Using the Three-Body Potential in LAMMPS

First, a brief introduction to the three-body potential followed by its two LAMMPS counterparts are given. Then, the commands needed to use the potential in LAMMPS are explained. Following are the instruction to add the potential to your LAMMPS. Finally, a few validity tests are shown.

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1 Introduction

In a molecular dynamics simulations (MD) of single valance particles, bond-swapping processes normally occur only when the temperature is similar or higher to the binding energy scale $k_BT/\epsilon \gtrsim 1$: thermal motion breaks bonded particle pairs allowing nearby particles different to the initially involved to reform the bond. Lowering the temperature drops the bond-swapping events frequency, but favors a higher number bonded pairs. The choice of an energy scale that simultaneously promotes bond-swapping events but keeps a high fraction of bonded pairs can be tricky and not always possible. Fortunately, in ref. 1, Sciortino proposes a bond-swapping mechanism in the shape of a three-body potential that can be used even at very low temperatures, conceding jointly bond-swapping events and high fraction of bonded pairs. The potential is computationally cheap, implicitly accounts for the single-bond per particle condition, can keep the potential energy unchanged throughout the bond-swapping process, and can even tune the bond-swapping event frequency.

1.1 The Three-Body Potential

The three-body potential can take in any arbitrary short-ranged bonding pairwise potential $V_{\text{bond}}(r)$ characterized with a minimum of depth ϵ located at a distance r_{min} (i.e. $\epsilon = |V_{\text{bond}}(r_{\text{min}})|$). Being the pairwise potential short-ranged, a cutoff radius r_{cutoff} can be defined above which the interaction is zero or can be neglected and the particle pair can be considered as no longer bonded. Given the bonding potential $V_{\text{bond}}(r)$, the three-body potential $V_{\text{threebody}}$ is defined as the product of two pairwise potentials

$$V_{\text{threebody}} = \lambda \sum_{i,j,k} \epsilon V_3(r_{ij}) V_3(r_{ik}) \tag{1}$$

with the sum over all triplets where particle i is simultaneously bonded to j and k, i.e. within a distance $r_{ij}, r_{ik} < r_{\text{min}}$. The pairwise potentials $V_3(r)$ are given by the bonding potential

$$V_3 = \begin{cases} 1 & r \leq r_{\text{min}} \\ \frac{-V_{\text{bond}}(r)}{\epsilon} & r_{\text{min}} \leq r \leq r_{\text{cutoff}} \end{cases} \tag{2}$$

The repulsive nature of the three-body potential compensates for the energy decrease when more than a single-bond per particle interaction takes place. The swapping mechanism is controlled by the λ parameter, it can be continuously tuned from enhancing ($\lambda = 1$) to suppressing ($\lambda > 1$) bond-swapping events.

1.2 LAMMPS Three-Body Potentials

Unfortunately, the bonding pairwise potential $V_{\mathrm{bond}}(r)$ arbitrariness could not be implemented to LAMMPS. Instead two specific-shaped, still rather malleable, potentials were chosen: the first one, called **lj3b**, is a generalized Lennard-Jones potential

$$V_{\mathrm{bond}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{2n} - \left(\frac{\sigma}{r}\right)^{n} \right] \tag{3}$$

the $2n - n$ powers facilitate locating the potentials minimum position $r_{\mathrm{min}} = 2^{1/n}\sigma$.

The second pairwise potential, called **fs3b** , is based on the Stillinger-Weber (sw) potential

$$V_{\mathrm{bond}(r)} = C\epsilon \left[\left(B\frac{\sigma}{r}\right)^{p} - \left(\frac{\sigma}{q}\right)^{n} \right] \exp\left(\frac{\sigma}{r - a\sigma}\right) \tag{4}$$

where C is a normalization constant used to set the depth of the potential equal to ϵ, i.e. $V_{\mathrm{bond}}(r_{\mathrm{min}}) = -\epsilon$. The exponential part ensures the vanishing of the potential at the cutoff distance $r_{\mathrm{cutoff}} \equiv a\sigma$. The additional parameters, B and a, and the unforced relation between p and q make this potential somewhat more general.

When implementing the three-body potentials to LAMMPS it made more sense to already include the pairwise interactions, meaning

$$V_{\mathrm{xx3b}} = \sum_{i,j} V_{\mathrm{bond}(r_{ij})} + V_{\mathrm{threebody}}(r_{ij}, r_{ik}) \tag{5}$$

with the first and second terms on the rhs given by eq. 1 and either eq. 3 or eq 4. Notice how the $V_{\mathrm{threebody}}$ already considers the the sum over the triplets. It's worth mentioning that the potential parameters can be species dependent, that is $\lambda_{ij}, \epsilon_{ij}, \sigma_{ij}, ...$ depend on what kind of particle i and j are.

2 Using LAMMPS Three-Body Potentials lj3b and fs3b

In LAMMPS, the particle interaction between particles is set with the `pair_style` command*. Depending on the pair style, the parameters that describe the potential (ϵ, σ, ...) must be declared explicitly or via a potential file in the `pair_coeff` command. The three-body pair style names are `lj3b` and `fs3b`, the potential parameters are read from a potential file that must end with **.lj3b** or **.fs3b**, accordingly. Given the different shape of the potentials, their file formats are slightly different between them; both are described in detailed below. The pair style syntax of the three-body potentials is the same as the sw (Stillenger-Weber), it is as follows

```
pair_style xx3b
pair_coeff * * [FileName].xx3b E1 E2 ...  EN
```

The first line sets either the **lj3b** or **fs3b** potential. In the second line, the `pair_coeff` command points all atom types "`* *`" to the "`[FileName].xx3b`" file containing the potential parameters, mapping in order each of the `N` atom types to one of the "$\mathtt{E_i}$" elements declared in the potential file.

As an example consider a system of three different atom styles. Particles of type "`1`" and "`3`" interact as `A`-elements, particles of type "`2`" interact as `B`-elements; and the `A` and `B` interaction parameters are written in the potential file "`AB.lj3b`". In LAMMPS the systems interaction would be set up as

```
pair_style lj3b
pair_coeff * * AB.lj3b A B A
```

As mentioned before, every potential has its own file format. Nonetheless, for every triplet species combination, a single line is written including the interaction parameters in a specific order. To account for symmetry of the interactions , e.g. `A-B` same as `B-A` interaction, some lines may be very similar.

The order of the interaction parameters in the **.lj3b** potential file is the following:

1. element1 [letter] - element bonded to both element2 and element3 (particle i in eq. 1)
2. element2 [letter]

*The `pair_style` command is also used for interactions involving more than two (a pair) particles

3. element3 [letter]
4. ϵ [floating point] - depth of the potential
5. σ [floating point] - particle size
6. r_{cutoff} [floating point] - cutoff radius
7. λ [floating point] - three-body potential modulator
8. n [floating point]
9. offset [0,1] - off/on flag to shift and cut the potential (more immediately below)

The offset flag is turned "on" when only the repulsive part of the potential wants to be included for a pair; when used $V_{bond}(r)$ is shifted by ϵ and its cutoff distance is shortened to its minimum $r_{\mathrm{cutoff}} = r_{\mathrm{min}}$. The offset can be either "`1`" (on) or "`0`" (off), any other value will give an error message. Naturally, the offset flag and the λ parameter cannot be both turned on for same single triplet interaction, you can't have the bond-swapping mechanism for purely repulsive interacting particles. Pair potential parameters are given in the lines where element2 and element3 are the same, see example below.

The parameters order for the **.fs3b** potential file is:

1. element1 [letter] - element bonded to both element2 and element3 (particle i in eq. 1)
2. element2 [letter]
3. element3 [letter]
4. ϵ [floating point] - depth of the potential
5. σ [floating point] - particle size
6. a [floating point] - cutoff radius proportionality factor ($r_{\mathrm{cutoff}} \equiv a\sigma$)
7. λ [floating point] - three-body potential modulator
8. B [floating point]
9. p [floating point]
10. q [floating point]
11. tol - additional performance-optimization parameter from the sw pair style (see ref. 2)
12. offset [0,1] - off/on flag to shift and cut the potential

Consider again the previous example of a system with three different atom styles interacting as either `A` or `B`-elements. Let's say now that the three-body interaction will be the simpler shaped `lj3b`, where same mapped species interaction `A-A` and `B-B` are completely repulsive but interspecies interactions `A-B` instead promote bond-swapping events. The potential file would look as follows

# ELEMENTS	ϵ	σ	r_{cutoff}	λ	n	offset
A A A	1.0	1.0	1.3	0.0	100	1
B B B	1.0	1.0	1.3	0.0	100	1
A B B	1.0	1.0	1.3	1.0	100	0
B A A	1.0	1.0	1.3	1.0	100	0
A A B	0.0	1.0	0.0	0.0	0	0
A B A	0.0	1.0	0.0	0.0	0	0
B B A	0.0	1.0	0.0	0.0	0	0
B A B	0.0	1.0	0.0	0.0	0	0

The "1" `offset` value in entry lines 1 and 2 restrict the same species interaction `A-A` and `B-B` to be only repulsive, while the $\lambda = 1.0$ in line 3 and 4 promote bond-swapping events of different species interactions `A-B`. The remaining lines describe turned off three-body mixed interactions, the $r_{\mathrm{cutoff}} = 0$ sets the cutoff radius to zero so that none of these interactions are actually calculated.

3 Adding the Three-Body Potentials to LAMMPS

Our aim is to have the three-body potentials as a LAMMPS built-in feature part of the MANYBODY package, in the meanwhile here we describe how you can add it "by hand". A requirement is to have downloaded LAMMPS source code and built it, ready-to-execute LAMMPS cannot be modified nor extended. The three-body potentials pair style is added to LAMMPS following the same steps you would for adding any other pair style as explained in the *Modifying & extending LAMMPS* chapter of the manual.[3] Depending on the process you used to build LAMMPS (CMAKE or MAKE) you must follow one of the following two procedures:

CMAKE:

- Add the `pair_lj3b.cpp`, `pair_lj3b.h`, `pair_fs3b.cpp` and `pair_fs3b.h` to your `src` directory, for consistency we added them inside the `src/MANYBODY` subdirectory
- In the terminal, go to your build directorym most likely its called `build`
- Compile LAMMPS with `cmake --build`

MAKE:

- Add the `pair_lj3b.cpp`, `pair_lj3b.h`, `pair_fs3b.cpp` and `pair_fs3b.h` to your `src` directory, for consistency we added them inside the `src/MANYBODY` subdirectory
- Write "pair_lj3b.h" and "pair_fs3b.h" in the `src/Makefile.list` file
- In the terminal run the "make machine" command you used to compile LAMMPS for the first time.

4 Validity Tests

4.1 Dumbbells - Comparison to the Reference

As a first test of the three-body potentials, we simulate ref. 1 system of dumbbell forming particles. The system is made of particles of two species: 400 particles of species **A** and 600 of species **B**, with total number density $\rho = 0.125$. Same-species particles interaction **A-A** and **B-B** is exclusively repulsive; while cross-species interaction **A-B** is attractive, single-bond per particle conditioned, and bond-swapping is promoted. The single-bond condition causes the formation of 400 **A-B** dumbbells, with the remaining 200 **B** particles avialable to swap. The bond-swapping events can be seen from the bond autocorrelation function $n_b(t)$, a function that gives the fraction of original bonds still remaining after t time has passed. The simulations are performed at a low temperature $k_BT/\epsilon = 0.03$ to ensure the swapping happens due to the three-body bond-swapping mechanism and not thermal fluctuations.

Both three-body potentials are tested, with the **lj3b** potential having exactly the same parameters as in ref. 1, the potential file looks like

# ELEMENTS	ϵ	σ	$r_{\texttt{cutoff}}$	λ	n	offset
A A A	1.0	1.0	1.3	0.0	100	1
B B B	1.0	1.0	1.3	0.0	100	1
A B B	1.0	1.0	1.3	1.0	100	0
B A A	1.0	1.0	1.3	1.0	100	0
A A B	0.0	1.0	0.0	0.0	0	0
A B A	0.0	1.0	0.0	0.0	0	0
B B A	0.0	1.0	0.0	0.0	0	0
B A B	0.0	1.0	0.0	0.0	0	0

The parameters used for the **fs3b** are given by the next potential file

# ELEMENTS	ϵ	σ	a	λ	B	p	q	tol	offset
A A A	1.0	1.0	1.3	0.0	1.0	100.0	50.0	0.0	1
B B B	1.0	1.0	1.3	0.0	1.0	100.0	50.0	0.0	1
A B B	1.0	1.0	1.3	1.0	1.0	100.0	50.0	0.0	0
B A A	1.0	1.0	1.3	1.0	1.0	100.0	50.0	0.0	0
A A B	0.0	1.0	0.0	0.0	0	0	0	0.0	0
A B A	0.0	1.0	0.0	0.0	0	0	0	0.0	0
B B A	0.0	1.0	0.0	0.0	0	0	0	0.0	0
B A B	0.0	1.0	0.0	0.0	0	0	0	0.0	0

The bond autocorrelation functions $n_b(t)$ in function of time are shown in fig. 1, the shape of the $V_{\text{bond}}(r)$ is included as an inset. The decay of **lj3b**'s and **fs3b**'s $n_b(t)$ is similar to the reference, corroborating that bond-swapping events take place. The **fs3b**'s $n_b(t)$ faster decay respect to the others is due to the wider well located at a slightly larger distance, the slower decay of the potential in r facilitates the approach of a third (swapping) particle.

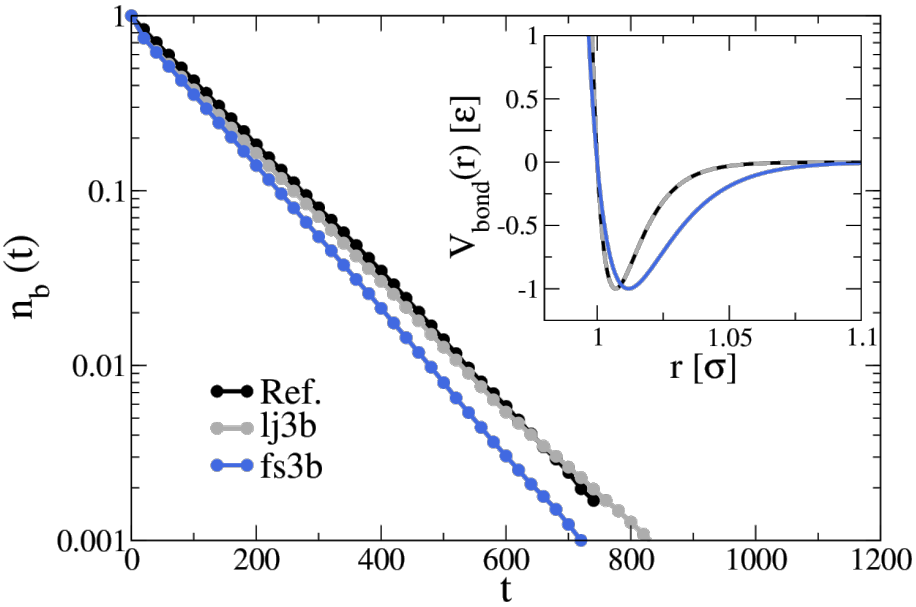

Figure 1. Bond autocorrelation function dependence on time for the reference and the **lj3b** and **fs3b** potentials. Time in MD units ($\sqrt{m\sigma^2/\epsilon}$).

4.2 Dumbbells - Bond-Swapping Tuning

Previously mentioned, the λ parameters allows tuning the frequency of the bond-swapping events. Fig. 2 shows the bond autocorrelation function for the dumbbell **lj3b** interacting system for different λ values. The potential parameters and the temperature are the same as in the previous example, that is $n = 100$, $r_{\text{cutoff}} = 1.3$ and $k_BT/\epsilon = 0.03$. Large effects with the increase of λ can be seen: the $\lambda = 1.1$ bonds have a lifespan about 4 times larger than the $\lambda = 1.0$ system, the original bonded pairs of the $\lambda = 1.3$ system practically remain together throughout all the simulation.

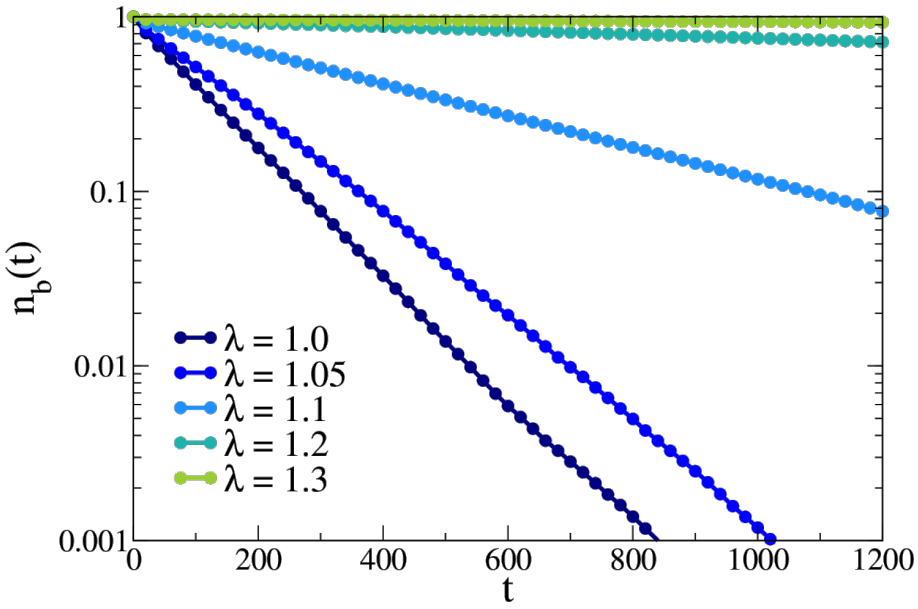

Figure 2. Bond autocorrelation function for the $n = 100$ **lj3b** potential with different λ values. Time in MD units ($\sqrt{m\sigma^2/\epsilon}$).

4.3 Potential Energy During a Swap Event

We now take a look at the potential energy contribution during a bond-swapping event. We use the **lj3b** potential with $n = 150$, $r_{\text{cutoff}} = 1.3$ and $\lambda = 1$ for a system three particle system (called particle 1, 2 and 3) at $k_BT/\epsilon = 0.01$. Fig. 3 shows the total potential energy and the contribution of each of the three particles for a short time window where two swap events take place. Initially particles 1 and 2 are bonded. Around time $t = 2$ particle 3 approaches the bonded pair by particle's 2 side, the three-body potential kicks in and particle 1 is swapped by particle 3. The 2-3 particle bond remains until particle 1 gets near the pair and again switches on the swapping-mechanism resulting in a bond made from particles 1 and 3. The potential energy contribution of each individual particle changes in time, nonetheless the total potential energy remains the same.

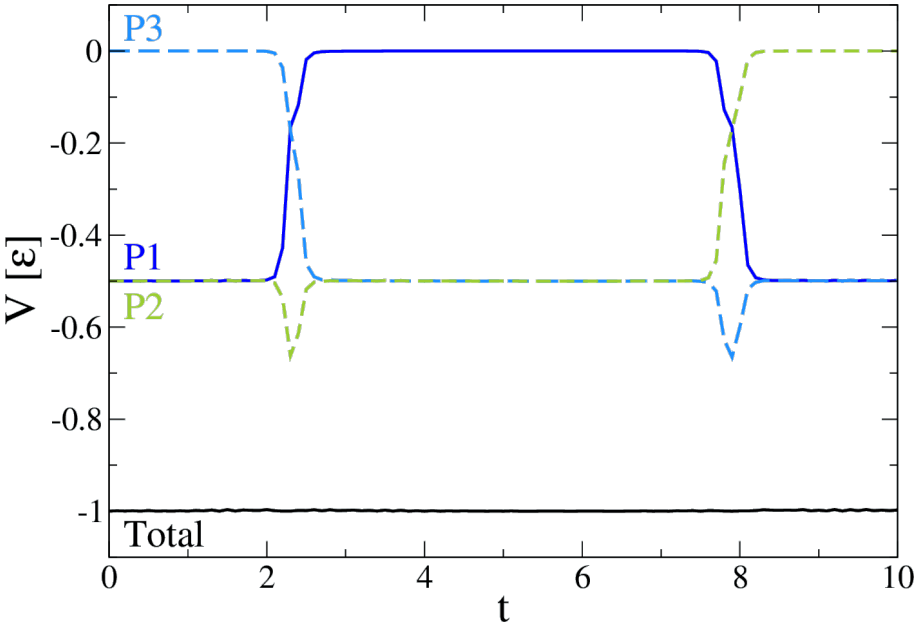

Figure 3. Potential energy contributions in time during bond-swapping events. The potential energy of the system remains almost constant ϵ while the contribution by each of three particles change according to whether they belong or not to the bond. Time in MD units ($\sqrt{m\sigma^2/\epsilon}$).

REFERENCES

[1] Sciortino, F., "Three-body potential for simulating bond swaps in molecular dynamics," *The European Physical Journal E* **40**(1), 3 (2017).

[2] "pair_style sw command." https://docs.lammps.org/pair_sw.html (2022). Accessed: 2022-09-30.

[3] "Modifying & extending lammps." https://docs.lammps.org/Modify.html (2022). Accessed: 2022-09-30.