Molecular Dynamics Simulation of Argon

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Abstract— **In this paper a molecular dynamics simulation of Argon is presented. A molecular dynamics simulation method is used to predict the *pressure*, *specific heat*, *pair correlation function*, and *self-diffusion coefficient* for matter whose interactions can be modeled by the Lennard-Jones potential. A microcanonical ensemble was considered for several different values for the temperature and density. A simulation time for 16.3 ms was reached per timestep for 864 particles, while calculating all the quantities presented. The results were compared with literature values of other simulations.**

I. INTRODUCTION

Molecular dynamics is concerned with the description of the atomic and molecular interactions that govern microscopic and macroscopic behaviors of physical systems. The molecular dynamics method was first introduced by Alder and Wainwright in the late 1950's to study the interactions of hard spheres [1]. The essence of molecular modeling resides in the connection between the macroscopic world and the microscopic world provided by the theory of statistical mechanics. We carry out computer simulations in the hope of understanding the properties of assemblies of molecules in terms of their structure and the microscopic interactions between them. This computational method calculates the time dependent behavior of a molecular system. The two main families of simulation technique are molecular dynamics (MD) and Monte Carlo (MC). In this research we shall concentrate on MD. The obvious advantage of MD over MC is that it gives a route to dynamical properties of the system: diffusion coefficients, pressure, specific heat and the pair correlation function. In our study we consider the case of an Argon gas, solid and liquid.

II. METHODS

A. Interactions of the particles

Since Argon is a noble gas it will only have a very limited way of interacting with its neighboring particles. The potential of a particle can be modeled by Lennard-Jones:
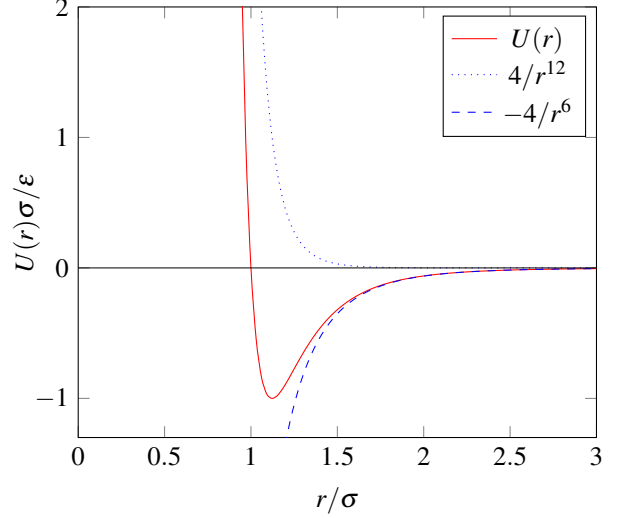
$$V(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (1)$$

The force is defined as the negative of the gradient of the potential:

$$F_{ij}(r_{ij}) = -\vec{\nabla} V(r_{ij}) = 24 \frac{\varepsilon}{r_{ij}^2} \left[2 \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \vec{r}_{ij} \quad (2)$$

So to calculate the force on particle i we sum over all the particles $j \neq i$:

$$F_i = \sum_{i \neq j} F_{ij} \quad (3)$$

Now we make the equations dimensionless by adopting the following units:

$$r_{ij} = r_{ij}^* \sigma, \quad m = m^* m_{Ar}, \quad E = E^* \varepsilon, \quad t = t^* \sigma \sqrt{\frac{m}{\varepsilon}} \quad (4)$$

Using these dimensionless parameters in the potential functions:

$$\frac{V(r_{ij})}{\varepsilon} = V^*(r_{ij}) = 4 \left[\left(\frac{1}{r^*} \right)^{12} - \left(\frac{1}{r^*} \right)^6 \right] \quad (5)$$

Doing the same for the force:

$$\mathbf{F}_{ij}(\mathbf{r}_{ij}) = 24 \frac{\varepsilon}{r_{ij}^{*2} \sigma} \left[2 \left(\frac{1}{r^*} \right)^{12} - \left(\frac{1}{r^*} \right)^6 \right] \mathbf{r}_{ij}^*$$

$$\frac{\varepsilon}{\sigma} \mathbf{F}_{ij}(\mathbf{r}_{ij}) = \mathbf{F}_{ij}^*(\mathbf{r}_{ij}) = 24 \frac{1}{r_{ij}^{*2}} \left[2 \left(\frac{1}{r^*} \right)^{12} - \left(\frac{1}{r^*} \right)^6 \right] \mathbf{r}_{ij}^* \quad (6)$$

Using this it is possible to *only* use dimensionless quantities, and thus from this point in the paper every equation will be written in terms of natural units.

Since $\mathbf{F}_{ij} = -\mathbf{F}_{ji}$ we see that every unique pair only has to be calculated once to find their force contributions on each other. If we write the forces as the tensor $\mathbf{F}_{ij}$ we observe that this results in the tensor being anti-symmetric, with zeros on the diagonal. For this reason only the upper triangle of this tensor will be calculated and the tensor is subsequently made anti-symmetric, resulting in only $N^2/2 - N$ computations instead of N^2. In total $N = 864$ particles will be used.

B. Time progression algorithm

Since the force on each particle is calculated according to the previous section, we will be able to increment the time

and calculate the new positions and velocities accordingly using Newton's laws. To increment time we are using a velocity-Verlet algorithm. This algorithm is given by [5]:

$$\mathbf{v}_i(t + \frac{\Delta t}{2}) = \mathbf{v}_i(t) + \frac{1}{2}\mathbf{a}_i(t)\Delta t \tag{7a}$$

$$\mathbf{x}_i(t + \Delta t) = \mathbf{x}_i(t) + \mathbf{v}_i(t + \frac{\Delta t}{2})\Delta t \tag{7b}$$

$$\mathbf{a}_i(t + \Delta t) = \mathbf{F}_i(\mathbf{x}, t + \Delta t) \tag{7c}$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2}\mathbf{a}_i(t + \Delta t)\Delta t \tag{7d}$$

Although this algorithm can be shortened, for computational purposes an extra half step was used in the calculation. The error contribution of this algorithm is of the order $\mathscr{O}(\Delta t^4)$. The actual error is larger due to the use of a cut-off radius, however, this has been neglected in this report.

C. Boundary conditions

We have implemented periodic boundary conditions to simulate a system of an infinite amount of boxes by only N boxes. Periodic boundary conditions imply that if a particle flies out of our system to the right/left it will reenter the system on the left/right.

D. Initial conditions

For the initial positions a FCC structure is chosen, since the atoms are then in the state with the lowest energy. The distance between the atoms depends on the density of the system.

The initial velocities are taken from a normal distribution such that every particle has a random speed in all three spatial directions. After these velocities are initialized they are rescaled to the right size such that the desired temperature of the system is attained. Rescaling of the velocities is discussed more in depth in section II-E.

After these random velocities have been initiated and agree with the desired temperature, the velocities are shifted such that the total velocity (momentum) of the system is 0. This is done through the following calculation:

$$\vec{v}_j = v_{j,rand} - \text{avg}(\vec{v}_{rand}) \tag{8}$$

Where $\text{avg}(\vec{v}_{rand})$ denotes the average value of all the velocities.

E. Reaching equilibrium

The moment the simulation starts the script has been made such that the kinetic energy agrees with the desired temperature, T_0. However, the moment the system is free to evolve, it will move towards an equilibrium position with a potentially different temperature. The system can be forced to attain an equilibrium with the desired temperature through the use of a *thermostat* [5]. To do this, the velocities are rescaled for the first 2500 timesteps ($t = 10$ in natural units) so that the kinetic energy agrees with the temperature. In the code this means that all velocities will be multiplied by $\lambda = \sqrt{(N-1)3T_0/2E_{kin}}$, with E_{kin} the total ensemble's kinetic energy. In the code this means:

$$\mathbf{v}_{t+1}^i = \mathbf{v}_t^i \cdot \sqrt{(N-1)3T_0/2E_{kin}} \tag{9}$$

After the first 2500 timesteps the potential energy should be close to equilibrium with the desired kinetic energy. From the simulations we can conclude that this method if sufficient to get to the desired temperature with an offset of less than 2%.

F. Measuring physical quantities

1) Pressure: The pressure is a quantity widely used in physics and is calculated via the Virial theorem from Clausius. The total Virial for a real system has two contributions: the ideal gas part, -3P V , 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:

$$P = 1 - \frac{1}{3NT}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} r_{ij}\frac{\delta U(r)}{\delta r_{ij}} - \frac{48\pi\rho}{9T\sqrt{r^2}}\left(\frac{2}{3(r^2)^4} - \frac{1}{r^2}\right) \tag{10}$$

The first part represents argon as an ideal gas, the second part the virial theorem and the third part is a correction for all the particles outside the cutoff distance. More about this has been written in section IV.

2) Specific heat: To measure the specific heat of the system we make use of a formula derived from a paper by Lebowitz et al. [2], and presented by J. Thijssen [5]:

$$\frac{\langle \delta K^2 \rangle}{\langle K \rangle^2} = \frac{2}{3N}\left(1 - \frac{3N}{2C_v}\right)$$

C_v can be directly calculated from this as:

$$C_v = \frac{3\langle K \rangle^2}{2\langle K \rangle^2 - 3N\langle \delta K^2 \rangle} \tag{11}$$

Where $\langle \ldots \rangle$ denotes the time averaged value. From eq. 11 the reader should note that in the limit of a perfect ideal gas assumption the specific heat goes to $3/2$ in natural units. More specifically $\lim_{\langle \delta K^2 \rangle \to 0} C_v = 3/2$. For the calculation of the specific heat it is important that the temperature is stabilized before any measurements are performed, after this a measurement over $\Delta t = 20$ natural units is performed in time steps of $\tau = 0.004$.

3) Pair correlation: The pair correlation function $g(r)$ is a useful tool to study the order of a system. It is a measure of the probability of finding a particle at a distance r and determined by counting the number of pairs $n(r)$ for every interval $[i\Delta r, (i+1)\Delta r]$ within the range $r = 0$ to $r = 0.5 \cdot$ boxsize (considering the periodic boundary conditions). In terms of $n(r)$ the pair correlation function is calculated as follows [5]:

$$g(r) = \frac{2V}{N(N-1)}\left[\frac{\langle n(r) \rangle}{4\pi r^2 \Delta r}\right] \tag{12}$$

4) Diffusion coefficients: The Einstein relation is also called the mean square displacement relation. For self-diffusion coefficients, the relationship is [3]:

$$D = \lim_{t \to +\infty}\frac{1}{6Nt}\left\langle \sum_{j=1}^{N}[r_j(t) - r_j(0)]^2 \right\rangle \tag{13}$$

Where $\langle \dots \rangle$ denotes the time averaged value and $[r_j(t) - r_j(0)]^2$ the distance the particles traveled. Due to periodic boundary conditions it is better to calculate this as follows:

$$r_j(t) - r_j(0) = \sum_1^t v_j(t)\delta t \qquad (14)$$

III. DETERMINING THE ERROR

To calculate an error for the *pressure, specific heat, diffusion coefficient,* and the *pair correlation function*, a large sample size of 20 samples will be made, each consisting of 5000 time steps. The final simulations will be run with 864 particles to minimize the effects of the periodic boundary conditions. From the 20 samples a mean will be calculated with an error of $u(\cdot) = \text{std}(\cdot)/\sqrt{N_{samples}}$.

However, for the temperature and the potential energy the mean and standard error will be determined over all the time samples.

IV. TAIL CORRECTION

To speed up the code a cut-off radius has been used when calculating the forces between the particles, the potential, and the virial contribution to the pressure. Although this has negligible contribution to the dynamics of the system, the error in introduces to potential energy and the pressure cannot be ignored. For this reason a correction has been made to the potential energy and the pressure [5]:

$$\langle U \rangle = \langle U \rangle_{cut-off} + 2\pi\rho(N-1)\int_{r_{cut-off}}^{\infty} r^2 U(r)g(r)dr \quad (15)$$

$$\frac{P}{nk_BT} = 1 - \frac{1}{3Nk_BT}\left\langle \sum_i \sum_{j>i} r_{ij}\frac{\partial U(r_{ij})}{\partial r_{ij}}\right\rangle$$
$$- \frac{2\pi\rho}{3k_BT}\int_{r_{cut-off}}^{\infty} r^3\frac{\partial U(r)}{\partial r}g(r)dr \qquad (16)$$

The correction part of these equations is contained in the right-most term. Furthermore, the assumption has been made that $g(r)|_{r=r_{cut-off}} \approx 1$, such that the integrals can be determined without having to make the domain (and thus the amount of particles) too large.

V. OVERVIEW OF CODE PROCEDURE

A general overview of the code can be found below. The code has been simplified such that the general structure can still be seen, although it does not specify where exactly the data is generated. More detail can be found in the code itself.

VI. RESULTS & DISCUSSION

In total the script runs for a total of 27 minutes, looping over 102,500 timesteps with 864 particles. This means one timestep takes 16.3 ms per timestep. This includes calculating every quantity presented in this report.

The methods described in the previous section were used to determine the average temperature T, the kinetic U_{kin} and potential energies, U_{pot}, the pressure $\beta P/\rho$, the specific heat, C_v, and the diffusion coefficient, D, for various values of

```
1:  Initialize all variables
2:  initiate() return initial positions, velocities, forces
3:  loop for N_t timesteps do:
4:    if t < time for equilibrium then
5:       Re-scale velocities to desired Temperature
6:    if t ≥ time for equilibrium then
7:       make_time_step() return
8:       new positions, velocities, forces + data
9:       if A sample has been completed then
10:         Save the sample's measurement
11:      else
12:         Save the data for next loop
13: Process all the samples
14: Write data to file
15: Make and save plots
```

density, ρ, and initial temperature, T_0, depicted in table I. The first three rows of results have initial values for ρ and T_0 identical to the molecular data for thermodynamic quantities of the Lennard-Jones liquid simulated by J. Thijssen [5] as a definite check to compare the results. It is observed that the values found for $\beta P/\rho$ and U_{pot} do not exactly match the values presented in the literature, this can be explained because the average temperature T is not precisely equal to the desired value. A notable error however is seen for the pressure at $\rho = 0.7$ and $T_0 = 1$. An explanation for this error could be that in this case there is a coexistence of the gas phase. Our simulation model is not yet advanced enough to account for such disturbances. The last row of table I represents a simulation done to check the diffusion coefficient with a literature value presented in a study done by L. Wei-Zong [3].

The total energy of the system is constant after reaching equilibrium, which is desired. Before equilibrium is reached one can observe that the kinetic energy remains constant, thus keeping the temperature constant. The moment the thermostat is turned off, small fluctuations in kinetic and potential energy can be observed, but the total energy remains constant. This is a good check for the validity of the simulation.

Besides the energy remaining constant, a check has also been done for the total momentum of the system. The results of the check can be seen in Fig. 1, and it is indeed observed that the momentum remains constant at the initial value of zero.

A. Gas phase

In the gas phase for $\rho = 0.3$ and $T_0 = 3$ a simulation was done for the energies, pressure, specific heat, pair correlation function and diffusion coefficient. The results are presented in figure 2a, figure 2b on page 6 and table I on page 4. The pair correlation function as given in figure 2b on page 6 gives us insight upon the spatial distribution of the molecules in the gas. As expected we see that no particles are closer than $r = 1$ to each other as expected from the Lennard-Jones potential. The observed peak at about $r = 1$ is expected due to

TABLE I.   Results for a number of different simulations with different parameters for ρ and T_0

ρ $(1/\sigma^3)$	T_0 (ε/k_b)	T	$u(T)$	$\beta P/\rho$	$u(\beta P/\rho)$	C_v (k_b/σ^3)	$u(C_v)$	$D(\sigma\sqrt{\varepsilon/m})$	$u(D)$	$U_{pot}(\varepsilon)$	$u(U_{pot})$
0.88	1	1.00	0.02	3.1	0.2	2.64	0.03	0.0408	0.0003	-5153	24
0.8	1	0.98	0.02	1.2	0.2	2.39	0.02	0.0650	0.0006	-4791	21
0.7	1	1.01	0.02	0.1	0.1	2.20	0.02	0.111	0.001	-4214	21
0.3	3	2.97	0.02	1.10	0.08	1.644	0.003	1.084	0.006	-1514	32
1.2	0.5	0.50	0.01	25.4	0.6	2.85	0.04	$6.1\cdot10^{-5}$	$0.7\cdot10^{-5}$	-6493	12
0.6873	1	0.99	0.02	-0.09	0.1	2.13	0.01	0.1129	0.0009	-4151	19

TABLE II.   Literature values for pressure and potential energy from J. Thijssen [5], diffusion coefficient from L. Wei-Zong [3]

$\rho(1/\sigma^3)$	$T_0(\varepsilon/k_B)$	T	$\beta P/\rho$	$U(\varepsilon)$	$D(\sigma\sqrt{\varepsilon/m})$
0.88	1.0	0.990	2.98	-5.704	-
0.80	1.0	1.010	1.31	-5.2710	-
0.70	1.0	1.014	1.06	-4.662	-
0.6873	1.0	-	-	-	0.1191

the valley in the Lennard-Jones potential. Also the potential energy of the particles in the gas state is higher than that in other states due to the higher temperature, which causes the particles to move closer to their neighbours.

B. Liquid phase

In the liquid phase for $\rho = 0.8$ and $T_0 = 1$ a simulation was done for the energies, pressure, specific heat, pair correlation function and diffusion coefficient. The results are presented in figure 2c, figure 2d and table I. Due to a lower temperature than the gas phase the argon atoms have a lower kinetic energy. Therefore the potential energy is also lower, as expected. Looking at the pair correlation function of the argon atoms in the liquid phase gives us inside upon the spatial distribution of the atoms. In a liquid most of the particles are found around $r = 1$, also peaks occur at $r = 2$ and $r = 3$. The results are quite satisfactory comparing them to those found by Rahman [4].
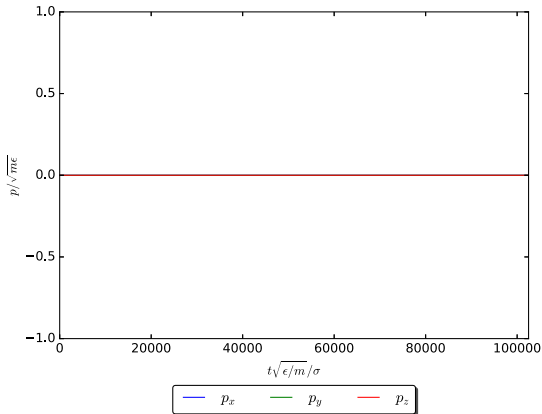

Fig. 1.   Momenta of the system. Note here that during the whole simulation, the total momentum of the system stayed constant at a value of 0. This is one of the checks to see if the dynamics of the system is working properly.

C. Solid phase

The results of the simulation of argon in the solid phase for $\rho = 1.2$ and $T_0 = 0.5$ depicted in figure 2e and figure 2f correspond with the expectations. Due to a lower temperature of the system the argon atoms have a lower kinetic energy compared to the gas and liquid phase leading to small variations in the displacement within the potential well of the Lennard-Jones potential. In magnitude, the potential energy of the atoms thus is higher. It is especially interesting to analyze the pair correlation function for a solid. Because the atoms oscillate from their locations in an FCC lattice, the positions of the peaks refer to the inter-particle distances and the width of the peak is a measure for the magnitude of the oscillations. Considering the initial FCC structure, a peak is expected at $r/\sigma = 1$, $r/\sigma = \sqrt{2}$, $r/\sigma = \sqrt{3}$ etc. as observed in figure 2f.

VII.   CONCLUSION

In the present study, pressure, specific heat, the pair correlation function, self-diffusion coefficients and potential and kinetic energies of a 864-particle Lennard-Jones fluid, gas and solid have been investigated. The obtained results are in closely resemble literature values and our expectations except for a large error in the pressure at density $\rho = 0.7$ and initial temperature $T_0 = 1$, an explanation for this error could be that this is due to the coexistence of the gas phase in the Lennard-Jones liquid. As a validity check, the total sum of the momenta and the sum of the potential and kinetic energy after rescaling are found constant. A typical running time for the simulation is 27 minutes, looping over 102,500 timesteps.

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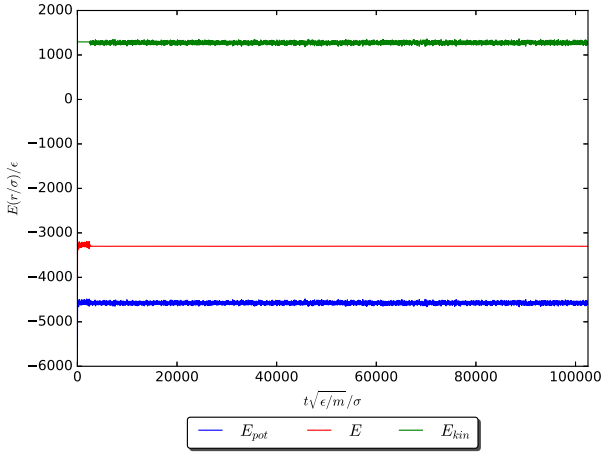[5] Jos Thijssen. *Computational Physics*. Cambridge University Press, second edition, 2007.
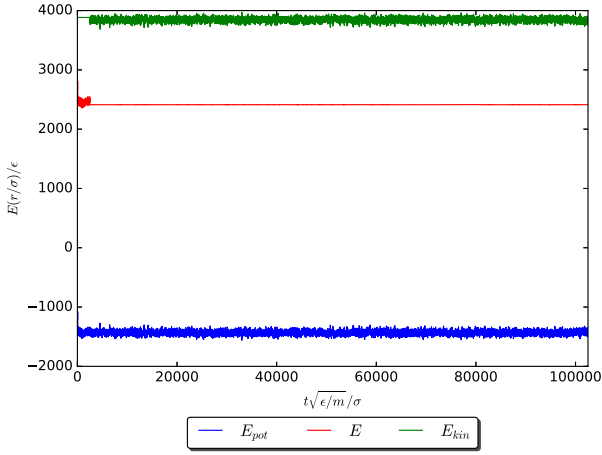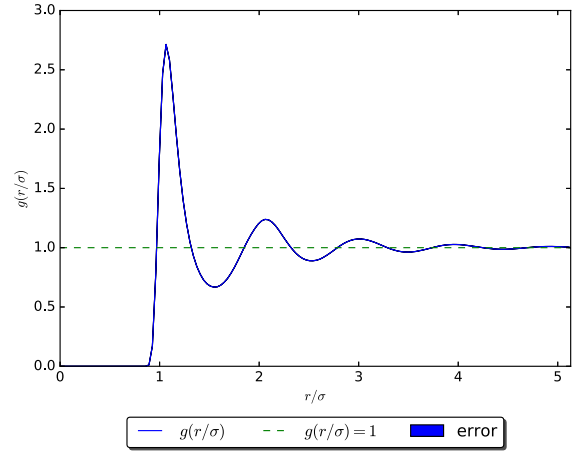
(a) Energies of the system for $T = 3$ and $\rho = 0.3$ as a function of time-steps. The Argon is in the gas phase with these parameters.
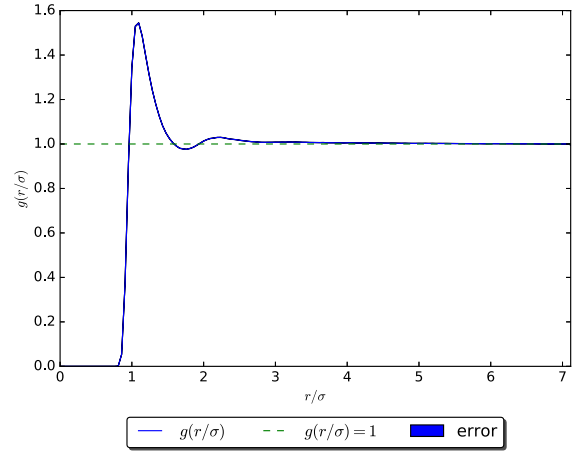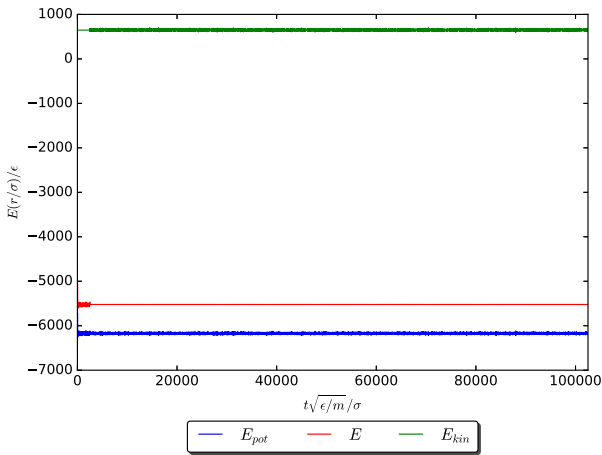
(b) Pair correlation function of the system for $T = 3$ and $\rho = 0.3$ as a function of the radius.
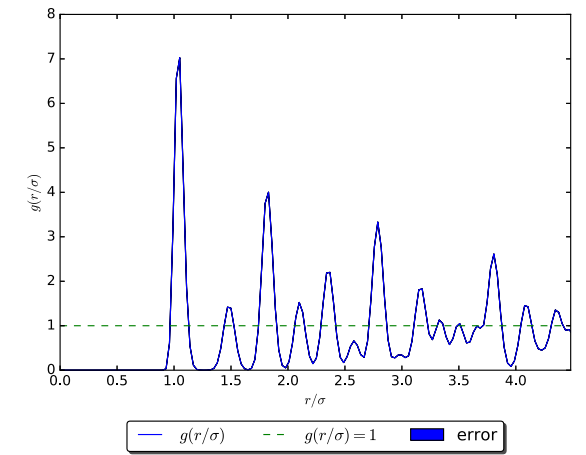
(c) Energies of the system for $T = 1$ and $\rho = 0.8$ as a function of time-steps. The Argon is in the liquid phase with these parameters.

(d) Pair correlation function of the system for $T = 1$ and $\rho = 0.8$ as a function of the radius.

(e) Energies of the system for $T = 0.5$ and $\rho = 1.2$ as a function of time-steps. The Argon is in the solid phase with these parameters.

(f) Pair correlation function of the system for $T = 0.5$ and $\rho = 1.2$ as a function of the radius.

Fig. 2. Results of three simulations. Presented on the left are plots of the potential energy, kinetic energy and the total energy versus time. On the right are plots of the pair correlation function. From top to bottom the figures are of a gas, liquid, and solid phase respectively. Notice that for gas phase the kinetic energy is much bigger in size than the potential energy. This relation is completely reversed in the situation of the solid, where the potential energy dominates. Furthermore, the pair correlation function for a gas shows a somewhat even distribution of particles after 1 σ, however in the case of the solid a clear structure can be seen, corresponding to the distances in an FCC crystal.