

Tutorial

6: Molecular Dynamics: Lennard-Jones liquid

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1 Velocity Verlet Integrator

In this section, the *Velocity Verlet* integrator is briefly reviewed.

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

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

In this method, the positions, velocities and accelerations can be calculated at the same time.

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1.1 Tasks

1. Read the code `vv.c` and understand it. In this program, only one particle is used, and the acceleration is set to be constant. In the next section, it will be extended into a real Lennard-Jones system.
2. Show that the *Verlet* and *Verlocity Verlet* algorithms lead to identical trajectories. The *Verlet* integrator is expressed as

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \Delta t^2 a(t) \quad (3)$$

The velocities don't explicitly appear in the *Verlet* integrator, which can be obtained in the following approach

$$v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{\Delta t} \quad (4)$$

Think about the advantage and drawbacks of *Verlet* integrator (compared with *Velocity Verlet* integrator).

2 MD Simulation on Lennard-Jones liquid

The Lennard-Jones (LJ) potential is written as

$$U^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (5)$$

where the parameters ϵ and σ define the interaction strength and the particle excluded volume. The r^{-6} is the attractive part in the Lennard-Jones potential, whereas the r^{-12} is the repulsive term.

From the potential, the **force** can be obtained (in the reduced units)

$$F_x = -\frac{dU^{LJ}(r)}{dr_x} = 48 \left(\frac{1}{r^{14}} - 0.5 \frac{1}{r^8} \right) r_x \quad (6)$$

where F_x , r_x are the x -components of the force and the distance.

The **pressure** is calculated via the virial theorem of Clausius, which states that the virial is equal to $-3Nk_B T$. The total virial for a real system has two contributions: the ideal gas part, $-3PV$, and the interaction between the particles. The later is defined as the sum of the products of the coordinates of the particles and the forces acting on them. Therefore,

$$P = \frac{1}{V} \left[Nk_B T + \frac{1}{3} \sum_{i=1}^{N-1} \sum_{j=i+1}^N (r_{ij} F_{ij}) \right] \quad (7)$$

The **temperature** is directly related to the kinetic energy of the system as follows:

$$U^{kinetic} = \sum_{i=1}^N \frac{m_i v_i^2}{2} = \frac{3N}{2} k_B T \quad (8)$$

where m_i , v_i are the mass and the velocity of particle i , N is the number of particles.

2.1 Static properties of LJ liquid

Besides the total energy, potential energy, kinetic energy, temperature and pressure, the **radial distribution function** (rdf) is calculate in the present tutorial,

$$g(r) = \frac{1}{\rho 4\pi r^2 dr} \sum_{ij} \langle \delta(r - |r_{ij}|) \rangle \quad (9)$$

where $\delta(x)$ is the function: $\delta(0) = 1$, and $\delta(x) = 0$ for $x \neq 0$.

The rdf is important for three reasons:

1. for pairwise additive potentials, knowledge of the rdf is sufficient information to calculate thermodynamic properties, particularly the energy and pressure.
2. there are very well developed integral-equation theories that permit estimation of the rdf for a given molecular model
3. the rdf can be measured experimentally, using neutron-scattering techniques.

2.2 Dynamic properties of LJ liquid

Two dynamic properties are studied in the present tutorial:

mean-square displacement (msd)

$$\Delta r^2 = \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \quad (10)$$

and **velocity autocorrelation function** (vacf)

$$C(t) = \langle v(0)v(t) \rangle \quad (11)$$

2.3 Tasks

1. ¹ Read the codes and understand *md.c*, *init.c*, *mdloop.c*, *integrate.c* and *force.c*. In the *integrate.c*, the *velocity verlet* integrator is absent. Add it in the appropriate position.

Notice that in the code the truncated and shifted potential is used (Why ?), that is,

$$U_{shifted}^{LJ}(r) = \begin{cases} U^{LJ}(r) - U^{LJ}(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases} \quad (12)$$

where $r_c = 2.5\sigma$ is used.

2. In this program, the average values and standard deviations of the total energy, potential, kinetic, temperature and pressure are given. The energies should be similar with Fig. 1.
3. Plot the *rdf.dat*. Look at radial distribution function.
4. Plot the *msd.dat*. Look at mean-square displacement.
5. Plot the *vacf.dat*. Look at velocity autocorrelation function. $C(0) \simeq ?$ Why?

¹D. Frenkel and B. Smit, *Understanding molecular simulations*, Molsim 2005

3 Links

3.1 Radial distribution function

- <http://www.ccr.buffalo.edu/etomica/app/modules/sites/Ljmd/Background1.html>
- <http://cbp.tnw.utwente.nl/PolymeerDictaat/node14.html>

3.2 Mean-square displacement

- <http://www.ccr.buffalo.edu/etomica/app/modules/sites/Ljmd/Background2.html>

3.3 Velocity autocorrelation function

- <http://www.compsoc.man.ac.uk/lucky/Democritus/Theory/vaf.html>

4 Related figures

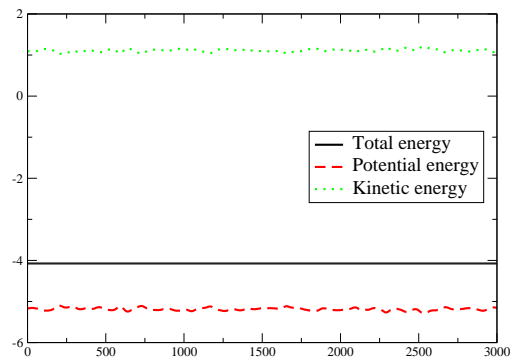


Figure 1: Total, potential and kinetic energy per particle as a function of the number of steps.

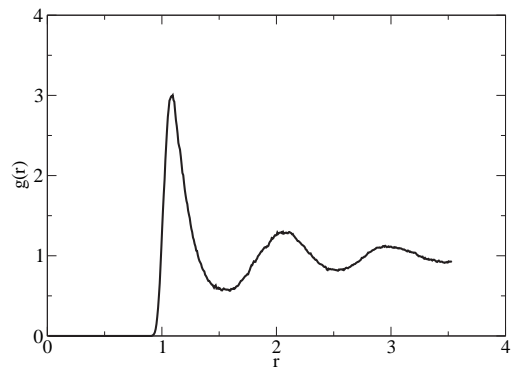


Figure 2: Radial distribution function.

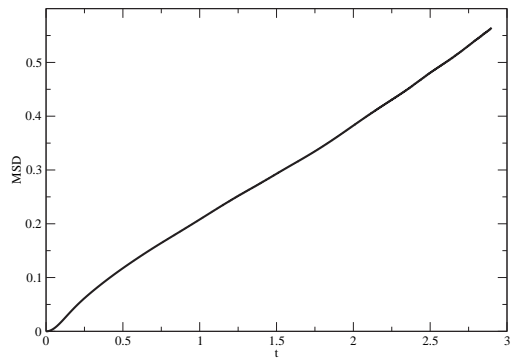


Figure 3: Mean-square displacement.

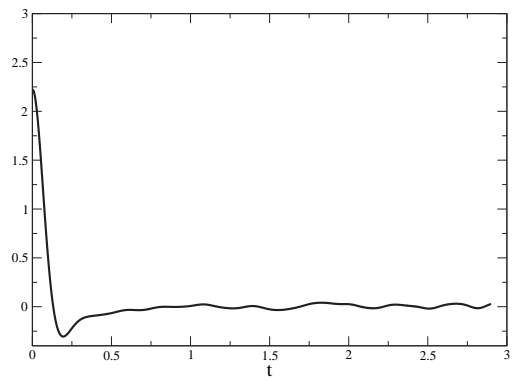


Figure 4: Velocity autocorrelation function.