

# **Molecular Dynamics Vision**

**Version 1.0, Build 0506**

**User Manual**

**March 2003**

# 1. Introduction

Since the development of computers, molecular simulation techniques have been developed rapidly to study thermodynamics, transport properties and phase behaviour of various molecules in a system. In general, there are two types of molecular simulations: Molecular Dynamics and Monte Carlo simulations. In Molecular Dynamics simulations, interaction energies among particles are calculated and are resolved into forces acting on each particle, which gives a change in its velocity and position. On the other hand, Monte Carlo simulations are done by calculation of probability of a particular state by putting particles in a random position. When a large number of positions are tested, we could obtain a structure of particle arrangement that gives a lowest energy state. Both simulation methods give rise to an equilibrium state of a system (provided that we do not apply an external biased force to the system) where we can obtain some thermodynamic data such as temperature and heat capacity.

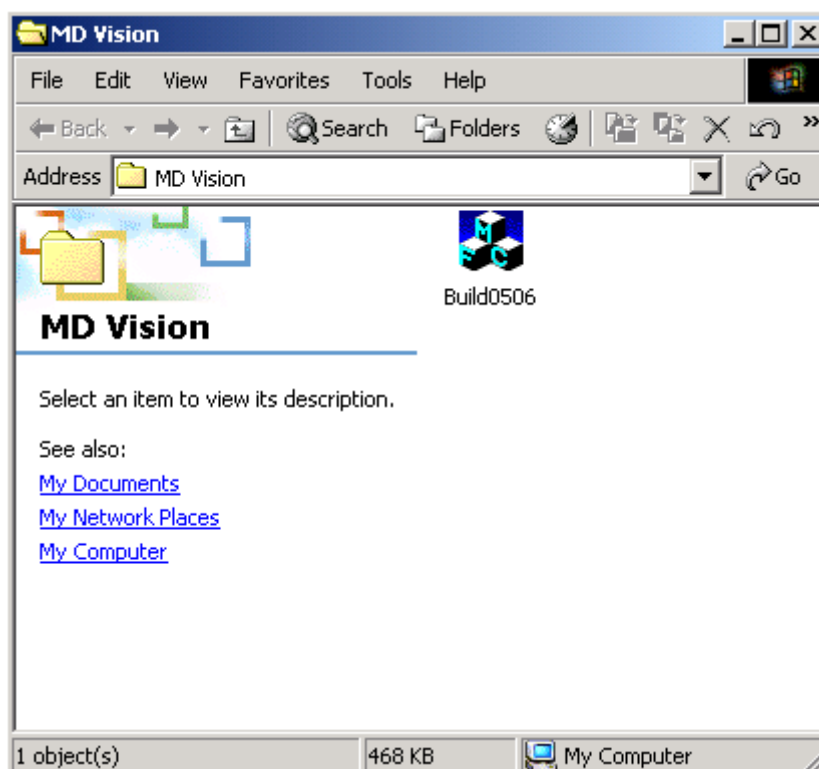
The study of classical thermodynamics and statistical mechanics usually involves complicated equations of algebra and calculus. Although in most of the time, the mathematical expressions could be explained by some equivalent physical meanings, such explanations are quite vague and abstract. In the study of statistical mechanics, the Boltzmann distribution gives information about the most probable state of energy of a system. However, we always find it difficult to relate the physical properties of an individual particle to macroscopic properties of the whole system, such as kinetic energy, by just looking the equations. Since it is not easy to study the principles of the physical quantities by just understanding numerous equations, we need a visualization program that can show the structure and movement of individual particles during the simulation process as well as the average thermodynamics data of the ensemble.

Real-time monitoring the process of molecular simulations becomes possible nowadays with the advancement of sophisticated personal computers equipped with high speed central processing units (CPU) and graphical acceleration video display cards. With a visualization software, we are able to observe some movement and diffusion of particles and compare the effect of temperature, pressure, and density to the physical behaviour of particles (just as the kinetic theories we were taught to explain the physical properties of a system in secondary school). We can also see how the properties of particles change during a phase transition (e.g. from a solid state to a liquid state) and know the meaning of an increase in entropy when a mixture of two regular packed particles move randomly, results in a chaotic state. The aim of this visualization program is to show the real-time movement of particles in a system during the Molecular Dynamics simulations and try to get a pictorial idea of thermodynamic and transport properties of the system under different physical conditions and phases. In the following chapters, the operation of the program and related principles in thermodynamics will be explained in details.

## 2. Using the Program

Before learning all the stuff of molecular simulations, we should get familiar with the visualization program by learning at least some of the buttons and meanings of parameters in the program. This chapter is aimed at providing information on how to start the program.

The current version of visualization program is **Build0506.exe**. Once you have got the program, you should put it into a new folder (Fig. 2-1). It is recommended that you start every new set of simulation in a new folder because some output files will be generated once the simulation has completed.



**Figure 2-1.** To run the visualization program, double click the program in the folder.

When you open the program (Fig. 2-2), you will see a window consists of three panels: The toolbar at the top, the visualization panel on the left and parameter panel on the right. The parameters and the effects of choosing different options will be explained below.

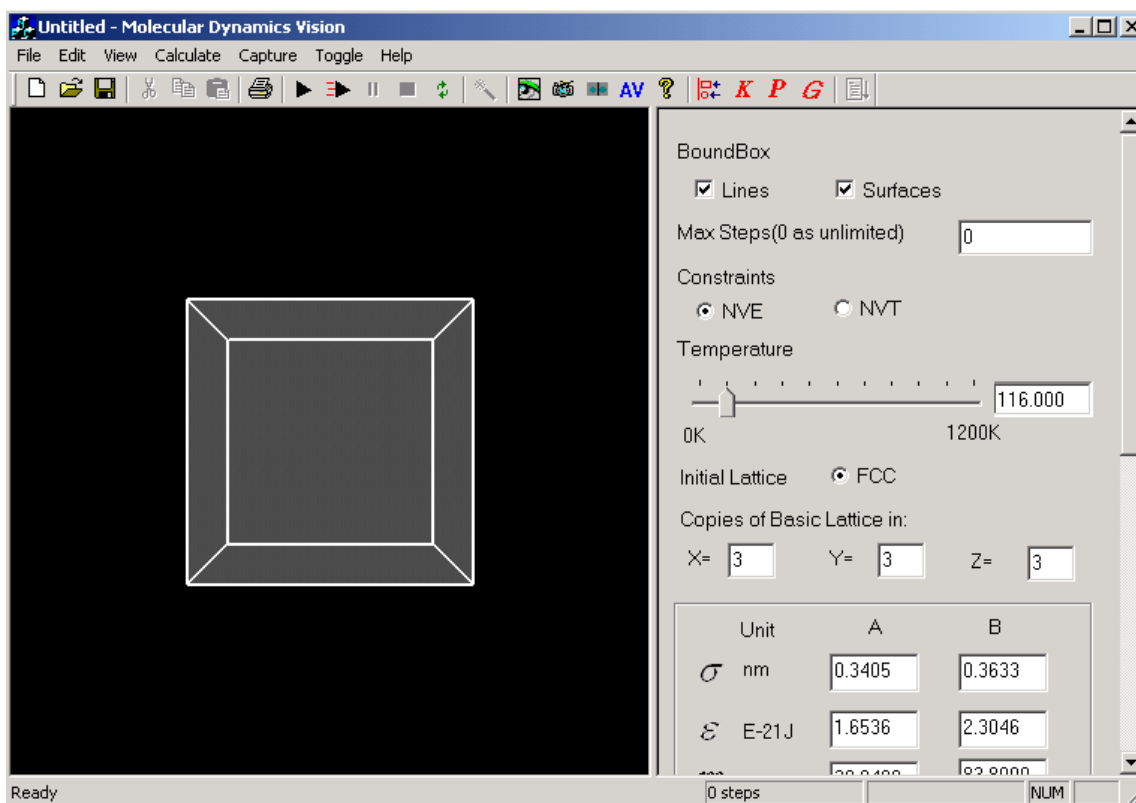


Figure 2-2. Main program.

## 2.1 Parameter and Setup Panel

The parameter panel is shown in Figure 2-3 and it is used for setting different physical conditions of the system as well as visualization effect of the animation appears in the left panel. The settings are described below and the physical principles of some parameters will be explained.

**BoundBox** – You should check the “Lines” box in order to show the boundaries of the simulation cell in the visualization panel. If you check the “Surface” box, you will see the surface boundary of the cell turns semi-transparent. Particles leaving or entering the box can be seen more clearly using this option.

**Max Steps** – You may enter a number in the box in order to set the number of time steps the simulation should run. In each simulation steps in Molecular Dynamics (MD) simulations, the forces acting on each particle are calculated and their velocities and new positions are solved using the Verlet algorithm. Instead of assigning a particular time step, you can enter “0” so that the simulation runs continuously. You can see how many time steps have been run in the status bar.

**Constraints** – You can choose either Microcanonical (NVE) or Canonical (NVT) ensemble for the simulation. If you choose the “NVE” option, total energy of the system will be kept constant during the simulation. If you choose “NVT”, temperature of the system will be kept constant by the help of a temperature rescaling technique.

**Temperature** – You have to choose an initial temperature by scrolling the bar to an appropriate value, or enter the value in the box at far right. During the simulation, you can change the values of temperature and observe the change in the speed of movement of particles as well as thermodynamic data.

**Initial Lattice** – The default initial state of the system is a face-centred cubic (FCC) structure.

**Copies of Basic Lattice** – A basic lattice in the simulation is a box filled with 4 particles arranged tetrahedrally. If you set the copies of the cell in x, y, z direction to, for examples, 2, the cell will duplicate in all directions and there will be  $4 \times 2 \times 2 \times 2 = 32$  particles in the system. You can enter a number from 1 to 5 in each box but the numbers entered must be the same for each direction.

### Molecular Parameters of a Binary LJ Mixture

Under the “Copies of Basic Lattice” section, there is a frame which contains some parameters for the particles. The program is designed for a mixture of 2 types of particles. Therefore 2 sets of parameters for species A and B can be assigned separately. There are 3 columns inside the box. The first column is the physical names and units. The second and third columns contain some boxes for the input of values for the 2 species.

**Size of Particles ( $\sigma$ )** – The first row in the frame is the size of particles in the unit of  $10^{-9}$  (nano) meter. The interaction among particles is calculated by the Lennard-Jones potential:

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

where  $\epsilon$  is the depth of the potential well and  $\sigma$  is the distance at which the function has its minimum interaction potential (Fig. 2-5). The Lennard-Jones (LJ) potential is a common way to calculate interaction between 2 particles and gives accurate results compared with

BoundBox  
 Lines       Surfaces  
 Max Steps(0 as unlimited)   
 Constraints  
 NVE       NVT  
 Temperature  
 0K  1200K   
 Initial Lattice       FCC  
 Copies of Basic Lattice in:  
 X=       Y=       Z=

Unit	A	B
$\sigma$ nm	<input type="text" value="0.3919"/>	<input type="text" value="0.3654"/>
$\epsilon$ E-21J	<input type="text" value="1.2680"/>	<input type="text" value="1.5642"/>
$m$ a.m.u.	<input type="text" value="28"/>	<input type="text" value="32"/>
$\rho^* \rho\sigma^3$	<input type="text" value="0.0013"/>	<input type="text" value="0.0003"/>
Num	<input type="text" value="84"/>	<input type="text" value="24"/>
Color	<input type="color" value="red"/>	<input type="color" value="green"/>
Arrangement	<input type="radio"/> Regular	<input checked="" type="radio"/> Random

Cut Off   $\sigma_{AA}$   
 Time Step   $\sigma_{AA} (m/\epsilon_{AA})^{1/2}$   
 Steps Every Frame  
   
 Display Speed(Frame/Second):

**Figure 2-3.** The parameter panel.

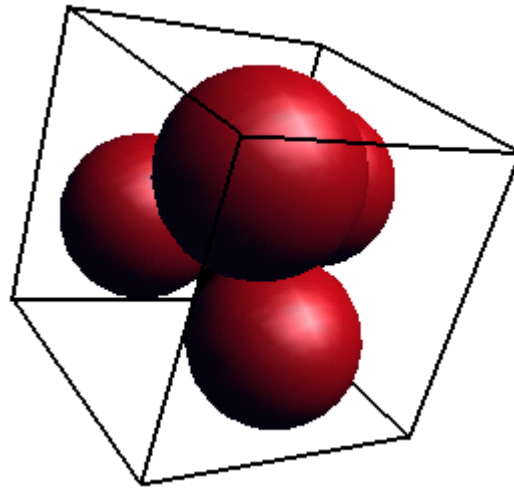
experimental data in the simulations of monoatomic particles. Some of the LJ parameters for different molecules are listed in Table 2-1.

**Lennard-Jones Paramter ( $\epsilon$ )** – Depth of the potential well in LJ function. The unit in the input box is in  $10^{-21}$  J per particle.

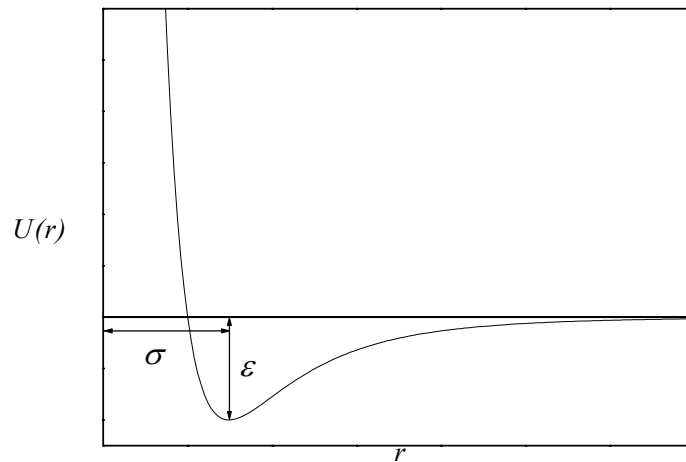
**Mass of Particles ( $m$ )** – Mass of particles in terms of atomic mass unit (a.m.u.)

**Table 2-1.** Lennard-Jones (12,6) potential parameters (Source: F. Cuadros, I. Cachadiña and W. Ahamuda, *Molec. Engineering*, **6**, 319 (1996).)

	$(\epsilon/k)/K$	$\sigma/10^{-9}$ m
Ar	111.84	0.3623
CCl <sub>4</sub>	378.86	0.6241
Cl <sub>2</sub>	296.27	0.4485
CO <sub>2</sub>	201.71	0.4444
F <sub>2</sub>	104.29	0.3571
Kr	154.87	0.3895
N <sub>2</sub>	91.85	0.3919
O <sub>2</sub>	113.27	0.3654
Xe	213.96	0.4260



**Figure 2-4.** A unit cell of the simulation



**Figure 2-5.** Lennard-Jones function with parameters.

In molecular simulations, the particle number in a system is less than 1000 and the number is small compared with the Avogadro constant ( $N_A = 6.022 \times 10^{23}$ ). If real units such as metre are used, the data generating from the model will be in a very small scale and not convenient for interpretation and comparison. Therefore the parameters in the simulations are usually expressed in a dimensionless unit and do not have a high order of power. In the simulations, the

physical quantities are reduced by the above 3 parameters or the combination of them. For examples the internal energy of a particle ( $U$ ) is reduced by the LJ parameter ( $\varepsilon$ ),

$$U^* = \frac{U}{\varepsilon}$$

so a value of  $-5.0$  in the simulation is equivalent to  $-5.0 \times 1.6544 \times 10^{-21} = -8.27 \times 10^{-21}$  J per molecule in real units. The parameters of density, cut off and time steps are expressed in reduced units and their relationship with the real units will be shown below.

**Reduced Density ( $\rho^*$ )** – The reduced number density of a system is defined by number of particles ( $N$ ) in the system in a unit volume of box ( $V$ ) and is related to the density of the model in real units by

$$\rho^* = \frac{N}{V^*} = \frac{N\sigma^3}{V} = \rho\sigma^3$$

In the equation, the symbols with an asterisk (\*) are reduced units. Note that the number density is different from the density in  $\text{kg m}^{-3}$  we normally use. In order to convert, say, density of water from  $1000 \text{ kg m}^{-3}$  to reduced unit of number density, we need to first divided the value by the mass of one mole of water. That is

$$\begin{aligned} \rho &= \frac{1000 \text{ kg m}^{-3}}{0.018 \text{ kg}} = 55556 \text{ mol m}^{-3} \\ &= 55556 \text{ mol m}^{-3} \times 6.022 \times 10^{23} = 3.3456 \times 10^{28} \text{ molecules m}^{-3} \end{aligned}$$

Assuming that the size of a water molecule to be  $3.17 \times 10^{-10} \text{ m}$

$$\rho^* = \rho\sigma^3 = 3.3456 \times 10^{28} \times (3.17 \times 10^{-10})^3 = 1.066$$

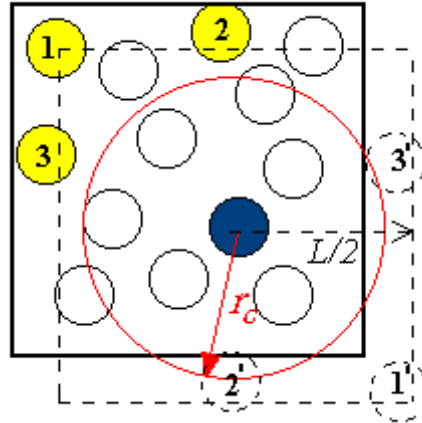
Therefore the reduced number density is 1.066.

**Number of Particles** – The number of particles in the box is automatically set when you set the number of repeating cell in x, y, z directions. However, you can set the number of particles in each species. If you want to perform a simulation of single species, you should set the number of particles and reduced density in B to be 0.

**Arrangement of Structure** – It determines the initial structure of the molecules. There are 2 options in the “Arrangement” section: Regular or Random. If you choose the “regular” option, the initial structure will be face-centred cubic.

**Cut Off** – A periodic boundary condition is applied to a finite number of particles to represent an infinite bulk system. The simulation cell is repeated in all 3 dimensions. Practically it is impossible to calculate the interactions between one particle and the infinite number of images as a result of periodic boundary condition. The interactions of particles far away from the central atom are small, and it is very time consuming to calculate such interactions. In order to effectively calculate the interaction of a particle, a potential cut-off is used. The principle of a potential cut-off is shown in Figure 2-6. For a given particle (blue in colour), only interactions with other particles in the box half the box length measured from its centre are considered. So its interactions with the image particles 1' to 3' are also considered but those with the real particles 1, 2, and 3 (yellow) are ignored. The red circle encloses the cut-off region where the particles outside the region do not have any

interactions with the centre particle (blue). The cut-off distance ( $r_c$ ) of LJ potential must not be larger than half the length of simulation box ( $L$ ) because a large value of  $r_c$  would lead to a repeat calculation of interaction potentials with particles created by image conversion. The cut-off distance is reduced by the size of particle A in this visualization program.



**Figure 2-6.** Periodic boundary conditions and potential cut-off.

**Time Step** – In Verlet algorithm, the position of a particle ( $r$ ) at time  $t + \delta t$  takes the form

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

where  $v(t)$  and  $a(t)$  are velocity and acceleration of the particle at the time  $\delta t$  before. From the equation it is clear that we need to specify a time interval value for solving the position of particles, and that's why we need to define the magnitude of a time step. In the program, the time step is expressed in reduced unit ( $t^*$ ) and it is related to real time interval ( $t$ ) by

$$t^* = t \cdot \frac{1}{\sigma} \sqrt{\frac{\varepsilon}{m}}$$

where  $\sigma$  is the size of particle,  $\varepsilon$  is the LJ parameter and  $m$  is the mass of a particle. For examples, given that  $\sigma = 0.3405$  nm,  $m = 6.63 \times 10^{-26}$  kg,  $\varepsilon = 1.65 \times 10^{-21}$  J for Argon, a time step of 1 nano-second means a reduced unit of 463.

During the simulation, the number of time step performed is shown in the right hand side of the bottom information bar.


**Steps Every Frame** – Adjust the number of steps of simulation runs before displaying the configuration in the visualization panel and recording the thermodynamic data.

**Display Speed** – Adjust the number of frames displayed per second for the animation.





## 2.2 The Toolbar


The buttons in the toolbars are located just below the menu bar. Some of them are important functions during the simulation process while some of them are redundant. The useful buttons are listed below.


**New**  – Open a new project.


**Open**  – Open a saved file and continue a previously stopped simulation.


**Save**  – Save the present configuration. The positions and velocities of the particles are saved in a file with the “.sta” extension.


**Start Simulation**  – Once you input the correct parameters in the parameter panel, you can press the “Play” button to start the simulation. You will see particles in the box moving in the visualization panel.


**Start Simulation (without visualization)**  – You can start the simulation without showing the animation. This option will speed up the simulation of long runs. If you run the program in this way, you must first set the maximum steps.


**Pause**  – You can stop a simulation temporarily by pressing the “Pause” button. You can resume the simulation by pressing the “Play” button, or “Play without visualization” button if you have input a maximum simulation steps.


**Stop**  – The simulation would end immediately if you press the stop button. Once the simulation is stopped, data of kinetic energy, potential energy, pressure, pair distribution functions and the current configuration will be saved individually in 5 separate files. The files are saved in the same folder where the program is located.

**Reset**  – The reset button reset the simulation cell in the visualization panel to its initial configuration. It does not change the particles’ information.


**Highlight a Particle**  – Pressing the “Pick up a Ball” button will change the cursor to a wizard stick, which you can select any particle in the simulation cell and change its colour. The function is very useful if you want to trace the motion of a particular particle during the simulation.


**Capture Current Status**  – Press this button to save the current configuration in a “.sta” file.


**Capture Current Bitmap**  – Save the snapshot of the simulation you see in the screen to a bitmap (.bmp) file.

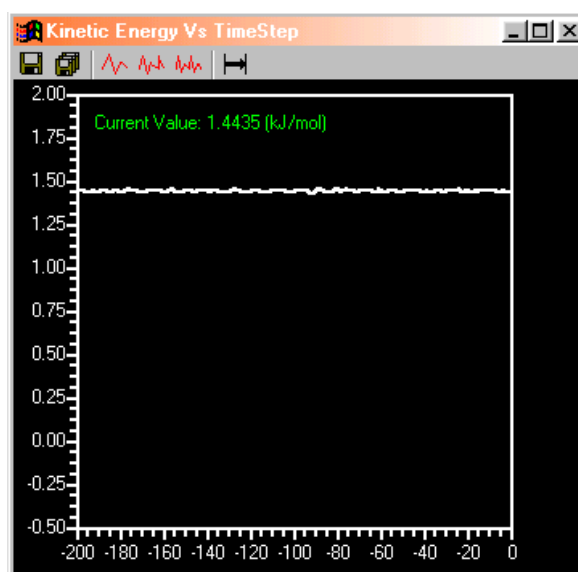
**Record the Simulation**  – You can record the simulation process by pressing “Record the simulation” button. The process is saved in the “.rec” format and can only be read by this program. If you want to view the simulation in progress using other software, use “Record as avi” button instead.

**Record the Simulation as avi File**  – Start saving the simulation process as a movie in “.avi” format.

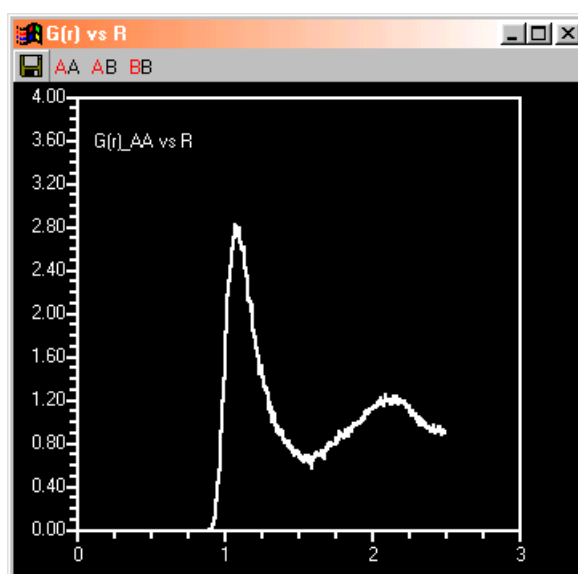
**Time Record of Thermodynamic Data**  – Pressing the 3 buttons will trigger 3 new windows showing the plots of pressure versus time, kinetic energy versus time and potential energy versus time (Fig. 2-7).

**Pair Distribution Functions**  – The pair distribution function  $g(r)$  gives the probability of finding a pair of atoms a distance  $r$  apart, relative to the probability expected for a completely random distribution at the same density. You will see a window showing the function (Fig. 2-8) when you press the “G” button. The distribution is updated and displayed continuously as simulation proceeds.

**Results**  – Pressing the button shows some general information of the simulation in progress such as temperature, volume and time steps of the system as well as parameters of the molecules.






**Figure 2-7.** A window showing plots of kinetic energy of the system as a function of timestep.




**Figure 2-8.** A window showing a plot of pair distribution function.


## Guide for Windows Showing the Plots


In the windows showing the plots of thermodynamics data, there are a few buttons which help in monitoring the change more efficiently.




**Save Plot**   – In the plots of Pressure/ KE/ PE against time step, there are 2 save buttons. Only the second one “Save all plots”  works. This button saves the data points into a text file from the start of the simulation till the instance you press the button. Note that at the end of the simulation, all the data points will be saved automatically.

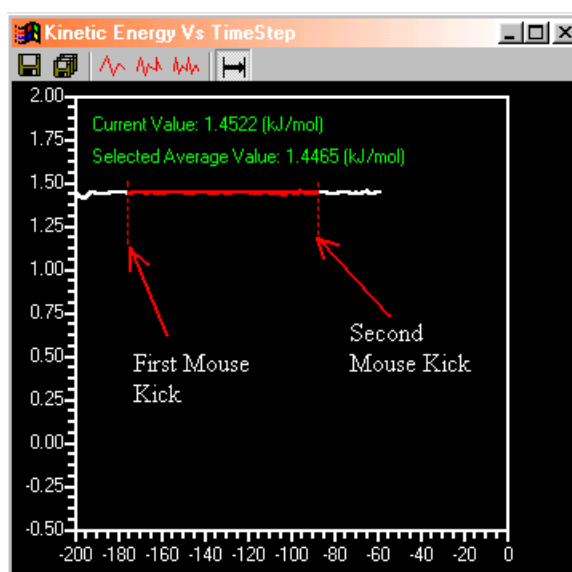
In the saved file of KE versus time, standard deviation of kinetic energy of particles at each step is calculated in the third column.

**Change Time Scale**  – Change the scale in the time step axis. The 3 buttons change the scale to 100, 200 and 400 steps respectively.

**Enable Selection**  – When you press the “Enable selection” button, you can calculate the average value of the thermodynamics data of certain region in the graph. To calculate the average value in a selected region, make one click by the mouse on the left side of the graph and a second one on the right (Fig. 2-9). The interval between the mouse click will be highlighted in red and the average value of the selected region will be shown on the graph. The function is useful to start accumulating data for averages after equilibration.

**Save G(r) Plot**  – In the  $g(r)$  versus time step plot, the “Save” button saves the current function.

**Change G(r) Functions**    – The 3 buttons allow you to change to view different pair distribution functions of: 2 type A particles (AA), between type A and type B particles (AB) or 2 type B particles (BB).



**Figure 2-9.** Select a region of graph to show its average value by two mouse clicks.

## 2.3 The Visualization Control Panel

The visualization panel is located on the left hand side of the program and it shows the ‘real’ time movement of molecules in a cubic box. The ‘real’ time means display as produced by simulations. When you have specified certain parameters and input to the simulation and click the “Start” button in the toolbar, you will see the particles moving in the box. You can control the perspectives of the simulation box with the help of a mouse and the keyboard. The “Bound Box” and “Display Speed” section in the parameter panel are used to set the display in visualization panel and were explained in Section 2.1. Other function keys are listed below.

Action	Effect in Simulation Box
Press the left mouse button and move forwards/ backwards	Box rotate along horizontal axis
Press the left mouse button and move it left/ right	Box rotate along vertical axis
With the ‘Ctrl’ key in keyboard pressed, press the left mouse button and move forwards/ backwards	The box moves up/ down
With the ‘Ctrl’ key in keyboard pressed, press the left mouse button and move it left/ right	The box moves left/ right
‘↑’ key in keyboard/ scroll backwards in mouse	Zoom out, camera position changes
‘↓’ key in keyboard/ scroll forwards in mouse	Zoom in, camera position changes
‘→’ key in keyboard/ Press ‘Ctrl’ key + scroll backwards in mouse	Zoom out, camera position does not change
‘←’ key in keyboard/ Press ‘Ctrl’ key + scroll forwards in mouse	Zoom in, camera position does not change

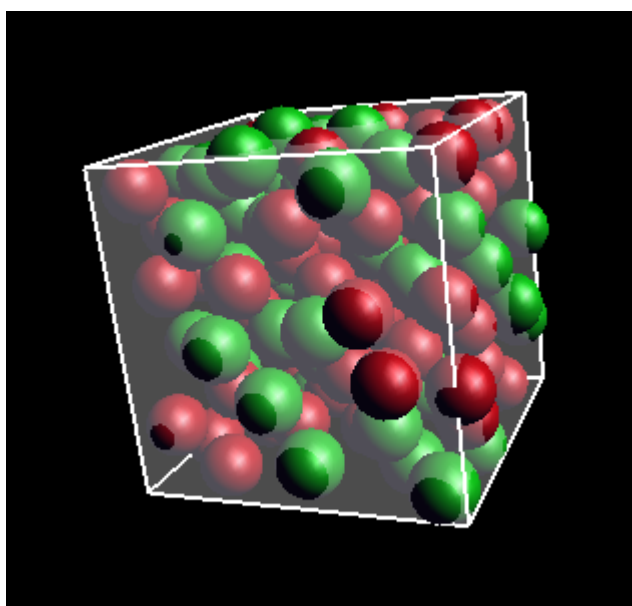


Figure 2-10. Visualization panel at the start of a simulation.

### 3. An Example of How to Perform a Simulation

This chapter will show you how to run a simulation using Molecular Vision program. All the necessary actions result in getting the simulation done will be illustrated by an example.

Suppose you are going to perform a simulation about properties of air at room temperature. You can setup a model consists of nitrogen and oxygen molecules. First you need to gather information about the property of air (nitrogen and oxygen).

Physical quantity	Air	Nitrogen (N <sub>2</sub> )	Oxygen (O <sub>2</sub> )	Others
Composition in Air by mole (%)	100	78.084	20.947	0.969
Molar Mass (g mol <sup>-1</sup> )	28.96	28	32	---
Density (kg m <sup>-3</sup> )	1.2929*	---	---	---

\* The value is density of dry air at sea level

The value of mass density is converted to number density in reduced unit with a value 0.001618. Assuming that the partial pressures of nitrogen and oxygen are proportional to their mole ratio, the reduced densities of the 2 gases are 0.0013 and 0.0003 respectively. Using the values of LJ parameters in Table 2-1, we obtain the values of  $\varepsilon$  and  $\sigma$  for nitrogen and oxygen. The value of  $\varepsilon$  is expressed in the form of  $\varepsilon/k$  and you need to multiple the value by Boltzmann constant in order to obtain the value in units of Joule. For a cell of 108 molecules, the ratio of number of particles in N<sub>2</sub> and O<sub>2</sub> are 84:24.

The reduced volume of the gas equals to number of particles in the cell divided by reduced density. That is  $108/0.001618 = 66750$ . The length of the box is calculated by taken cubic root and is equal to 40. Therefore in the simulation of gas, the potential cut-off can be as large as  $20\sigma$ . In simulation of higher density of model, however, we need to set a smaller value of potential cut-off. The time step is chosen to be  $1 \times 10^{-14}$  s. Reducing the value by the mass and LJ parameters of nitrogen we get a reduced time step of 0.004214. Putting all the data into the parameter panel (Fig. 2-3) and assign the program to run for 100,000 steps, we can press the “Play” button to start the simulation and watch the animation in the visualization panel (Fig. 3-1). Alternatively, we can press the “Start without visualization” button to just run the program and get the result. During the simulation, you can open the plot windows to see the variation of thermodynamics data (Fig. 3-2). When you increase the temperature during the simulation, you should see the molecules in the box speed up and kinetic energy of the system increase.

When the simulation is finished, you can see the output of thermodynamics data in the same folder as where the program is located (Fig. 3-3). The status of the simulation is saved in the “Status1.sta” file which you can open it at any time in the future to continue the simulation. The text files show the data every  $N$  steps you have specified in the “Steps Every Frame” column in the parameter panel. The values of potential and kinetic energies are expressed in kJ per mole and values of pressure are expressed in  $10^6$  Pa. In this simulation, the values for KE, PE and pressure are  $3.718 \pm 0.001$  kJ mol<sup>-1</sup>,  $-0.005 \pm 0.005$  kJ mol<sup>-1</sup> and  $(0.82 \pm 0.01) \times 10^5$  Pa respectively. The potential energy of the system is very low and it means it is similar to an ideal gas state. The pressure is lower than the literature value by 20% because in real gas, there exists moisture and other types of gases.

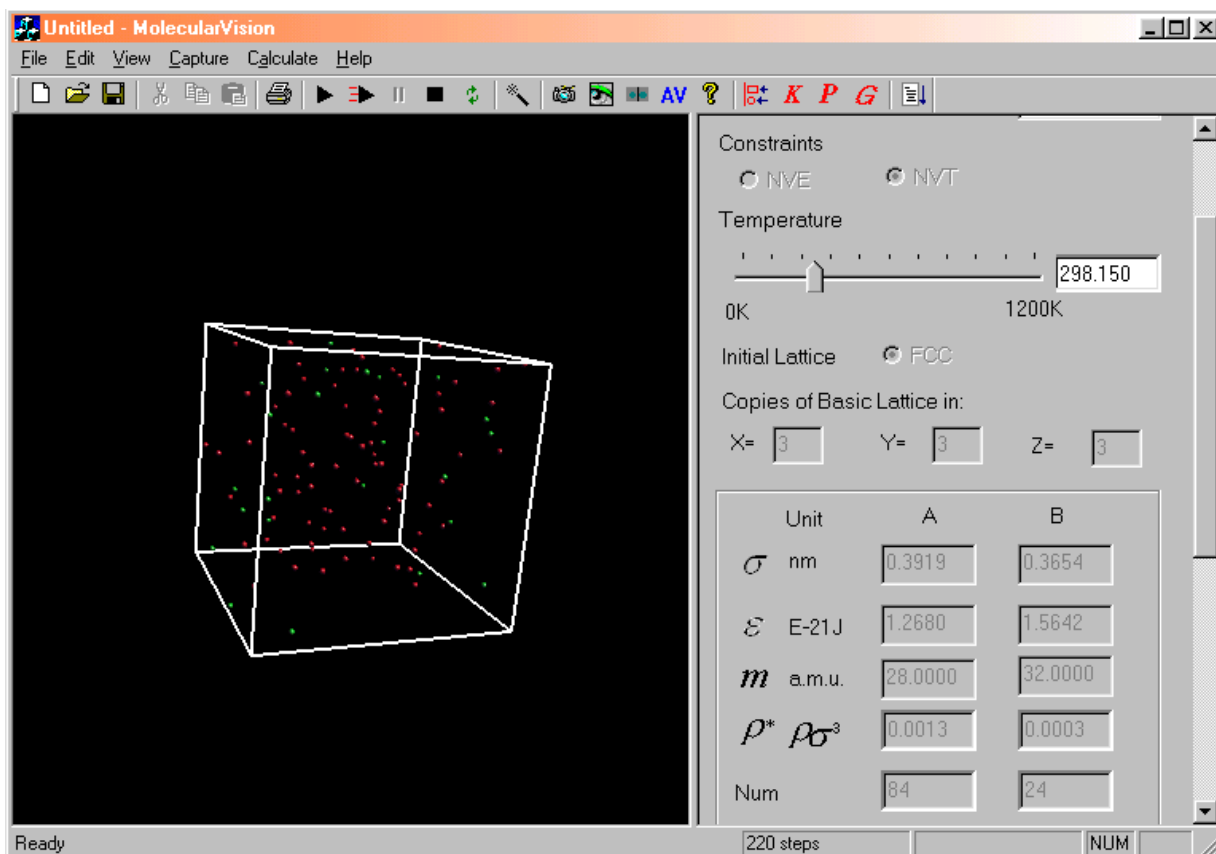


Figure 3-1. Simulations of air in room temperature and pressure

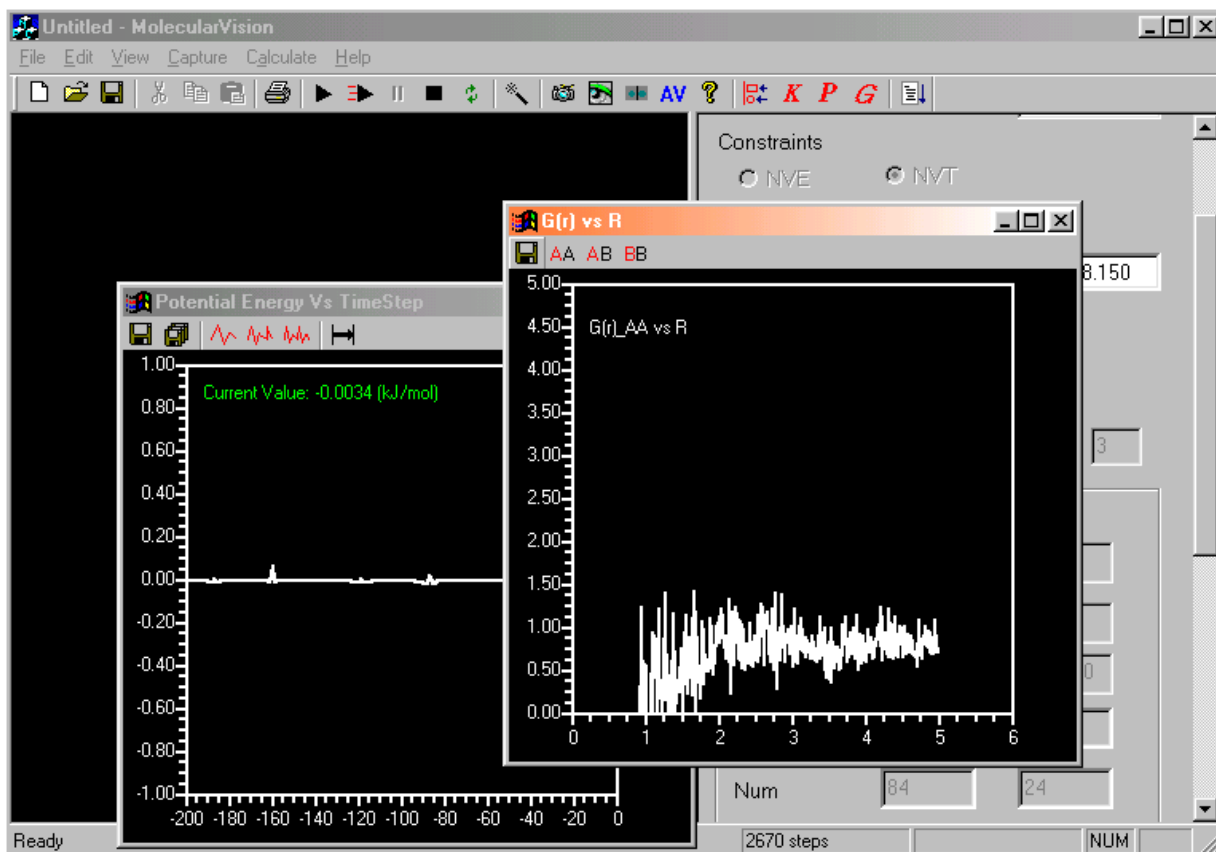
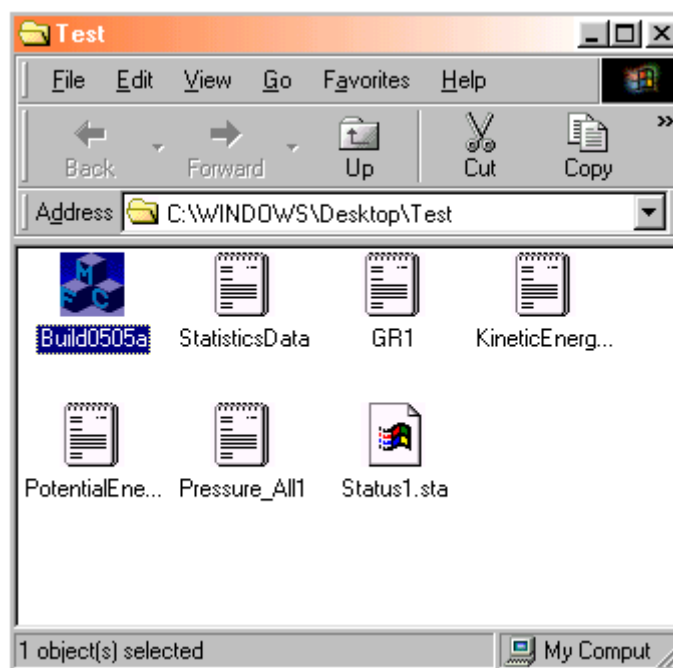


Figure 3-2. Windows showing the pair distribution function during simulation.



**Figure 3-3.** Files generated at the end of the simulation.

The above example shows a simulation of the gas phase. Apart from that, the visualization program can be used to simulate solid and liquid phase. A user can see from the simulation cell in the visualization panel the difference in density and speed of particles when you set a different density and temperature. Upon performing several sets of simulations, it is hoped that the user can get familiar with the thermodynamics of atoms or compounds with the help of the visualization features in the program.

## System Requirements

- **Software:** Windows 98, Windows 98 SE, Windows Me, Windows 2000 and Windows XP
- **CPU:** Pentium II Processor or above
- **Display Card:** Video Card with Open GL support. The visualization features in the program may fail in a PC equipped with ATI Rage display card.

This molecular dynamics simulation and visualization software has been developed by Kwong-Yu Chan, Wenping Wang, Bin Wang and Yuk-Wai Tang. Financial support was received from The University of Hong Kong through a Teaching Development Grant (2000-2001).