Thermodynamic identities derived from an Argon gas model

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Abstract

A system of 500 argon atoms that interact based on the Lennard-Jones potential is modeled. Using thermodynamic identities the heat capacity, pressure and structure factor are obtained. The resulting properties agree with the experimental values and the patterns found are in correspondence with expectations. This indicates that the used model pretty well describes a real argon gas.

I. Introduction

The study of physical many-particle systems becomes mathematically incredibly difficult or even impossible as the number of particles increases. The implementation of computational models can instead be used in order to obtain information about these kinds of systems, which can be compared to experimental results. Here the molecular dynamics of 500 argon atoms are simulated, whereafter various thermodynamic quantities can be obtained, such as pressure and the heat capacity. Such a simulation of argon gas molecules has already been carried out in 1967 by Verlet [1].

Running a simulation instead of an actual experiment enables one to plug in initial conditions that are experimentally demanding and moreover much more detailed information about the system can be obtained up to the single particle level. Secondly, the particle interaction theory can be tested against the experimental data.

This paper will firstly discuss the modeling of the argon atoms and the derivation of some physical quantities in section II. In section III the results obtained for heat capacity, structure factor and the pressure are discussed and in IV a conclusion is given including some recommendations for improvement and future research. [3]

II. Methods

The modeling of an argon gas is initialized by putting 500 particles in a 3-dimensional box with a certain starting temperature and density. The initial position of the particles form a fcc lattice and the initial velocity in each direction is drawn from a normal distribution with standard deviation $\frac{k_B T}{m}$ to ensure that the starting temperature is close to the input temperature.

The two-particle interaction is modeled by the Lennard-Jones potential

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

where $\epsilon = 10.3 meV$ and $\sigma = 0.34 nm$. The equations of motion are governed by Newtons 2nd law, however these become very complicated due to the fact that each pair of particles interact with each other and the fact that a computational implementation means a finite time step Δt. The algorithm that is used to obtain the path that every single particle covers in time is the Verlet [1] algorithm which is schematically shown by

$$\vec{v}_i(t) = \frac{\vec{F}_i}{2} \Delta t$$
$$\vec{r}_i(t) = \vec{v}_i(t) \Delta t = \frac{\vec{F}_i}{2} (\Delta t)^2$$
$$\text{Calculate } \vec{F}_i$$
$$\vec{v}_i(t) = \frac{\vec{F}_i}{2} \Delta t$$
$$\vec{v}_i(t) = \lambda \vec{v}_i(t)$$

which is the so called leap-frog implementation. The error that is introduced by this method is in the order of Δt^3.

The implementation assumes periodic boundaries, so in the second step of the algorithm the particles that leave the box enter on the other side. Furthermore, the force on a particle is obtained by differentiating the potential caused by every other particle in the box to the position, which is the

limiting factor in the simulation since this requires calculations that scale with N^2.

The described model[1] can handle two types of ensembles, the microcanonical (N, V, E) and the canonical (N, V, T). For the latter, an additional step is added to ensure a constant temperature meaning that the velocities have to be rescaled by

$$\lambda = \sqrt{\frac{\frac{3}{2} N k_B T}{E_{kin}}} \qquad (2)$$

where E_{kin} is the kinetic energy in the system. The initial parameters for the ensembles do not guarantee a system in equilibrium, in general, it requires a certain waiting time before equilibrium is reached. Equilibrium is assumed if the kinetic energy is approximately constant for a microcanonical ensemble and the total energy is more or less constant for the canonical case.

Once the system is in equilibrium it can be used to obtain the physical quantities such as the heat capacity, the pressure, the correlation function, the diffusion coefficient, the thermal conductivity, chemical potential, mean free path and so on. Here, the heat capacity, pressure and correlation function are discussed[2]. The used time steps in the model are $8.6 fs$ and the measuring time is minimally $43 ps$ to ensure a sufficient amount of statistical data.

Heat capacity The heat capacity at constant volume can be calculated by the thermodynamic identity $C_V = \frac{\partial E}{\partial t}$, which involves the fluctuation of the total energy. However, for the microcanonical ensemble, where the total energy is held constant, the heat capacity is calculated from the fluctuation of the kinetic energy

$$C_V = \frac{3 \langle K \rangle^2}{2 \langle K \rangle^2 - 3 \langle \delta K^2 \rangle} \qquad (3)$$

where $\langle K \rangle$ is the average of the kinetic energy and $\langle \delta K^2 \rangle$ is the average of the fluctuation squared.

Pressure The pressure is calculated using the virial theorem which gives a correction on the pressure due to the forces of the particles acting on each other compared to the assumption of an ideal gas. The total pressure of the system equals the sum of the ideal gas part and correction term

$$P = \rho k_B T - \frac{1}{3V} \left\langle \sum_i \sum_{j<i} \vec{F}_{ij} \cdot \vec{r}_{ij} \right\rangle \qquad (4)$$

where $\vec{F}_{ij} \cdot \vec{r}_{ij}$ is the dot product of the mutual force and the relative coordinates of two particles.

Structure factor The structure factor is obtained by counting the number of particles in a shell and dividing by the shell volume. Given by

$$g(r) = \frac{2V}{N(N-1)} \frac{1}{4\pi r^2 \Delta r} \langle N_{shell} \rangle \qquad (5)$$

$$N_{shell} = \sum_{i,j,j \neq i} \int \int_r^{r+\Delta r} \delta(\vec{r}' - \vec{r}_i) \delta\left(\left|\vec{r}' - \vec{r}_j\right| + r^*\right) dr^* d\vec{r}'$$

Where N_{shell} counts the number of particles in a shell with radius $[r, r + \Delta r]$ for every particle in the system. The structure factor can, among other information, tell something about the phase of the system.

To obtain an estimate of the mentioned physical quantities including the error a method is used called data blocking. For this the system in equilibrium produces data that is stored every single step and based on this data the correlation time is obtained by

$$\tau = \sum_{n=0}^{\infty} \frac{c(n)}{c(0)} \qquad (6)$$

where c is the autocorrelation of the data. The data is divided into blocks with a minimal length of the correlation time and the data is sampled in each block giving an estimate of the quantity to obtain[2].

III. Results

Heat Capacity The results for the heat capacity (for constant volume) for a wide range of temperatures is shown in figure 2. From theory [4] each degree of freedom is expected to contribute $\frac{1}{2} k_B$ to the heat capacity. For an ideal gas the degrees of freedom is 3 per particle (velocity in 3 directions) and for the solid state limit 6 per particle (velocity + vibrations in 3 directions), which is called the Dulong-Petit Law.

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[1]The code for the model can be found at [5]

[2]The structure factor is obtained every time interval that is know to sufficiently exceed the correlation time
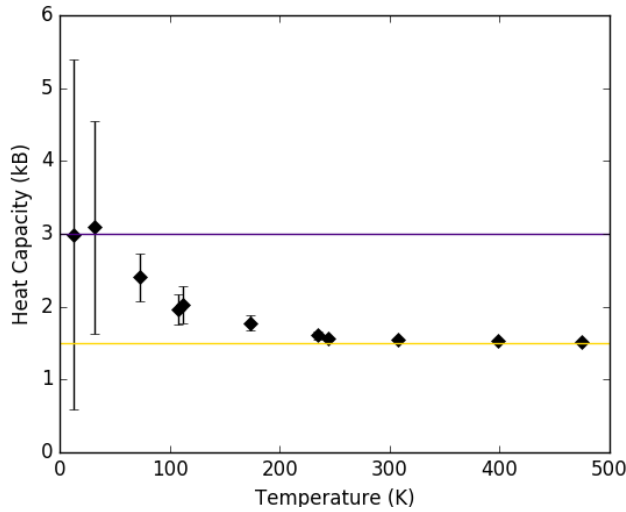
Figure 2: Heat capacity versus temperature including the errors. The yellow line indicating the theoretical limit for the ideal gas state and the purple line for the solid state limit

As can be seen the heat capacity does indeed converge to the expected value for the ideal gas and solid state limit. However, for the solid state the uncertainty becomes very large which is an indication that the system is not yet in equilibrium or does not converge to an equilibrated state. Furthermore for the state in between, a phase transition can be observed, at a temperature between approximately $75K - 150K$ which is well in correspondence to the melting $(84K)$ and boiling $(87K)$ point of argon [3].

The slow convergence towards the ideal gas state is explained by the non-negligible contribution of the Lennard-Jones interaction for temperatures up to $250K$.

Structure factor The structure factor is showed for different densities and temperatures in figure 1. The different combinations indicate different states of the system, for low temperature and high density the system is expected to be in a solid state. This is represented by the turquoise data points in the figure that show clear peaks at certain distances, which indicates that the atoms form a certain structure (or stay in the fcc structure) with fixed relative distances. These distances in solid state are mainly determined by the potential, since the kinetic energy is relatively low. Therefore, the atoms position themselves around the minimum of the potential which is at $0.38nm$ which can very well be seen in the results. Also, for the cases with increasing temperature and decreasing density the first peak is seen at this distance, however the structure of the system fades with increasing distance which is as expected since the kinetic energy breaks the initial fcc structure. For all combinations of density and temperature the density of particles up to approximately $0.3nm$ is zero in correspondence with the modeling of the potential, which increases very rapidly with lower distances prohibiting the particles to enter this close.
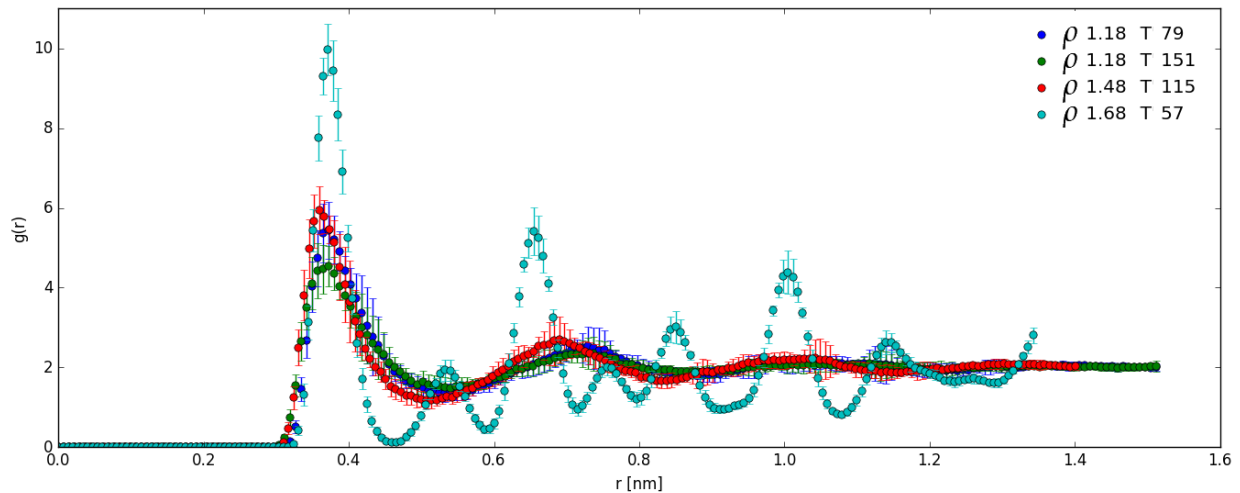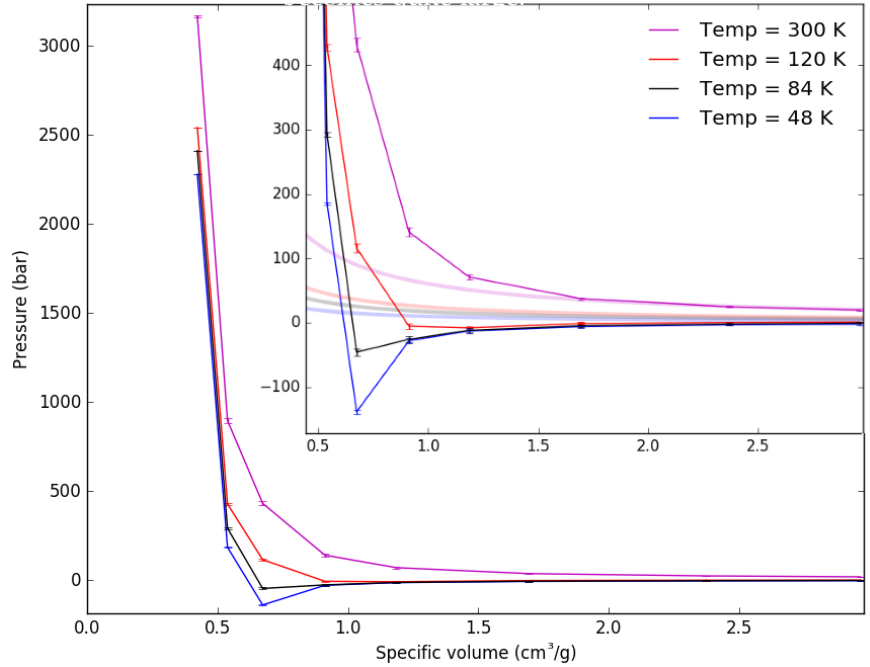

Figure 1: Structure factor for different combinations of density and temperature indicating different states of the system. The turquoise data points indicate the solid state limit whereas the green one is in the gas state. The blue and red combinations represent states in between.

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Pressure Figure 1 shows the results for the pressure to specific volume data for different temperatures which very much resemble the isotherms of a van der Waals gas [4]. For low density the system is expected to be in the gas state, in which case the pressure will converge to the ideal gas pressure which is the case as can be seen in the inset. Furthermore the pressure increases with temperature which is in accordance with equation 4. From the figure it can be seen that the virial correction term has more impact on the pressure as the temperature decreases and density increases. This can be attributed to the fact that with decreasing temperature and increasing densities the atoms will be closer together, resulting in higher forces acting on each other. For specific volumes ranging from 0.5-1.5, depending on the temperature, a phase transition can be observed. Within this region negative pressures occur due to the fact that the particles get trapped in the potential well without enough kinetic energy to escape resulting in chunks of particles with nothing in between, hence some kind of a vacuum is created. For even higher densities the particles are trapped in a lattice, where their relative distances become shorter than the minimum of the Lennard-Jones potential. This causes the particles to repel each other creating a pressure that increases very rapidly with increasing density due to the steep potential which is observed in the simulation.

IV. Conclusion

This paper describes the successful implementation of a model that calculates the time evolution of an argon gas. From this model several thermodynamic quantities are obtained after the system has reached equilibrium.

The first one, the heat capacity, converges nicely to the expected values for the ideal gas and solid state limit, however the uncertainty in the solid state becomes quite large. The phase transition in between is in correspondence with the expected temperature range obtained in experiments.

The structure factor, which gives an indication for the state in which the system is, shows patterns that are in line with expectations. For low temperature and high density, the structure factor shows clear peaks at certain distances in line with the used Lennard-Jones potential and the assumption that the atoms form a lattice. For the other extreme, the ideal gas, the pattern of the structure factor rapidly fades.

At last, the pressure was obtained showing isotherms which very much resemble the ones from a van der Waals gas. Three regimes were distinguished where the behavior of the pressure was explained by the position of the particles with respect to the potential used.

The correspondence of the obtained quantities shows that the used interacting potential is a very good approximation of the real interaction between argon atoms.

Future research could look at larger systems containing more atoms to improve the statistical data or the measuring time can be increased. Also the

time step can be reduces to decrease the introduced error. Also other quantities can be studied with the described model, such as the diffusion coefficient, the thermal conductivity, chemical potential, mean free path and so on.

References

[1] Verlet,L. 1967. Computer "Experiments" on Classical Fluids. I Thermodynamical Properties of Lennard-Jones Molecules, 159, 89-103

[2] Thijssen, J.M., 2013. Computational Physics, 2nd edition, CAMBRIDGE UNIVERSITY PRESS

[3] Patent-Invent, *Chemistry Quick Facts*. Feb. 2016. URL http://www.chemistry.patent-invent.com/chemistry/elements/argon.html

[4] Yoshioka, D., 2006. Statistica Physics. An Introduction, SPRINGER

[5] Tim Gebraad, *GITHUB: Computational-Physics-Argon*. Feb. 2016. URL https://github.com/TimGebraad/Computational-Physics-Argon.git