

# Final Master Thesis: initial benchmark

Roger Bellido

*Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona.*

(Dated: May 10, 2022)

## I. INTRODUCTION

In this first part, a benchmark was necessary to ensure that the LAMMPS script created was correct. The obtained results were compared against [1], using a methodology as close as it could be to the one presented in the article.

First of all, the simulated system is a water-methanol mixture. The concentration of both components can be varied, but for the benchmark of interest, the proportions are: 90% water and 10% methanol.

In this case, the water is simulated as a spherical atom with a core-softened potential. Methanol, on the other hand, is simulated as a dimer molecule, where one of the monomers is the methyl part of the alcohol ( $\text{CH}_3$ , apolar) and the other one is the hydroxyl ( $\text{OH}$ , polar). The bond between the two monomers is supposed to be rigid, so both are kept at the same distance at all times. Results could change upon considering a harmonic bond. The interactions are as follows:

- Lennard-Jones potential:  $\text{CH}_3\text{-CH}_3$
- Lennard-Jones using Lorentz-Berthelot mixing rules:  $\text{CH}_3\text{-OH}$ ,  $\text{CH}_3\text{-H}_2\text{O}$
- Core-softened potential:  $\text{OH-OH}$ ,  $\text{OH-H}_2\text{O}$ ,  $\text{H}_2\text{O-H}_2\text{O}$

The expressions of the mentioned potentials are:

$$U^{LJ}(r) = \frac{4}{3} 2^{\frac{2}{3}} \epsilon \left[ \left( \frac{\sigma}{r} \right)^{24} \left( \frac{\sigma}{r} \right)^6 \right] \quad (1)$$

using the parameters

$$\begin{aligned} \frac{\sigma_{LJ}}{a} &= 1.0 \\ \frac{\epsilon_{LJ}}{U_A} &= 0.1 \end{aligned}$$

The Lorentz-Berthelot mixing rules can be summed up as

$$\begin{aligned} \sigma_{mix} &= \frac{1}{2}(\sigma_{LJ} + a) \\ \epsilon_{mix} &= \sqrt{\epsilon_{LJ} U_A} \end{aligned}$$

For the core-softened potential,

$$U^{CS}(r) = k_1 + k_2 + k_3 \quad (2)$$

$$k_1 = \frac{U_R}{1 + \exp\left(\frac{\Delta(r-R_R)}{a}\right)} \quad (3)$$

$$k_2 = -U_A \exp\left(-\frac{(r-R_A)^2}{2\delta_A^2}\right) \quad (4)$$

$$k_3 = U_A \left(\frac{a}{r}\right)^{24} \quad (5)$$

with parameters

$$\begin{aligned} \frac{U_R}{U_A} &= 2, \quad \frac{R_R}{a} = 1.6 \\ \frac{R_A}{a} &= 2, \quad \left(\frac{\delta_A}{a}\right)^2 = 0.1 \\ \Delta &= 15 \end{aligned}$$

The cited article [1] uses a specific non-dimensional units defined as:

$$\begin{aligned} T^* &= \frac{k_B T}{U_A} \\ \rho^* &= \rho a^3 \quad \text{where} \quad \rho = \frac{N}{V} \\ P^* &= \frac{a^3}{U_A} P \end{aligned}$$

Arbitrarily, the values for the parameters  $a$  and  $U_A$  have been set to 1.

The most characteristic plot aimed to replicate would be the top one from FIG.1, where the pressure values chosen to run the simulations are highlighted in yellow.

As can be seen comparing FIG.1 and FIG.2, a similar behaviour can be observed. However, the accuracy does not seem to be as high as it could be desirable. The main guess is that is because of the pressure fluctuations observed in the simulation, that TABLE I sums up. Also, the differences in the values of the diffusion coefficient and the pressure are related to the definition of the non-dimensional units commented before.

A possible solution to the pressure fluctuation could be the use of the extra tool keyword *drag* in LAMMPS, which adds a damping effect. Its main con is that it has an effect on energy conservation and on the distribution of positions and velocities.

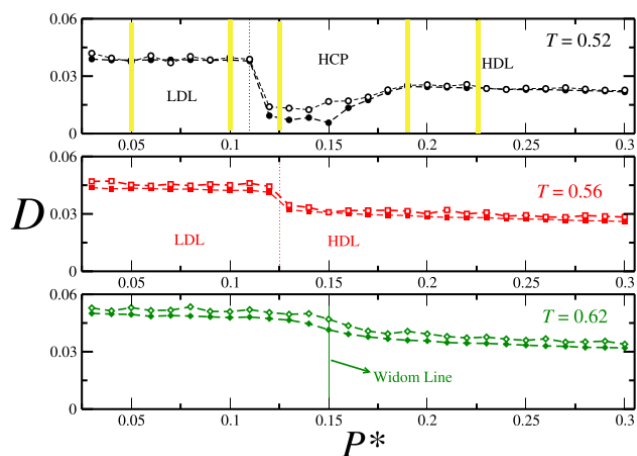


FIG. 1: Original figure from [1] which this first part aims to replicate using LAMMPS. In yellow, the pressure values used to obtain data.

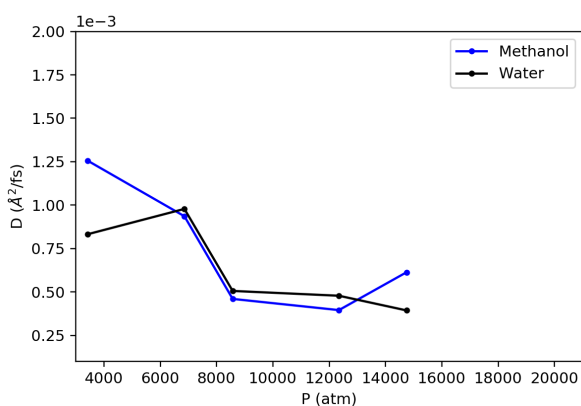


FIG. 2: Values obtained from the performed simulations. Compared to 1, the behaviour of the diffusion coefficient can be guessed, but it is much more dim.

- [1] M. Sodr  Marques, V. Fonseca Hernandes, E. Lomba, J.R. Bordin, *Competing interactions near the liquid-liquid phase transition of core-softened water/methanol mixtures*, J. Mol. Liq. 320 (2020) 114420.
- [2] G. Muna , T. Urbic, *Structure and thermodynamics of*

*core-softened models for alcohols* J. Chem. Phys. 142, 214508 (2015)

- [3] <https://docs.lammps.org/molecule.html>

P (atm)	$P_{damp}$	$\langle P \rangle$	$\sigma_P$	$\epsilon_{\langle P \rangle}$
3429.56	1200	3387.58	1380.82	$\pm 97.39$
6859.12	1200	6828.67	1541.97	$\pm 108.76$
8573.90	1200	8416.38	3409.60	$\pm 240.49$
12346.41	1150			$\pm$
12346.41	1200	12387.12	3426.61	$\pm 241.69$
12346.41	1250	12230.85	3493.25	$\pm 246.39$
14747.10	1200	14616.20	3733.16	$\pm 263.32$

TABLE I: The first column shows the attempted pressure value, followed by a parameter set in the barostat related to the stiffness of the piston construction. Next, the mean of the simulation and the standard deviation. Finally, the error associated to the mean. All shown values are computed using the last  $2 \times 10^6$  values of the simulation, to ensure the relaxation of the system.