MW2 Model

System

Box

- Orthorombic
- Dimensions are constants
- 2D or 3D periodic boundary condition

Species

- Name
- Count
- Mass
- Charge
  - point: $\rho_i(r) \equiv q_i \delta(r - r_i)$
  - gaussian: $\rho_i(r) \equiv Q_i \left(\frac{\eta^2}{\pi}\right) e^{-\eta^2 |r - r_i|^2}$
- Mobility
  - mobile: x, y, z, vx, vy, vz, fx, fy, fz
  - fixed: x, y, z

Molecules

- Name
- Sites
- Constraints
  - bond length constraints (Rattle)
  - linear molecules
- Intramolecular harmonic potentials
  - bond: $V(r_{ij}) = k_0(|r_{ij}| - r_0)^2$
  - angle: $V(r_i, r_j, r_k) = k_0(|\theta_{ijk}| - \theta_0)^2$

Electrodes

- Name
- Sites
- Potential
- Minimize energy to compute charges on electrode sites
  - conjugate gradient algorithm (tolerance, maximum iteration count)
  - inverse matrix (to be implemented)

Temperature control

- chained Nose-Hoover thermostat
- velocities periodic rescaling

Electrostatic Interactions

Coulomb potential

$$V(r_{ij}) = \int_{\mathbb{R}^3} dr' \int_{\mathbb{R}^3} dr'' \frac{\rho_i(r')\rho j(r'')}{|r_{ij}+r''-r'|}$$

- Long range interaction $\rightarrow$ Ewald summation
- Cut-off for real space sum: r_{cut}
- Tolerance on real space term minimum magnitude: ϵ_{real}
- Tolerance on reciprocal space term minimum magnitude: $\epsilon_{\mathrm{recip}}$

Lennard-Jones potential

$$V_{ij}(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}]$$

- Cut-off for all pairs: $V(r > r_c) = 0$
- Energy is shifted: $\tilde{V}_{ij}(r_{ij}) = V_{ij}(r_{ij}) - V_{ij}(r_c)$
- Force is not shifted: $F_{ij}(r_{ij}) = -\nabla V_{ij}(r_{ij})$

Born-Mayer potential with Fumi-Tosi parametrisation

$$V(r_{ij}) =$$
$$Be^{-\eta r_{ij}} - \frac{C}{r_{ij}^6}\left[1 - \sum_{k=0}^{6} \frac{d_{dd}^k r_{ij}^k}{k!} e^{-d_{dd} r_{ij}}\right] - \frac{D}{r_{ij}^8}\left[1 - \sum_{l=0}^{8} \frac{d_{dq}^l r_{ij}^l}{l!} * e^{-d_{dq} r_{ij}}\right]$$

- Cut-off for all pairs: $V(r > r_c) = 0$

Algorithms

Minimum image distance

```
dx = x_2 - x_1
scale = floor(dx / a + 0.5_wp)
dx = dx - a*real(scale,wp)
```

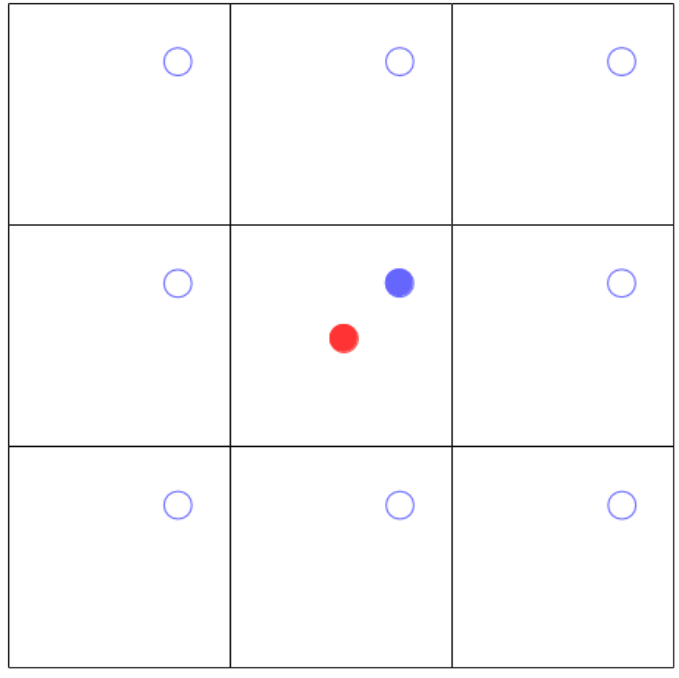

Figure 1: minimum image distance

NVE Time Integration

- Velocity - Verlet algorithm original formulation
  - $r(t+dt) = -r(t-dt) + 2r(t) + dt^2\ a(t)$
  - $v(t) = (r(t+dt) - r(t-dt))/2dt$
- Actual implementation
  - $v(t+dt/2) = v(t) + \frac{1}{2}dt\ a(t)$
  - $r(t+dt) = r(t) + dt\ v(t+dt/2) + \frac{1}{2}dt^2\ a(t)$
  - $a(t+dt) = m^{-1}f(r(t+dt))$
  - $v(t+dt) = v(t+dt/2) + \frac{1}{2}dt\ a(t+dt)$
- 2nd order centered finite difference method $O(dt^2)$
- Symmetric, reversible in time and symplectic (energy conservation)

Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules, Loup Verlet, Phys. Rev. 159, 98, 5 July 1967

NVT Time Integration

- Chained Nosé-Hoover Thermostat
  - $\dot{q}_i = \frac{p_i}{m_i}$
  - $\dot{p}_i = -\frac{\partial V(q)}{\partial q_i} - p_i \frac{p_{\eta_1}}{Q_1}$
  - $\dot{\eta}_i = \frac{p_{\eta_i}}{Q_i}$
  - $\dot{p_{\eta_1}} = \left[\sum_{i=1}^{N} \frac{p_i^2}{m_i} - NkT\right] - p_{\eta_1} \frac{p_{\eta_2}}{Q_2}$
  - $\dot{p_{\eta_j}} = \left[\frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT\right] - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}}$
  - $\dot{p_{\eta_M}} = \left[\frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT\right]$
- Conserved quantity $H(p, q, \eta, p_\eta) = V(q) + \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i=1}^{M} \frac{p_{\eta_i}^2}{2Q_i} + NkT\eta_1 + \sum_{i=2}^{M} kT\eta_i$
- $Q_1 = NkT/\omega^2$ and $Q_j = kT/\omega^2$ with ω the average "frequency" of the thermostats.

Nosé-Hoover chains: The canonical ensemble via continuous dynamic, G.J. Martyna, M.L. Klein., M. Tuckermann, J. Chem. Phys., Vol. 97, No. 4, 15 August 1992

NVT Time Integration - Implementation

- $v(t+dt/2) = v(t) + \frac{1}{2}dt(a(t) - v(t) * v_{\eta_1}(t))$
- $r(t+dt) = r(t) + dt\ v(t+dt/2) + \frac{1}{2}dt^2\ a(t)$
- $a(t+dt) = m^{-1}f(r(t+dt))$
- $\eta_i(t+dt) = \eta_i(t) + dt * v_{\eta_i}(t) + \frac{dt^2}{2}a_{\eta_i}(t)$
- $\tilde{v}^{(0)} = v(t+dt/2) + \frac{1}{2}dt\ a(t+dt)$
- $\tilde{v}_{\eta_i}^{(0)} = v_{\eta_i}(t-dt) + 2dt\ a_{\eta_i}(t)$
- do k = 1, max_iteration
  - $\tilde{v}^{(k)} = \frac{1}{1+\frac{dt}{2}\tilde{v}_{\eta_1}^{(k-1)}}\tilde{v}^{(k-1)}$
  - $\tilde{a}_{\eta_1}^{(k)} = \frac{1}{Q_1}(\sum_{i=1}^{N} m_i|\tilde{v}_i^{(k)}|^2 - NkT) - \tilde{v}_{\eta_1}^{(k-1)} * \tilde{v}_{\eta_2}^{(k-1)}$
  - $\tilde{v}_{\eta_1}^{(k)} = v_{\eta_1}(t) + \frac{dt}{2}(a_{\eta_1}(t) + \tilde{a}_{\eta_1}^{(k)})$
  - $\tilde{a}_{\eta_i}^{(k)} = \frac{1}{Q_i}(Q_{i-1}\tilde{v}_{\eta_{i-1}}^{(k)}\tilde{v}_{\eta_{i-1}}^{(k)} - kT) - \tilde{v}_{\eta_i}^{(k-1)}\tilde{v}_{\eta_{i+1}}^{(k-1)}$
  - $\tilde{v}_{\eta_i}^{(k)} = v_{\eta_i}(t) + \frac{dt}{2}(a_{\eta_i}(t) + \tilde{a}_{\eta_i}^{(k)})$
  - if $(\sum_{i=1}^{N} m_i|\tilde{v}_i^{(k)} - \tilde{v}_i^{(k-1)}|^2 \leq NkT\epsilon)$ EXIT
- $v(t+dt) = \tilde{v}^{(k)}$
- $v_{\eta_i}(t+dt) = \tilde{v_{\eta_i}}^{(k)}$
- $a_{\eta_i}(t+dt) = \tilde{a_{\eta_i}}^{(k)}$

Rattle

- force associated with intramolecular constraints: $g\left(r(t), v(t)\right)$
- dynamics with constraints: $a(t) = f\left(r(t)\right) + g\left(r(t), v(t)\right)$
- time integration:
  - $v(t + dt/2) = v(t) + \frac{1}{2} dt (a(t) + \tilde{g_r}(t))$
  - $r(t + dt) = r(t) + dt\ v(t + dt/2) + \frac{1}{2} dt^2\ a(t)$
  - $v(t + dt) = v(t + dt/2) + \frac{1}{2} dt (a(t + dt) + \tilde{g_v}(t))$
- $\tilde{g_r}(t))$ and $\tilde{g_v}(t))$ are approximation to $g\left(r(t), v(t)\right)$ such that $r(t + dt)$ and $v(t + dt)$ satisfy the constraints
  - $|r_j(t) - r_i(t)|^2 - d_{ij}^2 = 0$
  - $|v_j(t) - v_i(t)| \cdot |r_j(t) - r_i(t)| = 0$

Rattle: A "Velocity" version of the Shake Algorithm for Molecular Dynamics Calculations, H.C. Andersen, J. Comp. Phys., Vol. 52, 24-34 (1983)

Rattle - Implementation 1st part

Evaluate $\tilde{g}_r(t)$ for each molecule independently

- $\tilde{v}^{(0)} = v(t) + \frac{1}{2} dt \; a(t)$
- $\tilde{r}^{(0)} = r(t) + dt \; v^{(0)} + \frac{1}{2} dt^2 \; a(t)$
- do k = 1, max_iter
  - do c = 1, num_constraints
    - if (all constraint are satisfied) exit iteration loop
    - if $(|\tilde{r}_{ij}^{(k-1)}|^2 - d_{ij}^2 < \epsilon)$ cycle
    - $g_r = \frac{|\tilde{r}_{ij}^{(k-1)}|^2 - d_{ij}^2}{2dt(r_{ij}(t) \cdot \tilde{r}_{ij}^{(k-1)})(m_i^{-1} + m_j^{-1})}$
    - $\tilde{r}_i^{(k)} = \tilde{r}_i^{(k-1)} + dt g_r m_i^{-1} r_{ij}(t)$
    - $\tilde{v}_i^{(k)} = \tilde{v}_i^{(k-1)} + g_r m_i^{-1} r_{ij}(t)$
    - $\tilde{r}_j^{(k)} = \tilde{r}_j^{(k-1)} - dt g_r m_j^{-1} r_{ij}(t)$
    - $\tilde{v}_j^{(k)} = \tilde{v}_j^{(k-1)} - g_r m_j^{-1} r_{ij}(t)$
  - end do
- end do
- $r(t + dt) = \tilde{r}^{(k)}$
- $v(t + dt/2) = \tilde{v}^{(k)}$

Rattle - Implementation 2nd part

Evaluate $\tilde{g_v}(t)$ for each molecule independently

- $\tilde{v}^{(0)} = v(t + dt/2) + \frac{1}{2} dt \; a(t + dt)$
- do k = 1, max_iter
  - do c = 1, num_constraints
    - if (all constraint are satisfied) exit iteration loop
    - if $(r_{ij} \cdot \tilde{v}_{ij}^{(k-1)} < \epsilon)$ cycle
    - $g_v = \frac{r_{ij} \cdot \tilde{v}_{ij}^{(k-1)}}{|r_{ij}|^2 * (m_i^{-1} + m_j^{-1})}$
    - $\tilde{v}_i^{(k)} = \tilde{v}_i^{(k-1)} + g_v m_i^{-1} r_{ij}(t + dt)$
    - $\tilde{v}_j^{(k)} = \tilde{v}_j^{(k-1)} - g_v m_j^{-1} r_{ij}(t + dt)$
  - end do
- end do
- $v(t + dt) = \tilde{v}^{(k)}$

Ewald summation - Definitions

- point charge distribution: $\rho_i(r) \equiv q_i \delta(r - r_i)$
- gaussian charge distribution: $\rho_i(r) \equiv Q_i \left(\frac{\eta^2}{\pi}\right) e^{-\eta^2 |r - r_i|^2}$
- lx, ly, lz: box length dimension
- r_c: cut-off radius for real space interaction
- ϵ_{real}: tolerance parameter for real space sum convergence
- ϵ_{recip}: tolerance parameter for reciprocal space sum convergence
- α: Ewald gaussian smearing width (do not confuse with η !)
  - $\alpha = \frac{\sqrt{(-\log(\epsilon_{\text{real}} * r_c))}}{r_c}$
- $\vec{k} = (\frac{2\pi k_x}{a}, \frac{2\pi k_y}{b}, \frac{2\pi k_z}{c})$: reciprocal space vector
- k_c: cut-off radius for reciprocal space vector
  - $k_c = \sqrt{(-\log(\epsilon_{\text{recip}}))4\alpha^2}$
  - $k[xyz]_{max} = \text{floor}(k_c * l[xyz]/(2\pi))$

Ewald summation - Point charge distribution

- 3D PBC
  - $U_{sr} = \frac{1}{2} \sum_{i,j} q_i q_j \sum_{\vec{n}}{}' \frac{\mathrm{erfc}(\alpha|\vec{r_{ij}}+\vec{n}|)}{|\vec{r_{ij}}+\vec{n}|}$
  - $U_{lr} = \frac{1}{ab} \sum_{i,j} q_i q_j \sum_{\vec{k}\neq\vec{0}} \frac{\cos\left(\vec{k}\cdot\vec{r_{ij}}\right)}{|\vec{k}|^2} e^{-\frac{|\vec{k}|^2}{4\alpha^2}}$
  - $U_{self} = -\frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2$
- 2D PBC
  - $U_{sr} = \frac{1}{2} \sum_{i,j} q_i q_j \sum_{\vec{n}}{}' \frac{\mathrm{erfc}(\alpha|\vec{r_{ij}}+\vec{n}|)}{|\vec{r_{ij}}+\vec{n}|}$
  - $U_{lr} = \frac{1}{ab} \sum_{i,j} q_i q_j \sum_{\vec{k}\neq\vec{0}} \int_{-\infty}^{\infty} du \, \frac{\cos\left(\vec{k}\cdot\vec{\xi_{ij}}+uz_{ij}\right)}{|\vec{k}|^2+u^2} e^{-\frac{|\vec{k}|^2+u^2}{4\alpha^2}}$
  - $U_{k=0} = -\frac{\sqrt{\pi}}{ab} \sum_{i,j} q_i q_j \left(\frac{e^{-z_{ij}^2\alpha^2}}{\alpha} + \sqrt{\pi}|z_{ij}|\mathrm{erf}(\alpha|z_{ij}|) \right)$
  - $U_{\mathrm{self}} = -\frac{\alpha}{\sqrt{\pi}} \sum_i q_i^2$

Ewald summation - Gaussian charge distribution

- 3D PBC
  - $U_{sr} = \frac{1}{2} \sum_{i,j} Q_i Q_j \sum_{\vec{n}}{}' \frac{(\mathrm{erfc}(\alpha|\vec{r_{ij}}+\vec{n}|) - \mathrm{erfc}(\eta_{ij}|\vec{r_{ij}}+\vec{n}|))}{|\vec{r_{ij}}+\vec{n}|}$
  - $U_{lr} = \frac{1}{ab} \sum_{i,j} Q_i Q_j \sum_{\vec{k}\neq\vec{0}} \frac{\cos\left(\vec{k}\cdot\vec{r_{ij}}\right)}{|\vec{k}|^2} e^{-\frac{|\vec{k}|^2}{4\alpha^2}}$
  - $U_{\mathrm{self}} = \frac{1}{\sqrt{\pi}} \sum_i Q_i^2 \left(\frac{\eta_i}{\sqrt{2}} - \alpha\right)$
- 2D PBC
  - $U_{sr} = \frac{1}{2} \sum_{i,j} Q_i Q_j \sum_{\vec{n}}{}' \frac{(\mathrm{erfc}(\alpha|\vec{r_{ij}}+\vec{n}|) - \mathrm{erfc}(\eta_{ij}|\vec{r_{ij}}+\vec{n}|))}{|\vec{r_{ij}}+\vec{n}|}$
  - $U_{lr} = \frac{1}{ab} \sum_{i,j} Q_i Q_j \sum_{\vec{k}\neq\vec{0}} \int_{-\infty}^{\infty} du \, \frac{\cos\left(\vec{k}\cdot\vec{\xi_{ij}}+uz_{ij}\right)}{|\vec{k}|^2+u^2} e^{-\frac{|\vec{k}|^2+u^2}{4\alpha^2}}$
  - $U_{k=0} = -\frac{\sqrt{\pi}}{ab} \sum_{i,j} Q_i Q_j \left(\frac{e^{-z_{ij}^2\alpha^2}}{\alpha} + \sqrt{\pi}|z_{ij}|\mathrm{erf}(\alpha|z_{ij}|)\right)$
  - $U_{\mathrm{self}} = \frac{1}{\sqrt{\pi}} \sum_i Q_i^2 \left(\frac{\eta_i}{\sqrt{2}} - \alpha\right)$

Ewald summation - Mixed system

- 3D PBC
- $U_{sr} = \sum_{i,j} q_i Q_j \sum_{\vec{n}} \frac{(\mathrm{erfc}(\alpha|\vec{r_{ij}}+\vec{n}|)-\mathrm{erfc}(\eta_j|\vec{r_{ij}}+\vec{n}|))}{|\vec{r_{ij}}+\vec{n}|}$
  - $U_{lr} = \frac{2}{ab} \sum_{i,j} q_i Q_j \sum_{\vec{k}\neq\vec{0}} \frac{\cos\left(\vec{k}\cdot\vec{r_{ij}}\right)}{|\vec{k}|^2} e^{-\frac{|\vec{k}|^2}{4\alpha^2}}$
- 2D PBC
  - $U_{sr} = \sum_{i,j} q_i Q_j \sum_{\vec{n}} \frac{(\mathrm{erfc}(\alpha|\vec{r_{ij}}+\vec{n}|)-\mathrm{erfc}(\eta_j|\vec{r_{ij}}+\vec{n}|))}{|\vec{r_{ij}}+\vec{n}|}$
  - $U_{lr} = \frac{2}{ab} \sum_{i,j} q_i Q_j \sum_{\vec{k}\neq\vec{0}} \int_{-\infty}^{\infty} du \, \frac{\cos\left(\vec{k}\cdot\vec{\xi_{ij}}+uz_{ij}\right)}{|\vec{k}|^2+u^2} e^{-\frac{|\vec{k}|^2+u^2}{4\alpha^2}}$
  - $U_{k=0} = -\frac{2\sqrt{\pi}}{ab} \sum_{i,j} q_i Q_j \left(\frac{e^{-z_{ij}^2\alpha^2}}{\alpha} + \sqrt{\pi}|z_{ij}|\mathrm{erf}(\alpha|z_{ij}|) \right)$

Constant potential energy minimization

- Equipotential constraint: $\frac{\partial U_c}{Q_{i_e}} = V_e$
- $U_T = U - \sum_{e=1}^{N_{\text{elec}}} \sum_{i=1}^{N_e} V_e Q_{i_e} \Rightarrow \frac{\partial U_T}{Q_{i_e}} = 0$
- $U_T = \frac{1}{2} Q^T A Q - Q^T b + c$
  - $\frac{1}{2} Q^T A Q = U_{c_{gg}}$
  - $Q^T b = Q^T V - U_{c_{pg}}$
  - $c = U_{c_{pp}} +$ other interactions
- Solve $AQ = b$
  - matrix inversion: compute coefficient of A^{-1} (not yet implemented)
  - iterative algorithm: Conjugate Gradient

Put it all together

- $t = 0$
- initialize system (runtime.inpt)
- initialize position (data.inpt)
- initialize velocity (data.inpt or random distribution)
- compute charge on electrodes
- compute forces on mobile species
- Begin MD loop
  - update velocities and positions
  - if (NVT) update species' and thermostats's positions and velocities
  - if (molecule with constraints) apply 1st part of rattle
  - compute charge on electrodes at $t + dt$
  - compute forces on mobile species at $t + dt$
  - Update velocities for the second half-step
  - if (molecule with constraints) apply 2nd part of rattle
  - if (NVT) iteratively update species and thermostat velocities
  - output
  - $t = t + dt$
- End MD loop

Missing features

To request the addition of a feature, create an issue on the gitlab:

https://gitlab.maisondelasimulation.fr/amarinla/mw2/issues