Computational Physics:
Simulation of argon in a cubic volume

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Abstract

The subject of this report is a simulation of a cubic volume filled with argon atoms. From the system of interacting particles the specific heat C_v, the pressure, expressed as $P/\rho k_B T$, and the pair correlation function $g(r)$ are derived and compared to the theory, the literature and the physical expectations. The conclusion is that the described simulation produces the values for thermodynamic quantities that were also found in literature discussing well known simulations by Verlet [1], Rahman [2] and Thijssen [3] and that this indicates that the program simulates a volume of argon atoms properly.

1 Introduction

The model discussed in this report is a simulation of a cubic volume filled with argon. It is a nice and smooth introduction into the field of molecular dynamics simulations; it is a noble gas with neutral charge, so the interactions between the particles is very simplistic. These kind of computer programs are a perfect way to analyze a thermodynamic system on a very fundamental level. The major benefit of a simulation over an experiment, is that it gives the user the possibility to manipulate virtually any parameter of the system. Realizing this in an experimental setup can be very troublesome.

2 Theory

In order to simulate the movement of the argon atoms a discretized form of Newton's equations of motion is used. The acceleration of the particles is caused by a force coming from a potential between the atoms. From the system of moving particles a number of thermodynamic quantities are derived.

2.1 Natural units

In order to ease computation, the used quantities are expressed in units related to the system. Lengths, energies and temperatures are expressed in units relevant to the Lennard-Jones potential. The new unit of mass is the mass of one argon atom. The Boltzmann constant k_B is expressed in units of itself, $k_B = 1\ [k_B]$. The new definition of these units also introduces a new time unit, which is called τ for simplicity. Another consequence of the natural units is that velocity and momentum are now equally valued.

Quantity	Unit	Value in SI units
Length	σ	0.34 nm [2]
Energy	ϵ	$120 k_B = 1.656 \cdot 10^{-21}$ Joule [2]
Temperature	ϵ/k_B	120 Kelvin [2]
Mass	m_{argon}	$6.63 \cdot 10^{-26}$ kg [4]
Time	$\sqrt{\frac{m_{\text{argon}}\sigma^2}{\epsilon}} \equiv \tau$	$7.99 \cdot 10^{-24}$ s

2.2 Interaction between the particles

The interaction between argon atoms can be modeled by an intermolecular potential. Argon has a neutral charge, so there is no Coulomb force between the particles. Furthermore we approximate the interaction between the particles as being pairwise. This allows us to only use the Lennard-Jones potential as the interaction between a pair of atoms. The Lennard-Jones (L-J) potential is given by: [3]

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

where ϵ is the depth of the potential well, σ is the distance at which the potential is zero, and r is the distance between the atoms. From the potential we can calculate the force acting on the particle:

$$\vec{F}_{LJ}(r) = -\vec{\nabla} U_{LJ}(r) = 4\epsilon \left[\left(\frac{6\sigma}{r} \right)^{7} - \left(\frac{12\sigma}{r} \right)^{13} \right] \hat{r} \tag{2}$$

In order to reduce computation time the force between particles further than the cut-off range $r_c = 2.5\sigma$ is considered negligible and is not calculated.

2.3 Equations of motion

The motion of the particles will be calculated using the velocity Verlet algoritm.[3] Each time step the new position and velocity will be calculated with the following equations:

$$x(t + \Delta t) = x(t) + v(t)\Delta t + \frac{F(t)}{2m}\Delta t^2 + \mathcal{O}(\Delta t^3) \tag{3}$$

$$v(t + \Delta t) = v(t) + \frac{1}{2}\left[\frac{F(t)}{m} + \frac{F(t + \Delta t)}{m} \right]\Delta t + \mathcal{O}(\Delta t^3) \tag{4}$$

2.4 Specific heat, C_v

The specific heat tells us how the temperature of the system reacts to the addition of energy. It is therefore a very useful thermodynamic quantity. In this simulation the total energy of the system is constant. The specific heat can be extracted from the fluctuations of the kinetic energy, E_{kin}, with the formula derived by Lebowitz. [3]

$$\frac{\text{Var}[E_{\text{kin}}]}{\mathbb{E}[E_{\text{kin}}]} = \frac{2}{3N}\left(1 - \frac{3N}{2C_v} \right) \tag{5}$$

where $\mathbb{E}[E_{\text{kin}}]$ and $\text{Var}[E_{\text{kin}}]$ denote the expectation value and the variance of the kinetic energy respectively. When slightly rewritten this equation becomes:

$$C_v = \frac{1}{\frac{2}{3N} - \frac{\text{Var}[E_{\text{kin}}]}{\mathbb{E}[E_{\text{kin}}]}} \tag{6}$$

This is the equation that is implemented in this simulation. The specific heat is given in units of k_B. If C_v is divided by the number of particles, N, a prefactor is derived. If the system is in a gaseous phase then this factor is $\frac{3}{2}$ due to the equipartition theorem, and if the argon is in the solid phase the factor will be 3. The latter conclusion is based on the law of Dulong-Petit. [5]

2.5 Pair correlation function, $g(r)$

The pair correlation function of $g(r)$ tells us how many particles one can find in a spherical shell of thickness Δr at distance r from a particle. In order to determine the pair correlation function, the distances between

the particles are put into a histogram with a number of bins with thickness Δr. The amount of hits in a bin that encompasses distance r is called $n(r)$. This value is then divided by a volume element $4\pi r^2 \Delta r$ to get the number of particles per volume of the spherical shell. As value for r the distance in the middle of the histogram bins is used. The only thing that separates this quotient from the pair correlation function is a prefactor, which multiplies it with the total volume and divides it by the number of particle pairs $N(N-1)/2$. The function $g(r)$ is dimensionless and has the asymptotic value of $g(r) \equiv 1$ for $r \to \infty$. [3]

$$g(r) = \frac{2V}{N(N-1)} \left[\frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \right] \tag{7}$$

2.6 Thermostat function

The base form of this simulation is as an (N,V,E) ensemble; the system is a fixed volume closed off from the environment so the total energy and number of particles is constant. Because of the fact that tracking the total energy is unfeasible in an experiment, a system with constant temperature is virtually always used. To mimic such a setup a thermostat is applied. This is a piece of code that rescales the velocity of the particles per time step to a value associated with the desired temperature. The velocity of particle i, $\vec{v}_i$ is rescaled to $\lambda \vec{v}_i$, with the following equation for λ for every component of the velocity: [3]

$$\lambda = \sqrt{\frac{(N-1)3k_B T_D}{\sum_{i=1}^{N} mv_i^2}} \tag{8}$$

where T_D is the desired temperature. This rescaling will be active in a small portion of time at the beginning of the simulation. If after that the temperature does not fluctuate any more, then the system is in equilibrium.

2.7 Pressure P

The pressure of the system, P, is calculated with the virial equation: [3]

$$\frac{P}{\rho k_B T} = 1 - \frac{1}{3Nk_B T} \left\langle \sum_i \sum_{j>i} r_{ij} \frac{\partial U(R)}{\partial r_{ij}} \right\rangle_{\text{cut-off}} - \frac{2\pi N}{3k_B TV} \int_{r_{\text{cut-off}}}^{\infty} r^3 \frac{\partial U(r)}{\partial r} g(r) dr \tag{9}$$

with $\rho = N/V$. The left hand side is expressed in this way because $P/\rho k_B T$ is a dimensionless quantity. The term between the angled brackets is the product of the distance and the derivative of the potential between two particles, summed up for all atom pairs not further than r_c apart. The third term of the right hand side is used to compensate for the potential energy that is otherwise lost when applying a cut-off range. In this term the g is approximated with $g(r) = 1$, the asymptotic value for g for large distances. The integral now becomes quite trivial and reduces to a constant value.

The pressure can be calculated for every time step but the results that are shown in section 4.3 is the time average of these values.

3 Simulation setup

The simulated system is a cubic volume with sides of length L. The value of this parameter is determined, through the volume V, by the desired density $rho = N/V$, and number of particles N in the system. Unless otherwise noted, a number of 864 particles is used. The program runs in time steps of $\Delta t = 0.004 \, \tau$.

3.1 Initial conditions

As usual, the particles in this simulation start with an initial position and velocity. The only constraint that is put on the initial position is that in solid phase the argon particles should be in a face-centered cubic

(FCC) lattice. [6] In this way the argon will be a neatly ordered solid at high density and low temperature and if the simulation has parameters of a liquid or gas phase then the initial velocity will have randomized the positions of the particles when the system has reached equilibrium. A consequence of this initial condition is that the simulation will only run in situations where there is an integer amount of unit cells in the x-, y- and z-direction. The number of particles will then be $N = 4N_{\text{u.c.}}^3$, where $N_{\text{u.c.}}$ is the number of unit cells along each vertex.

The initial velocity is determined by the temperature of the system through the Maxwell-Boltzmann distribution. This distribution is achieved by drawing each of the components of the initial velocity from a normal distribution $N(\mu, \nu)$ with $\mu = 0$ and $\nu = \sqrt{k_B T/m}$. As the last step of determining the initial velocity, the average momentum of the system is put to zero by reducing the velocity components of the particles by the mean value of the velocity in that direction.

3.2   Boundary conditions

The simulated volume has periodic boundary conditions. This means that while simulating a small system, there are an infinitely repeating number of images of the same small volume along every axis. It is as if the simulated system is a part of a much larger volume filled with argon. A consequence of the periodic boundary conditions is that in the situation where an atom leaves the volume on the right side, an image of this particle will enter the system on the left side. In this way the atoms will move in a natural way while the number of particles stays constant.

This simulation also follows the closest image convention; this means that the every particle only reacts with the closest version of another atom, even if this is an image that lies outside of the volume.

3.3   Error calculation

In a simulation, just as with any experiment, there of course has to be an estimate of the error. This is done by a procedure called data-blocking. The time series of data derived from the simulation is divided into a number of blocks N_{blocks}. In this way one obtains multiple short time series. These short series are also called data blocks. If the length in time of these blocks is larger than the correlation time, these short time series will be uncorrelated. These blocks can then be interpreted as multiple independent simulations. After the system has reached equilibrium, the setup becomes very uncorrelated in time and the correlation time will be very small. The data blocks can therefore be quite short. Only when, for example, calculating the specific heat for low temperatures a large block length can be beneficiary to get a measurement with a small uncertainty. The thermodynamic quantities A_i will be calculated for every data block i. Then we have: [3]

$$\langle A \rangle = \frac{1}{N_{\text{blocks}}} \sum_i A_i, \quad \text{Error}(A) = \frac{\sigma_{A_i}}{\sqrt{N_{\text{blocks}}}} \tag{10}$$

where σ_{A_i} is the standard deviation of the collection of measured values A_i for all data blocks. If the measured quantity can be determined every time step, then A_i is the time average over one of the data blocks.

4 Results

Unless otherwise noted the parameters associated with the solid, liquid and gas phases are:

Phase	Density ρ $[\sigma^{-3}]$	Temperature T $[\epsilon/k_B]$
Solid	1.2	0.5
Liquid	0.8	1.0
Gas	0.3	3.0

4.1 Specific heat, C_v

Table 1: Calculated values of C_v in solid, gas and liquid phase.

Phase	Density ρ $[\sigma^{-3}]$	Temperature T $[\epsilon/k_B]$	C_v $[k_B]$	C_v/N $[k_B]$
Solid	1.2	0.5	2500 ± 106	2.89 ± 0.12
Liquid	0.8	1	2148 ± 58	2.21 ± 0.04
Gas	0.3	3	1416.1 ± 5.0	1.639 ± 0.006

Table 1 was calculated by running the simulation for 15000 time steps divided into 15 data blocks for the noted combinations of parameters. It can be seen that the error in the specific heat increases with decreasing temperature. Because of the fact that at lower temperatures the fluctuations in the kinetic energy are smaller, a larger amount of time steps are needed to get a calculation of the variance with a reasonable accuracy. If the length of the data blocks are kept the same, the C_v will have an increasing error with decreasing temperature.

In table 1 one can see that in the solid and the gas phase the factor C_v/N is roughly 3 and 3/2 as would be expected by the Dulong-Petit law and the equipartition theorem respectively.

4.2 Pair correlation function, $g(r)$

The pair correlation function and its error was derived from 15 data blocks of 1000 time steps in length. In the figures below the error is indicated in a red shading around the mean value of $g(r)$ in blue. Unfortunately, the error can hardly be seen due to its small size.
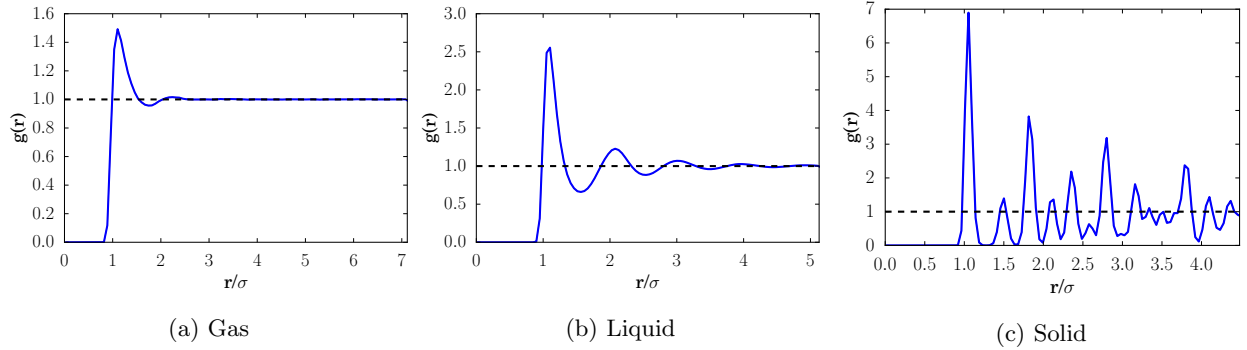

(a) Gas

(b) Liquid

(c) Solid

Figure 1: The pair correlation function g(r) in gas, liquid and gas phase.

The most notable features of the pair correlation function is that for every phase there are no particles closer together than $r = 1\ \sigma$ and that there is a peak at r slightly above $1\ \sigma$. These characteristics are caused by the Lennard-Jones potential. The high potential for $r < 1\ \sigma$ causes a strong repulsion between the atoms and the potential well for slightly higher values of r results in a slight attraction.

The figure 1b is very reminiscent of the graph made by A. Rahman in 1964. [2] In figure 1c one can see a periodic pair correlation function as is expected of a crystalline solid. In the graphs of the liquid and the gas phase one can see that for large r, $g(r)$ indeed goes asymptotically to 1.

4.3 Pressure, P

The pressure and its error are derived from fifteen data blocks of a 1000 time steps each.

Table 2: Values for $P/\rho k_B T$ for various (ρ, T) combinations.

Density ρ $[\sigma^{-3}]$	Temperature T $[\epsilon/k_B]$	Pressure $P/\rho k_B T$
0.40	1.491	0.448 ± 0.008
0.50	1.361	0.330 ± 0.008
0.70	0.990	-0.039 ± 0.016
0.80	0.999	1.25 ± 0.02
0.88	1.011	3.07 ± 0.02

The measured values for the dimensionless pressure are equal to the ones found in the literature. [1] [3] In the three measurements with the highest densities, where the system is in a liquid phase, $P/\rho k_B T$ increases when the density does. This is something what would be expected.

In figure 2 one can see a plot of the pressure divided by $k_B T$ in a system with 256 particles as a function of the density ρ for three different temperatures. The isotherms at T = 2.74 ϵ/k_B, T = 1.36 ϵ/k_B and T = 1.10 ϵ/k_B are at temperatures above, near and below the critical temperature of liquid-gas phase transition respectively. The fact that the isotherm of T = 1.36 ϵ/k_B has a section in which the line runs horizontal indicates that it is at, or at least very near, the critical temperature.
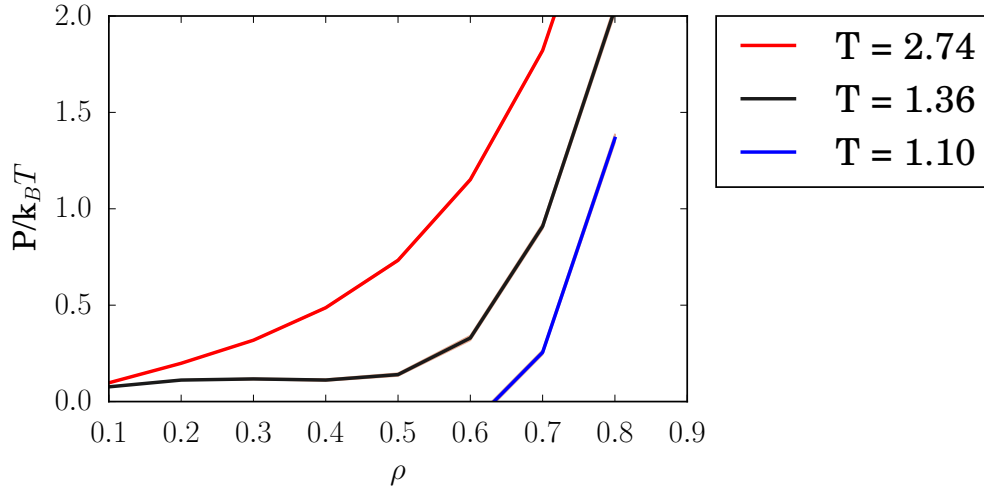

Figure 2: A plot of three isotherms in units of $[\epsilon/k_B]$ in a graph of P $k_B T$ in units of $[\sigma^3]$ against the density ρ in units of $[\sigma^{-3}]$.

In this figure the error of the pressure calculation is plotted in the graph, but it is unfortunately too small to see. The lines plotted in figure 2 are also similar to the graph found in the paper by Verlet. [1]

5 Conclusion

The measured quantities are equal or similar to values found in the literature and predictions made based on the theory. Notable examples are the values of C_v/N for gaseous and solid argon, which are the same as the theory, and the pair correlation function for liquid argon, which matches the literature [1], and for argon in the solid phase, which behaves as one would expect from a crystalline solid. The isotherms in the graph which plots $P/k_B T$ against the density ρ share their shape with those in the paper by Verlet [1], this indicates that the calculation of the pressure also behaves in the way it should behave. Based on all these findings one can conclude that the computer program discussed in this report, complete with the physical analysis containing the pairwise Lennard-Jones potential and the velocity Verlet algorithm, is an adequate simulation of a volume of argon. This model can in the future be used for additional studying of molecular dynamics.

References

[1] Loup Verlet. Computer" experiments" on classical fluids. i. thermodynamical properties of lennard-jones molecules. *Physical review*, 159(1):98, 1967.

[2] A Rahman. Correlations in the motion of atoms in liquid argon. *Physical Review*, 136(2A):A405, 1964.

[3] Jos Thijssen. *Computational physics*. Cambridge University Press, 2007.

[4] Michael E Wieser, Norman Holden, Tyler B Coplen, John K Böhlke, Michael Berglund, Willi A Brand, Paul De Bièvre, Manfred Gröning, Robert D Loss, Juris Meija, et al. Atomic weights of the elements 2011 (iupac technical report). *Pure and Applied Chemistry*, 85(5):1047–1078, 2013.

[5] Daniel V Schroeder. *An introduction to thermal physics*, volume 60. Addison Wesley New York, 2000.

[6] Neil W Ashcroft and N David Mermin. Solid state physics. 1976.