# 1 TPS for a diatomic molecule in a WCA-fluid

## 1.1 Model

Consider $N$ two-dimensional particles of mass $m$ interacting via the purely repulsive Weeks-Chandler-Andersen potential,

$$V_{\rm WCA}(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \epsilon & \text{if} \quad r \le r_{\rm WCA} \equiv 2^{1/6}\sigma, \\ 0 & \text{if} \quad r > r_{\rm WCA}, \end{cases} \tag{1}$$

where $r$ is the interparticle distance and $\epsilon$ and $\sigma$ are parameters specifying the strength and the interaction radius of the potential, respectively. In addition, two of the $N$ particles interact via the double well potential

$$V_{\rm dw}(r) = h\left[1 - \frac{(r - r_{\rm WCA} - w)^2}{w^2}\right]^2. \tag{2}$$

Here, $r$ is the distance of the two particles belonging to the diatomic molecule. The parameter $h$ controls the height of the barrier between the stable states located at $r = r_{\rm WCA}$ (the compact state) and $r = r_{\rm WCA} + 2w$ (the extended state), respectively. The system evolves according to Hamilton's equations of motion in a simulation box with periodic boundary conditions.

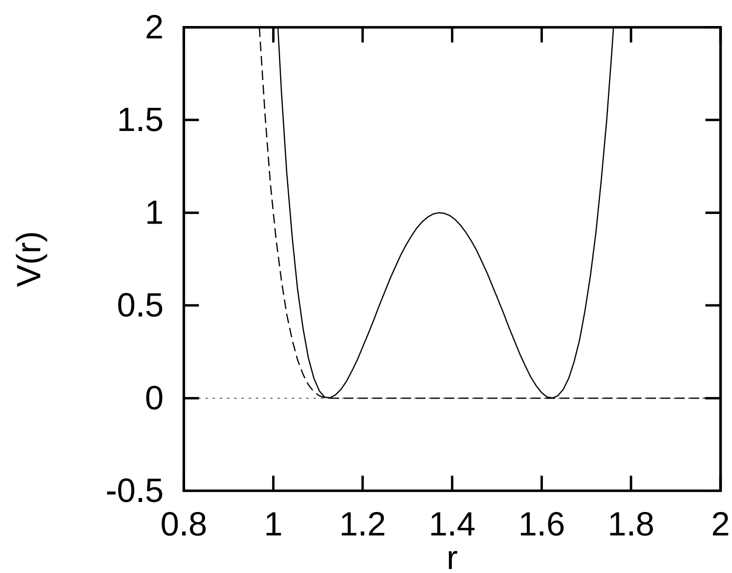


**Fig 1:** Potential energy functions: WCA (broken line), WCA+bistable potental (solid line).

It is practical to use reduces units, where lengths are measured in units of $\sigma$, energies in units of $\epsilon$, masses in units of $m$, times in units of $\tau \equiv (m\sigma^2/\epsilon)^{1/2}$, and transition rate constants in units of $\tau^{-1}$.

Since the system evolves at constant total energy $E$ with a fixed center of mass, the appropriate distribution function of initial conditions $x_0$ is the microcanonical distribution with the additional constraint of a vanishing total momentum $P$,

$$\rho(x_0) = \delta\left(\mathcal{H}(x_0) - E\right)\delta\left(P\right). \tag{3}$$

Accordingly, the momentum displacement $\delta p$ used in the shooting algorithms must be chosen to conserve both the total energy $\mathcal{H}$ and the total momentum $P$ of the system.

For shooting moves all the components of the momentum displacement vector $\delta p$ are chosen from a Gaussian distribution with a certain width. Next, components of $\delta p$ corresponding to a non-vanishing total momentum are removed. Then, $\delta p$ is added to the old momentum $p_t^{\mathrm{o}}$ yielding the new momentum $p_t^{\mathrm{n}} = p_t^{\mathrm{o}} + \delta p$ which is rescaled to conserve the total energy $E$.

The interatomic distance $r$ provides the natural order parameter for the definition of the stable regions $A$ and $B$: we define regions $A$ and $B$ to contain all configurations with $r < R_A$ and $r > R_B$, respectively. Obviously, $R_A$ and $R_B$ should lie on different sides of the separating barrier and allow the stable regions to accommodate most of the equilibrium fluctuations around the potential energy minima. Typical values are $R_A = 1.30\sigma$, $R_B = 1.45\sigma$, a barrier width of $w = 0.25\sigma$, and a barrier height of $h = 6\epsilon$. Consequently, the top of the barrier is at $r \sim 1.37\sigma$, and the minima of the bistable potential are at $r \sim 1.12\sigma$ and $r \sim 1.62\sigma$. To increase the speed of the simulation small particle numbers should be chosen, e. g. $N = 9$.

An MD-code and a path sampling code are provided on the workstations. In these programs the equations of motion are integrated with the velocity-Verlet algorithm.

## 1.2 Things to do

1. Follow a an MD-trajectory for a certain time and watch how the intramolecular distance evolves, i.e. plot $r$ as a function of time. Do it for different densities.

2. Calculate the time correlation function $C(t)$ for a low barrier with straightforward MD.

3. Calculate the transmission coefficient for different particle densities.

4. Take the path sampling code and find out if subsequent pathways are very different. You could, for example, compare the evolution of the intramolecular distance along the pathways.

5. Find the optimum $\delta p$.

6. Calculate the path average $\langle h_B(t) \rangle_{AB}$ with the transition path sampling program.

7. Where is the plateau?

8. Calculate $C(t)$ by umbrella sampling.

9. Calculate a transition rate constant.

10. Determine the transition state ensemble