33} and finite-angle wetting
 122 transitions have, to the best of our knowledge, never been observed experimentally. There-
 123 fore, the correct qualitative wetting behavior in our system is not achieved with standard
 124 cutoffs and if undetected could potentially lead to false conclusions. **Differences between**
 125 **short and long-ranged interactions have been highlighted for other interfacial phenomena,**
 126 **such as drying³⁴ or grain boundary melting³⁵.**

128 We further study the effect of the most commonly used correction schemes to cutoffs:

1. A shifted potential (sp) which ensures that the value of the potential energy U does not jump at the cutoff distance, given by:

$$U_{\text{sp}}(r) = U_{\text{LJ}}(r) - U_{\text{LJ}}(r_c) \quad (2)$$

The corresponding force F remains unaltered:

$$F_{\text{sp}}(r) = F_{\text{LJ}}(r) \quad (3)$$

2. A switching function (switch) which brings the force to zero between an inner $r_{c,1}$ and an outer cutoff $r_{c,2}$ (we choose 3 and 4 σ):

$$F_{\text{switch}}(r) = F_{\text{LJ}}(r) \quad r \leq r_{c,1} \quad (4)$$

$$F_{\text{switch}}(r) = \sum_{k=0}^3 C_k (r - r_{c,1})^k \quad r_{c,1} < r \leq r_{c,2}$$

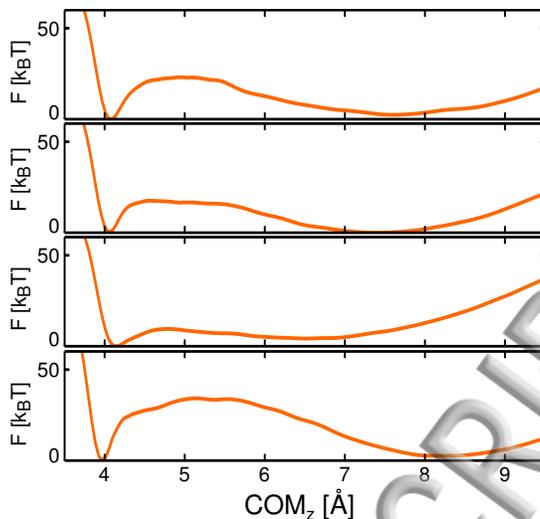


FIG. 3. Free energy profiles of wetting approximately at the transition temperature with uncorrected setup (cut) and for different correction schemes [shifted potential (sp), force switch (switch) and shifted force (sf)] applied with a cutoff at 3σ . None of the schemes show the correct behavior, which is shown in figure 2 to be a single basin.

129 where C_k are constants determined to ensure a smooth behavior²¹.

3. A shifted-force potential (sf), which ensures that force and potential do not jump:

$$\begin{aligned}
 U_{\text{sf}}(r) &= U_{\text{LJ}}(r) - U_{\text{LJ}}(r_c) - (r - r_c)F_{\text{LJ}}(r_c) \\
 F_{\text{sf}}(r) &= F_{\text{LJ}}(r) - F_{\text{LJ}}(r_c)
 \end{aligned}
 \tag{5}$$

130 The latter approach was found to give good results for a homogeneous system and even
 131 allowed for a reduction of the cutoff³⁶. Our results for these three corrections can be found in
 132 figure 3. Unsurprisingly the shifted potential does not yield any significant difference over the
 133 plain cutoff since forces remain unaltered. The smooth cutoff via switching function seems
 134 to improve the situation, however the fact that the transition temperature lies between the
 135 ones we found for a plain cutoff at 3 and 4σ suggests that the improvement stems from the
 136 effectively increased interaction range rather than the fact that the force vanishes smoothly.
 137 Interestingly, the shifted force with the same cutoff performs worst out of all candidates as
 138 the barrier increases by a factor of two, which increases the likelihood that simulations are
 139 performed in the metastable state without realizing it. The fact that none of the considered
 140 correction schemes significantly improved the character of the wetting free energy profile

leads us to conclude that it is not the way in which the cutting is done that matters most,
142 but rather the effective cutoff distance as well as the overall interaction strength at that
143 distance.

144 As an initial attempt to understand the results obtained we looked at the potential
145 energies of the various systems with the different cutoffs considered. This, however, did
146 not reveal any obvious explanation. However, one possible interpretation for the creation
147 of metastable states in our systems with shorter cutoff can be obtained by considering
148 the droplet state (not assuming anything about the stability relative to the film state).
149 For a transition towards the film state, there needs to be thermal fluctuations of water
150 molecules that are above the contact layer in the downwards direction (the fact that COM_z
151 has proven a good reaction coordinate supports this statement). With an infinite interaction
152 range all molecules that are losing height contribute to these fluctuations since they have
153 an interaction with the substrate. Therefore we expect the interaction energy to change
154 monotonically and the free energy to follow monotonically either up or down depending on
155 the balance of the interfacial free energies (see figure 2, $r_c = 8\sigma$). But if the interaction
156 range is finite, not all molecules contribute to an increased interaction with the substrate
157 even if they decrease their height (and subsequently weaken the water-water interaction
158 of the system by leading to deviations from a perfect spherical droplet). In other words,
159 there is a minimum distance from the substrate that has to be surpassed by a molecule
160 for it to contribute to a fluctuation increasing the interaction energy, otherwise it will (on
161 average) actually decrease the total interaction energy. This minimum fluctuation for a
162 single molecule translates into the macroscopic states (droplet and film) being connected by
163 a barrier shaped free energy profile rather than a monotonic one (see figure 2, $r_c = 3\sigma$). The
164 entropic contributions to the free energy are unlikely to change this, since they are essentially
165 dominated by the environment a molecule is in (quasi-static contact layer or quasi-liquid
166 water on top). The entropic change between these two states will be monotonic for a single
167 water molecule and therefore also for the whole droplet.

168 Finding a general recipe for how to avoid such unphysical wetting states is difficult.
169 Other aspects like e.g. the substrate density or the liquid-liquid interaction strength will
170 have an influence on how strongly the fluctuations in the droplet state are affected by r_c .
171 Generally, cutoffs that are deemed acceptable from the inter-molecular perspective do not
172 necessarily mean that the interaction between macroscopic states such as a film/droplet and

174 substrate is sufficiently captured. This is especially important in an interfacial simulation
175 setting such as a slab, where a cutoff-caused change in interaction from the substrate side is
176 not compensated by an equal change from the vacuum side. Consequently, only employing
177 much larger cutoffs or techniques to calculate the long-range part of the dispersion force³⁷⁻³⁹
178 can ensure that unphysical effects are avoided. A minimal sanity check for future wetting
179 studies could be to start simulations from both a wetting film and a spherical liquid snapshot.
180 If both of them end up in the same configuration the existence of an unphysical metastable
181 wetting state is unlikely.

182 In light of the vast amount of work that is done in the MD community using similar
183 interactions, our findings urge extreme caution when dealing with truncated non-bonded
184 potentials in simulations of interfacial phenomena. We have seen both quantitative and
185 qualitative differences for the wetting transition. The former could be accounted for by
186 changing other interaction parameters to reproduce the transition at the right temperature
187 T_0 . This assumption is fundamental to fitting force fields with truncated potentials to
188 obtain quantitative agreement with e.g. experimental values. But it does not hold for the
189 character of the transition because it arises purely from the value of the cutoff itself. If
190 the resulting metastability of states remains undetected, the use of truncated interaction
191 potentials could lead to wrong inferences about physical properties being made. While
192 this conclusion has resulted from a simulation of wetting, similar implications could hold
193 for other interfacial phenomena such as capillary flow^{40,41}, evaporation/condensation^{42,43},
194 mixtures⁴⁴⁻⁴⁶ or heterogeneous nucleation⁴⁷⁻⁵¹ where it is commonplace to use truncated
195 interactions.

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