

P.393 - Collision Mini-Project

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The goal of this project is to simulate some number of water molecules bouncing around in a box under a Leonard-Jones Potential. The simulation also calculates the torques, from the electric dipole moments, that the molecules exert on each other. The user has control of the size of the box, the number of molecules, the temperature in the box (this determines the initial velocities of the molecules), the time step and the speed of the animation. Additionally the user can specify a factor to increase the moment of inertia of the water molecules. The last setting was required because there are un-realistic parts of the simulation which cause the molecules to spin at unrealistically fast speeds due to the torques from the dipole moments. For the molecules to be large enough to be easily seen in the simulation the box must be a size so that the molecules are much closer together than they would be in a real water vapor. The torque from the dipole moment drops off at the rate of $\frac{1}{r^3}$ where r is the separation distance between two molecules. This means that if the molecules are ten times closer together then is realistic the torques will be 1000 times greater than is realistic. Additionally the simulation only has a small number of molecules while a real gas would have a very large number of molecules with randomly aligned dipole moments which would, for the most part, average out close to zero. Using a higher than realistic moment of inertia then keeps the molecules from spinning uncontrollably fast in the simulation. To change the parameters of the simulation the simulation must be reset with the exception of the speed of the simulation (how many time steps are computed per updating the animation) which can be changed while the simulation is running. As a note, when entering a new value in the text boxes the user needs to press enter with the text box selected for the simulation to record the changed value.

1 The Physics

The Leonard-Jones Potential is a rough model of how molecules interact with each other. The potential includes an attractive and a repulsive component between molecules. At some distance σ the attractive and repulsive components are equal and cancel out. For distances in between molecules less than σ the repulsive force is much stronger and molecules repel each other but when the distance is greater than σ the inverse is true and the molecules attract. In this sense the parameter σ can be thought of as the diameter of a molecule. The Leonard-Jones Potential between two molecules is given by, [1]

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{Leonard-Jones Potential} \quad (1)$$

The $\left(\frac{\sigma}{r} \right)^{12}$ term is an approximation to the Pauli Repulsion, which occurs from molecules coming close enough together that their electron orbitals overlap. When $r < \sigma$ the $\frac{\sigma}{r}$ term is greater than 1 and grows **very** quickly as r gets smaller. Therefore this term constitutes a strong repulsion at distances less than the "size" of the molecule. The $\left(\frac{\sigma}{r} \right)^6$ term on the other hand represents a long range attractive force between molecules. When $r > \sigma$, $\frac{\sigma}{r} < 1$ and this term is greater than the repulsive term constituting an overall attraction between two molecules farther apart than σ .

To compute the motion of the molecules we need the forces experienced between two molecules rather than the potential. This can be done from Newtonian Mechanics where a conservative force can be written in terms of a potential as,

$$\vec{F} = -\nabla V$$

Applying this to Eq.(1) we have the force between two particles is,

$$\vec{F} = 24\epsilon \left[2\frac{\sigma^{12}}{r^{13}} - \frac{\sigma^6}{r^7} \right] \hat{r} \quad (2)$$

The simulation will use realistic values for the parameters in question for water molecules as stated in [2].

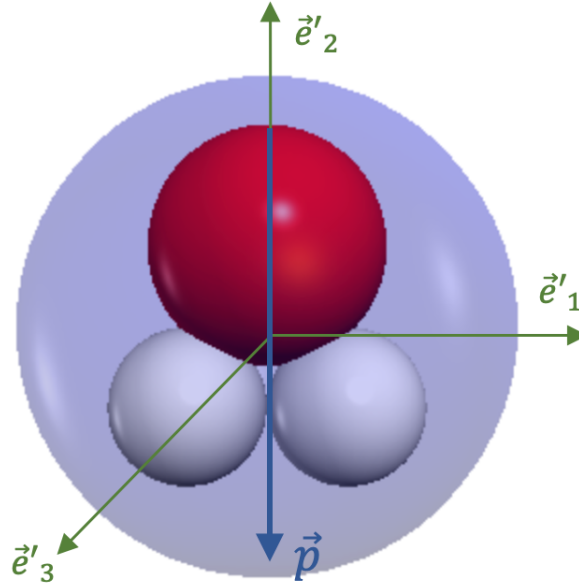
$$\sigma = 2.725 \text{ \AA}$$

$$\epsilon = 491.15 \times 10^{-23} \text{ J}$$

$$m = 30.103 \times 10^{-27} \text{ kg}$$

Water molecules are polarized so they have a non zero dipole moment which will cause the molecules to exert torques on each other. The dipole moment of a water molecule points from the negatively charged Oxygen atom towards the center of the two positively charged hydrogen atoms Fig.(1). The dipole moment is given by $\vec{p} = -6.2 \times 10^{-20} \vec{e}'_2 \text{ [C} \cdot \text{\AA]}$ [3].

Figure 1: Dipole Moment of H₂O



The contribution to the electric field due to a dipole can be calculated with, [4]

$$\vec{E}_{dip}(\vec{r}) = \frac{3(\vec{p} \cdot \hat{z})\hat{z} - \vec{p}}{4\pi\epsilon_0 z^3} \quad (3)$$

Where \vec{r} is the field point in question and \vec{z} is the separation vector from the dipole moment to the field point. Now that the electric field is know the torque on each molecule can be calculated as,

$$\vec{\tau} = \vec{p} \times \vec{E} \quad (4)$$

Where here \vec{p} is the dipole moment of the molecule the torque is acting on and \vec{E} is the total electric field from all of the other molecules.

2 The Simulation

When the simulation begins the number of molecules specified are initiated at random positions within the box and with random orientations. The initial rotational velocity is close to zero for all the molecules with a small random initial rotation velocity in a random direction. The velocities are sampled from the Maxwell velocity distribution based on the user chosen temperature and in a random direction.

The force on any single molecule is the sum of the forces on it from all other molecules.

$$\vec{F}_i = \sum_{j \neq i}^n 24\epsilon \left[2 \frac{\sigma^{12}}{r_{ij}^{13}} - \frac{\sigma^6}{r_{ij}^7} \right] \hat{r}_{ij} \quad (5)$$

Where n is the number of molecules in the simulation and $\vec{r}_{i,j}$ is the vector from molecule i to molecule j . The acceleration can then be calculated from the force using Newton's second law. The velocity can be updated at each time step then as,

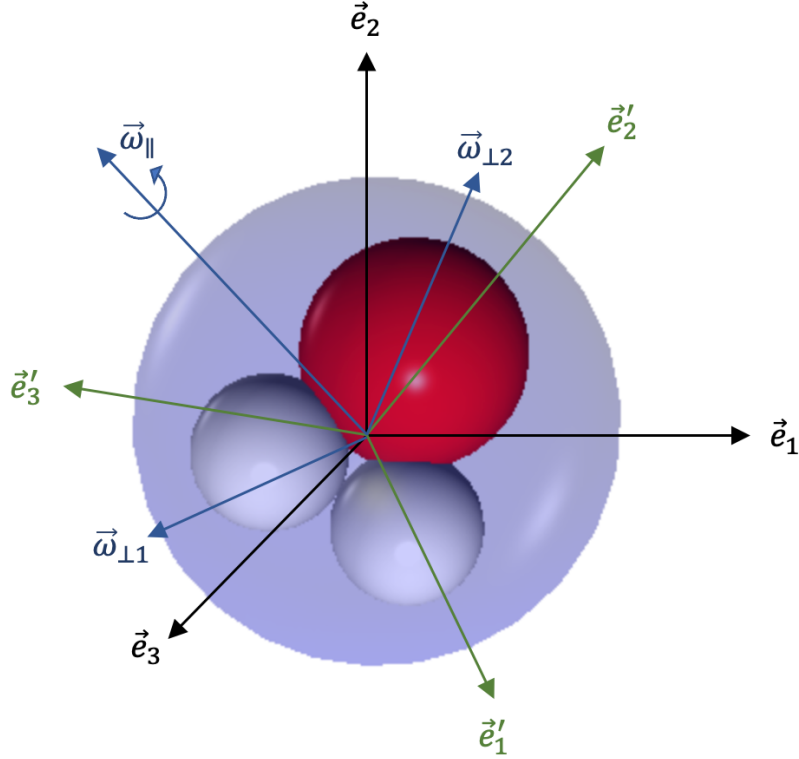
$$\vec{v}_i = \vec{v}_{i,0} + \vec{F}_i \frac{\Delta t}{m} \quad (6)$$

To add to the visual effect the water molecules are drawn as a larger red sphere to represent the oxygen atom and two smaller white sphere to represent the hydrogen atoms, all with a translucent blue sphere representing the total molecule's "size" i.e. the distance at which it will repel or "collide" with another molecule. The molecules are drawn so that they are all rotating as they move around the box. The molecule is easy to draw in a coordinate system where the oxygen's position lines up with the y-axis and the centers of all three atoms are in the x-y plane. We can then represent the orientation of the molecule as it rotates by a 3x3 matrix which represents a change of basis from the molecules natural coordinates to standard cartesian coordinates. This transformation matrix is made by simply stacking the primed basis vectors as columns in a matrix.

$$\mathbf{T}_{e' \rightarrow e} = \begin{bmatrix} \vec{e}'_1 & \vec{e}'_2 & \vec{e}'_3 \end{bmatrix} \quad (7)$$

Now rotations in three dimensions are complicated but they can be done simply in two dimensions. If we change the coordinate system so the z-axis of our natural rotational coordinates lines up with the

Figure 2: Rotating Coordinates



axis of rotation then the rotation can be done by simple matrix multiplication with a transformation matrix,

$$\mathbf{R}(\theta) = \begin{bmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (8)$$

Now to transform the orientation basis vectors into the natural rotational coordinates, the $\vec{\omega}$ basis as shown in Fig.(2), we need to form another change of basis matrix. It is easy to build the matrix which changes basis back from the rotational coordinates to the standard cartesian coordinates by just stacking the rotational coordinate basis vectors written in terms of the standard unit vectors as columns in a 3×3 matrix.

$$\mathbf{A}_{\omega \rightarrow e} = [\vec{\omega}_{\parallel} \quad \vec{\omega}_{\perp 1} \quad \vec{\omega}_{\perp 2}] \quad (9)$$

And to perform the change of basis in the other direction we simply need to invert this matrix. So all together the rotations of the molecules can be done by a chain of matrix multiplication. $\mathbf{A}^{-1}\mathbf{T}$ takes the orientation matrix which is the molecules natural coordinate basis vectors written in standard cartesian unit vectors and transforms them to be written in terms of the natural rotation basis vectors. Now we can multiply $\mathbf{R}(\theta)$ by the resulting matrix to rotate the molecules orientation vectors by the angle θ which is calculated by $\theta = |\omega|\Delta t$ giving the angle of rotation for one time step. Now that the molecules orientation has been rotated we just need to chain on the change of basis matrix $\mathbf{A}_{\omega \rightarrow e}$ to transform the orientation vectors back to being written in terms of standard cartesian unit vectors.

$$\mathbf{T}_{e' \rightarrow e}^{(final)} = \mathbf{A}_{\omega \rightarrow e} \mathbf{R}(\theta) \mathbf{A}_{\omega \rightarrow e}^{-1} \mathbf{T}_{e' \rightarrow e} \quad (10)$$

Now to calculate the change in ω during a time step we need to find the angular acceleration. The first step is to find the net torque on any molecule. To do this we need the electric field at the molecule due to all the other molecules. This can be calculated using Eq.(3).

$$\vec{E}(\vec{r}_i) = \sum_{j \neq i}^n \frac{3(\vec{p}_j \cdot \hat{r}_{ji})\hat{r}_{ji} - \vec{p}_j}{4\pi\epsilon_0 r_{ji}^3} \quad (11)$$

This means the net torque on the molecule due to its dipole moment is,

$$\vec{\tau}_i = \vec{p}_i \times \vec{E}(\vec{r}_i) \quad (12)$$

Now that we have the net torque on each molecule we calculate the angular acceleration using the following formula for the net torque on a rigid body which follows from Newton's second law. [5]

$$\vec{\tau} = \mathbf{I} \vec{\alpha} + \vec{\omega} \times \mathbf{I} \vec{\omega} \quad (13)$$

Where \mathbf{I} is the inertial tensor and $\vec{\alpha}$ is the angular acceleration. In terms of the primed coordinate system as shown in Fig.(2) the inertial tensor is, [6]

$$\mathbf{I}' = \begin{bmatrix} 1.09 \times 10^{-27} & 0 & 0 \\ 0 & 1.91 \times 10^{-27} & 0 \\ 0 & 0 & 3.00 \times 10^{-27} \end{bmatrix} \quad [\text{kg } \text{\AA}^2]$$

However $\vec{\tau}$ and $\vec{\omega}$ are in standard cartesian coordinates (unprimed) so to calculate the angular acceleration ($\vec{\alpha}$) it is going to be easiest to transform the inertial tensor from its simplest (diagonalized) form to be written in the standard unprimed coordinates. We already have a transformation matrix from primed to unprimed coordinates, $\mathbf{T}_{\vec{e}' \rightarrow \vec{e}}$. Therefore the inertial tensor transformed into the unprimed coordinates is,

$$\mathbf{I} = \mathbf{T} \mathbf{I}' \mathbf{T}^{-1} \quad (14)$$

Plugging this into Eq.(13) and solving for $\vec{\alpha}$ we get an equation we can use to calculate the angular acceleration at each time step for each molecule.

$$\vec{\alpha} = (\mathbf{T} \mathbf{I}' \mathbf{T}^{-1})^{-1} (\vec{\tau} - \vec{\omega} \times \mathbf{T} \mathbf{I}' \mathbf{T}^{-1} \vec{\omega}) \quad (15)$$

And finally we can update the molecules angular velocity for the current time step using this value.

$$\vec{\omega}_i = \vec{\omega}_{i,0} + \vec{\alpha}_i \Delta t \quad (16)$$

References

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