Molecular Monte Carlo Simulation of Hard Sphere Fluid

Alena Klindziuk

PHYS 610 Methods of Molecular Simulation

We investigate the radial distribution function (RDF) and pressure of a hard sphere fluid in a molecular Monte Carlo simulation. This system is modeled as impenetrable, non-interacting, non-overlaping spheres, which represents atoms or molecules that experience strong repulsion in proximity to one another. The energy function of hard sphere fluid is given by

$$\mathrm{U} = \frac{1}{2}\sum_{\mathrm{i}\neq\mathrm{j}} \mathrm{u}(|\mathbf{r}_\mathrm{i} - \mathbf{r}_\mathrm{j}|)$$

where the intermolecular potential is

$$u(r) = \begin{cases} \infty & \text{for } r < d \\ 0 & \text{for } r > d \end{cases}$$

where d is the diameter of the sphere. The thermodynamic properties of the hard sphere fluid are independent of temperature, and vary with density. For example, the pressure depends on density according to

$$\frac{\beta p}{\rho} = 1 + \frac{2}{3}\pi d^3 g(d^+)$$

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.

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

Molecular Monte Carlo technique was used to obtain the ensemble averages used to calculate the histogram of the number of particles found at each value or radial distance from each other. See Appendix for details of the simulation. The $g(r)$ functions are for various densities are in Figures 1 through 3. The density values for each graph appear in the legend in terms of reduced density, $\eta = \rho\pi d^3/6$. Qualitatively, at lower densities $g(r)$ is uniformly 1 with a small increase in the contact region. As the density increases, the number of particles in contact with the original sphere increases and so does the RDF. At density nearing that of solid, shown in Figure 4, the RDF increases sharply suggesting asymptotic behavior and signifying first order liquid-solid phase transition. At a radial distance far from contact with the original particle, the RDF averages to 1 in all cases. Note however, that at highest density sampled, the RDF far from contact region has peaks, which are caused by the initial simple cubic configuration of the particles that is retained throughout the simulation due to high density.

Quantitatively, Table 1 summarizes the $g(d^+)$ values obtained from the graphs in Figures 1 -3 for the each of the corresponding ρ and the resulting p scaled by a factor of β/ρ. Since the $g(r)$ has a steep slope at contact for high density samples, these values have greater standard deviation resulting in higher standard error, $SE = \sigma/\sqrt{N-1}$ where σ is the standard deviation and N is the sample size. The pressure data obtained from the simulation, along with the theoretical pressure curve given by the Carlahan-Starling equation of state are plotted against η in Figure 5. For reduced density values below the phase transition, the data lies within the standard error of the theoretical curve. However, for almost solid density near $\eta = 0.5$, the pressure obtained from the simulation is significantly higher than that given by the equation of state, and the error can not account for that. The Monte Carlo technique can not be used to calculate the pressure of the solid phase of the hard sphere fluid because when the particles are closely packed, as for $\rho > 1.0$ and $\eta > 5.2$ no displacement of a random particles can be made without generating an overlap. Hence at nearly solid density, the simulation produces inacurate results.

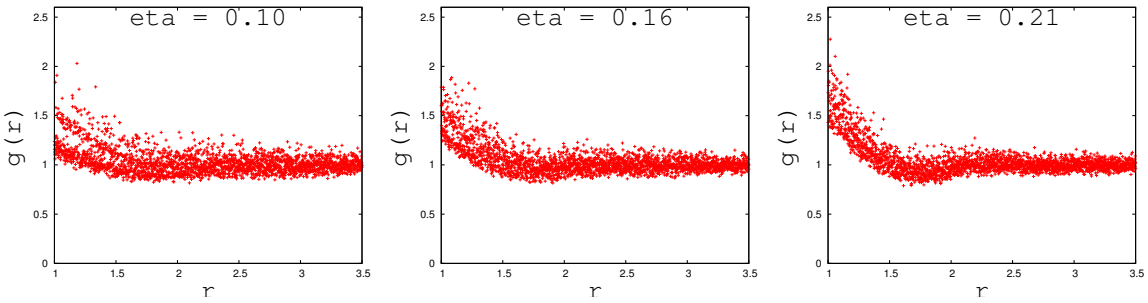

Figure 1: Radial distribution function for $\rho = 0.2$, $\rho = 0.3$, $\rho = 0.4$.

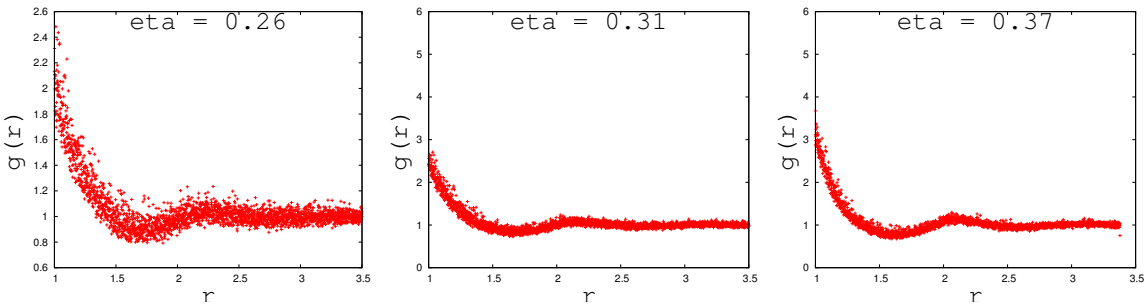

Figure 2: Radial distribution function for $\rho = 0.5$, $\rho = 0.6$, $\rho = 0.7$.

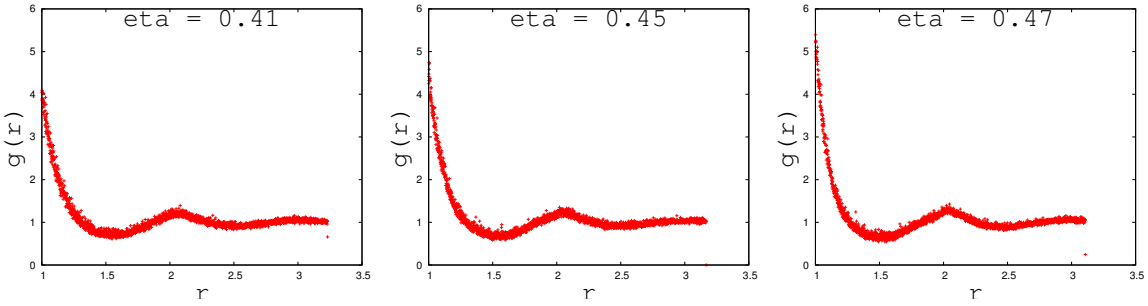

Figure 3: Radial distribution function for $\rho = 0.8$, $\rho = 0.85$, $\rho = 0.9$.

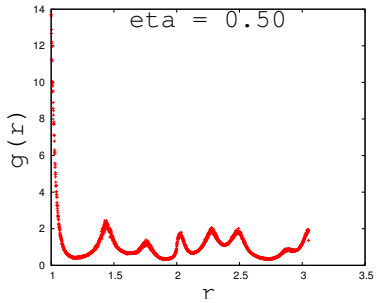

Figure 4: Radial distribution function for $\rho = 0.95$.

Table 1: RDF at contact and pressure calculated from the simulation data.

ρ	η	g(d$^+$)	$\beta p/\rho$	SE
0.2	0.10	1.3	1.54	2.62
0.3	0.16	1.5	1.94	2.40
0.4	0.21	1.8	2.51	1.76
0.5	0.26	2.2	3.30	2.55
0.6	0.31	2.6	4.27	2.06
0.7	0.37	3.2	5.69	2.16
0.8	0.42	3.9	7.53	2.15
0.85	0.46	4.4	8.83	3.19
0.9	0.47	5.0	10.42	6.39
0.95	0.50	14.0	28.86	7.88

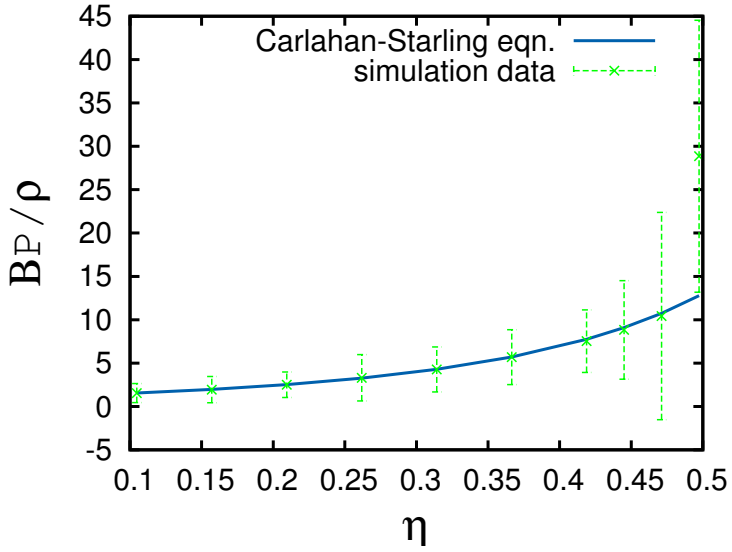

Figure 5: Pressure of hard sphere fluid as obtained from the simulation in comparison with the Carnahan-Starling equation of state.

1 Appendix

The Monte Carlo simulation was performed for 216 particles which were initially arranged on a simple cubic lattice. The particle diameter was fixed, so the volume of the unit cell varied with the chosen density. Data was collected after 100,000 Monte Carlo steps (single particle displacements) with a sampling frequency of 1 in every 1,000 steps. The first 1000 steps were not included in the $g(r)$ calculation. The RDF histogram bin width was 0.001.