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Simple Harmonic Oscillator Model of O_2 Molecule in Vacuum: A Classical Molecular Dynamics Study

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ABSTRACT

The simple harmonic oscillator model allows a basic understanding of all processes and can be used to analyse optical vibrational modes and electronic transitions in atoms, molecules and crystals, in order to derive general properties of harmonic generation to all orders. In particular, we are done to investigate single, ten, and twenty harmonic oscillator of O_2 molecule using GROMACS 4.55. Time is the important factor in simulation because the best result of simulation can be obtained by increasing the number of steps and by decreasing the timesteps. Since the properties only depend on time and not on the specific microscopic model, they can also be adopted for the quantum-mechanical description by using in the classical molecular dynamics.

Keywords: *classical molecular dynamics, harmonic oscillator, GROMACS*

Introduction

Computation and simulation are top role in modern science. They are bridge between theoretical and experimental methods to obtain data in science. The harmonic oscillator is extremely useful in chemistry as a model for the vibrational motion in a diatomic molecule (Guillaume L, 2003), (J. J. Rael et al, 2000) and (Charles B et al, 1990). The atoms are viewed as point masses which are connected by bonds which act approximately like springs obeying Hooke's law (Ugural, et al, 2003), (Keith., 1971) and (Simo, J. C, 1998). To get started with it, a simple model of bond vibration of diatomic molecule O_2 can be done. They are many approaches to investigate bond vibration (F. lachello, 1998), (Philip M, 2002) and (O. S. van Roosmalen., 1998). One of them is harmonic oscillator. Here, oxygen atom is a type to describe the atoms in the diatomic molecule. Two oxygen atoms are treated as a classical object which are connected by a spring. The ilustration and force formulation of Hooke's law of harmonic oscillator which working in the spring is in the equation 1 and Figure 1.

$$F = -k \triangle x \qquad (1)$$

Where F is the resulting force, x is the displacement of the mass from equilibrium ($x = r - r_q$) and k is the force constant.

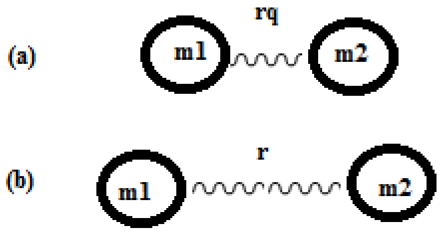

Figure 1. Ilustration of a simple harmonic oscillator

In this study, the series package is GROMACS 4.55. It used to gain the settings for classical force simulation. GROMACS is a molecular dynamics package to perform molecular dynamics simulations and energy minimization (Berk Hess et al, 2008). Molecular dynamics simulation is based in Newton's equations of motion (N. Goga et al, 2015). The simulations use classical mechanical descriptions of energy as a motion.

Methodology of Simulation

In single harmonic oscillator simulation, one molecule O_2 was put in a vacuum 3D box. The mass of an atom (m_O) was 16 amu. The distance at which the potential was minimum (b_0) was set to be 0.11 nm, the force constant that contribute to the vibration (k) was 500 kJ. mol $^{-1}$. nm^{-2}

In GROMACS, nuclei and electron are usually treated as an entities which is described by lennard-Jones potential as follows in equation 2,

$$U(r) = 4\,\varepsilon\,[\,(\sigma/r)^{12} - (\sigma/r)^{6}\,] \qquad (2)$$

ε is depth of potential well, σ is the finite distance at which the inter-particle potential is zero, and r is distance between two particles. (C6 1.0e-6, C12=1.0e-10). Molecular dynamics simulation will be performed with 10000 steps which 0.001 ps timesteps. The center of mass is not fixed in a certain coordinate to study the effect of vibration to translational motion. Periodic boundary condition is not applied. If it will be applied, the size of 3D box has to be increased to make sure that there is no interaction among O_2 molecule.

In weakly coupled harmonic oscillator simulation, two systems are investigated: 10 harmonic oscillators and 20 harmonic oscillators in constant volume. Ten oscillators are studied at constant energy and twenty oscillators are studied at constant energy and constant temperature (Berendsen thermal coupling). The simulation are performed using periodic boundary conditions in which models an infinite system and at constant density.

Results and Discussion

Single harmonic oscillator of O_2 molecule in vacuum

The energy can be regarded as vibrational energy only because rotational and translational motions do not occur. The data of potential energy, kinetic energy, total energy, average distance, and bond length of simulation are shown in Table 1.

Table 1. Calculation result of single harmonic oscillator O_2 molecule (time =10 ps)

Energy	Average	Error Estimate	RMSD	Tot-Drift (kJ/mol)
Potential	0.2011	9.8e-05	0.141613	0.00656422
Kinetic	0.1989	1.0e-05	0.141608	-0.00650921
Total	0.4000	1.1e-05	2.79793e-05	5.50065e-05

The motion motion O_2 molecule is periodic. Because the given force constant is quite high, and the period is quite small. Force constant is proportional to the total energy. The force constant is not the only parameter that affect the period. The other one is the mass of the atoms involved in the motion. The larger force constant applied, the larger total energy is showed in O_2 molecule.

The investigations are continued by the modification of timesteps to know the maximum timestep (algorithm is stable). The timesteps of 0.01ps is good to represent the energy and bond length average but the timesteps of 0.2 ps is bad to represent them because the average bond lenght differs and the standard deviation is high.

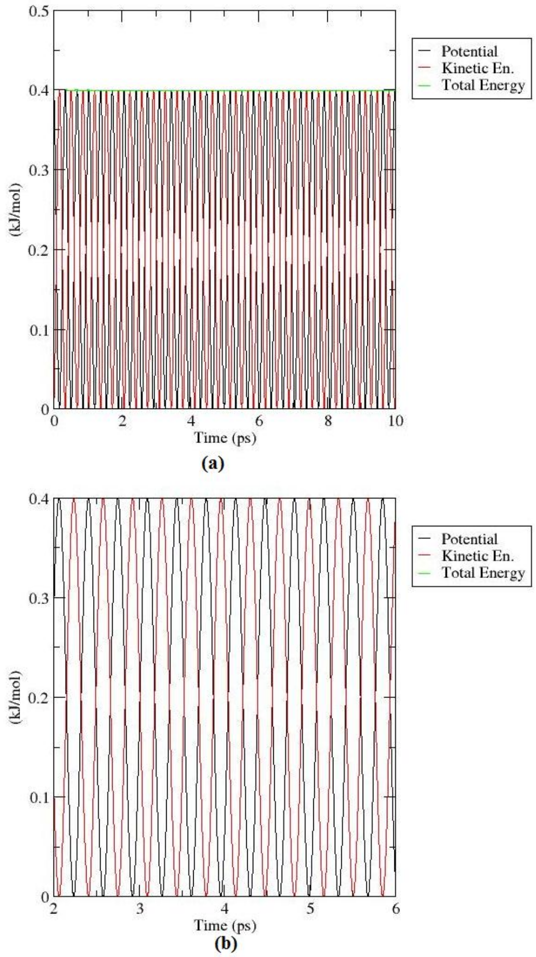

Figure 2. Potential, kinetic and total energy as a function of time (a) and at 2-6 ps (b)

Table 2. Calculation result of single harmonic oscillator O_2 molecule (time = 2-6 ps)

Energy	Average	Error Estimate	RMSD	Tot-Drift (kJ/mol)
Potential	0.20123	5.5e-05	0.141727	0.0151076
Kinetic	0.19877	6.2e-05	0.141722	-0.0015013
Total	0.40000	1.4e-05	3.0052e-05	9.46684e-05

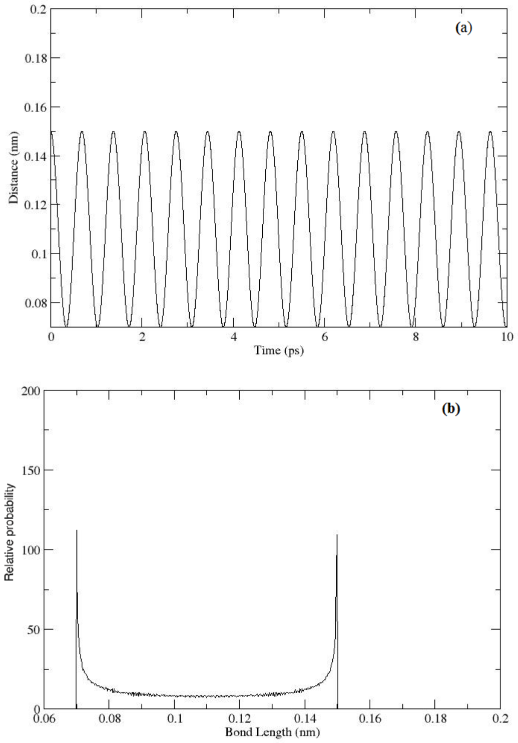

Figure 3. (a) Average distance of single harmonic oscillator of O_2 molecule, and (b) Distribution of harmonic bond distance as a function of bond length

In Figure 3 (a), there are 14.5 oscillators in 10 ps. The motion is periodic with frequency 1.26 . $10^{12}s^{-1}$. The result of simulation approaches the result of hand calculation as follow,

$v = 1/2\pi\sqrt{k/\mu} = 1/2\pi\sqrt{2k/m} = 1/2\pi \sqrt{2(0.8303\ Jm^{-2)} / 16. (1.66.\ 10^{-27}\ kg)} = 1.26.\ 10^{12}\ s^{-1}$

The other analysis with different time (2-6 ps) simulation is showed in Table 2 and Figure 2 (a).

In order to improve energy conservation by reducing time, the timestep try to be reduced but it makes a problem which is higher computational cost. In this experiment 0.001 ps is enough to represent the system and conservation energy that can be maintained. The result of reducing time-step can be seen in Table 3. Natural frequency is a function of force constant and mass of atom. Many variations of natural frequency can be made by manipulating force constant and mass atom.

Table 3. Total energy, average, error estimate, RMSD and Tot-Drift

time-steps	Average	Error Estimate	RMSD	Tot-Drift (kJ/mol)
0.001	0.400007	1.1e-05	2.79793e-05	5.50065e-05
0.0001	0.40004	2.6e-06	6.78162e-06	8.23066e-06
0.00001	0.400186	8.6e-06	0.000167623	-1.27036e-05

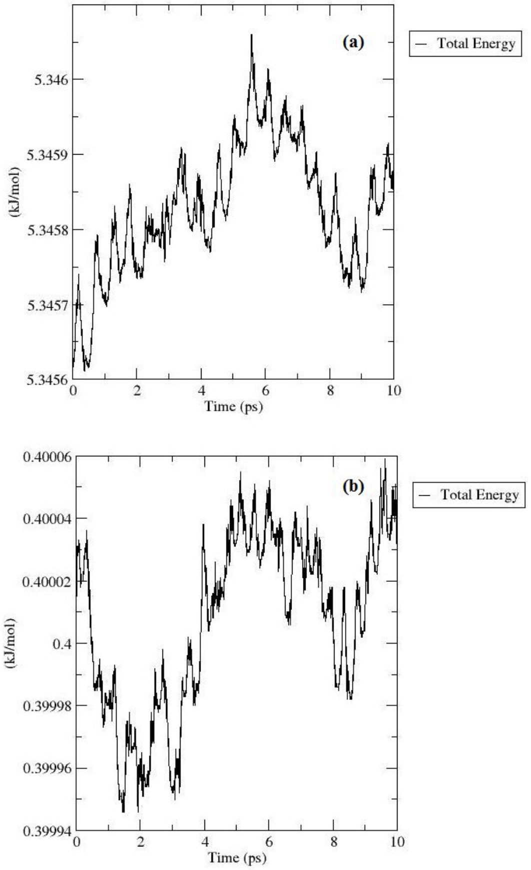

Figure 4. (a) Total energy as a function of time and (b) at velocity=0

The total energy is well conserved. There is a little noise which comes from numerical calculation error. It is shown in Figure 4 (a). that the energy does not drift. It fluctuated about a mean. In order to achieve highly accurate results, the improvement of the conservation energy is not by reducing in time step because the improvement is very small. The energy conservation is not influenced by the starting conditions. We can see from the total energy in Figure 4 (b). It shows that the trend in the tot-Drift does not respect the bond lenght at zero time. The effect of force constant can be seen in Table 4. It shows that the high force constant is also high in the average and tot-Drift energy. The effect of mass can be seen in Table 5. The mass affect the frequency but it does not have effect on the total energy nor on the drift.

Table 4. Total energy and total energy drift in different force constant

Mass (u)	Average	Tot-Drift
1	0.641259	0.00056722
4	0.646058	0.0132756
11	0.643103	0.00931154
22	0.641551	0.00465577

Variational of initial bond length ro change the total energy. The |ro-bo| considered as the amplitude of vibration.

Table 5. Total energy and total energy drift in different mass

Force constant ($kJ\ mol^{-1}\ nm^{-2}$)	Average	Tot-Drift (kJ/mol)
20	0.0160013	4.00047e-06
80	0.0640213	6.40074e-05
200	0.1600133	0.000399982
400	0.3205330	0.001599982
500	0.4008330	0.002499840
800	0.6421330	0.006399710

Figure 5. is the distribution of

harmonic bond distance as a function of bond lenght in difference of distribution and distance.

The result of single harmonic simulation shows that the graph does not look like Boltzman distribution, It is only vibration can occur and the atom spends more time in maximum and minimum bond length. The initial atomic coordinate play an important role because it determines the amplitude and energy of vibration but the frequency of vibration still the same.

Weakly coupled harmonic oscillator of O_2 molecule in vacuum

The distribution of harmonic bond length of ten and twenty harmonic oscillators at constant energy are given in Figure 6 (a) and (b). The distribution is actually the same between ten and twenty oscillators. Comparing Figure 6 (a) and (b) to distribution at single oscillator (Figure 2 b). It shows that they differ in the magnitute of the probability. The distribution of large system also shows that the peak of single oscillator is not the same with ten and twenty oscillator.

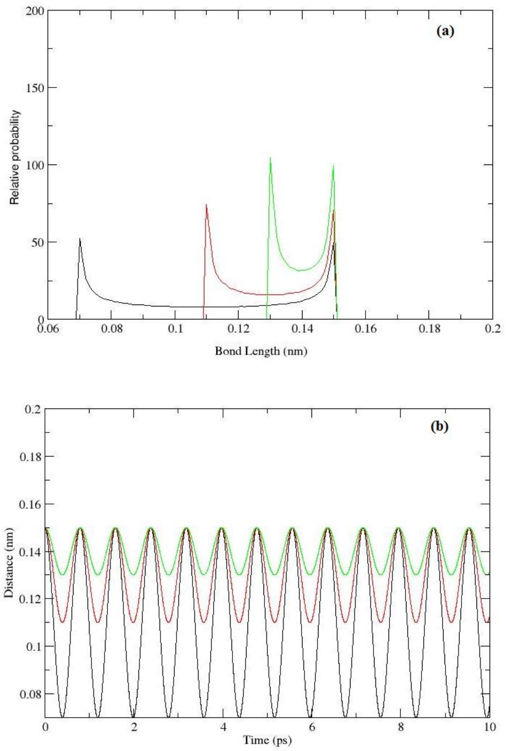

Figure 5.(a) Distribution at bond lenght 0.11 nm (black), 0.13 nm (red), 0.14 nm (green) as a function of bond distance, (b). Distance at bond lenght 0.11 nm (black), 0.13 nm (red), 0.14 nm (green) as a function of time (ps)

Based on this graph, there are many harmonic bonds lengths which have zero distribution. The distributions of larger systems also show peaks between the highest and lowest values of the distance and characteristic that is not showed by the single oscillator. Moving to observe the larger systems, from a first look we can note that the distribution relative at the 20 oscillators is more attened. Thus, the highest values of the probability are lower in the bigger system. Moreover, the 10 oscillators distribution show values of probability almost equal to 0 between peaks while the 20 oscillators one doesn't.

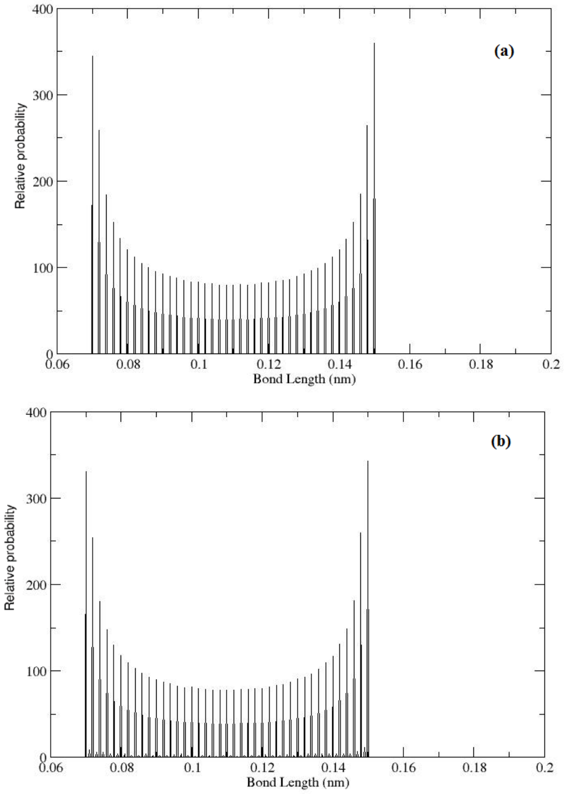

Figure 6. Distribution of ten (a) and twenty (b) harmonic oscillators as a function of bond lenght (nm)

The molecules will not collide each other because the translational and rotational motion do not influence too much. If the simulation is done in constant temperature, the energy comes in and out to the system to maintain the temperature become constant. When the simulation is done in 300K, the distribution will be different because translational and rotational motion are influence significantly. The molecule can collide each other and they transfer energy among them. The amount of energy transfer depend on intial momentum and orientation collision.

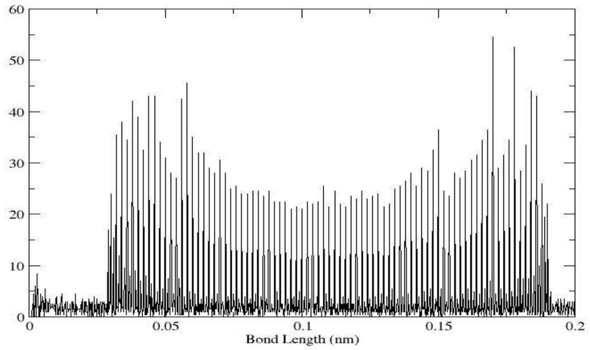

Figure 7. Distribution of twenty oscillators at constant temperature as a function of bond lenght (nm)

Figure 7 shows that the difference trend between the distribution of twenty oscillator system at constant energy and constant temperature is not much.

Focusing in Figure 6 b and 7 we can see the marked difference between the distributions obtained for the 20 oscillators system at constant energy (Figure 6 b) and at constant temperature (Figure 7). The latter distribution is even more attened than the first one; the entity of the highest values of the probability drops even lower if we keep constant the temperature.

Consequently there is a less pronounced dominant position of these highest values. It is also noted a greater quantity of peaks. We can say that there are less defined peaks.

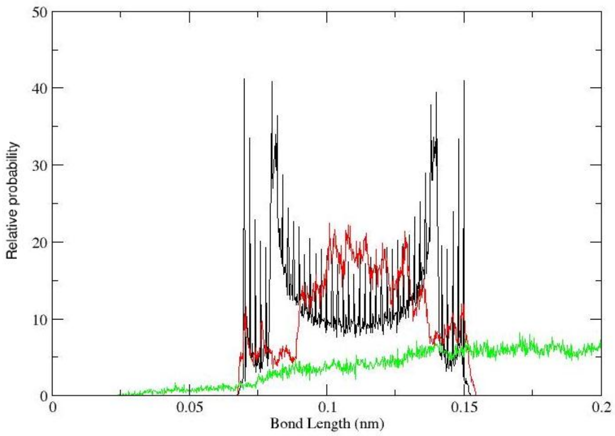

Figure 8. Distribution at 10 oscillator constant energy (black), 20 oscillator constant energy (red), 20 oscillator at constant temperature (green) as a function of bond distance.

The entities of the distribution at constant energy are higher than the distribution of the constant temperature. The distribution simulation at constant energy spreaded in small region compare to the energy distribution of simulation with constant temperature. If the simulation continue until 100 ns, the distribution will look like a Boltzman distribution and it will confirm a Maxwell-Boltzman distribution (Kevin J, 2018) . These is caused by the higher number of energy exchanges that the oscillators can do in a wider period of time. If the period of the simulation could be infinity, we will get a perfect Gaussian representing the Boltzmann distribution. The comparison between simulation with constant energy and constant temperature at 10 ns is in Figure 8.

Conclusion

Single, ten, and twenty oscillators have been finished to investigate. Time is the important factor in simulation because the best result of simulation can be obtained by increasing the number of steps and by decreasing the timestep. but it need higher computational cost. A simulation experts will use an optimum number of steps and timesteps so they can obtain an excellent data with minimum computational cost.

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