FYS4460 Project 1

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In this project we study a monatomic gas consisting of Argon atoms using molecular dynamics.

I. INTRODUCTION

II. THEORY

A. Integration

We assume that our particles adhere to Newtonian motion based on the interatomic forces and use the velocity-Verlet method to integrate motion in our system.

B. Interatomic force

The interatomic force is based on a chosen Lennard-Jones potential.

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \qquad (1)$$

where r is the distance between two atoms, σ is chosen to be $\sigma = 3.405\,\text{Å}$ and $\varepsilon = 1.0318 \cdot 10^2\,\text{eV}$.

Taking the gradient of the potential gives us the force as

$$\mathbf{F} = \frac{24\varepsilon}{r^2} \left[\left(2\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \mathbf{r} \qquad (2)$$

III. IMPLEMENTATION

A. Initial velocities and temperature

To mimic a given temperature upon starting the system, we select speeds from a Boltzmann distribution, meaning that the x-, y- and z-components of the velocity have zero mean and standard deviation $\sqrt{k_B T / m}$.

B. Periodic boundary conditions

Our system is limited in size, but to mimic a larger system, we use periodic boundary conditions.

C. Neighbor cells

To make the calculations go faster, we decide on a cutoff distance for the force. Outside this cutoff distance, we assume that the interatomic force is zero. Inside, it is still defined by the Lennard-Jones potential. In this project, we set the cutoff distance to be $r_{\text{cut}} = 3\sigma$.

To make use of this, we implement neighbor cells[1] as a division of our space into regions at least as large as r_{cut} in all directions.

IV. RESULTS

A. Boltzmann distribution of velocities

B. Energy fluctuations based on time step

From figure 3 we see that the energy fluctuations do not vary much with time step, at least not in terms of frequency nor magnitude. However, figure 3b indicates that any larger time step than this would cause errors since the frequency of time steps would be smaller than the frequency of the fluctuations. In fact it does, and tests show that larger time steps yield non-conserved energies, as shown in figure 4.

V. IMPACT OF THERMOSTATS

Even though the thermostats are very useful to make the transition to new temperatures smooth and easy, they introduce some nasty unphysical behavior. For instance, it is not a good idea to slowly tune the temperature while measuring the pressure to spot phase changes. One instance of this is shown in figure

A. Temperature evolution

If we start the system at $T = 300\,\text{K}$ in a perfect fcc grid, we won't stay at this temperature throughout the run. The reason is that the potential energy is practically zero in an fcc grid. We see this effect in figure 6.

B. Temperature fluctuations based on system size

As expected, we see that the fluctuations in temperature are reduced with system size, as shown in figure 7. This is because a larger system has a smaller deviation in velocities due to its size. Physically we may see this as any outliers more easily being "squashed" by the rest of the system when there are more particles available in larger systems rather than small ones.
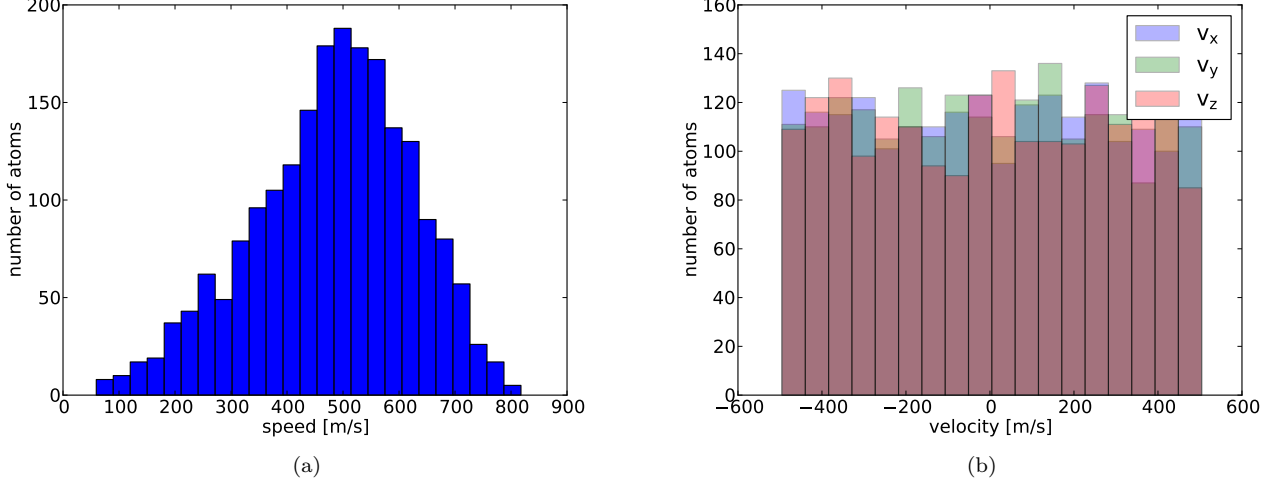
FIG. 1. Magnitudes (a) and components (b) of the velocities in the first time step after initializing with random uniform velocities in each direction, showing a non-Boltzmann distribution.
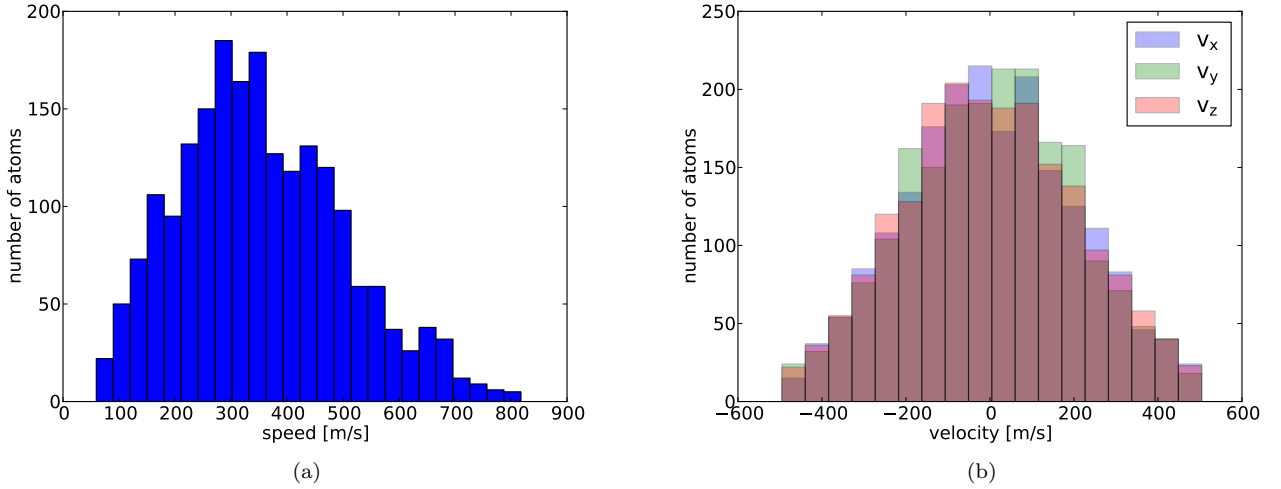

FIG. 2. Magnitudes (a) and components (b) of the velocities 100 time steps after initializing with random uniform velocities in each direction. This clearly shows a Boltzmann distribution of the magnitudes and a normal distribution of the components.

C. Pressure vs temperature

Within one isolated system, the relation between pressure and temperature is linearly inverse, meaning that the pressure is lowered with higher temperatures. This might be attributed to the fact that we are (for the most part) conserving energy within one isolated system. This is shown in figure V C.

However, between different systems, we see that the relation such that we get increasing pressure with increasing temperature (which makes sense). We even see a bump right above $300\,\mathrm{K}$ where we are likely encountering a phase change. This claim is backed up by visualizing the atoms in Ovito at $292\,\mathrm{K}$ and $330\,\mathrm{K}$, as seen in figure

9.

D. Diffusion

The displacement as function of time is shown in figure 10 for solid and liquid systems. We see that there is clearly no displacement in the solid system on average, while there is a definite trend in the liquid system.

From the relation $\langle r^2(t) \rangle = 6Dt$ (when $t \to \infty$) we find the approximated diffusion constant as

$$D = 4.5847 \cdot 10^{-9}\,\mathrm{m}^2 \tag{3}$$

(a) $\Delta t = 1.2 \cdot 10^{-14}\,\mathrm{s}$

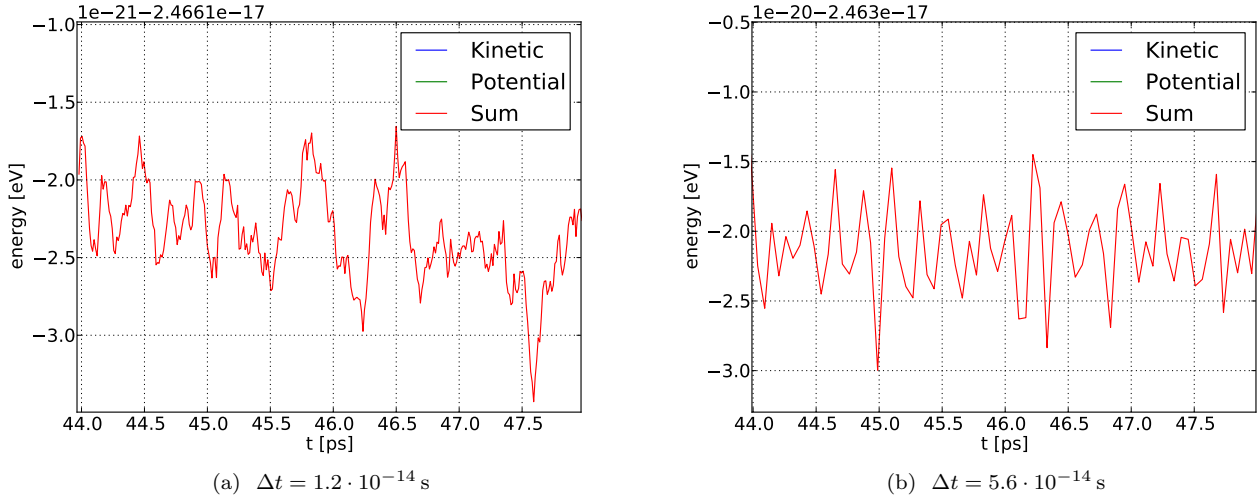(b) $\Delta t = 5.6 \cdot 10^{-14}\,\mathrm{s}$

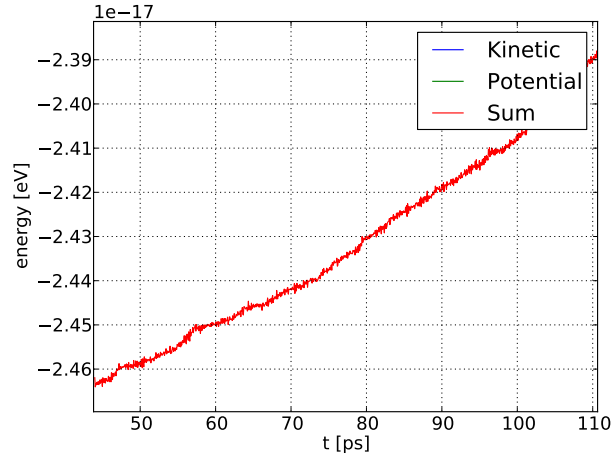FIG. 3. Fluctuations in kinetic energy as for a small time step (a) and a large time step (b).

FIG. 4. Kinetic energy for a large time step $\Delta t = 6.7 \cdot 10^{-14}\,\mathrm{s}$. We clearly see that the energy diverges - a feature not shown for smaller time steps.

E. Radial distribution

The radial distribution gives an indication of the mean atomic density within spherical shells around the atoms. This differs greatly between solid and liquid states. A plot of the radial distribution is shown in figure 11. Evidently the radial distribution at low temperatures $(10\,\mathrm{K})$ reveals the periodic structure in the solid. At higher tem-

peratures the structure is still visible, yet a bit smoothed. his is because there is more motion in the system which smooths out the exact locations of the atoms. For higher temperatures $(800\,\mathrm{K})$ there is apparently no such fine structure, although we may observe that it is more likely for atoms to appear close to others, indicating some temporary binding.

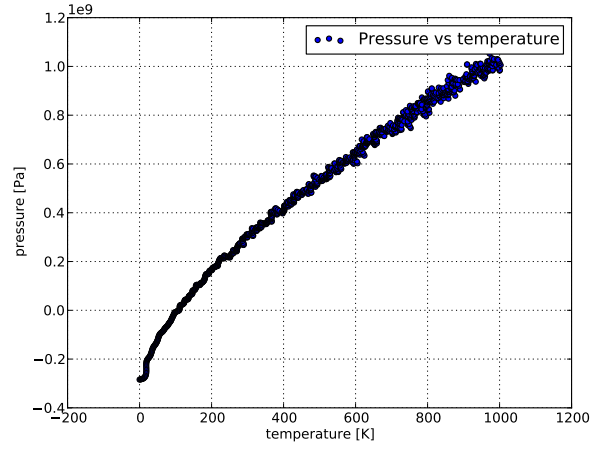[1] Neighbor cells are generally easier to combine with parallel code. Another approach is to use Verlet lists.

FIG. 5. Evolution of pressure and temperature under the use of a thermostat. Here we are completely missing the phase change at about $300\,\mathrm{K}$.
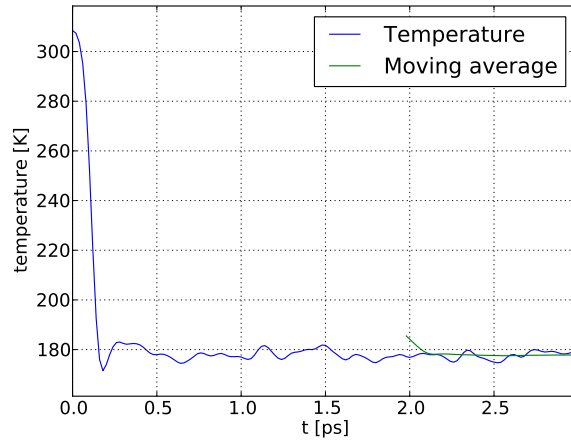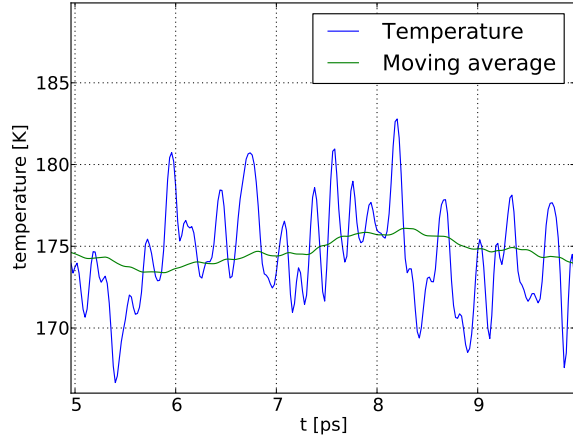

FIG. 6. Kinetic energy for a large time step $\Delta t = 6.7 \cdot 10^{-14}\,\mathrm{s}$. We clearly see that the energy diverges - a feature not shown for smaller time steps.
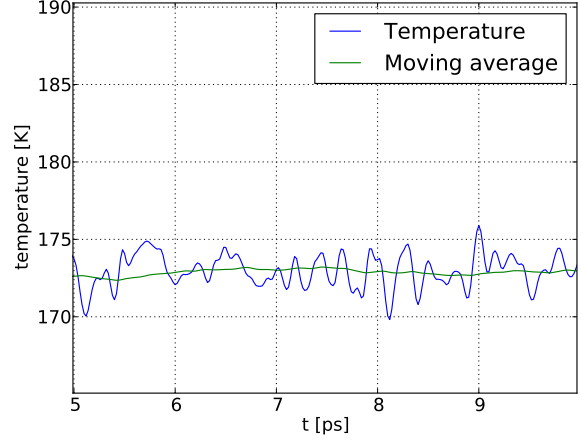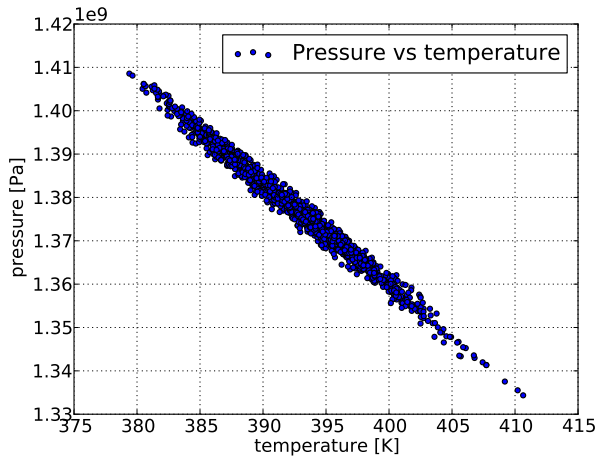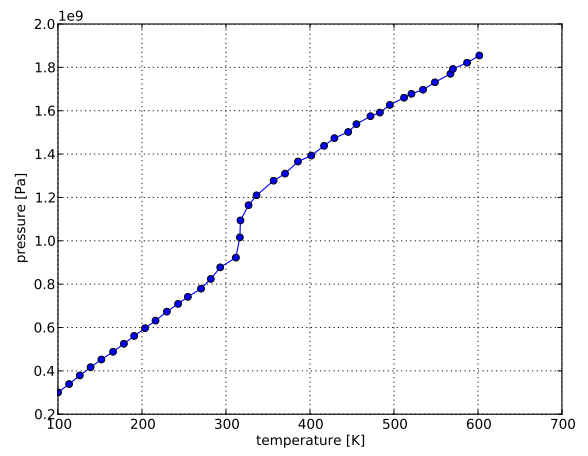
(a) System size $6 \times 6 \times 6$

(b) System size $12 \times 12 \times 12$

FIG. 7. Fluctuations in temperature for a small system (a) and a large system (b).

(a) System size $6 \times 6 \times 6$

(b) System size $12 \times 12 \times 12$

FIG. 8. Relation between temperature and pressure for a $8 \times 8 \times 8$ lattice (a) within one single system initialized with a thermostat at $400\,\mathrm{K}$) and (b) for systems initialized with multiple different temperatures. In (a) each dot represents a time step while in (b) each dot represents the mean pressure and temperature of one system.
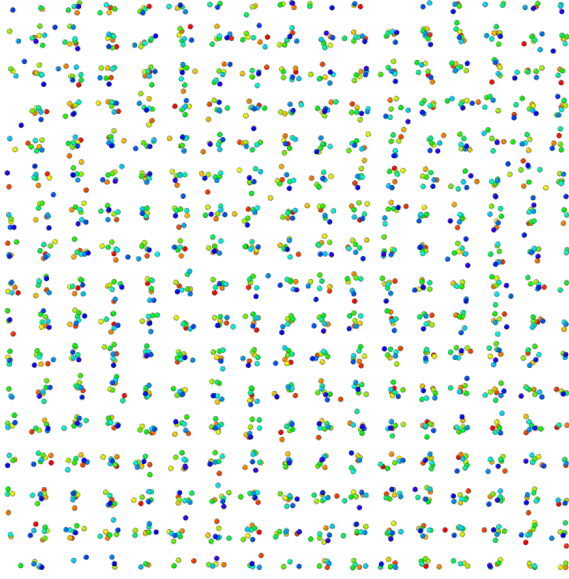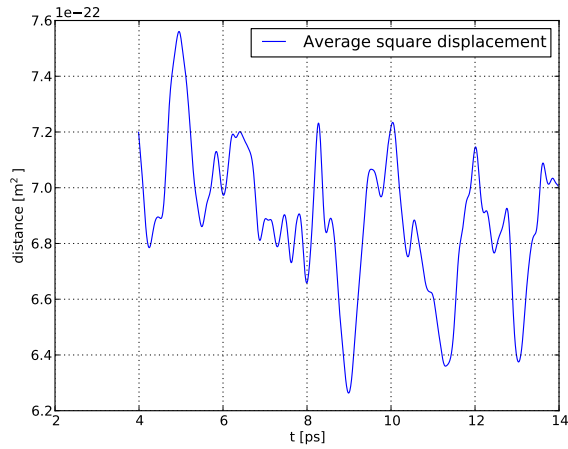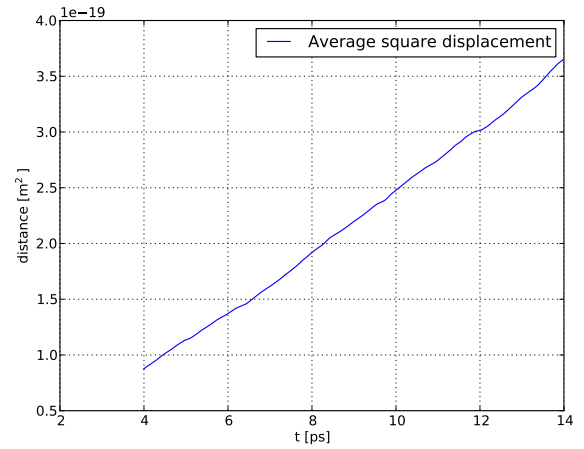
(a) 292 K, solid
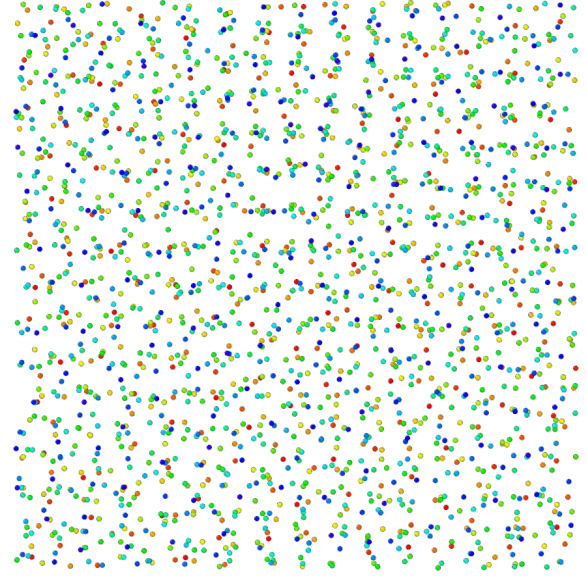
(b) 330 K, liquid

FIG. 9. Visualization of the atoms in an $8 \times 8 \times 8$ system (a) right before and (b) right after the phase change from solid to liquid.

(a) 50 K, solid

(b) 400 K, liquid

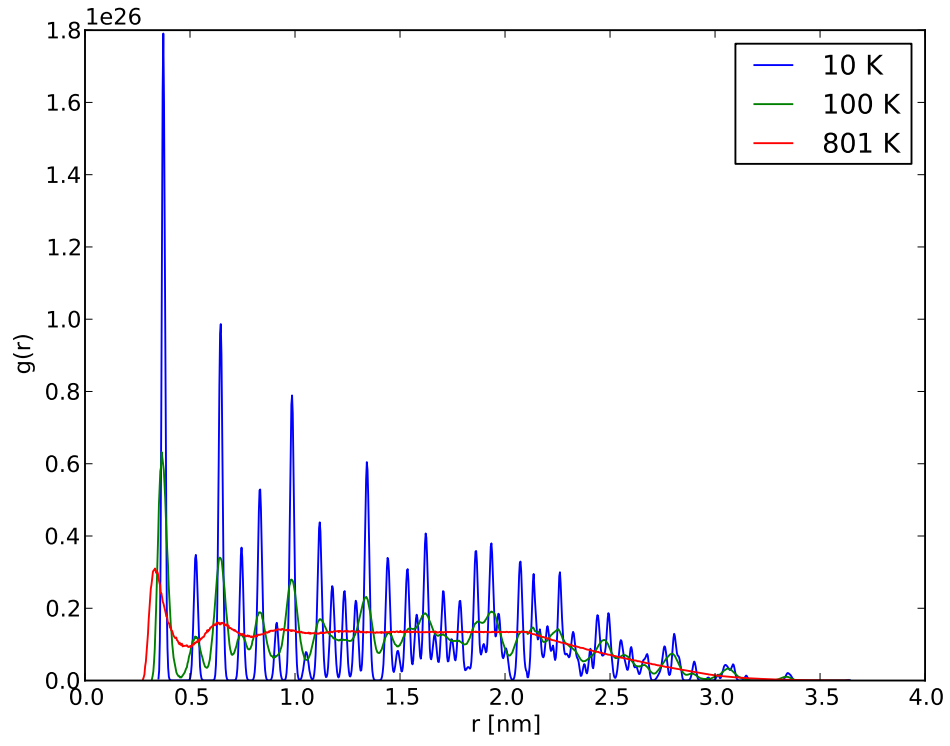FIG. 10. Displacement as function of time for (a) a solid system and (b) liquid.

FIG. 11. Radial distribution at different temperatures.