

Solution to Exercise 4.2-1 "Diffusion During Cooling"

Illustration

For the diffusion length L we have the well known equations:

$$L = \sqrt{2 D t} \quad \text{or} \quad L^2 = 2 D t$$

$$D = D_0 \exp \left(- \frac{E}{kT} \right).$$

- E is the activation energy of the diffusing species and k is the Boltzmann constant. Because of $T = T_0 \cdot \exp(-\lambda \cdot t)$ we obtain for L^2

$$L^2 = 2 D(t) t = 2 D_0 \int_0^\infty \exp \left(- \frac{E}{kT(t)} \right) dt$$

$$= 2 D_0 \int_0^\infty \exp \left(- \frac{E}{kT_0 \exp(-\lambda t)} \right) dt$$

$$= 2 D_0 \int_0^\infty \exp \left(- \frac{E}{kT_0} \exp(\lambda t) \right) dt$$

Now we have a purely mathematical exercise which is not too difficult, but not too easy either. In order to solve the integral, we try the substitution

- $u(t) = \frac{E}{kT_0} \exp(\lambda t), \quad dt = \frac{du}{\lambda u}$

- The boundaries must be changed too, we obtain

$$t = 0 \text{ changes to } u_0 = E/kT_0$$

$$t = \infty \text{ changes to } u = \infty.$$

This gives us

$$L^2 = \frac{2 D_0}{\lambda} \int_{u_0}^\infty \frac{1}{u} \exp(-u) du.$$

Now you must solve a simple looking integral. There are several ways of doing that

- 1. Find a good math book with lots of integrals and take the solution from there (the "Bronstein", however, won't do)
- 2. Do a sensible approximation and solve it yourself in a simple way
- 3. Go all the way and solve it completely - if you can.

- Here we go the second route.

We use a Taylor expansion for $1/u$ around u_0 because that's where u is felt most critically - for large values of u everything tends to be zero anyway. In full generality we have

$$\frac{1}{u} = \sum_{v=0}^{\infty} (-1)^v \frac{1}{u_0^{v+1}} (u - u_0)^v \approx \frac{1}{u_0} - \frac{u - u_0}{u_0^2}.$$

- If we keep it really simple, we could just use the first term, having $1/u \approx 1/u_0$; but we will go one step beyond this and take

$$\frac{1}{u} \approx \frac{1}{u_0} - \frac{u - u_0}{u_0^2}$$

- This gives us

$$\begin{aligned}
L^2 &= \frac{2 D_0}{\lambda u_0} \int_{u_0}^{\infty} \exp(-u) - \frac{u - u_0}{u_0} \exp(-u) du \\
&= \frac{2 D_0}{\lambda u_0} \int_{u_0}^{\infty} 2 \exp(-u) - \frac{u}{u_0} \exp(-u) du \\
&= \frac{2 D_0}{\lambda u_0} \left[-2 \exp(-u) + \frac{u+1}{u_0} \exp(-u) \right]_{u_0}^{\infty} \\
&= \frac{2 D_0}{\lambda u_0} \exp(-u_0) \left[1 - \frac{1}{u_0} \right] \\
&= \frac{2 D_0 k T_0}{\lambda E} \exp\left(-\frac{E}{k T_0}\right) \left[1 - \frac{k T_0}{E} \right] \\
\Rightarrow L &= \sqrt{\frac{2 D_0 k T_0}{\lambda E} \left[1 - \frac{k T_0}{E} \right]} \exp\left(-\frac{E}{2 k T_0}\right).
\end{aligned}$$

- The second term of the Taylor expansion brought in the factor $[1 - kT_0/E]$ and since $kT_0 \ll E$ in all normal cases, it is indeed not very important. If we neglect it, we may simply give the desired solution as

$$L = \left(\frac{2D_0 \cdot kT_0}{\lambda \cdot E} \right)^{1/2} \cdot \exp - \frac{E}{2kT_0}$$

Now we can look at some typical cases and see what this formula means. However, first we have to find the right values for λ

- For this we have to take the given values of the initial cooling rate, which we call λ' , and see what λ values correspond to these cooling rates.
- The initial cooling rate λ' is the derivative of the $T(t)$ function at $t = t_0 = 0$, we thus have

$$\frac{d}{dt} (T_0 \cdot \exp - \lambda \cdot t) \Big|_{t=0} = \lambda' = -\lambda \cdot T_0 \cdot \exp - \lambda \cdot t \Big|_{t=0} = -\lambda \cdot T_0$$

- and obtain

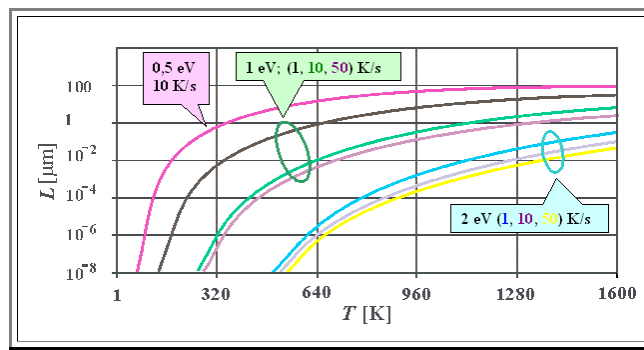
$$\lambda = \frac{\lambda'}{T_0}$$

- The "-" sign cancels, because our λ' must carry a minus sign, too, if it is to be a cooling and not a heating rate.

Replacing λ by λ'/T_0 yields the final formula:

$$L = \left(\frac{2D_0 \cdot kT_0^2}{\lambda' \cdot E} \right)^{1/2} \cdot \exp - \frac{E}{2kT_0}$$

- We have to evaluate this formula for cooling rates λ' given as $(-) 1 \text{ }^\circ\text{K/s}$, $10 \text{ }^\circ\text{K/s}$, $50 \text{ }^\circ\text{K/s}$, $10^4 \text{ }^\circ\text{K/s}$, and activation energies of $E = 1.0 \text{ eV}$, 2.0 eV , 5 eV . For D_0 we take $D_0 = 10^{-5} \text{ cm}^2\text{s}^{-1}$.
- The result (including the $[1 - kT_0/E]$ term is shown below



What can we learn from the formula and the curves?

1. The cooling rate is not all that important. Differences in the cooling rate of a factor of **50** produce only an order of magnitude effect or less since L is only proportional to $(1/\lambda)^{1/2}$.
2. The starting temperature T_0 is slightly more important than the activation energy E ; both have the same weight in the exponential, but T_0 appears directly in the pre-exponential while E enters only as square root.
3. The pre-exponential factor D_0 of the diffusion coefficient is exactly as important as λ' and E in the pre-exponential factor of the equation for L .

What can we do with the numbers? Quite simple:

1. L gives you the average of the largest distance between some point defect agglomerates, e.g. precipitates, because point defects farther away than L from some nuclei cannot reach it and must form their own agglomerate.
2. The average number of point defects in an agglomerate divided by L^3 gives a lower limit for the point defect concentration, because at least as many point defects as we find in an agglomerate must have been in the volume L^3 .