Understanding The Relationship Between Microscopic Mechanisms and Continuum Description of Diffusion

MSE 6270: Introduction to Atomistic Simulations
Homework #5

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1 Question 1

Using the same FCC crystal that you used in homework #4 (7×7×7 unit cells), but build it with the lattice parameter afcc = 5.78 A that is based on the experimental molar volume of liquid Ar at the melting temperature and 1 atm pressure.

Perform a simulation at constant volume and temperature T = 1.5Tm, where Tm is the melting you found in homework #4.

Run the simulations for a time sufficient to collect data for the calculation of the diffusion coefficient.

From HW#4 the melting temperature of Ar at pressure of 1 atm and molar volume of 24.6 $\frac{cm^3}{mole}$ was $T_m = 92K$. An FCC crystal with 7x7x7 unite cells was constructed with lattice parameter $a_{fcc} = 5.78$ A" and simulated at constant volume and temperature $T = 1.5T_m = 138K$.

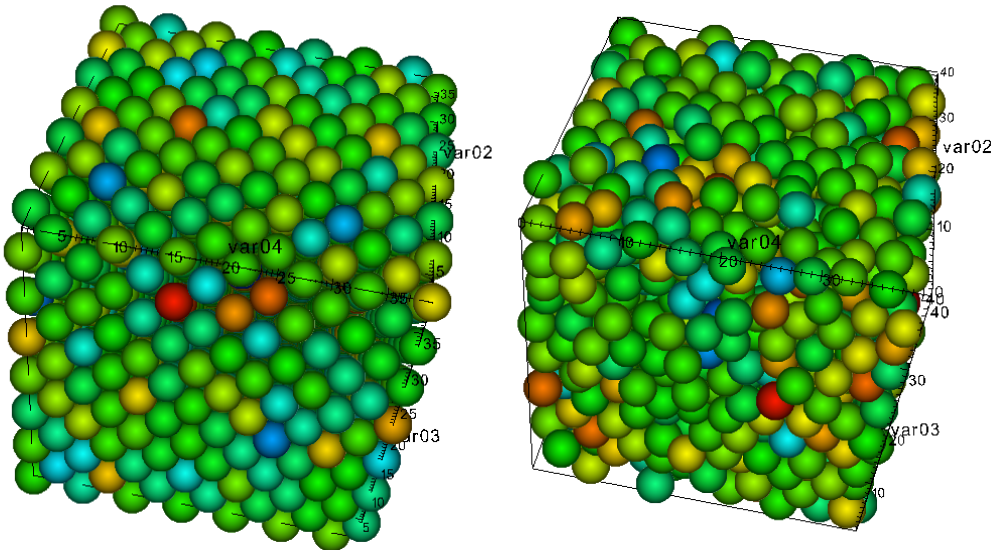


Figure 1: The FCC crystal was first equilibrated using constant pressure and equal velocity distribution (LFLAG = 1, KFLAG = 2) with periodic boundary conditions at temperature T = 138 K for t = 1 ps. The crystal on the left is the system before equilibration, and after equilibration on the right. Given that the temperature specified is above the melting temperature previously found, it is reasonable that no long range order is found in the system after equilibration and the FCC crystal is not in a solid state.

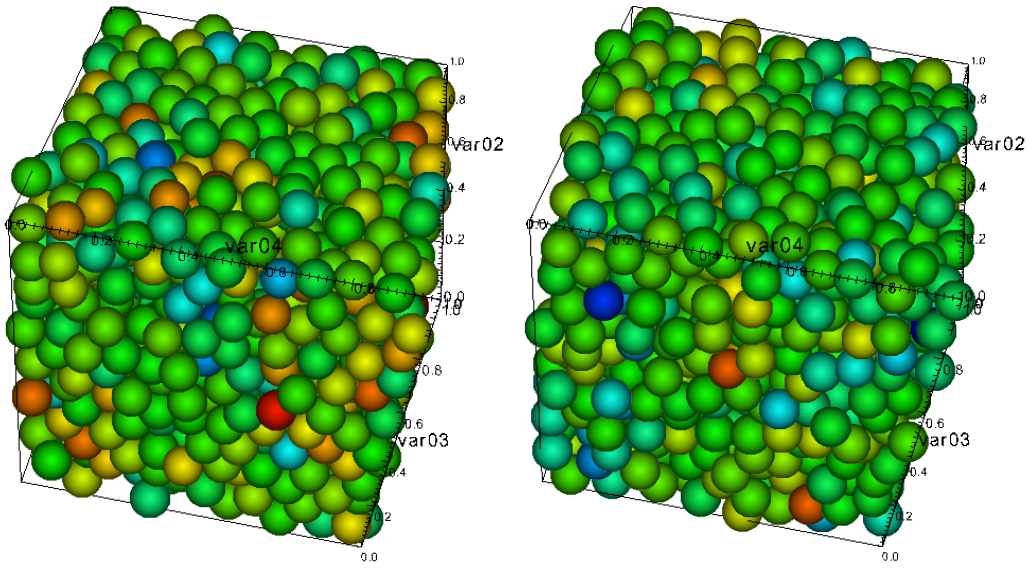


Figure 2: The FCC crystal after equilibration being heating for t = 100 ps (dt = 0.001 ps) with constant volume and constant temperature (LFLAG = 0, KFLAG = 5) and periodic boundary conditions in all three directions. On the left is the system at t = 0 ps, on the right at t = 100 ps. No qualitative difference is observed between the two system snapshots, and diffusion cannot be estimated since all atoms are of the same type.

2 Question 2

The mean squared displacement can be calculated using the average of atomic displacements as follows:

$$MSD = \left\langle \Delta\vec{r}(t)^2 \right\rangle \equiv \frac{1}{N}\sum_{i=1} N(\vec{r_i}(t) - \vec{r_i}(0))^2 \tag{1}$$

where the periodic boundaries must first be "unwrapped" to obtain the true atomic displacements from the simulation. The following algorithm (Matlab) was used to unwrap the displacements:

```
% "Unwrap" coordinates from periodic boundary simulation
% This undoes the gather() command that keeps atoms in simulation box
% Displacement vector is unwrapped instead of individual coordinates
for j=1:N
    r_prev = r(1,j); % j-th atom first timestep = true coordinates
    gt(1,j) = r(1,j);  % corrected cooridnates (1st timestep = true coordinates)
    % Loop through time trajectory of j-th atom
    for k = 2:length(pos_x(:,j))
        dr = r(k,j) - r_prev;          % displacement between current and previous timestep
        if dr > .5*box_size            % displacement too far "right"?
            dr = dr - box_size;        % replace displacement
        end
        if dr < -.5*box_size           % displacement too far "left"?
            dr = dr + box_size;        % replace displacement
        end
        gt(k,j) = gt(k-1,j) + dr;
        r_prev = r(k,j);
    end
end
```

Next, using the Einstein relation the diffusion coefficient, D, for $T = 1.5T_m$ can be calculate using:

$$MSD = \left\langle \Delta\vec{r}(t)^2 \right\rangle = A + 6Dt + fluctuations \tag{2}$$

which is a \$0$^{\text{th}}$\$f-order polynomial fit (linear fit) to the mean squared displacement vs time plot which was calculated above. Using linear regression, the coefficients can be found as:

Table 1: Diffusion coefficient and offset as calculated using linear regression of the MSD vs time plot of the atomic displacements in the simulation.

Coefficient	Value	Value
A (offset)	$20.5493 Angstrom^2$	$2.0549 \times 10^{-9} m$
D (diffusion)	$0.9371 \frac{Angstrom^2}{ps}$	$9.371 \times 10^{-9} \frac{m^2}{s}$

However, from the in-class lecture on mobility of atoms and diffusion (page 1), the Einstein relation is stated to be suitable for estimated D in MD simulations only for sufficiently high temperature, when $D > 10^{12} \frac{m^2}{s}$, which seems to be very high and perhaps a typo.

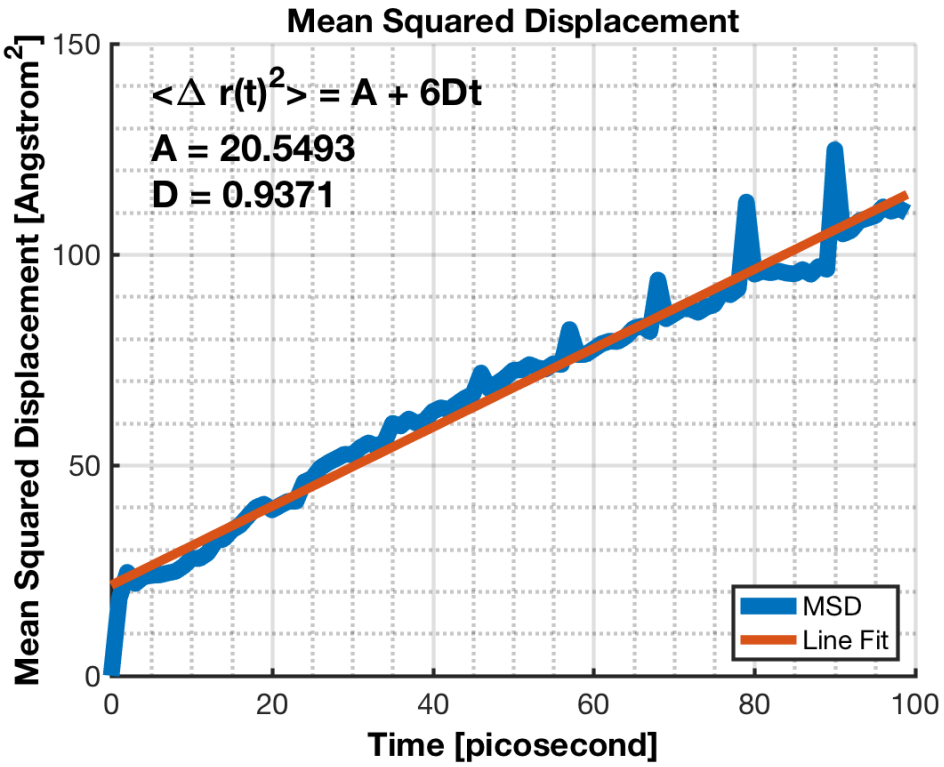


Figure 3: The mean squared displacement vs. time plot as calculated from atomic trajectories compared to their initial positions. A linear fit estimated the diffusion coefficient, D, as the slope of the data.

3 Question 3

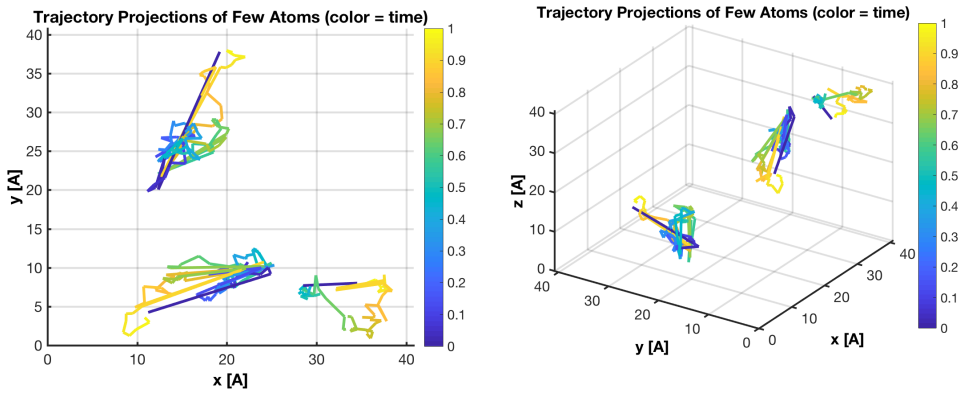


Figure 4: The trajectories of three particles are plotted over time with the color of the line corresponding to time (0 ps to 100 ps, brighter = later time). On the left is the projection of the trajectory to a 2D plane, on the right the same trajectories are plotted in 3D view. From the diffusion coefficient ($D = 0.9371A^2/ps$) it is expected that the 2D projection will show an area close to $0.9371A^2/ps \times 100ps = 93.71A^2$ or $9.68A$ in each direction (on average). The trajectories on the left closely resemble this behavior, with atomic displacements on average being close to 10 Angstroms in each direction.

4 Question 4

Similar to previous simulations, the assembled crystal was first equilibrated by simulation for 1 ps with equal velocity distribution is constant pressure (KFLAG = 2, LFLAG = 1) at T = 138 K. Since the total simulation time is only 1 ps, the value of Ngather was arbitrarily set.

After equilibration, the system was simulated with constant temperature and constant volume (KFLAG = 5, LFLAG = 0) at T = 138 K for 800 ps with dt = 0.004 ps. If we consider "significant mixing" to be the diffusion of atoms 15 Angstrom into each other, then we can predict the simulation time using knowledge of the diffusion coefficient as:

$$\frac{(2 \times 15 \quad [Angstrom])^2}{D \quad [Angstrom^2/ps]} = \frac{900 \quad [Angstrom^2]}{0.9371 \quad [A^2/ps]} = \frac{961 \quad [ps]}{0.004 \quad [steps/ps]} = 240250 \quad [steps] \tag{3}$$

Since the Ngather parameter gathers molecules back to the computation cell, it is reasonable to perform a gather step when atoms are expected to have traveled half of the simulation cell. With rigid boundaries in the z-direction, only the x and y directions will require gathering. Using our new knowledge of the diffusion coefficient D = 0.9371 A^2/ps and the known size of the x-y simulation box (x_{len} = 23.12 Angstrom both), we can calculated the number of simulation steps required for an atom to travel half the box distance:

$$\frac{1}{D}\left[\frac{ps}{A^2}\right] \times \frac{1}{dt}\left[\frac{steps}{ps}\right] \times \left(\frac{x_{len}}{2}\right)^2 [A^2] = 35650[steps - per - gather] \tag{4}$$

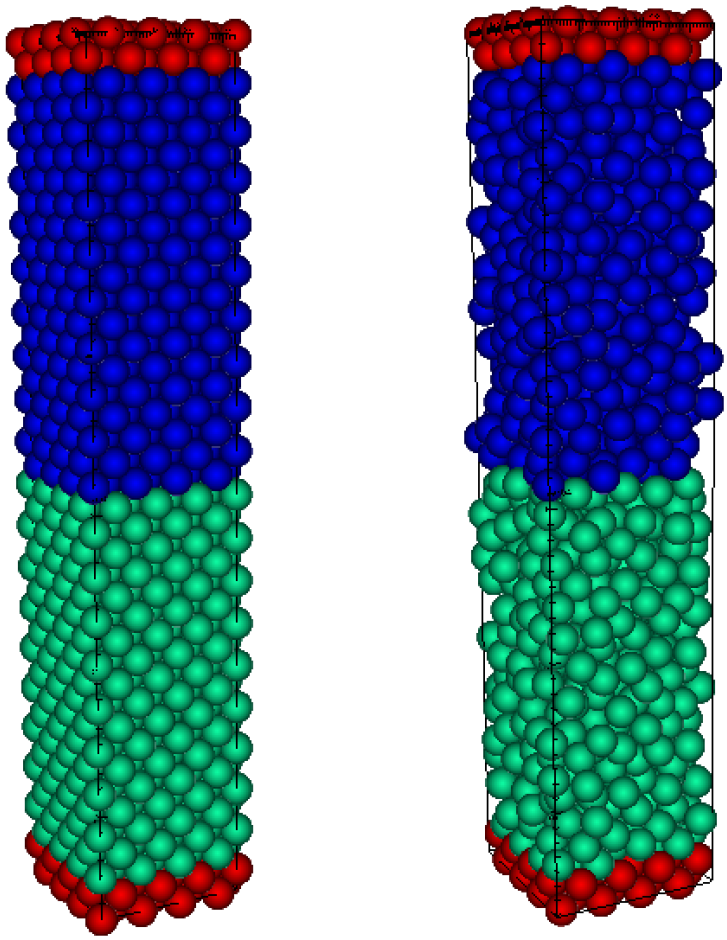
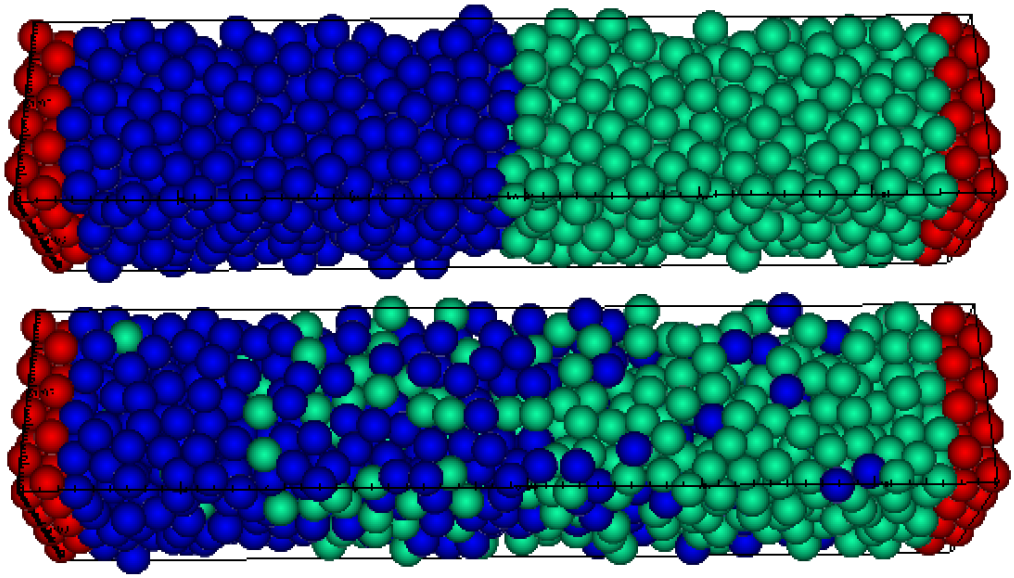


Figure 5: Equilibration of the 4x4x20 FCC crystal (1280 atoms) with $a_{fcc} = 5.78$ Angstrom. Rigid atoms are on the top and bottom with a corresponding rigid boundary condition in the z direction. The inner two types of atoms correspond to Ar and an isotope of Ar, with corresponding periodic boundary conditions in the X and Y direction. The axis of the figure is such that the z-axis is north (up).



5 References

1. The argon melting curve to very high pressures. C-S. Zha, R. Boehler, D. A. Young, M. Ross. The Journal of Chemical Physics 85, 1034 (1986)

2. Extended and accurate determination of the melting curves of argon, helium ice (H_2O), and hydrogen (H_2). F. Datchu, P. Laubeyre, R. LeToullec. Physical Review B 61, 6535 (2000)

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% Literature source for Argon % at T = 84 K, 1.53 10e-5 cm^2/sec % `https://aip.scitation.org/doi/abs/10.1063/1.1700899` % % at T = 295 K and 42 kPa, 0.423 cm^2/sec % `https://journals.aps.org/pr/pdf/10.1103/PhysRev.72.1256`

% at T = K and 87 kPa, 2.07 10e-5 cm^2/sec

% Unit conversion: % 1 $Angstrom^2$/ps = 10e-4 cm^2/sec = 10e-8 m^2/s