T1. Polycrystal diffusion

A1 Write the expression for v in terms of T and physical constants. From this, obtain the law of proportionality $D(T)$.

From thermodynamics we know that $v = \sqrt{3kT/m}$, where m is the particle's mass, and k is Boltzmann constant. Because characteristic jump time between inter-nodes is inversely proportional to transition probability $\times$ particle's speed, and because diffusion coefficient is inversely proportional to jump time, then $D(T) \propto v\exp(-E_g/kT) \propto \sqrt{T}\exp(-E_g/kT)$.

A2 Write down how the rms displacement of a particle Δr_{sq}, diffusion coefficient D and simulation time t are related to each other in the **three-dimensional case**. *Note:* the particle motion along each of the three axes in random walk can be considered independent. The diffusion coefficient D in **one-dimensional case is** related to the cell size a and characteristic jump time τ as $D = a^2/2\tau$. *Note:* if you cannot complete this task, in the future, consider $\Delta r_{sq} = \sqrt{Dt}$.

First, let's find rms particle displacement along one of the axes (we'll call this axis x). In this case movement will happen analogously to the one considered in preparational lectures, so rms particle displacement will be:

$$\overline{x^2} = na^2,$$

where n is total numner of jumps. Number of jumps can be estimated as:

$$n = t/\tau.$$

Considering $D = a^2/2\tau$, we obtain:

$$\overline{x^2} = 2Dt.$$

Finally, because movement along different axes can be considered as independent, then $\overline{y^2} = \overline{z^2} = 2Dt$. Using Pythagorean theorem, we obtain:

$$\Delta r_{sq} = \sqrt{\overline{x^2} + \overline{y^2} + \overline{z^2}} = \sqrt{6Dt}.$$

A3 Get the points to find $D(T)$ and linearize the resulting dependence. Find the energy E_g in arbitrary units with an accuracy of at least 2%. Explicitly state how you achieve this accuracy. Make measurements in $T \in [1; 10]$, $t \in [1; 10]$, and $N \in [10^2; 10^4]$.

Let's use results of the previous task to find diffusion coefficient. Because $\Delta r_{sq} = 6Dt$, then $D = \Delta r_{sq}^2/6t$. Combining this with results of task **A1**, we get $\Delta r_{sq}^2/6t\sqrt{T} = \exp(-E_g/kT)$. The easiest way now is to find the slope of dependency of $Y = \ln\left[\Delta r_{sq}^2 t^{-1}T^{-1/2}\right]$ on $X = 1/T$. How the accurace is guaranteed: First, it'd be good to have $\Delta r_{sq} \gg 1$. Second, $1/T$ changes by 0.9, and E_g is proportional to the dependency slope. To guarantee a 2% accuracy we need the sum of errors for min and max temperatures to be $\sigma_y(0.1) + \sigma_y(1.0) \leq 0.02 \cdot 0.9E_g$. Because $y = \ln[\Delta r_{sq}^2 T^{-1/2}]$, then $\varepsilon_r(0.1) + \varepsilon_r(1.0) \leq 0.009E_g$. We can simply check that for all points $\varepsilon_r \leq 0.0045E_g$. Let's obtain data points and put them in a table below:

t	10	10	10	10	10	10	10	10	10	10
T	1.000	1.111	1.250	1.429	1.667	2.000	2.500	3.333	5.000	10.00
N	10000	10000	10000	10000	10000	10000	10000	10000	10000	10000
Δr_{sq}	13.750	17.009	20.882	25.999	32.154	40.362	50.733	65.932	86.227	122.632
σ_r	0.053	0.066	0.081	0.102	0.127	0.156	0.198	0.257	0.336	0.477
X	1.000	0.900	0.800	0.700	0.6	0.5	0.4	0.3	0.2	0.1
Y	2.939	3.312	3.664	4.035	4.383	4.747	5.092	5.473	5.807	6.164



	1	2
1	1.	2.939
2	0.9	3.312
3	0.8	3.664
4	0.7	4.035
5	0.6	4.383
6	0.5	4.747
7	0.4	5.092
8	0.3	5.473
9	0.2	5.807
10	0.1	6.164

One can see that the required accuracy is indeed achieved. Let's plot $Y(X)$ and find its slope using InteractiveBuffer.nb. It will be equal to

$$-E_g = -3.58 \pm 0.02.$$

B1 What will be the coefficient α in such a structure?
Note: It is not necessary to solve this task to proceed to numerical modeling.

From the question paper we can conclude that grain boundaries which are perpendicular to the diffusion flow do not affect the effective diffudion coefficient, and then it will be:

$$D_{eff} \approx 2\delta D_{gb}/3 \implies \alpha = 2/3.$$

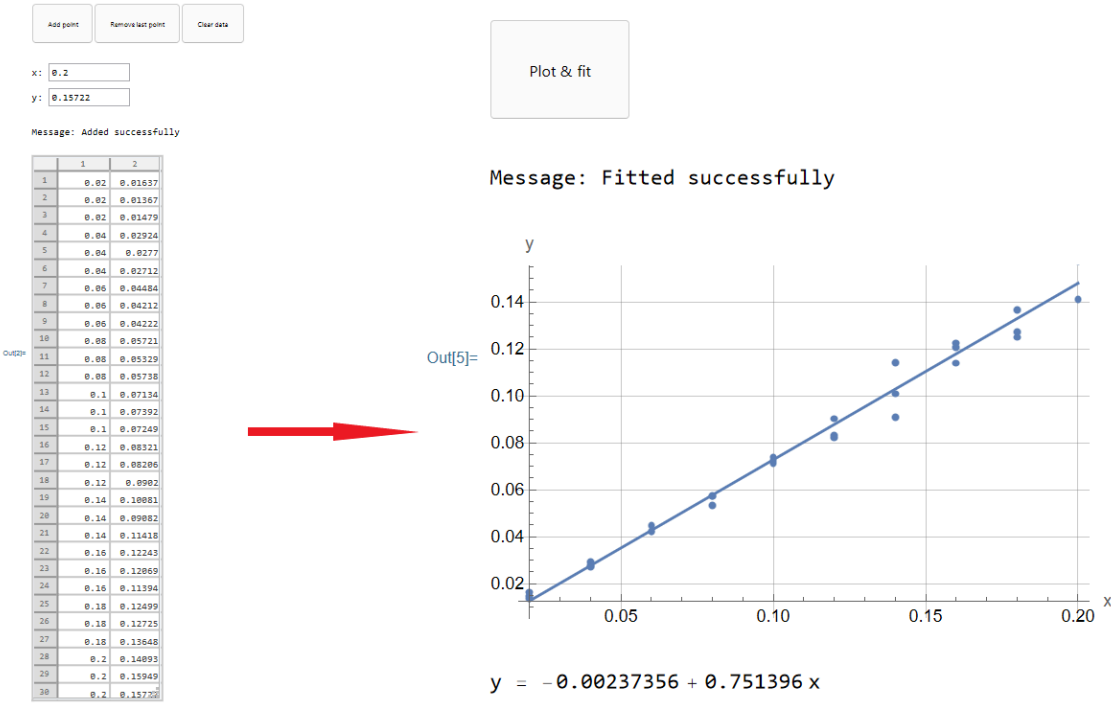
B2 Simulate diffusion in a polycrystal with $t \in [2;5]$, $D_{gb}/D \in [2;5]$, and $\delta \in [0.005; 0.05]$, to obtain the experimental value of α. Compare with the result of **B1**.
Note: As a result of the program operation, the dependence of the logarithm of the mean concentration $\ln \bar{c}$ of impurity particles on the square of the penetration depth z^2 is written to the file Bavg.csv. This dependence can be analyzed with the program B.nb.

It is clear that simulation results will be better for larger D_{gb}/D and smaller δ. It is also better to use maximum simulation time, since type A diffusion appears on large timescales. So, let's choose $(5, 5, 0.005)$ as our starting point. Plots in B.nb should ideally have a slope of $k = -\frac{1}{4D_{eff}t}$, so in arbitrary units we write:

$$D_{eff} = \frac{1}{4|k|t} = 1 + \alpha\delta(D_{gb}/D - 1).$$

Choosing $X = \delta(D_{gb}/D - 1)$ and $Y = \left[\frac{1}{4|k|t} - 1\right]$ as coordinates makes this dependency linear. The best way to make X change considerably is to increase δ. We can also suggest lowering Width slider in B.nb to mitigate possible edge effects. Let's obtain data points, put them in a table below and make a plot in InteractiveBuffer.nb:

t	5	5	5	5	5	5	5	5	5	5
D_{gb}/D	5	5	5	5	5	5	5	5	5	5
δ	0.005	0.010	0.015	0.020	0.025	0.030	0.035	0.040	0.045	0.050
$\lvert k\rvert$	0.049194 0.049325 0.049271	0.048579 0.048652 0.048679	0.047854 0.047978 0.047974	0.047294 0.047470 0.047286	0.046670 0.046558 0.046616	0.046159 0.046208 0.045863	0.045421 0.045837 0.044876	0.044546 0.044615 0.044885	0.044445 0.044355 0.043995	0.043823 0.043122 0.043207
Y	0.01637 0.01367 0.01479	0.02924 0.02770 0.02712	0.04484 0.04212 0.04222	0.05721 0.05329 0.05738	0.07134 0.07392 0.07259	0.08321 0.08206 0.09020	0.10081 0.09082 0.11418	0.12243 0.12069 0.11394	0.12499 0.12725 0.13648	0.14093 0.15949 0.15722
X	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20



	1	2
1	0.02	0.01637
2	0.02	0.01367
3	0.02	0.01479
4	0.04	0.02924
5	0.04	0.0277
6	0.04	0.02712
7	0.06	0.04484
8	0.06	0.04212
9	0.06	0.04222
10	0.08	0.05721
11	0.08	0.05329
12	0.08	0.05738
13	0.1	0.07134
14	0.1	0.07392
15	0.1	0.07249
16	0.12	0.08321
17	0.12	0.08206
18	0.12	0.0902
19	0.14	0.10081
20	0.14	0.09082
21	0.14	0.11418
22	0.16	0.12243
23	0.16	0.12069
24	0.16	0.11394
25	0.18	0.12499
26	0.18	0.12725
27	0.18	0.13648
28	0.2	0.14893
29	0.2	0.15949
30	0.2	0.15722

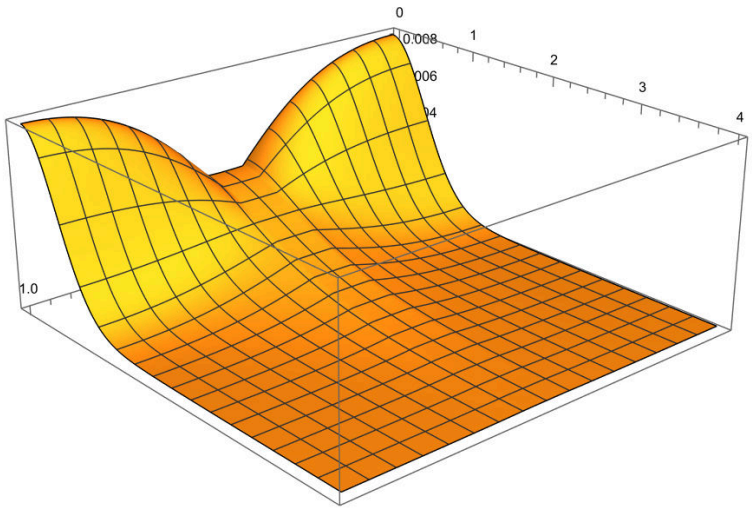
Simulation result give us $\alpha = 0.75 \pm 0.09$ which coincides with theoretical estimation within a margin of error.

C1 What can one say about the coefficients without resorting to numerical modeling? Find all values of coefficients that can be determined a priori.

The only "a priori"constraint here is the dimentional one. Conveniently, every factor in the r.h.s. except for a is dimentionless, so $\psi = -6/5$.

C2 Find the remaining coefficients by numerical simulation. Take measurements in the range of $t \in [0.005; 0.200]$, $D_{gb}/D \in [5; 50]$, $\delta \in [0.02; 0.20]$.As a result of the program's operation, the Cavg.csv file contains the dependence of the logarithm of the average concentration $\ln \bar{c}$ of impurity particles on the penetration depth $z^{6/5}$, and in the file Cmap.csv – the dependence of the logarithm of the concentration $\ln c$ on the penetration depth $z^{6/5}$ and the y coordinate along the solid surface. These dependencies can be analyzed using the C.nb program.

As it was stated in the question paper, the scale of type B diffusion should be much less than a (i.e. $\sqrt{2[D_{gb}/D]t} \ll 1$) and simultaneously much more than δa (i.e. $\sqrt{2t} \gg \delta$). Then, if we for example set input paramenters to be $(0.100; 25; 0.10)$, we will be able to achieve type B diffusion by varying any of input parameters in a wide range. We always can check whether simulated diffusion was of the type B or not by plotting the concentration profile to see if it looks like the one in the question paper. For example, here is concentration map for initial parameters $(0.100; 25; 0.10)$:



To find the slope of $k = \dfrac{\mathrm{d}\ln\bar{c}}{\mathrm{d}z^{6/5}}$ we will clip linear regions of plots generated in C.nb.

We can obtain ξ by simulating diffusion with different δ and plotting $\ln|k|(\ln\delta)$ in InteractiveBuffer.nb. η and ζ can be found in a similar manner (varying $[D_{gb}/D]$ and t correspondingly).

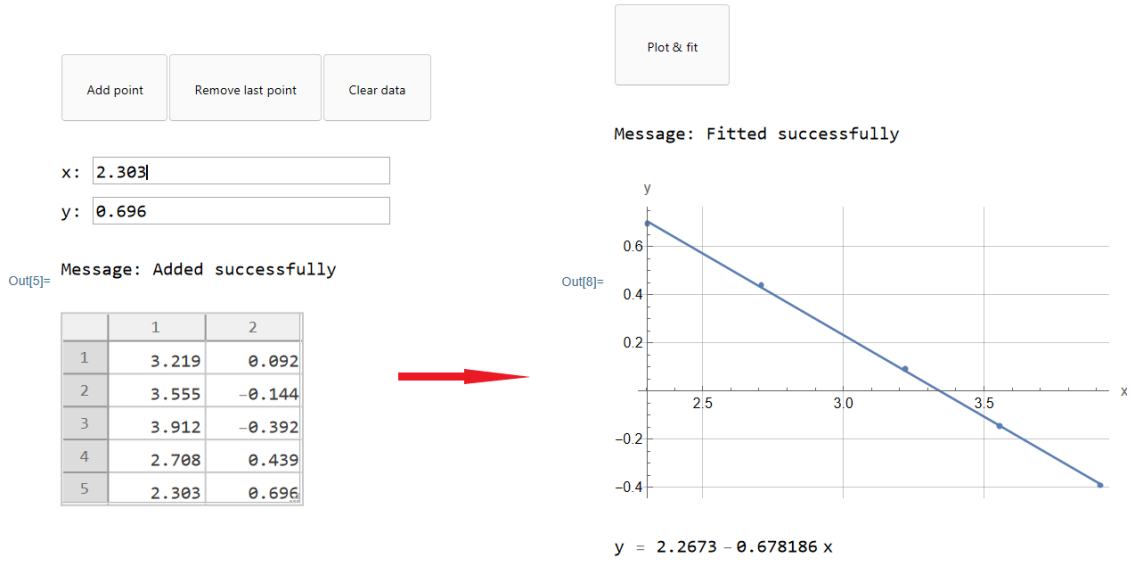
Let's obtain data points and put them in a table below ($\delta^{-0.39}[D_{gb}/D]^{-0.68}t^{-0.44} \equiv Z$):

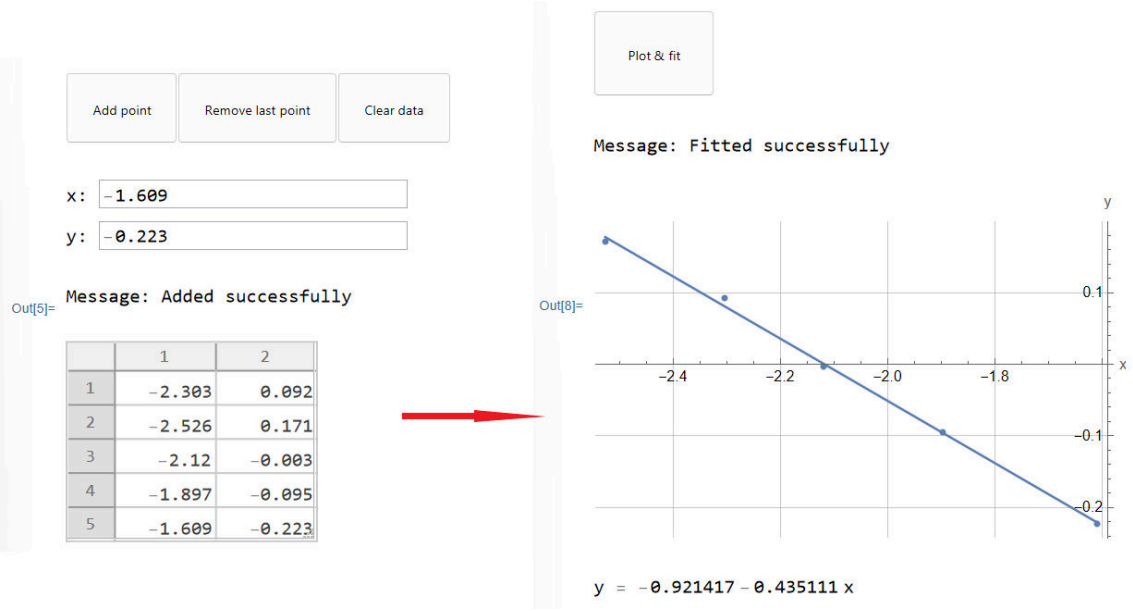
δ	0.100	0.080	0.060	0.120	0.150
k	-1.08567	-1.11796	-1.2865	-0.942494	-0.903676
$\ln\delta$	-2.303	-2.526	-2.813	-2.120	-1.897
$\ln\|k\|$	0.092	0.112	0.252	-0.059	-0.101
Z	0.758	0.826	0.925	0.706	0.647

D_{gb}/D	25	35	50	15	10
k	-1.08567	-0.865926	-0.675888	-1.55123	-2.00586
$\ln[D_{gb}/D]$	3.219	3.555	3.912	2.708	2.303
$\ln\|k\|$	0.092	-0.144	-0.392	0.439	0.696
Z	0.758	0.603	0.473	1.072	1.413

t	0.100	0.080	0.120	0.150	0.200
k	-1.08567	-1.18623	-0.99746	-0.908966	-0.799996
$\ln t$	-2.303	-2.526	-2.120	-1.897	-1.609
$\ln\|k\|$	0.092	0.171	-0.003	-0.095	-0.223
Z	0.758	0.836	0.699	0.634	0.558







Coefficients we are looking for are then just slopes of plotted lines, so:

$$\xi = -0.39 \qquad \eta = -0.68 \qquad \zeta = -0.44$$

C3 Find the value of C as accurately as possible.

Knowing ψ, ξ, η, and ζ, we can find C as a slope of dependency of $Y = |k|$ on $X = \delta^{-0.39}[G_{gb}/D]^{-0.68}t^{-0.44}$. Calculating X for points obtained in the previous task, we can make a plot with InteractiveBuffer.nb:

The slope is:

$$C = 1.42$$

Add point | Remove last point | Clear data

x: 0.558

y: 0.799996

Message: Added successfully

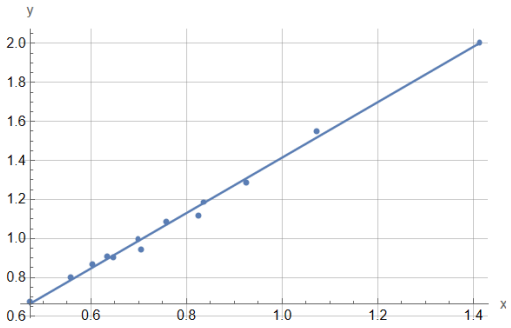
Out[5]=

	1	2
1	0.758	1.08567
2	0.826	1.11796
3	0.925	1.2865
4	0.706	0.942494
5	0.647	0.903676
6	0.603	0.865926
7	0.473	0.675888
8	1.072	1.55123
9	1.413	2.00586
10	0.836	1.18623
11	0.699	0.99746
12	0.634	0.908966
13	0.558	0.799996

Plot & fit

Message: Fitted successfully

Out[8]=



$y = -0.0081678 + 1.42207\,x$