Simulating Water Freezing Using Canonical Ensembles Method (NVT)

Numerical Algorithms Applied to Computational Quantum Chemistry

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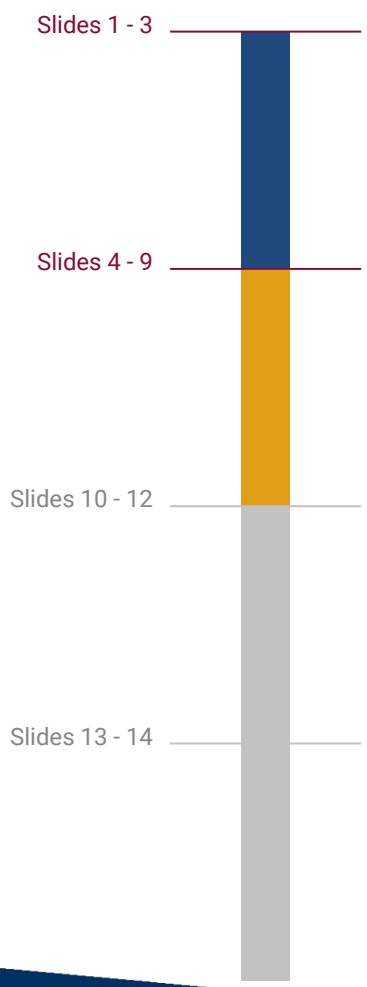
Key Focus Areas



Background

An accurate water simulation model is critical in many industries and chemical processes where water is a primary solvent (Energy, Pharmaceuticals etc..).

Numerical Modeling Algorithms

System Models (NPT, NVT), Structural Models (Simple Point Charge SPC, Transferable Intermolecular Potential TIP3P, SPC/E, TIP5P etc..).

Software Implementation

Software stack (frontend development, backend, Docker, CMake, GUI).

Simulation & Future Developments

Brief Simulation showcase, ongoing improvements and performance considerations.

Applications of Water Simulation Models

Pharmaceutical Research

R&D focused on solvation effects, and drug efficacy.

Simulations help predict binding affinities (small molecule and ligand binding)

- Stabilizing drug receptor complexes
- Prediction of ligand binding sites

Material Science

Materials hydration, Polymers & Nano material.

Water interaction at the molecular level with polymers.

- Polymer structure flexibility
- Enhanced Material design
- Thermal studies of materials in presence of water

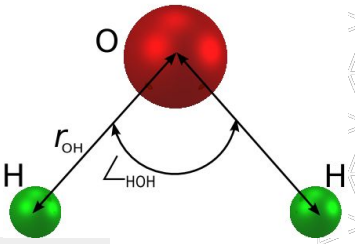
Nuclear Energy

Thermodynamics properties under various conditions.

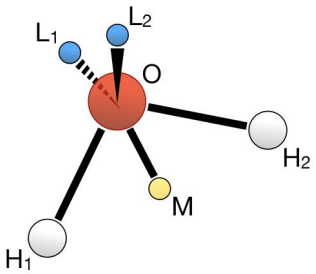
Thermodynamic behavior of water under extreme conditions

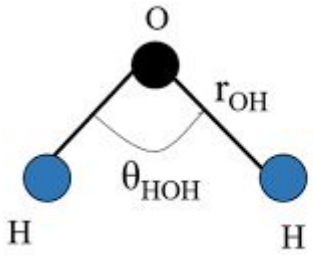
- Water studies in supercritical temperatures
- water density and entropy changes
- Radiation induced changes

Existing Structural Models

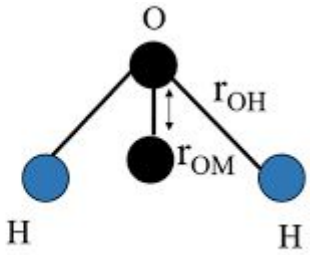


01	Simple Point Charge	• A rigid 3 - point model • Fixed atomic charges • Other variations include SPC/E
02	Transferable Intermolecular Potential	• Three point model optimized for MD • Used for bi-molecular studies • Other versions TIP3P, TIP4P, TIP5P
03	Polarizable Water Model	• Adjusts dipoles based on local environment • To model water's dielectric property • Other versions MB-Pol, POL3





TIP3P



TIP4P

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Canonical Ensembles vs Ensemble Methods

Canonical Ensemble Method (NVT)

Represents a system with a fixed number of particles (N), Volume (V), and temperature (T)

- Used for simulation requiring constant environmental conditions
- Applied i molecular dynamics and to investigate temperature dependent phenomenon such as crystallization

Ensemble Methods

Broader term simulations that under various conditions (microcanonical (NVE) and grand canonical ensembles

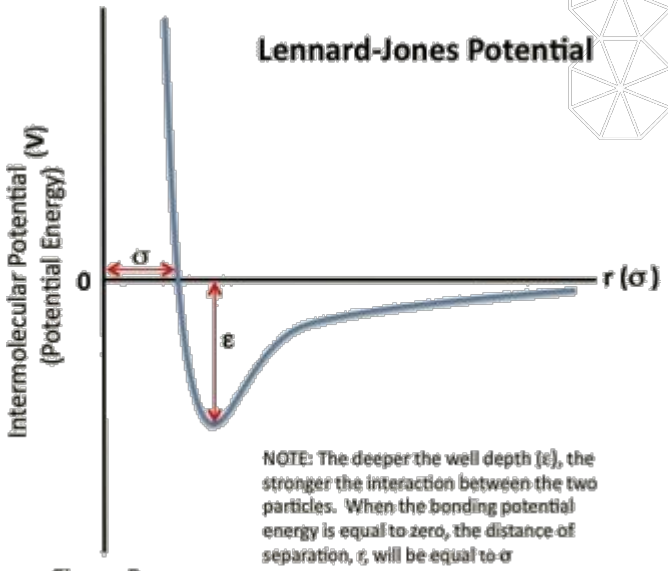
- Microcanonical is fixed energy, volume and number of particles (NVE)
- Used in Energy conservation studies
- Adsorption and phase

Our Objective:

Model water under constant thermodynamic conditions with gradual cooling and hydrogen bonding interactions using a hybrid SPC model with NVT system conditions.

Methods: Lennard Jones Potential

- Consider a simple point charge model interaction
  - Spherically symmetric atoms
    - i.e. no directional chemical bonds
    - intermolecular interactions
  - 12-6 Lennard-Jones Potential



$$U_{\text{total}} = \sum_{i<j} [U_{\text{LJ}}(r_{ij}) + U_{\text{Coulomb}}(r_{ij})]$$

$$U_{\text{LJ}}(r_{\text{OO}}) = 4\varepsilon_{\text{SPC}} \left[\left(\frac{\sigma_{\text{SPC/E}}}{r_{\text{OO}}} \right)^{12} - \left(\frac{\sigma_{\text{SPC/E}}}{r_{\text{OO}}} \right)^{6} \right]$$

- In this form, σ_{ij} is the equilibrium bond distance
  ε_{ij} is the magnitude of the binding energy

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Reference: Chem279 Lecture 2 slide 9 - 14

Izadi, S., & Onufriev, A. V. (2016, August 21). *Accuracy limit of rigid 3-point water models.* The Journal of chemical physics. https://pmc.ncbi.nlm.nih.gov/articles/PMC4991989/

Methods: LJ Force Calculations

- Derivative of LJ potential to get the forces at the different time steps

$$U_{\mathrm{LJ}}(r_{\mathrm{OO}}) = 4\varepsilon_{\mathrm{SPC}} \left[\left(\frac{\sigma_{\mathrm{SPC/E}}}{r_{\mathrm{OO}}} \right)^{12} - \left(\frac{\sigma_{\mathrm{SPC/E}}}{r_{\mathrm{OO}}} \right)^{6} \right]$$

$$\vec{F}_{\mathrm{LJ}}(r) = -\nabla V_{\mathrm{LJ}}(r) = 24\varepsilon \left[2 \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \frac{\vec{r}}{r^2}$$

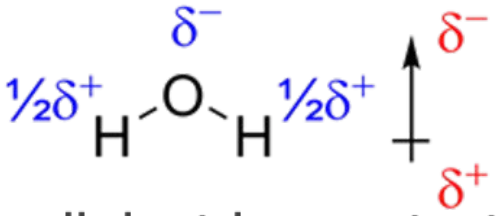
$$\vec{F}_{\mathrm{LJ}}(r) = 24\varepsilon \left[2 \left(\frac{\sigma}{r} \right)^{13} - \left(\frac{\sigma}{r} \right)^{7} \right] \vec{r}$$

Reference: Chem279 Lecture 2 slide 9 – 14

Methods: Dipole Moment and Coulombic Interactions

- Similar to non-directional dispersion interaction, we can include Coulomb force from charges
- Provides interactions between polar molecules (e.g. water) or charged species (e.g. salts, ionic liquids)

$$E_{ij}^{el} = \frac{Q_i Q_j}{\varepsilon R_{ij}}$$



Q_i are parameters, ε is (usually a dielectric constant)

- The coulombic interactions well be broken down into more specific forces

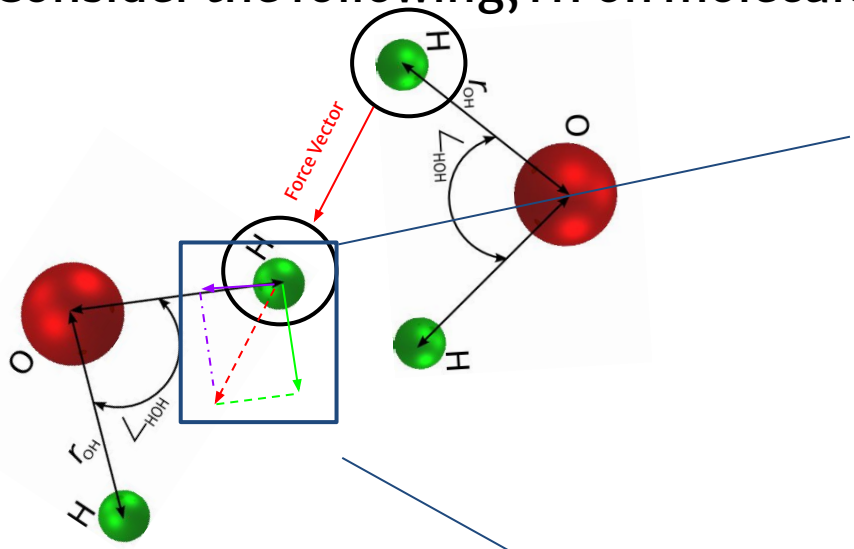
Methods: Coulombic Interactions cont.

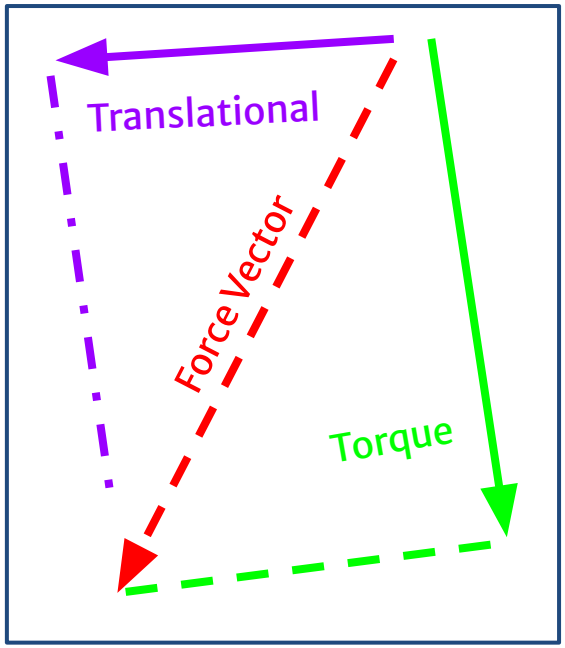
In order to apply these forces we need to break them down:

- Translation forces
- Rotational forces

See interactive Geogebra page below.

Consider the following, H1 on molecule 1 and H1 on molecule 2





https://www.geogebra.org/3d/na9arbmv

Kinetic Energy and Velocity Calculation

- Kinetic Energy

$$E_{\text{kin}} = \frac{1}{2}\sum_{i=1}^{N} m_i \mathbf{v}_i^2$$

$$K_i = \frac{1}{2} m_i \left(v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2\right)$$

$$\langle E_{\text{kin}} \rangle = \frac{1}{2} k_B T$$

- Velocity-Verlet Algorithm

$$\vec{a}_i = \frac{\vec{F}_i}{m_i}$$

$$\vec{r}(t+\Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2$$

$$\vec{a}(t+\Delta t) = \frac{\vec{F}(t+\Delta t)}{m}$$

$$\vec{v}(t+\Delta t) = \vec{v}(t) + \frac{1}{2}\left[\vec{a}(t) + \vec{a}(t+\Delta t)\right]\Delta t$$

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{1}{2}\vec{a}_i(t)(\Delta t)^2$$

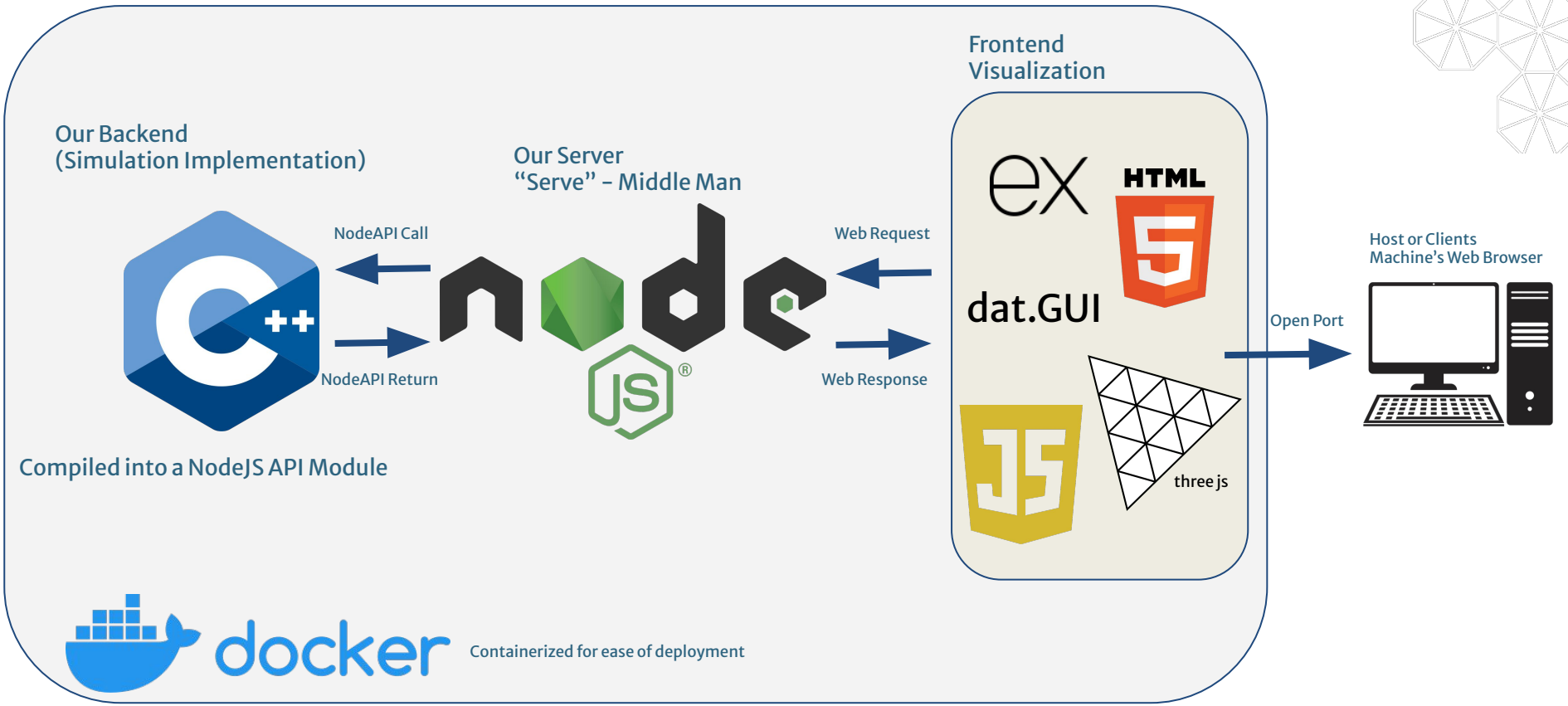
$$\vec{F}_i(t+\Delta t) = \text{Calculate Forces Based on } \vec{r}_i(t+\Delta t)$$

$$\vec{a}(t+\Delta t) = \frac{\vec{F}(t+\Delta t)}{m}$$

$$\vec{v}(t+\Delta t) = \vec{v}(t) + \frac{1}{2}\left[\vec{a}(t) + \vec{a}(t+\Delta t)\right]\Delta t$$

$$KE_{\text{total}} = \sum_{i=1}^{N} \frac{1}{2} m_i \left(v_{i,x}^2 + v_{i,y}^2 + v_{i,z}^2\right)$$

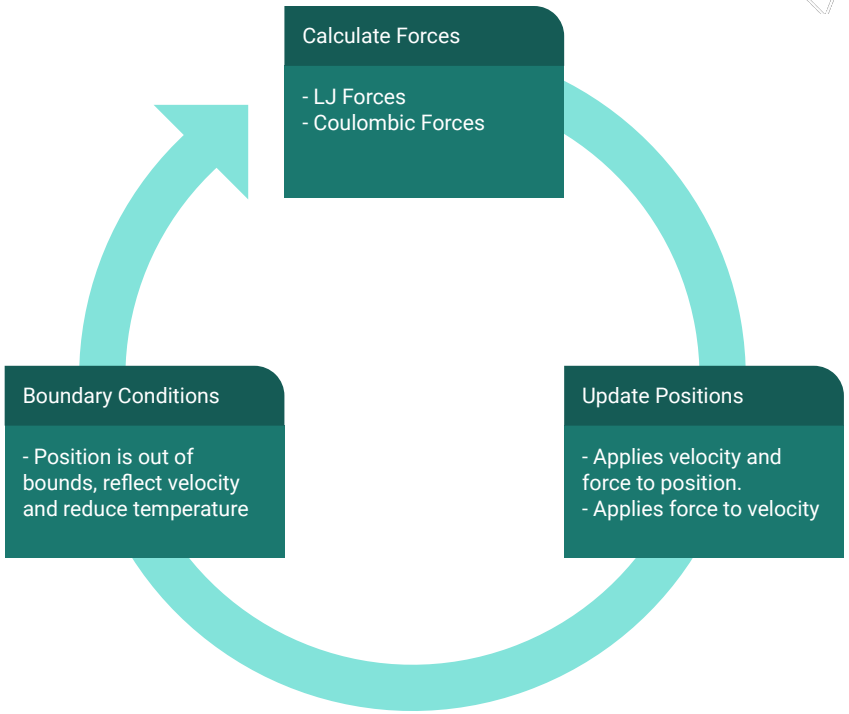
Software Stack



Backend Implementation

- Developed in all C++
- Compiled into a custom Node API module
- Runs simple simulation stack:
  - Declare initial variables
  - Calculate initial conditions
  - Run simulation step
    - “Zero” forces
    - Calculate forces
    - Update position
    - Apply boundary conditions

Each Simulation Step

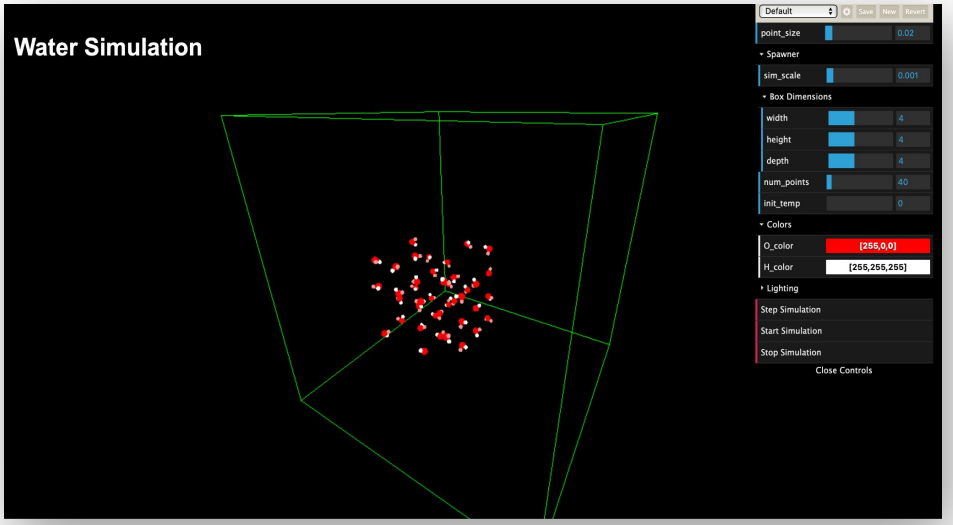


Front End Implementation

All implementation was designed to allow as many machines to run and visualize the simulation as possible.

To achieve this, we decided to use the web browser for visual. They have many more examples as well as resources to get 3D visualizations working vs. something like C++.

- HTML5
- Javascript
- ThreeJS
- dat.GUI
- Web requests
- WebGL (GLSL)



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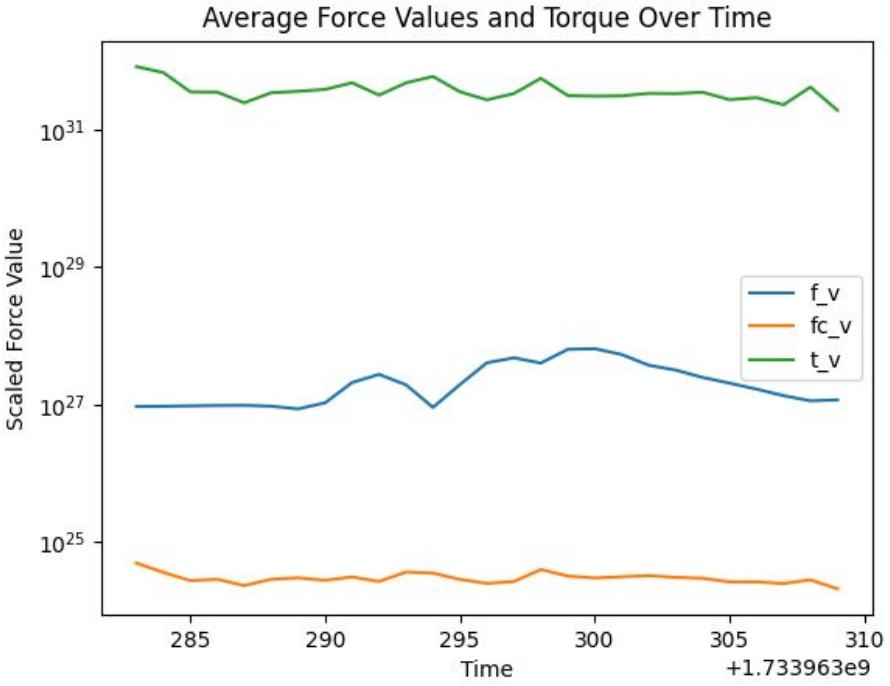
Simulation Showcase

Results

- Average LJ forces at each time step (f_v)
- Average of Coulombic Forces (fc_v)
- Average torque forces
  - directly correlated to dipole calculations



Discussions: Struggle Points

- Particles being initialized un-realistically close together
  - Causing LJ forces to "explode" the particles in a cramped space
- Units, Units, Units!!!
- Determination of simulation type (NVT, NPT, NVE…)
- "Ooh shiny" syndrome
  - We started all of our work on wanting to recreate another simulation someone else ran, this led to many initial misunderstandings of the equations and procedure for our code.
  - We all do it, no shame

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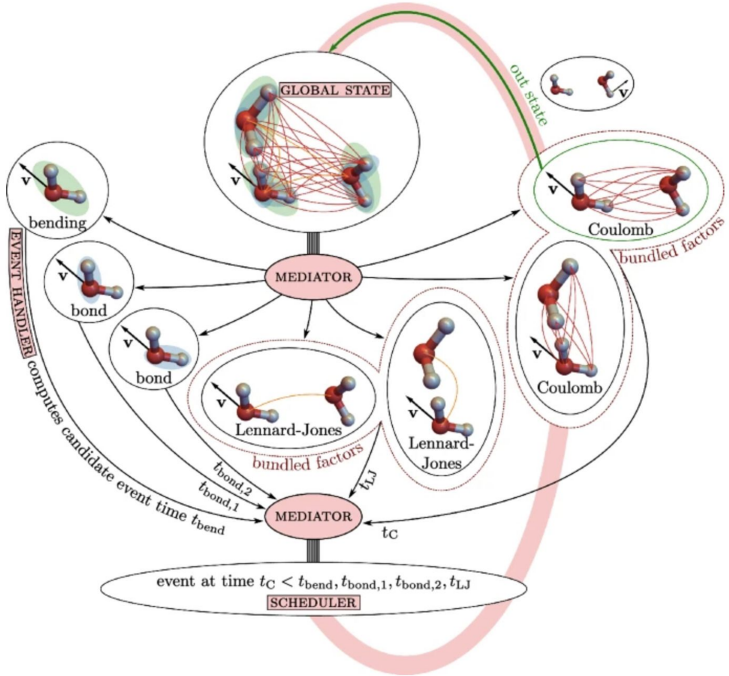
Sebastians videos
https://www.youtube.com/watch?v=rSKMYc1CQHE&t=954s

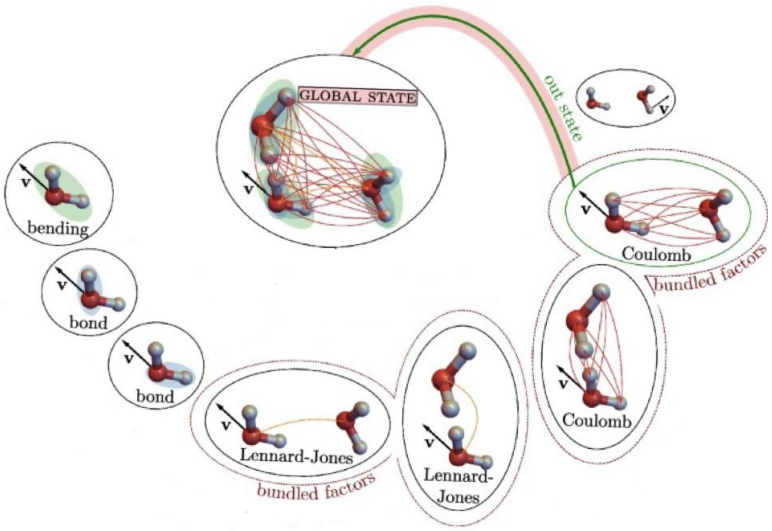
Discussions: Future Development

- Correctly implementing Coulombic forces (being worked on).
  - Static dynamics for correct rotational forces experienced.
- Lock down all initial parameters.
  - Prevent user from changing them during run time.
- Correct Initial bounds calculations on the UI side.
- Reset simulation button.
- Large-scale modularization.
  - Others implement their desired calculations.
  - Changing of molecules and atomic parameters.
  - Combine/merge energy and force calculations.
- Implement other properties of water
  - thermal expansion coefficient, isobaric heat capacity, dielectric constant
- Monte-Carlo Simulation for bond angle prediction to achieve optimal bonds.
- An error check mechanism to ensure all units match!!

Hydrogen - Oxygen Bond Angle Optimization

- Bond angle change performed with a monte carlo algorithm
- If the bond angle results low potential energy accept else continue.





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Höllmer, P., Maggs, A. C., & Krauth, W. (2024, July 16). *Fast, approximation-free molecular simulation of the SPC/FW water model using non-reversible Markov chains*. Nature News. https://www.nature.com/articles/s41598-024-66172-0

Live Simulation Showcase and Q&A's

Thank you!

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References

1. Höllmer, P., Maggs, A. C., & Krauth, W. (2024, July 16). *Fast, approximation-free molecular simulation of the SPC/FW water model using non-reversible Markov chains*. Nature News. https://www.nature.com/articles/s41598-024-66172-0
2. Izadi, S., & Onufriev, A. V. (2016, August 21). *Accuracy limit of rigid 3-point water models*. The Journal of chemical physics. https://pmc.ncbi.nlm.nih.gov/articles/PMC4991989/
3. Martin.chaplin@btinternet.com, M. C. (n.d.). Water models. https://water.lsbu.ac.uk/water/water_models.html
4. For detailed references please visit Notion page dedicated to this project: https://www.notion.so/Molecular-Dynamic-Simulation-of-Water-130778e8c4238072b858de53ea4cbc5b

Key Takeaways

Water simulation models are crucial for scientific research

- Complex computational methods enable molecular-level understanding
- Ongoing research continues to improve simulation techniques (ML-approaches)
- Interdisciplinary applications across pharmaceuticals, materials science, and energy

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