Molecular Dynamics of Lennard Jones Fluid

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PHYS 610 Methods of Molecular Simulation

We investigate the properties of particles in a Lennard-Jones potential in a molecular dynamics simulation. Lennard Jones potential represents an interaction between two particles and its associated energy function is

$$\mathrm{U} = \frac{1}{2}\sum_{\mathrm{i}\neq\mathrm{j}} \mathrm{u_{lj}}(|\mathrm{r_i} - \mathrm{r_j}|)$$

where the intermolecular potential is

$$u(r)_{lj} = 4[r^{-12} - r^{-6}]$$

where r is the interparticle separation. To avoid the computational costs associated wiht an infinite potential, it is reasonable to implement an approximation that cuts off the potential at some length, r_c and to add the approximate amount of energy that has been cut off for all particles at once. In this case, potential becomes

$$u(r) = \begin{cases} \infty & \text{for } r \leq r_c \\ 0 & \text{for } r \geq r_c \end{cases}$$

The so called tail correction for potential energy in this case is

$$u_{\text{tail}} = \frac{8}{3}\pi\rho[\frac{1}{3}(\frac{1}{r_c})^9 - (\frac{1}{r_c})^3]$$

and the tail correction for pressure is

$$P_{\text{tail}} = \frac{16}{3}\pi\rho^2[\frac{2}{3}(\frac{1}{r_c})^9 - (\frac{1}{r_c})^3]$$

where ρ is the number density. But we can also find the pressure without using the tail end correction by using the virial

$$P = \frac{\rho}{\beta} + \frac{\text{vir}}{V}$$

where V is the volume, and vir is the virial, which is

$$\text{vir} = \frac{1}{3}\sum_i \sum_{i\geq j} f(r_{ij}) \cdot r_{ij}$$

the pressure-density plot calculated in the simulation using the virial is shown in Figure 6 (right).

where ρ is the number density and $g(d^+)$ is the value of the RDF at contact. The RDF, $g(r)$, is a pair correlation function that describes how atoms in a disordered system are packed in relation to each other.

Radial distribution function is an important measure of the static structural properties of the liquid. It can be computes as

$$g(r) = \frac{1}{N}\frac{\sum_{i=1}^{N} \text{number of particles between r and r} + \Delta\text{r}}{4\pi r^2 \rho \Delta r}$$

where N is the number of particles. The radial distribution functions obtained in the simulation for various values of density are shown in Figures 1 and 2.

An important dynamical property to evaluate is the diffusion coefficient, which is related to the concentration c by

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$

then, the diffusion coefficient is

$$D = \frac{1}{6}\frac{\partial}{\partial t} < r^2 >$$

where $< r^2$ is mean squared displacement. Figure 4 shows the $< r^2$ trajectory for various number densities and the approximated slope of the linear portion of the curve curve. Figure 5 shows the log linear plot of $\frac{1}{6}\frac{\partial}{\partial t} < r^2 >$ vs time with a horizontal line to approximate the value of the diffusion coefficient. Figure 6 (right) plots the D for each density.

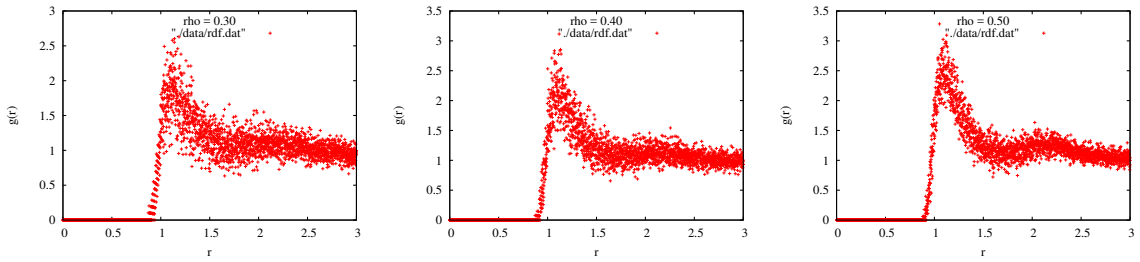

Figure 1: Radial distribution function for $\rho = 0.3$, $\rho = 0.4$, $\rho = 0.5$.

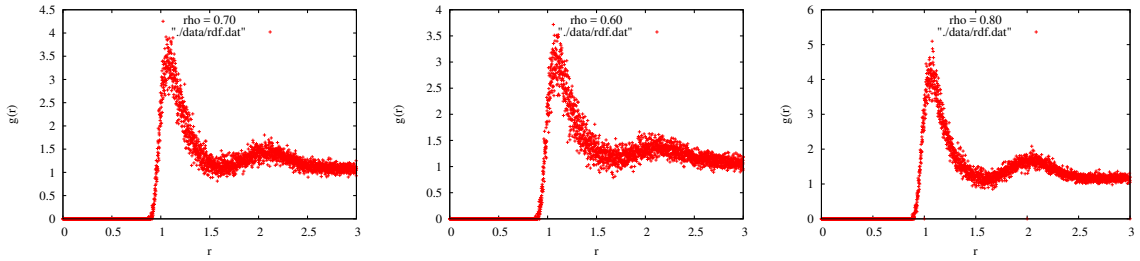

Figure 2: Radial distribution function for $\rho = 0.6$, $\rho = 0.7$, $\rho = 0.8$.

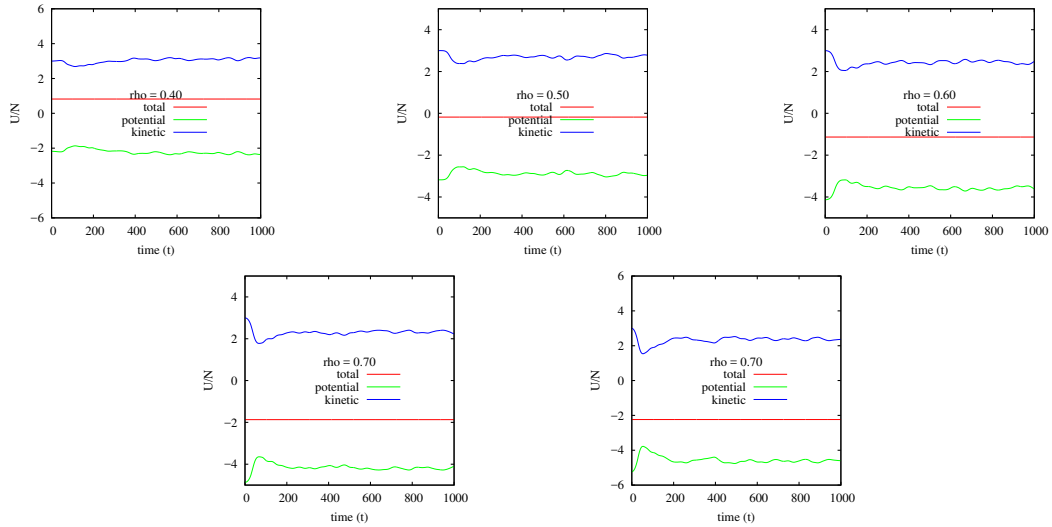

Figure 3: Time evolution of kinetic, potential and total energy for $\rho = 0.4$, $\rho = 0.5$, $\rho = 0.6$, $\rho = 0.7$, $\rho = 0.8$.

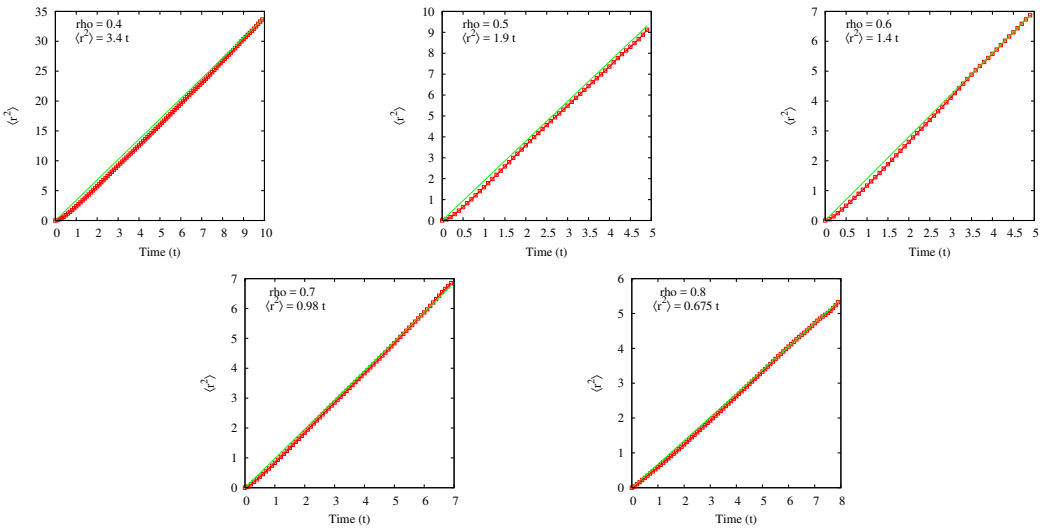

Figure 4: Mean squared displacement vs time for $\rho = 0.4$, $\rho = 0.5$, $\rho = 0.6$, $\rho = 0.7$, $\rho = 0.8$.

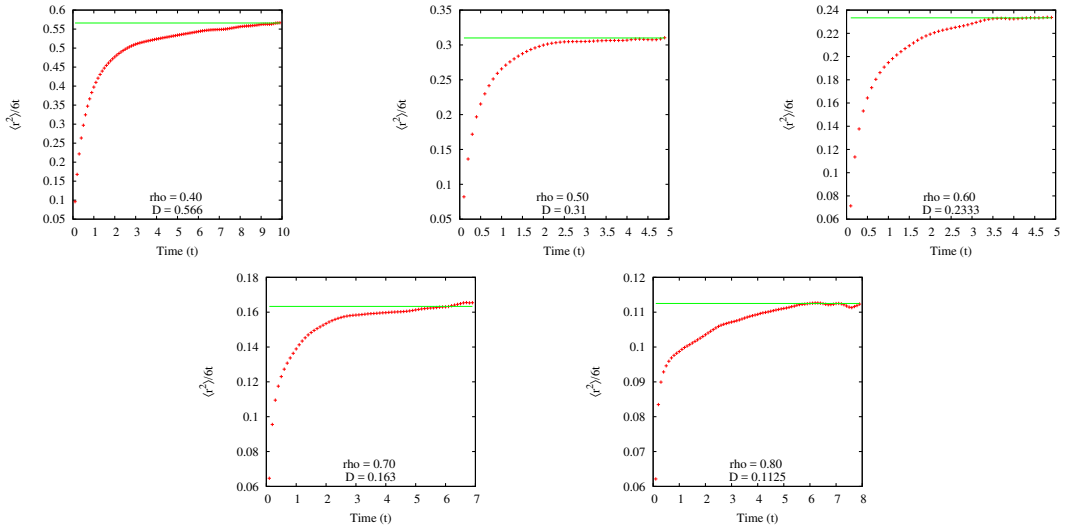

Figure 5: Diffusion coefficient vs time for $\rho = 0.4$, $\rho = 0.5$, $\rho = 0.6$, $\rho = 0.7$, $\rho = 0.8$.

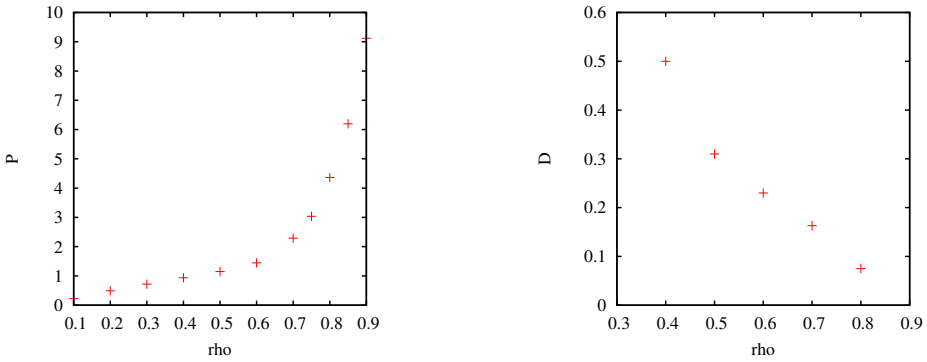

Figure 6: (left) Pressure vs density plot (right) diffusion coefficient vs density plot