Tutorial

6: Molecular Dynamics: Lennard-Jones liquid

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Contents

1 Velocity Verlet Integrator

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

$$r(t+\triangle t) = r(t) + \triangle t\, v(t) + \frac{1}{2}\triangle t^2\, a(t) \tag{1}$$

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

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 mathematically. The *Verlet* integrator is expressed as

$$r(t+\triangle t) = 2\,r(t) - r(t-\triangle t) + \triangle t^2\,a(t) \tag{3}$$

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

$$v(t) = \frac{r(t+\triangle t) - r(t-\triangle t)}{2\triangle t} \tag{4}$$

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 writen as

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

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)

$$F_x = -\frac{\mathrm{d}\,U^{LJ}(r)}{\mathrm{d}\,r_x} = 48\left(\frac{1}{r^{14}} - 0.5\frac{1}{r^{8}}\right)r_x \tag{6}$$

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

The **pressure** is calculated via the virial theorem of Clausius, which states that the virial is equal to -3Nk_BT. 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,

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

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

$$U^{kinetic} = \sum_{i=1}^{N}\frac{m_i v_i^2}{2} = \frac{3N}{2}k_BT \tag{8}$$

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,

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

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)

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

and **velocity autocorrelation function** (vacf)

$$C(t) = \langle v(0)v(t) \rangle \tag{11}$$

Both these two quantities are related with the self-diffusion coefficient.

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* integragtor is absent. Add it in the approciate position.

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

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

   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. Why the pressure fluctuates bigger than the other properties?

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

4. Plot the *rdf.dat*. Look at radial distribution function.

5. Plot the *msd.dat*. Look at mean-square displacement.

6. Plot the *vacf.dat*. Look at velocity autocorrelation function. $C(0) \simeq ?$ Why?

7. The force calculation is the slowest part of molecular dynamics simulations. In the present code, *force.c*, all particle pairs are searched, and the distances between them are calculated. Therefore, the CPU cost is very expensive, $O(N^2)$, i.e. very slow when $N \rightarrow \propto$. When the neighbour list method is included, it can be $O(N)$. See the following link about the neighbour list.

N	120	180	240	300	360	480	600
t							

Table 1: CPU time for varying number of particles, N.

3 Links

3.1 Truncated and shifted potential and long-range correction

- http://www.fisica.uniud.it/ ercolessi/md/md/node16.html

3.2 Radial distribution function

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

3.3 Mean-square displacement

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

3.4 Velocity autocorrelation function

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

3.5 Neighbour list

- http://beam.acclab.helsinki.fi/ knordlun/atomistiset/lecture3a.ps

4 Related figures

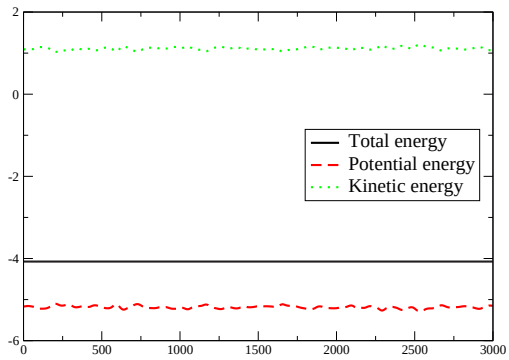

Figure 1: Total, potential and kinetic energy per particle as a function of the number of steps.

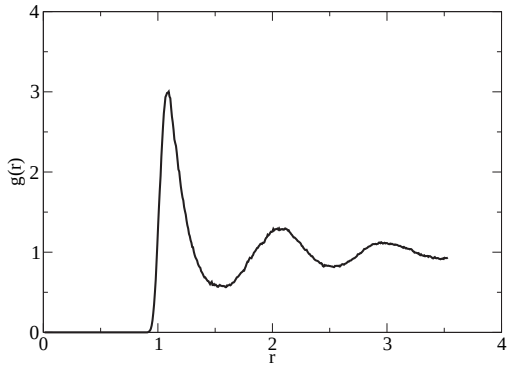

Figure 2: Radial distribution function.

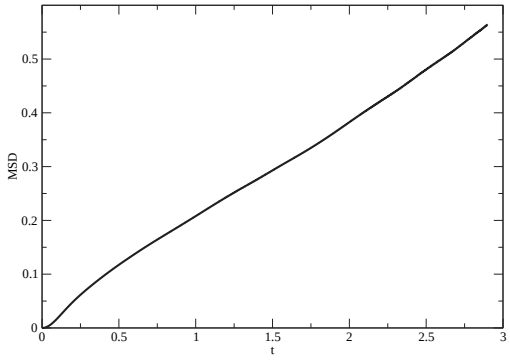

Figure 3: Mean-square displacement.

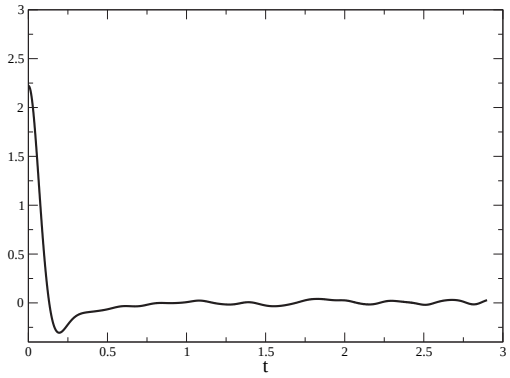

Figure 4: Velocity autocorrelation function.