

# 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 ( $7 \times 7 \times 7$  unit cells), but build it with the lattice parameter  $a_{fcc} = 5.78 \text{ \AA}$  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  $T = 1.5T_m$ , where  $T_m$  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  $24.6 \frac{\text{cm}^3}{\text{mole}}$  was  $T_m = 92K$ . An FCC crystal with  $7 \times 7 \times 7$  unit cells was constructed with lattice parameter  $a_{fcc} = 5.78 \text{ \AA}$  and simulated at constant volume and temperature  $T = 1.5T_m = 138K$ .

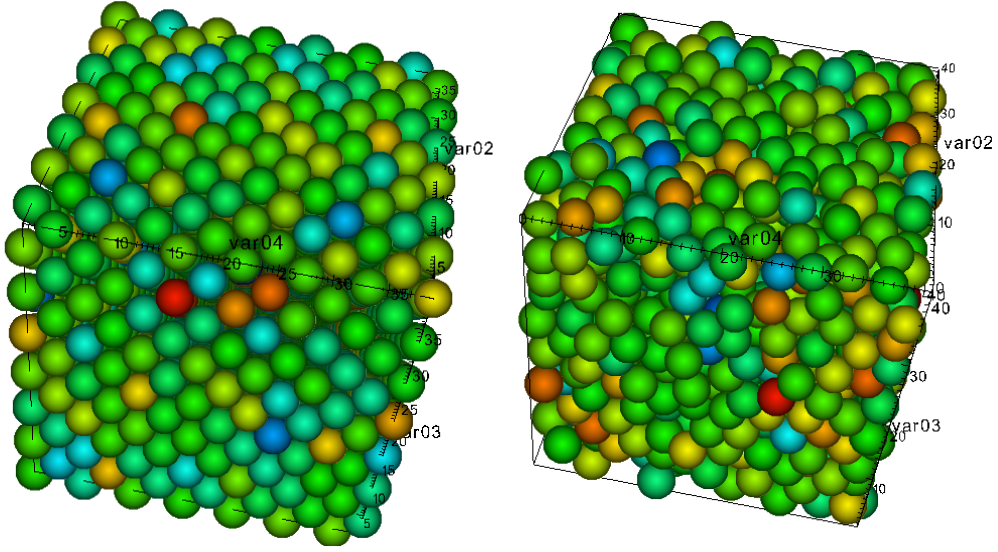


Figure 1: The FCC crystal was first equilibrated using constant pressure and equal velocity distribution (LFLAG = 1, KFLAG = 2) with periodic boundary conditions at temperature  $T = 138$  K for  $t = 1$  ps. The crystal on the left is the system before equilibration, and after equilibration on the right. 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.

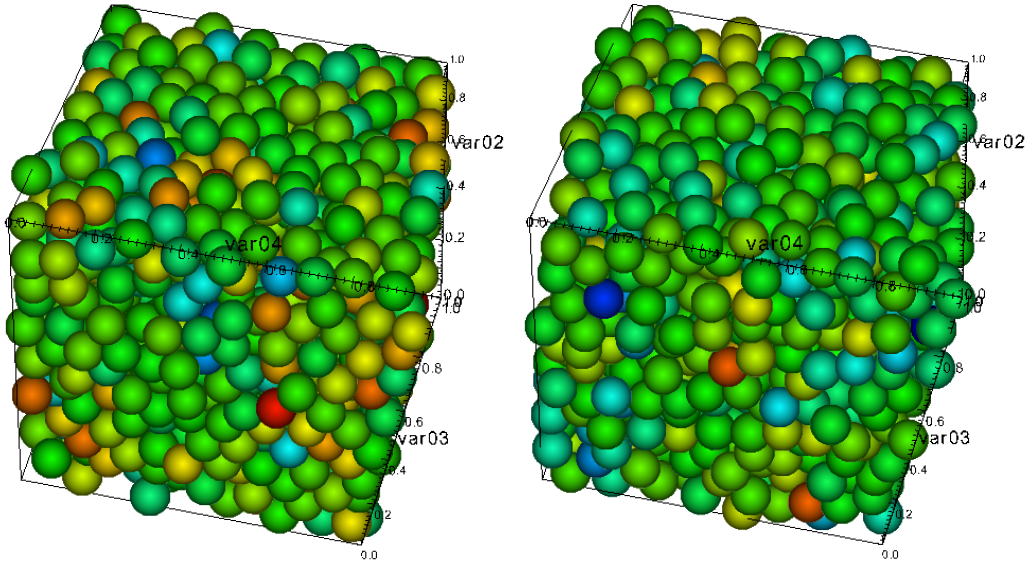


Figure 2: The FCC crystal after equilibration being heating for  $t = 100$  ps ( $dt = 0.001$  ps) with constant volume and constant temperature (LFLAG = 0, KFLAG = 5) and periodic boundary conditions in all three directions. On the left is the system at  $t = 0$  ps, on the right at  $t = 100$  ps. 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:

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

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 coordinates (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:

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

which is a 0<sup>th</sup>-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 <i>Angstrom</i> <sup>2</sup> | $2.0549 \times 10^{-9} m$            |
| 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.

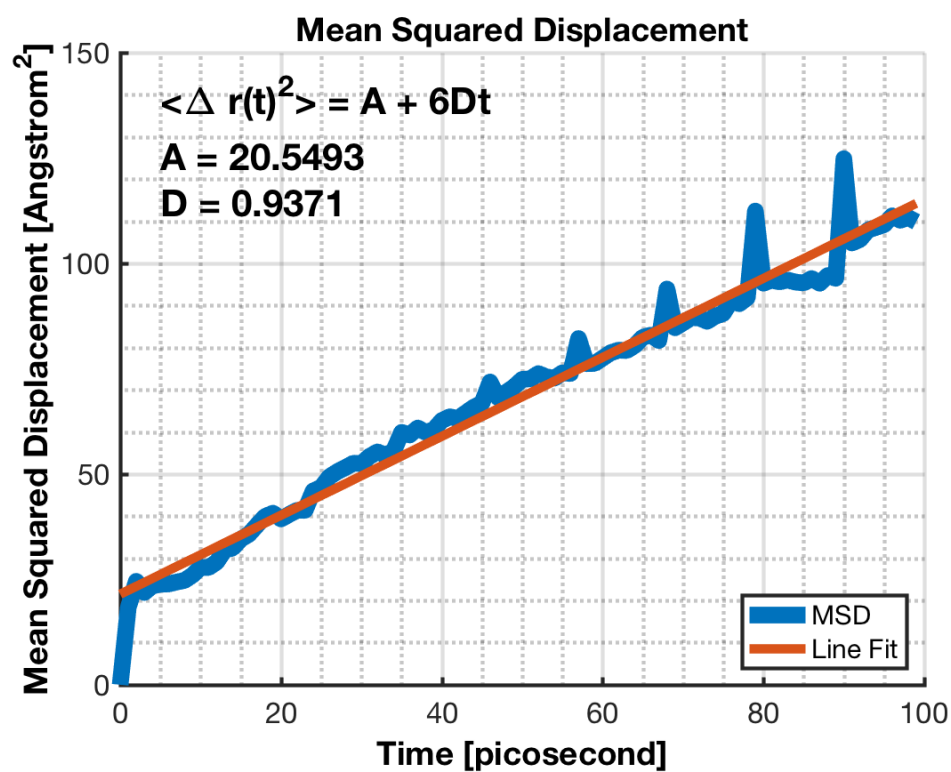


Figure 3: The mean squared displacement vs. time plot as calculated from atomic trajectories compared to their initial positions. A linear fit estimated the diffusion coefficient,  $D$ , as the slope of the data.

### 3 Question 3

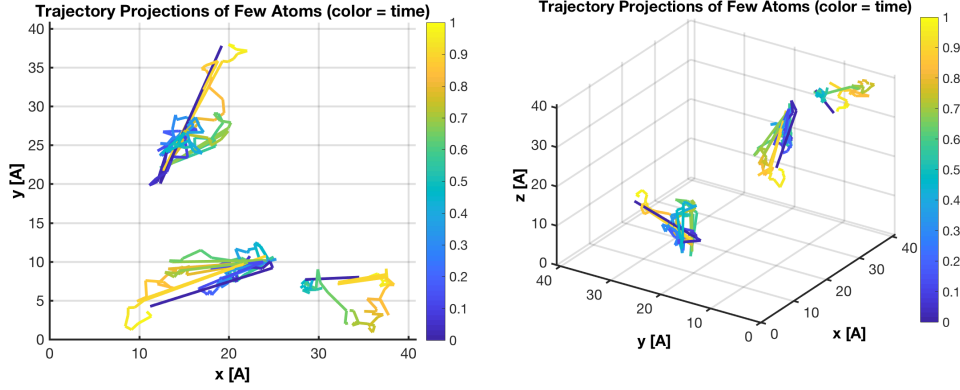


Figure 4: The trajectories of three particles are plotted over time with the color of the line corresponding to time (0 ps to 100 ps, brighter = later time). On the left is the projection of the trajectory to a 2D plane, on the right the same trajectories are plotted in 3D view. From the diffusion coefficient ( $D = 0.9371 \text{ \AA}^2/\text{ps}$ ) it is expected that the 2D projection will show an area close to  $0.9371 \text{ \AA}^2/\text{ps} \times 100 \text{ ps} = 93.71 \text{ \AA}^2$  or  $9.68 \text{ \AA}$  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 simulating  $t=1$  ps with equal velocity distribution and 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 961 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:

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

The predicted number of steps multiplied by the timestep of integration yields the total simulation time required to achieve diffusion of 15 Angstrom depth.

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  $D = 0.9371 \text{ \AA}^2/\text{ps}$  and the known size of the x-y simulation box ( $x_{len} = 23.12$  Angstrom both), we can calculate the number of simulation steps required for an atom to travel half the box distance:

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

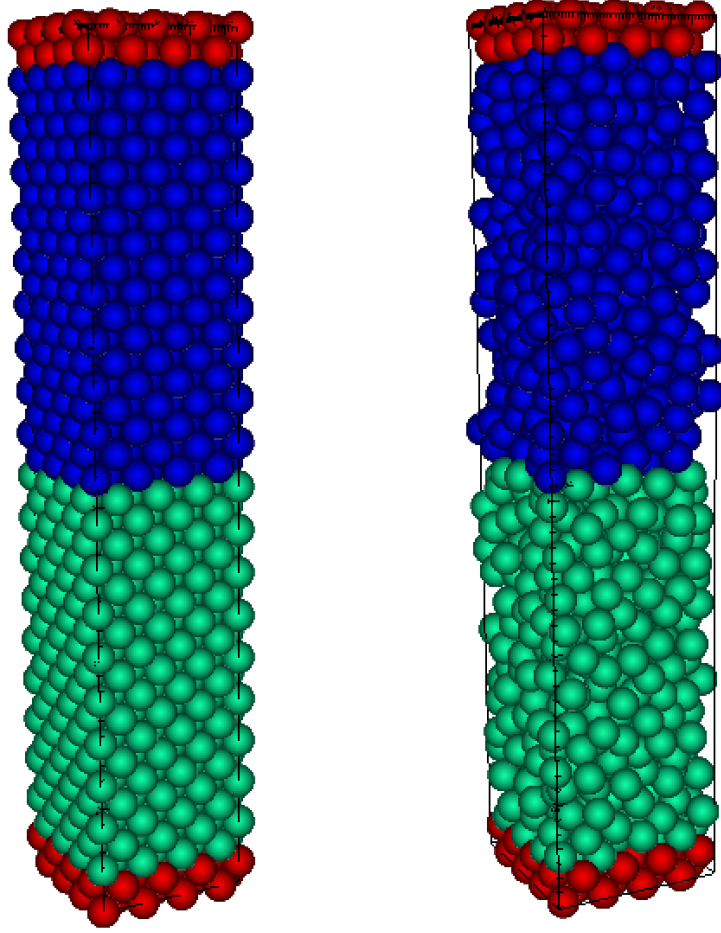


Figure 5: Equilibration of the  $4 \times 4 \times 20$  FCC crystal (1280 atoms) with  $a_{fcc} = 5.78$  Angstrom. Rigid atoms are on the top and bottom with a corresponding rigid boundary condition in the  $z$  direction. The inner two types of atoms correspond to Ar and an isotope of Ar, with corresponding periodic boundary conditions in the  $X$  and  $Y$  direction. The axis of the figure is such that the  $z$ -axis is north (up).

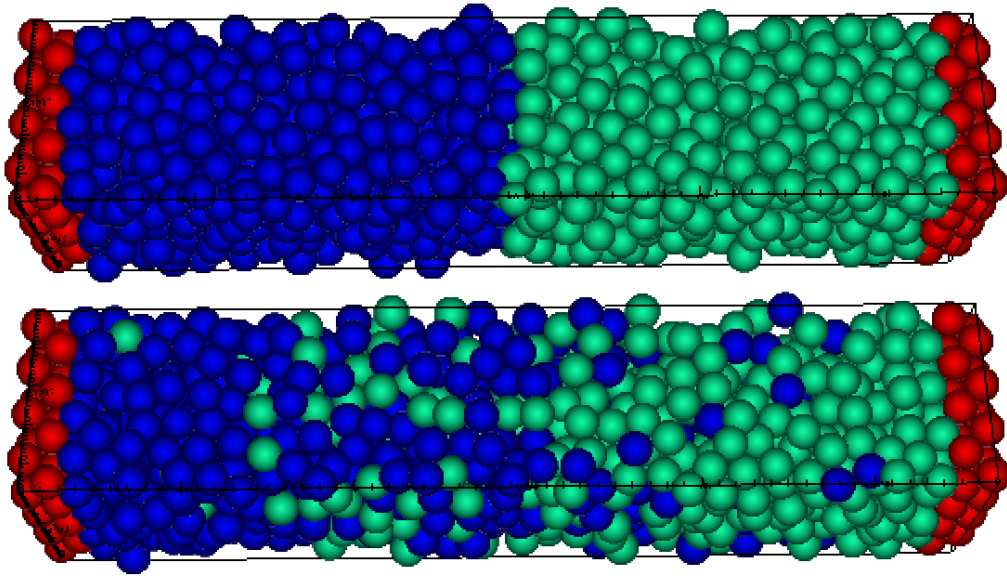


Figure 6: Top snapshot is at  $t = 0$  ps, bottom snapshot is at  $t = 961$  ps. As predicted, the Ar atoms self diffused across the artificial barrier up to 15 Angstrom on average. The atomic snapshot only shows the lateral surface of the simulation box, so a different analysis technique is necessary to determine mixing to a more accurate degree.

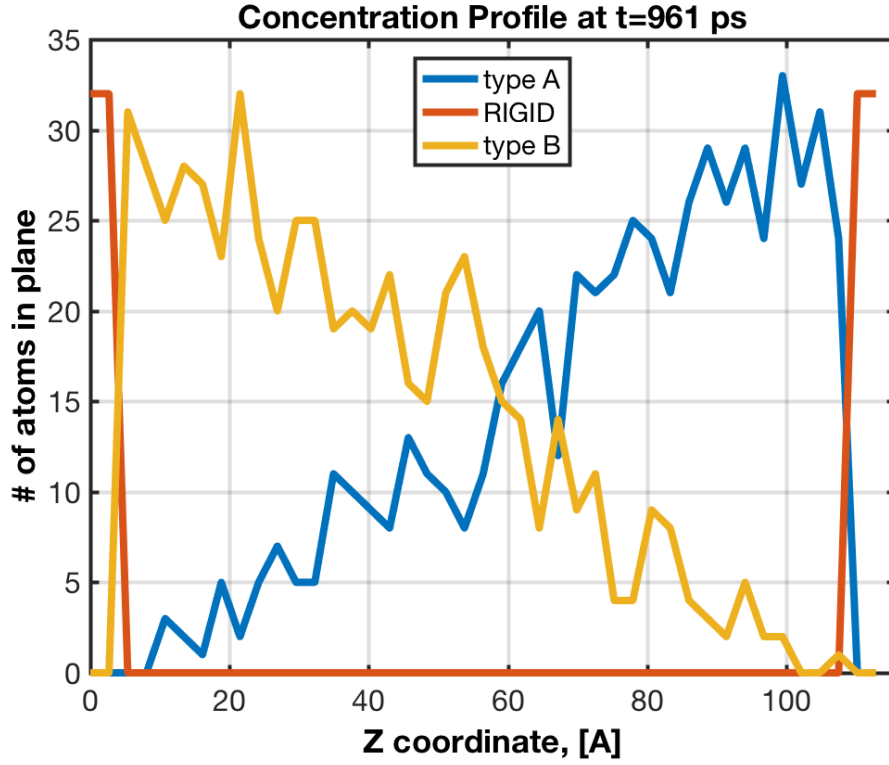


Figure 7: The concentration profile along the z-axis (horizontal in the figure above) is plotted where the atoms in each x-y plane with 2.6 Angstrom thickness are binned into a single data point. The initial concentration profile is showed atoms of type-A and type-B completely separated. The plot above shows significant self-diffusion of Argon, with an equal concentration of type-A and type-B atoms in the middle of the system ( $Z = 60$  Å), and roughly linearly increasing/decreasing further from the symmetric center of the system.



## 5 Question 5

A finite difference (FD) method (1D FTCS) was used (Matlab code below) to calculate the time evolution of the concentration profile from a continuum scale by simulating the diffusion equation. The general trend of diffusion is similar in both the FD and MD solutions, where the z-coordinate symmetrical center of the system has equal concentrations of both type-A and type-B atoms. However, given the small size and discrete nature of atoms in the MD simulation, the concentration profile reconstructed from atomic positions appears more linear than the continuum-level simulation.

More specifically, the FD reconstruction shows the atomic concentrations plateauing to a non-zero value ( $\sim 7$  atoms), whereas the concentration profile obtained from MD simulations has atomic concentration reaching 0. This is expected given the discrete nature of such a small system, where no atoms were present at the extreme ends of the simulation box (for the given simulation time and diffusion coefficient). Over all concentration profiles obtained both in the continuum and MD simulations are in good agreement with similar trends. However, the continuum-level model is not applicable to the nanoscale because it does not correctly reproduce the complete absence of atoms in the extreme ends of the simulations box (where no type-A atoms were found in the type-B side, and vice versa). Such a discrepancy will have important consequences for other physical and transport properties calculated from the MD system.

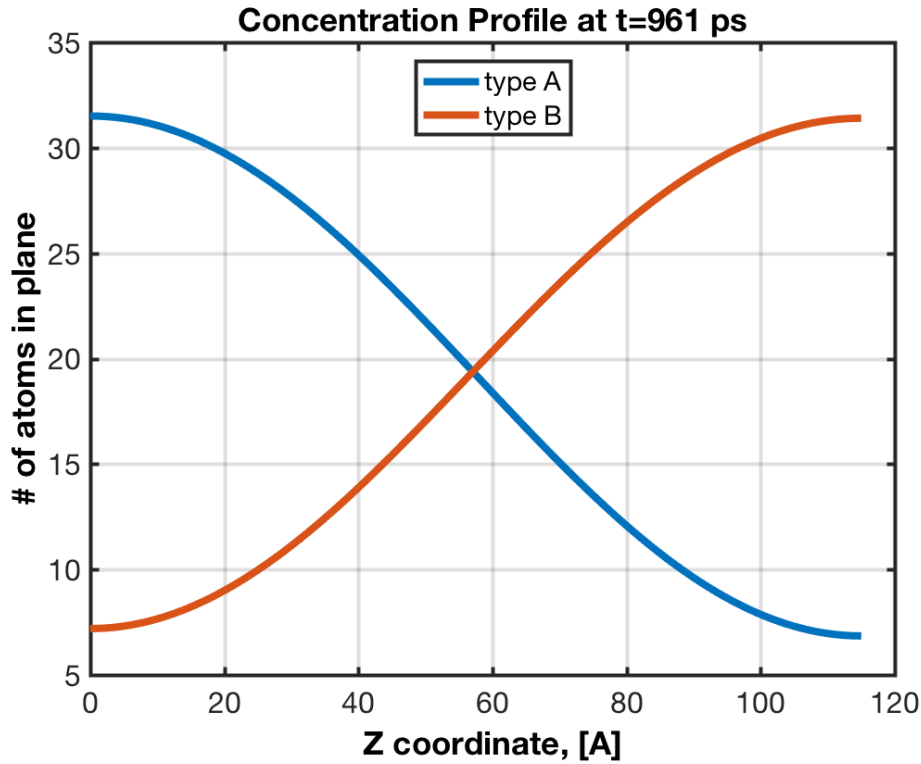


Figure 8: A one-dimensional forward-in-time centered-in-space (FTCS) finite difference method is used to calculate a continuum-level evolution of the concentration profile by solving the diffusion equation. The same parameters were used as in the MD simulation.

```
D = .9371;           % diffusion constant
L = 115.6;          % system size
dx = 1.25;          % step of spatial discretization
```

```

h = 0.5;           % timestep
max_t = 961;       % total simulation time
x = [0:dx:L];      % x vector

N = ceil(L / dx);  % Number of nodes
beta = (h*D/(dx^2)); % Constant used in main loop

if (2*D*h/(dx^2)) > .99
    disp('Von-Neumann_stability_condition_not_met!');
end

% Initial concentration profile
typeAlen = floor(length(x)/2); % half-length of z-coord
Ca(1,:) = zeros(1,length(x)); % type A atoms initial
Ca(1,1:typeAlen+1) = 38*ones(1,typeAlen+1); % type A atoms initial

Cb(1,:) = zeros(1,length(x)); % type B atoms initial
Cb(1,typeAlen:length(x)-1) = 38*ones(1,typeAlen+1); % type B atoms initial

% Loop over time
step = 2;
for t = 0:h:max_t
    for i = 2:N-1
        Ca(step,i) = Ca(step-1,i) + ...
            beta*(Ca(step-1,i+1) - 2*Ca(step-1,i) + Ca(step-1,i-1));
        Cb(step,i) = Cb(step-1,i) + ...
            beta*(Cb(step-1,i+1) - 2*Cb(step-1,i) + Cb(step-1,i-1));
    end
    Ca(step,1) = Ca(step-1,1) + 2*beta*(Ca(step-1,2) - Ca(step-1,1));
    Cb(step,1) = Cb(step-1,1) + 2*beta*(Cb(step-1,2) - Cb(step-1,1));
    Ca(step,N) = Ca(step-1,N) - 2*beta*(Ca(step-1,N) - Ca(step-1,N-1));
    Cb(step,N) = Cb(step-1,N) - 2*beta*(Cb(step-1,N) - Cb(step-1,N-1));
    step = step+1;
end

```

## 6 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<sub>2</sub>O), and hydrogen (H<sub>2</sub>). F. Datchu, P. Laubeyre, R. LeToullec. Physical Review B 61, 6535 (2000)