Molecular Dynamics Simulations of a Lennard-Jones System

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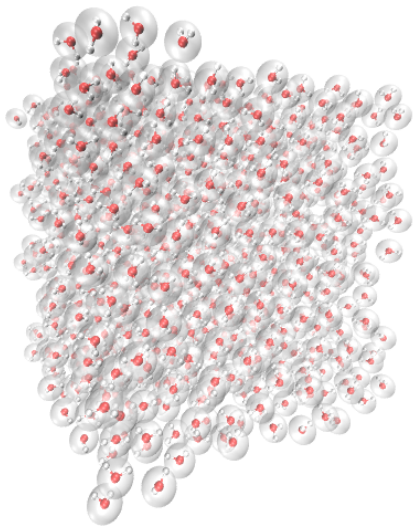


Course: Modeling and Simulation for Scientific Applications
Prof. Vangelis Harmandaris
Prof.Iannis Tanis

N-body Problem

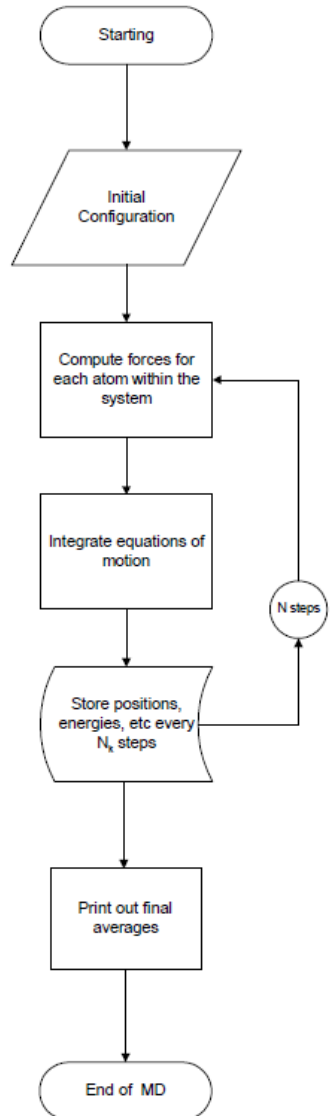
The N-body or Many-body Problem determines the motion of N atoms interacting with each other according to the Newton law of motion.

- Denote r_j, p_j the position and momentum of the i-th atom, $i = 1, \ldots, N$
- Solve the Hamiltonian Equations of motion
  $H(\mathbf{r}, \mathbf{p}) = K(\mathbf{p}) + U(\mathbf{r})$
  where $K(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}$
- So, $\dot{\mathbf{r}} = H_{\mathbf{p}} = \frac{\mathbf{p}}{m}, \quad \dot{\mathbf{p}} = -H_{\mathbf{r}} = -\frac{\partial U}{\partial \mathbf{r}}$
  where m total mass

Molecular Dynamics Simulation

MD is a computer method for simulating the physical movements of molecules.

- Integrate the equations of motion via Verlet algorithm
- Use Newton's law of motion $F(\mathbf{r}) = \mathbf{m}\frac{d^2\mathbf{r}}{dt^2}$ and
- Second order Finite Differences $\frac{d^2\mathbf{r}}{dt^2} = \frac{\mathbf{r}(t+dt)-2\mathbf{r}+\mathbf{r}(t-dt)}{dt^2}$
- So, Particles Positions formula: $\mathbf{r}(t+dt) = 2\mathbf{r}(t) - \mathbf{r}(t-dt) + \frac{Fdt^2}{\mathbf{m}}$ and
- Velocities formula: $\mathbf{v} = \frac{\mathbf{r}(t+dt)-\mathbf{r}(t-dt)}{2dt}$



Lennard-Jones Potential

It is common to estimate the energy with the two-body contributions: $U(\mathbf{r}) \approx \sum_{i,j} u(r_{ij})$

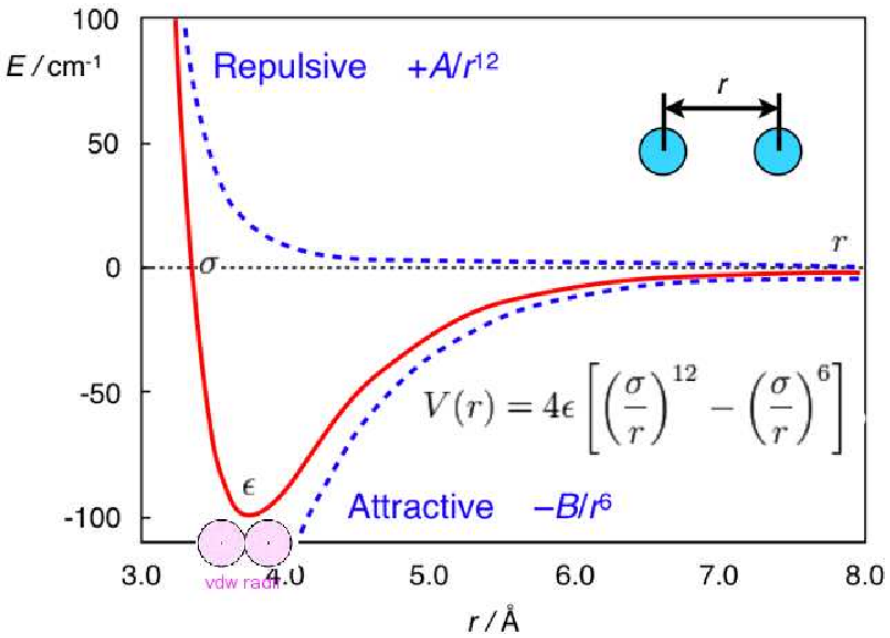


Figure: The Lennard-Jone Potential

The Lennard-Jones potential is an intermolecular pair potential and is applied to calculate the potential energy of the CG particles.

- Form of the L-J potential: $U_{LJ}(r_{ij}) = 4\epsilon\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right)$
- r_{ij} is the distance between two particles r_i and r_j,
- ϵ is the depth and σ the atom diameter.
- Repulsion:$\left(\frac{\sigma}{r_{ij}}\right)^{12}$ and Attraction: $\left(\frac{\sigma}{r_{ij}}\right)^{6}$

Analysis of MD Algorithm I

- A simulation Box with N particles
- $Volume = \frac{N}{\rho}, L = V^{1/3}$
- A cut-off radius r_c
- Periodic boundary conditions
- Minimum-image convention

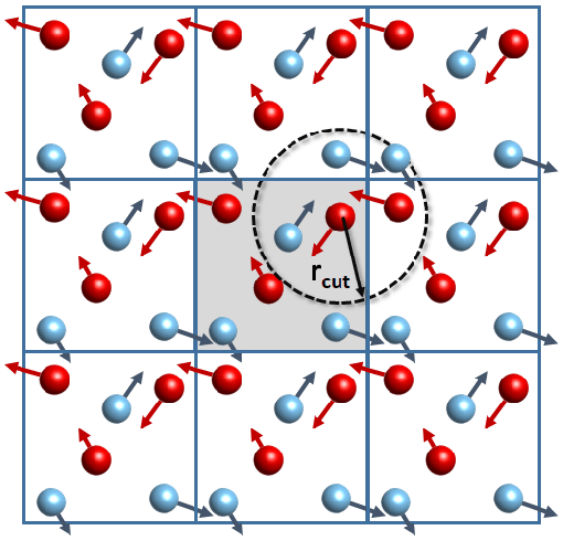


Figure: A two-dimensional periodic system with the minimum image convention.

Analysis of MD Algorithm II

- Initial coordinates: Given via crystal structure
  - First integration step
    $\mathbf{r}(t+dt) = \mathbf{r}(t) - dt\mathbf{v}(t) + 0.5F(t)dt^2$
  - Next integration steps
    $\mathbf{r}(t+dt) = 2\mathbf{r}(t) - \mathbf{r}(t-dt) + \frac{Fdt^2}{\mathbf{m}}$
- Velocities follow a Boltzmann distribution
  $v \sim N(0, \sqrt{(k_b/\mathbf{m})})$

MD algorithm

Goals:

Calculate

- The conserved Hamiltonian
- The conserved Momentum ~ 0
- Distribution of Distances between all particles
- Pair Distribution function $G(r)$

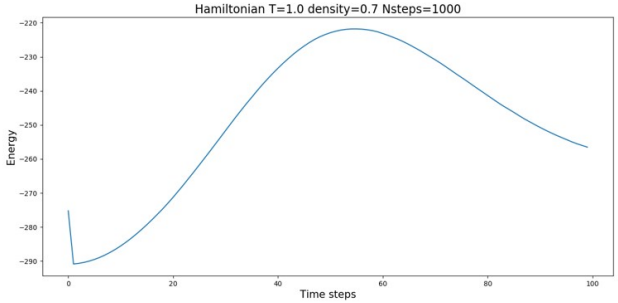
Selected parameters:

- Nstep= $10^3, 10^4$
- Density= $0.1, 0.5, 0.7$
- Temperature= $0.5, 1.0, 2.0$

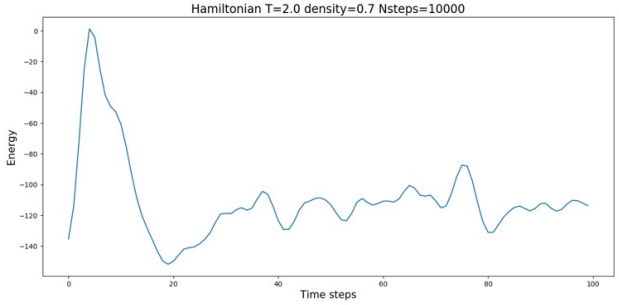
Set N, ρ, T, dt
Set number of steps *nsteps*
Initialize $\mathbf{r}(t_0), \mathbf{v}(t_0)$ and compute $\mathbf{r}(t_1)$ with equation (15)
for *j=1,...,nsteps* **do**
  $t = jdt$
  for *i=1,...,N* **do**
    $\mathbf{r}_i(t+dt) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-dt) + \frac{\mathbf{F}_i}{m_i}(t)$
    $\mathbf{v}_i = \frac{\mathbf{r}_i(t+dt) - \mathbf{r}_i(t-dt)}{2dt}$
  end
  Compute forces $\mathbf{F}(\mathbf{r}(t+dt))$
  Implement periodic Boundary Conditions
end

Figure: MD algorithm

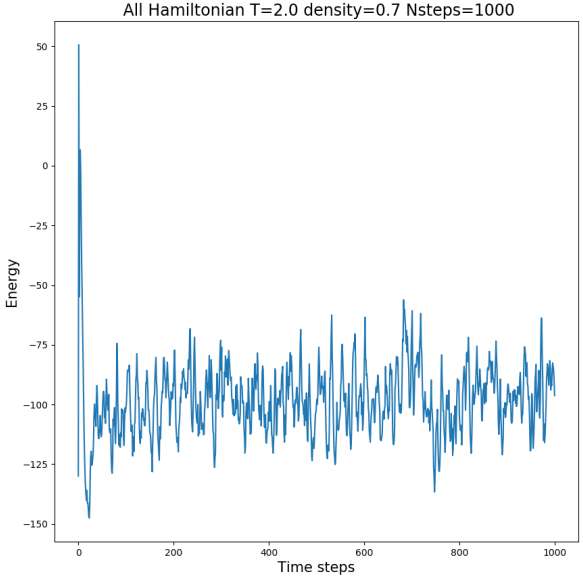
Results-Hamiltonian



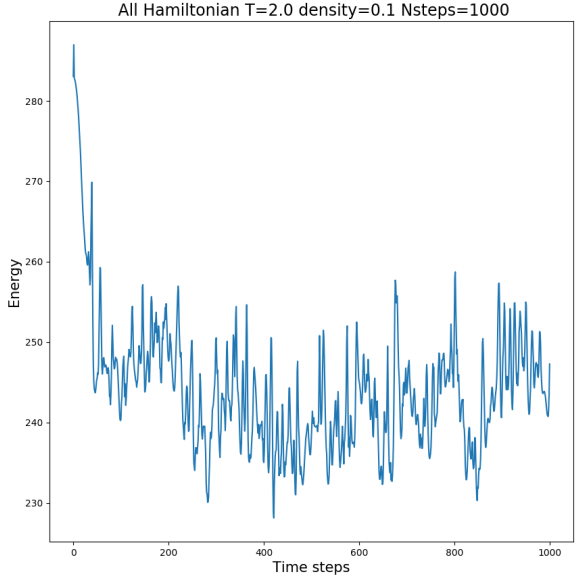
$\rho = 0.7, T = 1.0, dt = 0.0001, Nsteps = 1000$



$\rho = 0.7, T = 2.0, dt = 0.0001 Nsteps = 10000$



$= 0.7, T = 2.0, .dt = 0.01, Nstep = 1000$



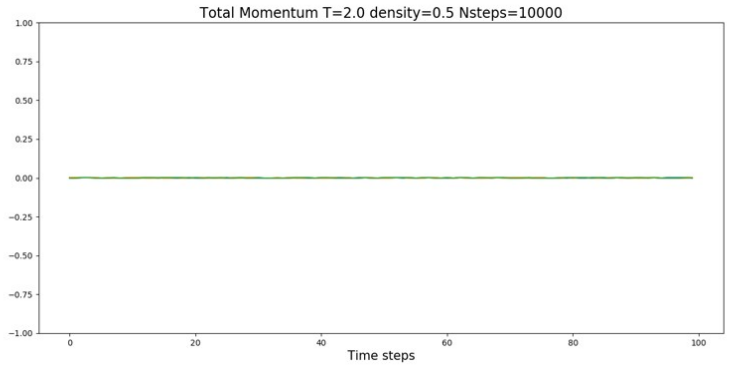
$\rho = 0.1, T = 2.0, dt = 0.01 Nstep = 1000$

Results-Hamiltonian I

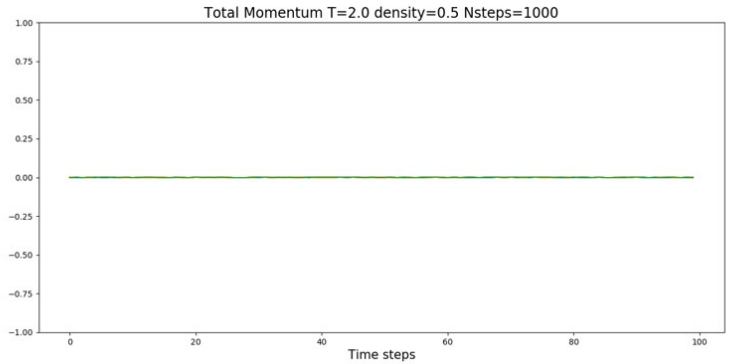
- Hamiltonian does not change for any temperature
- Hamiltonian can not be well conserved with a small number of time steps ($dt = 0.0001$) and Nsteps and starts getting stabilized after big number of steps.
- Hamiltonian stabilizes after a few steps ($dt = 0.01$)
- Systems with lower density, Hamiltonian is more unstable than the systems with higher density

Results-Momentum

Momentum is a conserved quantity at any value of temperature or density and remains equal to zero for all configurations



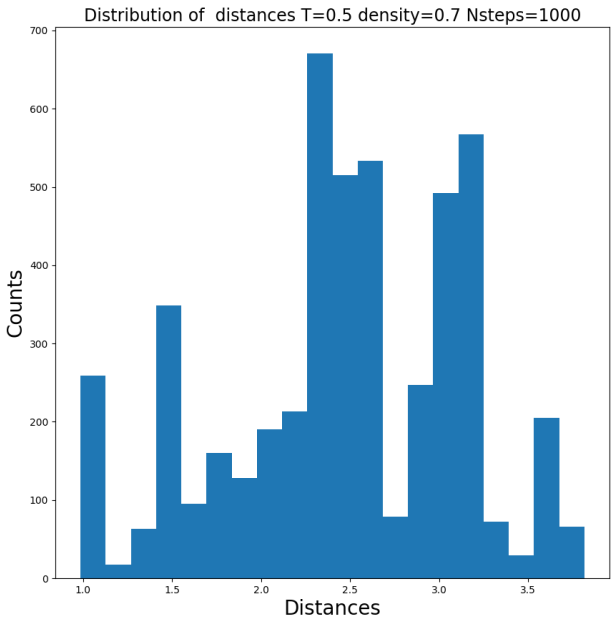
Momentum for
$\rho = 0.5, T = 2.0, Nstep = 10000$



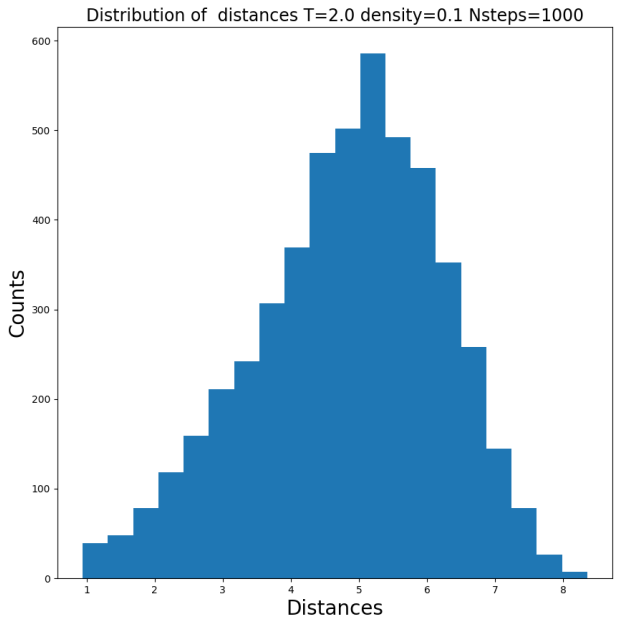
Momentum for
$\rho = 0.5, T = 2.0, Nstep = 1000$

Results-Distribution of Distances

The distribution of pair distances approximates the normal distribution. More clear when the Nstep and the time step increase.

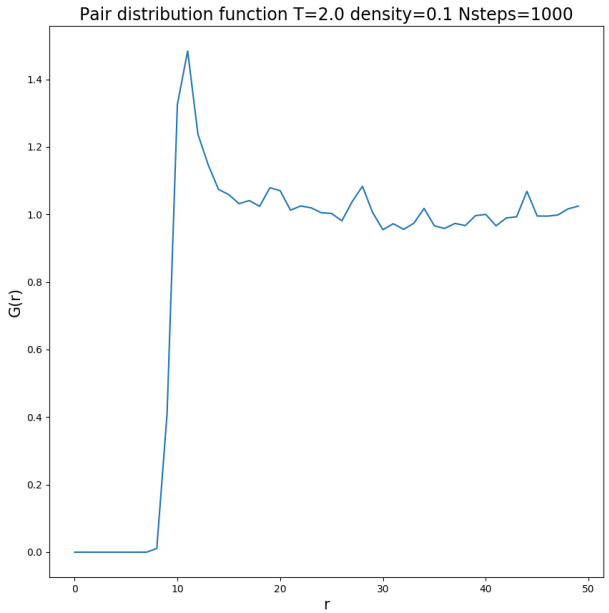


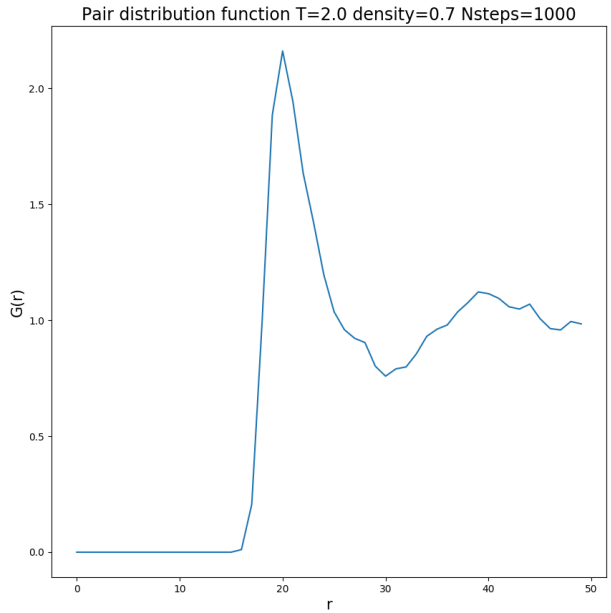
$\rho = 0.7, T = 0.5, dt = 0.0001, Nsteps = 10^3$



$\rho = 0.1, T = 2.0, dt = 0.0001, Nsteps = 10^4$

Results-Pair Distribution function $G(r)$





$\rho = 0.1, T = 2.0, Nstep = 1000$

- A radial distribution function of liquids.
- At short distances, $G(r) = 0$, due to the strong repulsive forces
- First peak: High probability of finding more molecules at this distance

$\rho = 0.7, T = 2.0, Nstep = 1000$

- $G(r) \approx 1$: the probability to find molecules is equal to zero
- Low density: fewer particles around the central particle

Conclusion

- Our system of liquid particles can reach the equilibrium state more quickly with larger time steps or more configurations.
- It works better though when we choose a larger time step and a small number of configurations, in order to reach the equilibrium state, because the results are already satisfactory in earlier time.
- The Hamiltonian of low density systems is more unstable, since these systems can not reach that well the equilibrium state.

Thank you all!