

**FYS4460:  
UNORDERED SYSTEMS AND PERCOLATION:  
MOLECULAR DYNAMICS TOPICS**

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1. TOPIC 1: MOLECULAR-DYNAMICS ALGORITHMS

Discuss the algorithms for molecular-dynamics modeling: Potentials, integration, cut-off, periodic boundary conditions, initialization, efficiency improvements.

- Molecular dynamics, an approximation to describing the the motion of molecules
- Forces described by potential energy:  $U = U(\mathbf{r}_i) = \sum_{ij} U_{ij}(r_i, r_j)$
- Simplest case does not depend on internal states
- Lennard-Jones potential:  $U(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)$

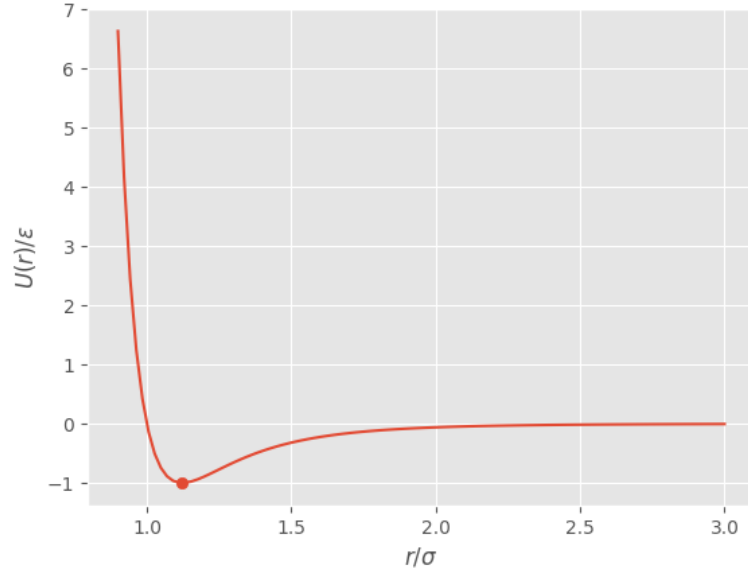


FIGURE 1.1. Illustration of the Lennard-Jones potential and it's minimum at  $r/\sigma = 2^{1/6}$ .

- Force acting on the atoms:

- $F(r) = -\frac{d}{dr}U(r) = 24\epsilon \left( \left(\frac{\sigma}{r}\right)^6 - 2\left(\frac{\sigma}{r}\right)^{12} \right)$

- Velocity Verlet algorithm:

$$\begin{aligned}
 (1) \quad & v_i(t + \Delta t/2) = v_i(t) + F_i(t)/m\Delta t/2 \\
 (2) \quad & r_i(t + \Delta t/2) = r_i(t) + v_i(t + \Delta t/2) \\
 (3) \quad & F_i(t + \Delta t) = -\nabla U(r_i(t + \Delta t)) \\
 (4) \quad & v_i(t + \Delta t) = v_i(t + \Delta t/2) + F_i(t + \Delta t)/m\Delta t/2
 \end{aligned}$$

- Making the equations of motion dimensionless

- Introduce  $r' = r/\sigma$  and  $t' = t/\tau$ , where  $\tau = \sigma\sqrt{m/\epsilon}$

- Equations of motion rewritten:

$$(5) \quad \frac{d^2}{dt'^2} \mathbf{r}'_i = \sum_j 24 \left( \left( \frac{1}{r'_{ij}} \right)^6 - 2 \left( \frac{1}{r'_{ij}} \right)^{12} \right) \left( \frac{\mathbf{r}'_{ij}}{r'^2_{ij}} \right).$$

- Calculation of the forces are expensive,  $\mathcal{O}(n^2)$

- Cut-off
- Initialization considerations
- Velocities
- Position
- Restrictions of simulating large systems
- Periodic boundary conditions
- Additional improvements

## 2. TOPIC 2: MOLECULAR-DYNAMICS IN THE MICRO-CANONICAL ENSEMBLE (1)

Discuss initialization and initialization effects. Temperature measurements and fluctuations. Comment on use of thermostats for initialization.

- Basic considerations of initialization
- Creating velocities in LAMMPS: `velocity all create 2.5 87287`
- Initial positions, more care must be taken

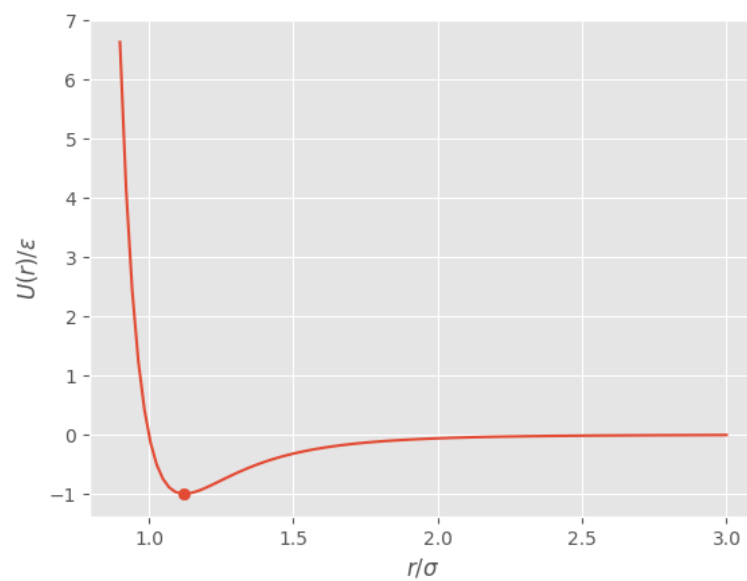


FIGURE 2.1. Illustration of the Lennard-Jones potential and its minimum at  $r/\sigma = 2^{1/6}$ .

- Random positions may cause trouble
- Unit cells
- Simple cubic lattice
- Face-centered cubic lattice
- Implementing this in LAMMPS:

```

variable      b          equal 5.72
variable      sigma      equal 3.405
variable      rhoStar    equal 4/((b/sigma)^3)
variable      nCells     equal 10

units lj
dimension 3
boundary p p p
atom_style atomic

lattice fcc rhoStar
region simbox block 0 nCells 0 nCells 0 nCells
create_box 2 simbox
create_atoms 1 box

```

- Reaching an equilibrium state
- When is it in equilibrium?
- Central limit theorem and velocity distributions
- Characterizing the velocity distribution:

$$(6) \quad \frac{\sum_i^n h_i(t) h_i(t_n)}{\sum_i^n h_i(t_n)^2}.$$

- Example for argon at  $T = 2.5$  in figure 2.3

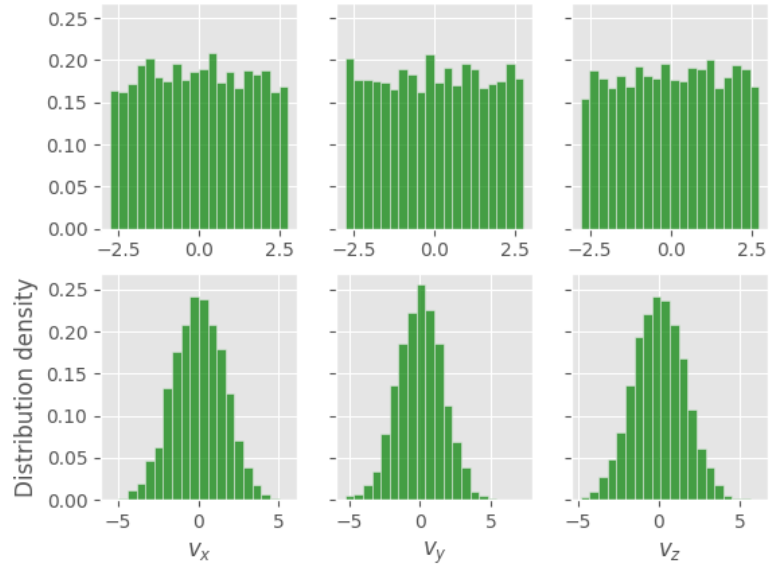


FIGURE 2.2. Histograms of the (top) initial and (bot) final velocity components of an argon gas.

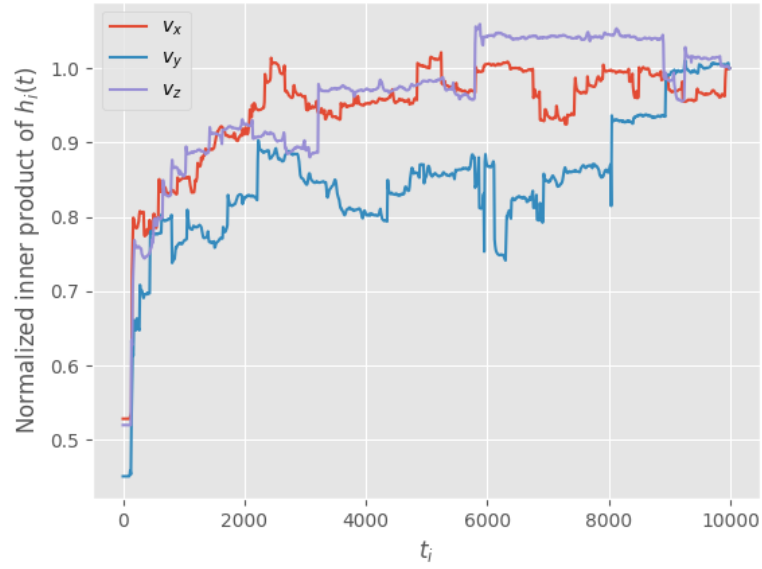


FIGURE 2.3. Normalized inner product of the velocity components of an argon gas.

- Another approach: monitor the temperature

- Build-in function in Lammmps based on the equipartition principle:

$$(7) \quad \langle E_k \rangle = \frac{3}{2} N k_B T.$$

- Initial temperatures for systems of different size in figure 2.4

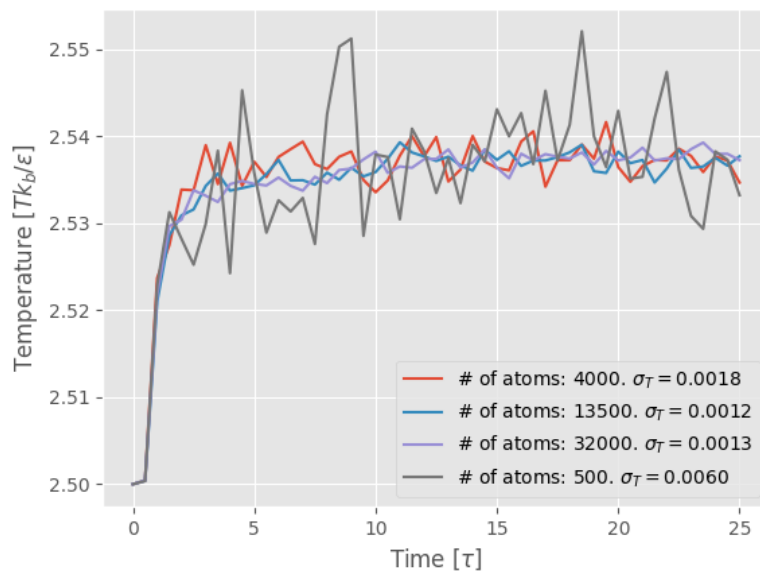


FIGURE 2.4. Temperature as a function of time in an argon gas.

- Challenges with initial temperatures and pressure

- Solution: Thermostats!

- NVE  $\rightarrow$  NVT

- Berendsen thermostat, rescales velocities by a factor

$$(8) \quad \gamma = \sqrt{1 + \frac{\Delta t}{\tau} \left( \frac{T_0}{T} - 1 \right)}.$$

- Simple to implement, but has it's challenges

- Not consistent with the canonical ensemble

- Nosè-Hoover thermostat, harder to implement, but standard in Lammmps

- LAMMPS commands:

```
fix 1 all temp/berendsen ${T0} ${T1} ${tau} #Berendsen
fix 1 all nvt temp ${T0} ${T1} ${tau}      #Nosé-Hoover
```

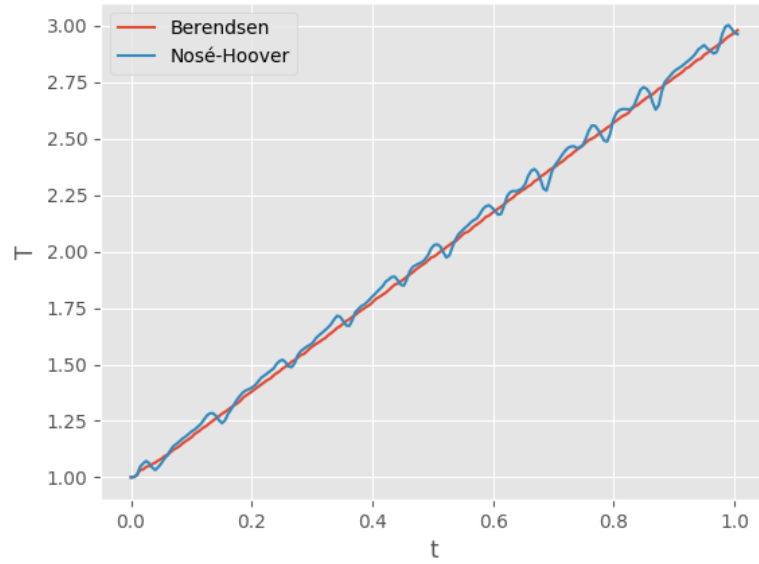


FIGURE 2.5. Comparison of the temperature of two systems while under the effects of the Berendsen and Nosé-Hoover thermostats.



### 3. TOPIC 3: MOLECULAR-DYNAMICS IN THE MICRO-CANONICAL ENSEMBLE (2)

How to measure macroscopic quantities such as temperature and pressure from a molecular-dynamics simulation. How is this done in your Lammmps simulation? What challenges do you expect? What can it be used for? Provide examples from your own simulations.

- An important reason for doing molecular dynamics simulations
- The Equipartition principle gives us a means to measure the temperature

$$(9) \quad \langle E_k \rangle = \frac{3}{2} N k T.$$

- Also used in Lammmps for temperature measurements
- Only an estimate
- Other considerations
- Temperature fluctuations
- Time-averaging

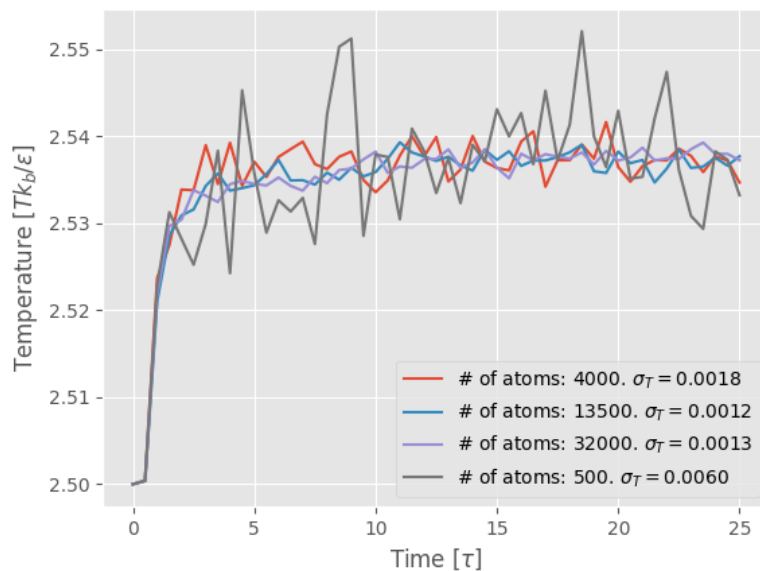


FIGURE 3.1. Time development of the temperature in systems of different sizes.

- Choice of time-step in the integration

- Conservation of momentum

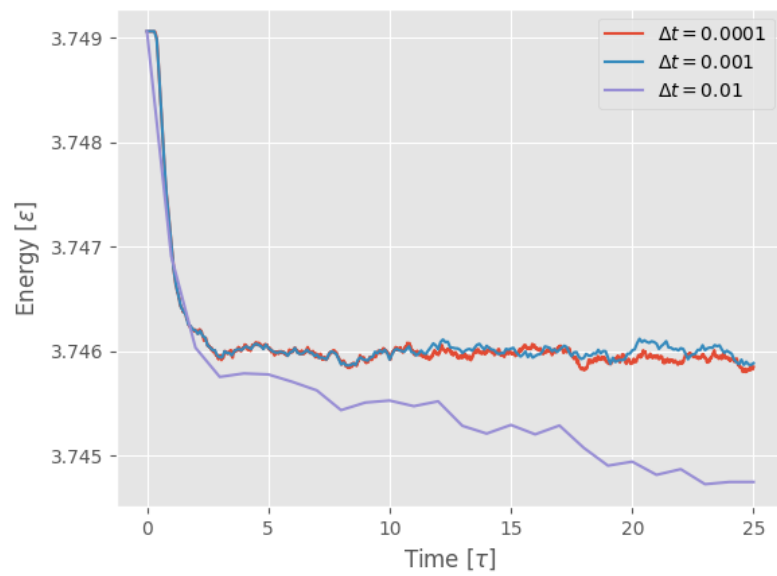


FIGURE 3.2. Time development of the total energy of the system for different time steps.

- Equation of state:  $PV = NkT$
- Some results from simulations

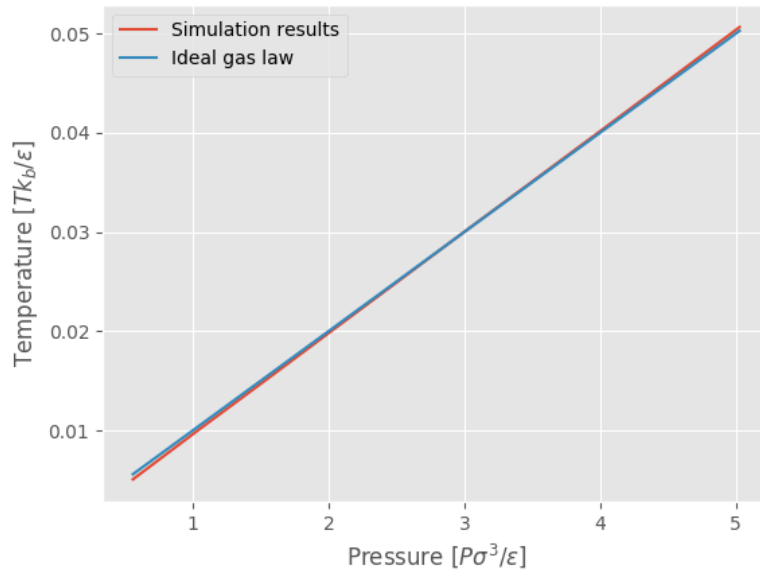


FIGURE 3.3. Pressure as a function of temperature of and argon gas.

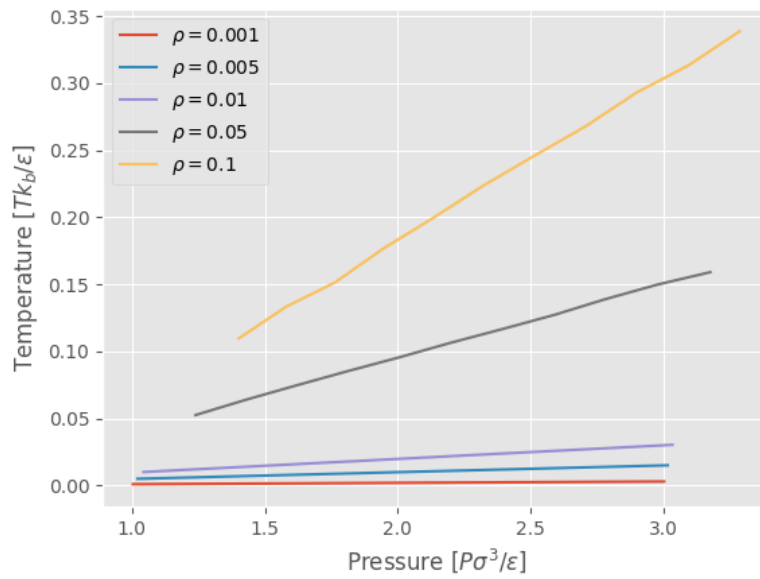


FIGURE 3.4. Pressure as a function of temperature of and argon gas at different densities.

- Van der Waals equation of state:

$$(10) \quad \left( P + a \left( \frac{N}{V} \right)^2 \right) (V - Nb) = Nk_b T.$$

- Can determine the factors in simulation
- Calculation of pressure in Lammmps:

$$(11) \quad P = \rho k T + \frac{1}{3V} \sum_{i < j} \mathbf{F}_{ij} \cdot \mathbf{r}_{ij}.$$

- The pressure tensor is also calculated
- Can be used to visualize pressure locally

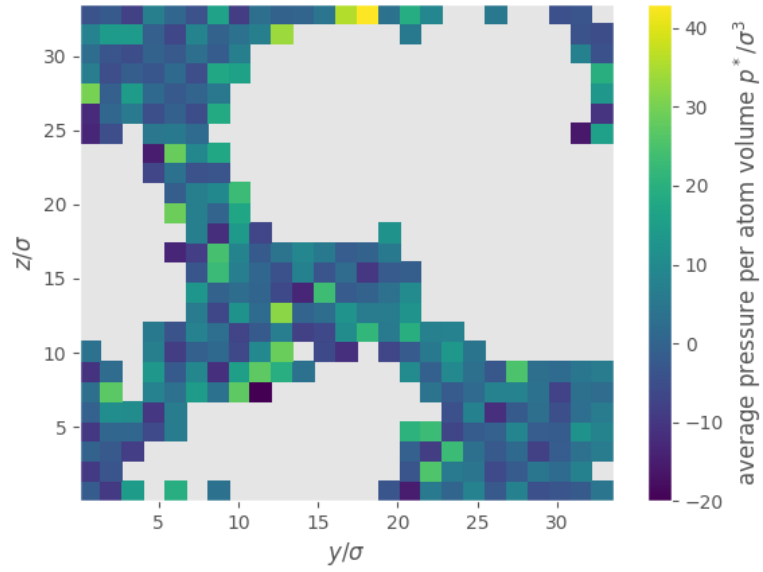


FIGURE 3.5. Cross section of a porous structure, showing the spatial pressure distribution of the system at  $T = 1.5$ . White areas represents a matrix of solid spheres.

#### 4. TOPIC 4: MEASURING THE DIFFUSION CONSTANT IN MOLECULAR-DYNAMICS SIMULATION

How to measure the diffusion constant in molecular dynamics simulations – limitations, challenges and results. Compare with theoretical estimates for diffusive behavior. Discuss difference between the potential models you studied.

- Definition
- Mean squared displacement:  $\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N (\mathbf{r}(t) - \mathbf{r}(t_0))^2$
- Measuring MSD in Lammmps: `compute msd all msd`
- Diffusion coefficient:  $\langle r^2(t) \rangle = 6Dt$
- Considerations when measuring  $D$
- Example from simulations of liquid argon:

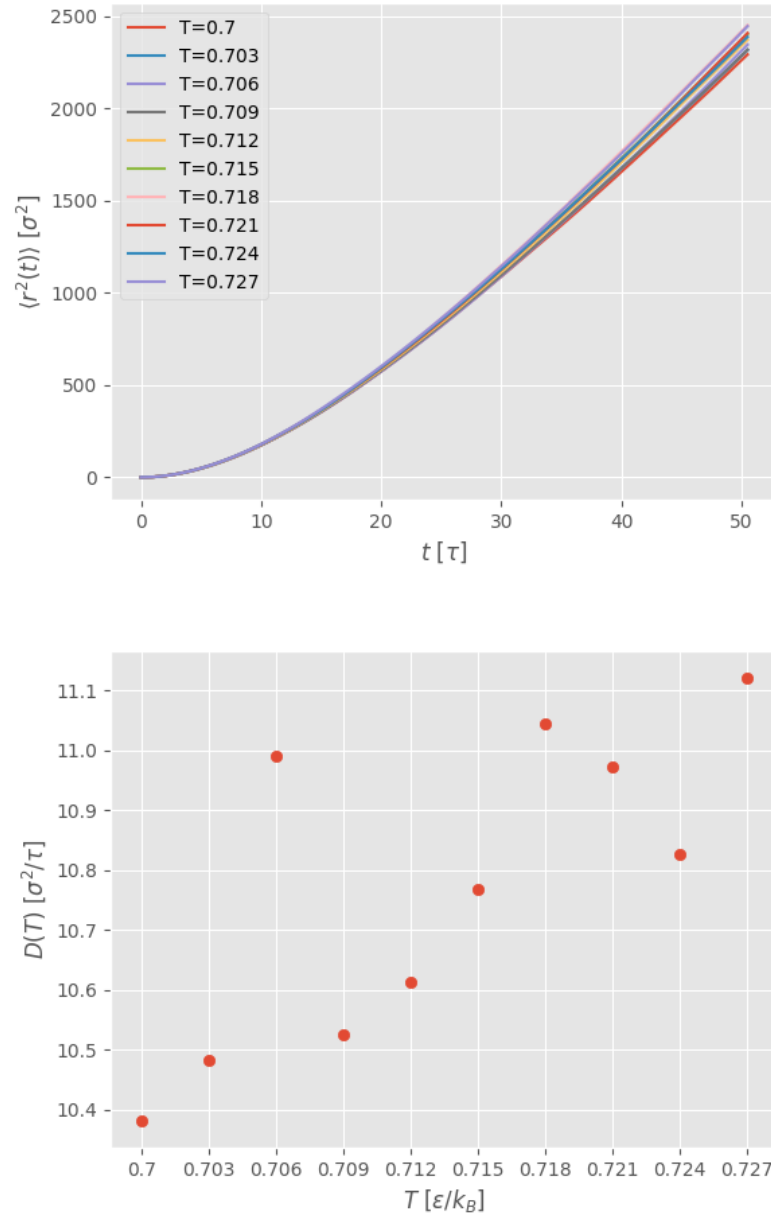


FIGURE 4.1. Mean squared displacement and diffusion constant of argon in the liquid temperature range

- Measure diffusion of Silicon

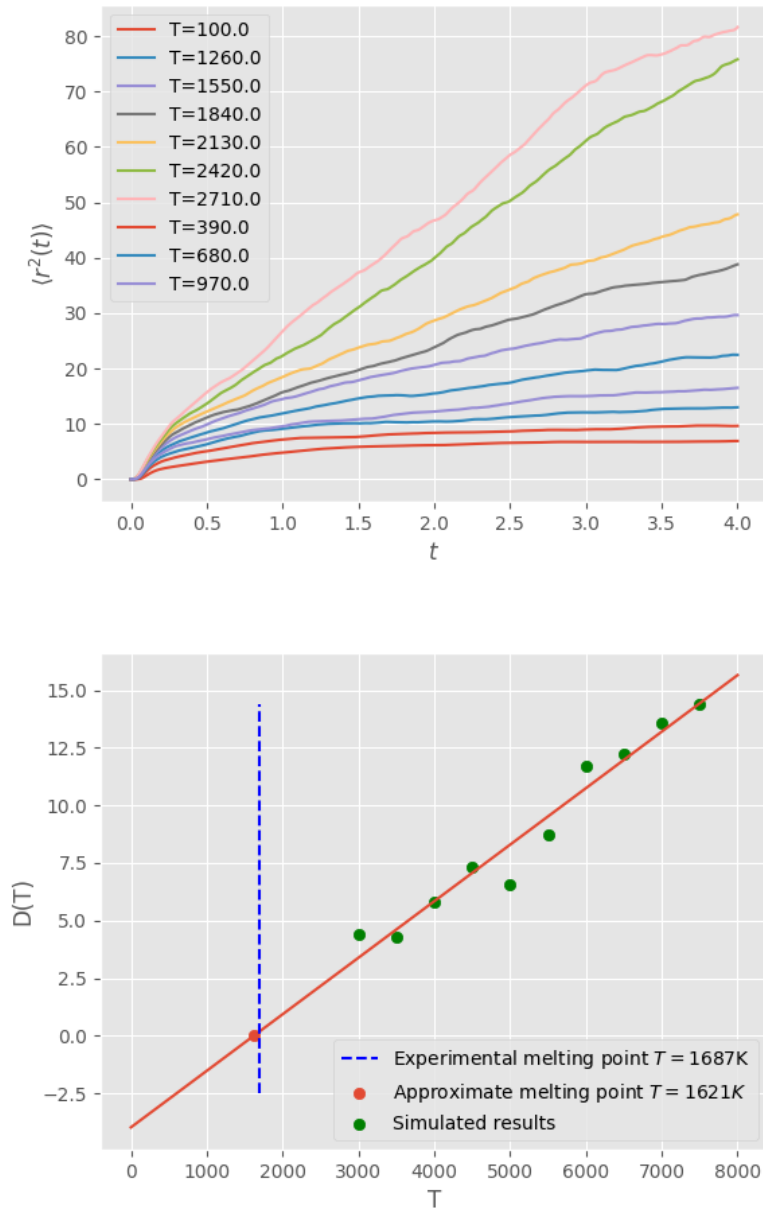


FIGURE 4.2. Mean squared displacement and diffusion coefficients of silicon for different temperatures, with an approximation to it's melting point.

- Results are more noisy than for Argon
- Useful nonetheless

- Diffusion of water using the SPC/E water model

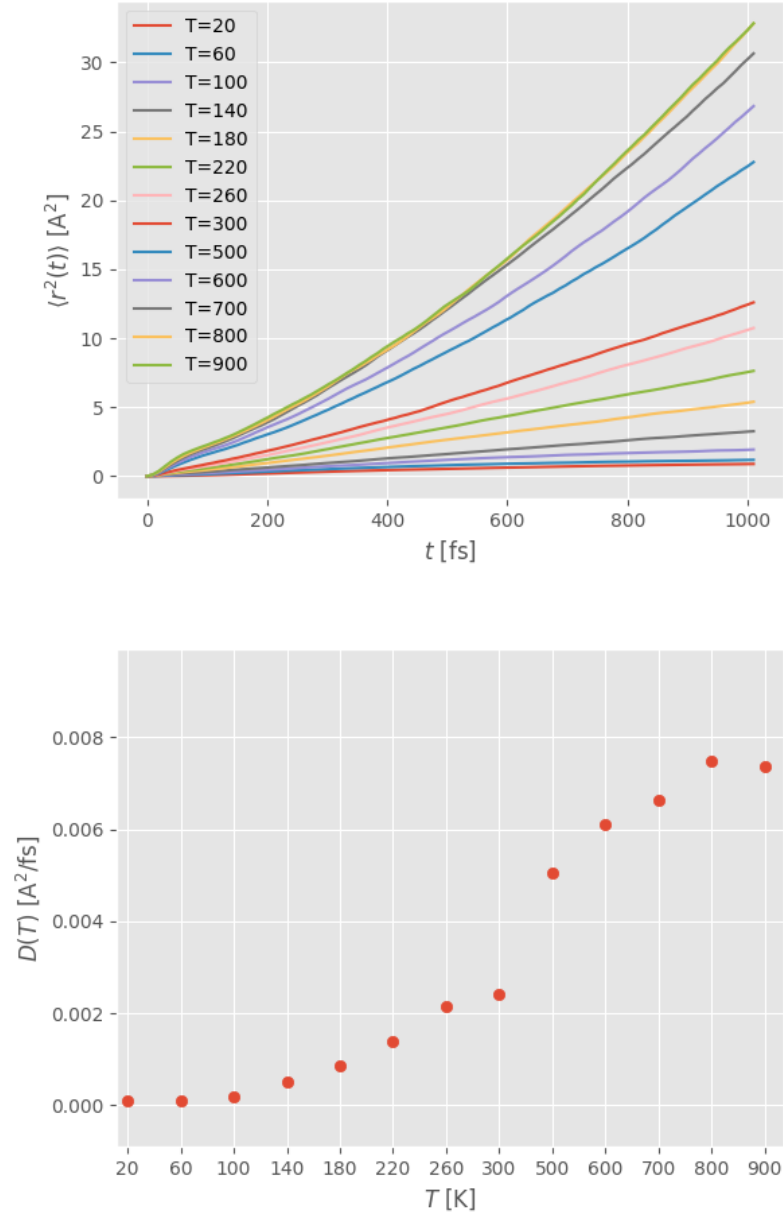


FIGURE 4.3. Mean squared displacement and diffusion constants of water over a range of temperatures.

- More non-linearity in the MSD of water for high temperatures
- Remarks about the model differences



## 5. TOPIC 5: INTERACTION MODELS IN MOLECULAR-DYNAMICS SIMULATIONS

Introduce the three potential models you studied. Discuss similarities and differences in your results with particular emphasis on initialization, efficiency,  $g(r)$  and  $D(T)$ . Provide examples from your own simulations.

- Potential energy dictates the behaviour of the system

- Bonded vs non-bonded interactions

- Assumption of the closed form of the potential energy:

$$(12) \quad U = U(\mathbf{r}_i) = \sum_{ij} U_{ij}(\mathbf{r}_i, \mathbf{r}_j) + \sum_{ijk} U_{ijk}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots$$

- Lennard-Jones potential:

$$(13) \quad U(r) = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right).$$

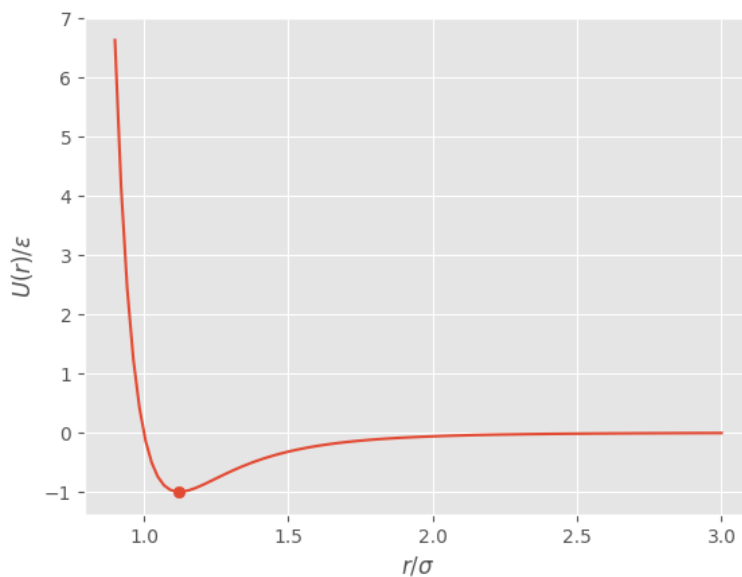


FIGURE 5.1. Illustration of the Lennard-Jones potential and its minimum at  $r/\sigma = 2^{1/6}$ .

- Setup of simulation in LAMMPS:

```
#3d Lennard-Jones gas
units lj
dimension 3
```

```
boundary p p p
atom_style atomic
```

```
lattice fcc 0.01
region simbox block 0 10 0 10 0 10
create_box 1 simbox
create_atoms 1 box
```

```
mass 1 1.0
velocity all create 2.5 87287
```

```
pair_style lj/cut 3.0
pair_coeff 1 1 1.0 1.0 3.0      #sigma, epsilon, cut-off
```

- Stillinger-Weber potential:

$$(14) \quad U(r) = \sum_{ij} U_2(r_{ij}) + \sum_{ijk} U_3(r_{ij}, r_{ik}, \theta_{ijk}),$$

- The potentials  $U_1$  and  $U_2$  are given by

$$(15) \quad U_1(r_{ij}) = A\epsilon \left[ B \left( \frac{\sigma}{r_{ij}} \right)^p - \left( \frac{\sigma}{r_{ij}} \right)^q \right] \exp \left( \frac{\sigma}{r_{ij} - a\sigma} \right),$$

$$(16) \quad U_2(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda\epsilon [\cos(\theta_{ijk}) - \cos(\theta_{ijk,0})]^2 \exp \left( \frac{\gamma\sigma}{r_{ij} - a\sigma} \right) \exp \left( \frac{\gamma\sigma}{r_{ik} - a\sigma} \right)$$

- Similarities to Lennard-Jones

- Differences
- Initial positions:

```
lattice custom $a
    &a1 1.0 0.0 0.0      #unit cube coords
    &a2 0.0 1.0 0.0
    &a3 0.0 0.0 1.0
    &basis 0.0 0.0 0.0    #atom placements
    &basis 0.0 0.5 0.5
    &basis 0.5 0.0 0.5
    &basis 0.5 0.5 0.0
    &basis 0.25 0.25 0.25
    &basis 0.25 0.75 0.75
    &basis 0.75 0.25 0.75
    &basis 0.75 0.75 0.25
```

- Stillinger-Weber potential in Lammmps: `pair_style sw`

- Other parameters in the potential must also be defined
- Water: Single Point Charge model (SPC/E)

$$(17) \quad U_{ij} = \sum_{ij} = \frac{kq_i q_j}{r_{ij}} 4\epsilon \left( \left( \frac{\sigma}{r_{OO,ij}} \right)^{12} \left( \frac{\sigma}{r_{OO,ij}} \right)^6 \right).$$

- Similarities to Lennard-Jones
- Setup in LAMMPS is more involved, use `moltemplate`
- Measurements of diffusion of the different models

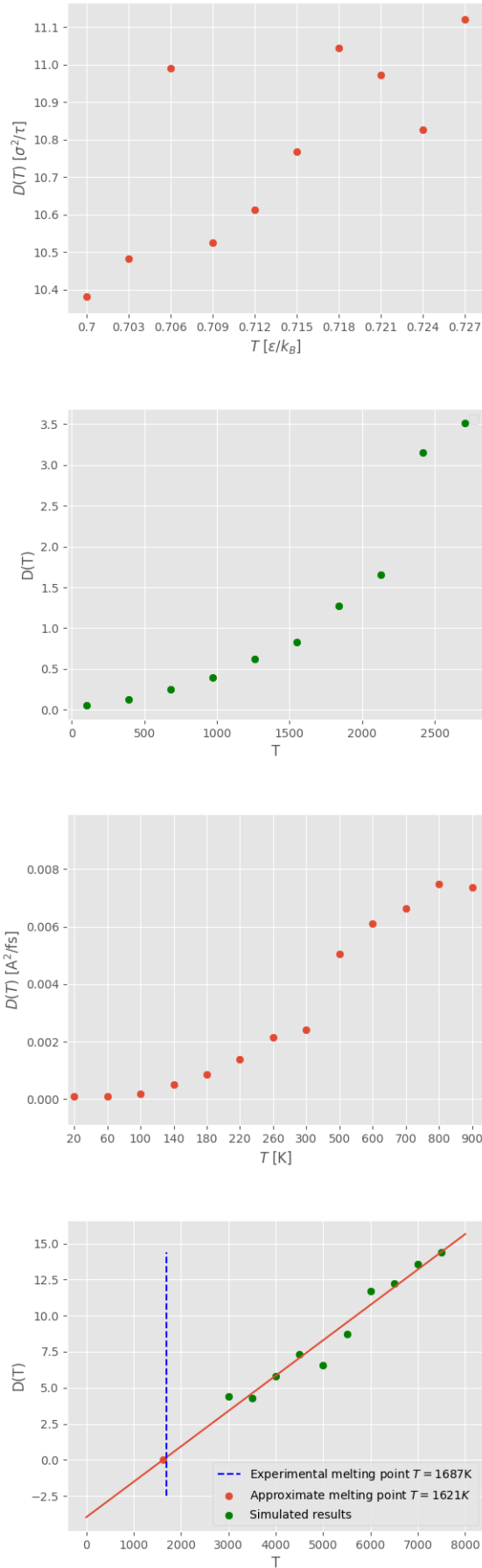


FIGURE 5.2. Diffusion constant as a function of temperature for (from top) argon, silicon and water, with bonus pic of silicons melting temperature.

- Measurements of the radial distribution function

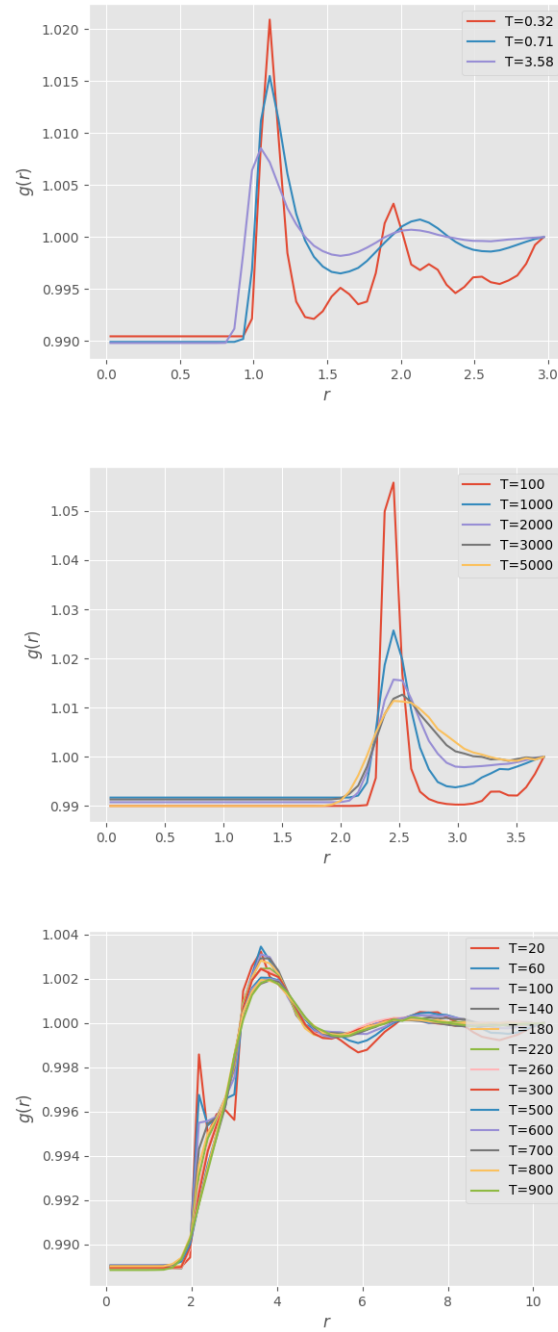


FIGURE 5.3. Radial distribution of (from top) argon, silicon and water.