PHYS-E0421 Solid-State Physics (5cr), Spring 2019
Exercise session 5
Model solutions

1. **Equilibrium concentration of divacancies**

We want to minimize the free enthalpy (Gibbs free energy) of the system, $G = U + pV - TS = H - TS$. Its change with respect to a defect-free crystal is

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= n(\Delta h_f - T\Delta s_f) - Tk_B\Delta(\ln\Omega)\end{aligned}$$

Above, h_f is the vacancy pair formation enthalpy, Δs_f is the entropic correction to the formation free energy due to structural relaxation of atoms Ω the number of different microstates for the system (for the defected system this is the number of combinations with n vacancies on $N_{a,c}$ cation and anion sites, for perfect crystal with no vacancies just 1).

$$\Omega = \frac{N_c!}{n!(Nc-n)!}\frac{N_a}{n!(N_a-n)!} = (\frac{1}{n!})^2\frac{N_c!N_a!}{(N_c-n)!(N_a-n)!}$$

$$\ln\Omega = \ln(N_c)! + \ln(N_a) - \ln(N_c-n)! - \ln(N_a-n)! - 2\ln(n)!$$

We simplify the expression using the Stirling's approximation,

$$\ln x! = x\ln x - x, \quad x \gg 1.$$

This will give

$$\ln\Omega = N_c\ln(N_c) + N_a\ln(N_a) - (N_c-n)\ln(N_c-n) - (N_a-n)\ln(N_a-n) - 2n\ln(n)$$

We find the extrema by setting the derivative to zero,

$$\frac{\partial(\Delta G)}{\partial n} = \Delta h_f - T\Delta s_f - k_B\frac{\partial(\Delta\ln(\Omega))}{\partial n} = 0.$$

Approximating $n \ll N_{a,c}$ gives the final result

$$\begin{aligned}\frac{\partial(\Delta ln(\Omega))}{\partial n} =& 2\ln(n)2 + \ln(N_c n) + 1 + \ln(N_a n) + 1 = \ln(\frac{N_cN_a}{n^2}), \\ k_BT\ln(\frac{N_cN_a}{n^2}) &= \Delta h_f - T\Delta s_f\end{aligned}$$

The final result is

$$n \approx \sqrt{N_aN_c}e^{-\Delta h_f/2k_BT}e^{\Delta s_f/2k_BT}.$$

2. **Equilibrium concentration of point defects**

From the last page of the exercise sheet: $H_v \approx 1.26$ eV and $H_i \approx 3.24$ eV (We assume that $\Delta V \approx 0$. Then the formation enthalpy is simply the formation energy). The atomic fractions are calculated using

$$\frac{n}{N} = e^{-H_f/k_B T}.$$

For the vacancies we get atomic fractions of 6.8×10^{-22} (300 K) and 4.5×10^{-7} (1000 K), and for the interstitials 3.7×10^{-55} (300 K) and 4.7×10^{-17} (1000 K).

3. **Defect diffusion**

Diffusion constant $D = a^2\nu$, where a is the lattice constant and ν is the jump probability to nearest neighbor site per unit time. If the random jumps are thermally activated transitions to the other side of the energy barrier E, we have

$$\nu = \nu_0 e^{-E/kT} \tag{1}$$

where ν_0 can be interpreted as the jump trial frequency and we get

$$D = a^2 \nu_0 e^{-E/kT}. \tag{2}$$

We know D at two temperatures from which we can solve the two unknowns, E and ν_0:

$$\frac{D_1}{D_2} = e^{-E/k\cdot(1/T_1 - 1/T_2)} \tag{3}$$

$$\Rightarrow E = \frac{k \ln\left(\frac{D_1}{D_2}\right)}{1/T_2 - 1/T_1} = 0.85 \text{ eV} \tag{4}$$

and

$$\nu_0 = \frac{D_1}{a^2} e^{-E/kT_1} = \frac{D_2}{a^2} e^{-E/kT_2} = 1.48 \cdot 10^{13} \text{ s}^{-1} \tag{5}$$

4. **Defect diffusion, Elliott 3.13**

(a) The diffusion equation in 1D is

$$\frac{\partial n_i}{\partial t} = D_i \frac{\partial^2 n_i}{\partial x^2}, \tag{6}$$

where i indexes different atom types. For the given ansatz

$$n_i(x,t) = n_i^0 e^{-k^2 D_i t} e^{ikx} \tag{7}$$

we obtain

$$\frac{\partial n_i(x,t)}{\partial t} = -k^2 D_i n_i^0 e^{-k^2 D_i t} e^{ikx} = -k^2 D_i n_i(x,t) \tag{8}$$

and

$$D_i \frac{\partial^2 n_i(x,t)}{\partial x^2} = -k^2 D_i n_i^0 e^{-k^2 D_i t} e^{ikx} = -k^2 D_i n_i(x,t), \tag{9}$$

which are equal. Thus, the given ansatz is the solution for the diffusion equation.

Note that since the diffusion equation is a *linear* equation, a sum of terms each of which has the form of the general solution above, but different values of k, is also a solution.

Additionally, note that at time $t = 0$ the general solution is of form

$$n_i(x, t = 0) = n_i^0 e^{ikx} \tag{10}$$

(b) Now, the initial distribution is

$$n_i(x,0) = N_i \delta(x-x_0) = \frac{N_i}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x_0)} dk. \tag{11}$$

Note that this of the same form as the general solution in Eq. (10). Here we just have an integral over different values of k. Thus, by the reasoning above, we can get the time dependence by using the time dependence of the general solution of Eq. (7)

$$n_i(x,0) = \frac{N_i}{2\pi} \int_{-\infty}^{\infty} e^{-k^2 D_i t} e^{ik(x-x_0)} dk \tag{12}$$

(one can also subsitute this to the diffusion equation to see that it is fulfilled). Let's evaluate the integral

$$\begin{aligned} n_i(x,0) &= \frac{N_i}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x_0)-k^2 D_i t} dk & (13) \\ &= \frac{N_i}{2\pi} \int_{-\infty}^{\infty} e^{-D_i t [k - i(x-x_0)/2D_i t]^2} e^{-(x-x_0)^2/4D_i t} dk & (14) \end{aligned}$$

and make the change of variable $y \equiv \sqrt{D_i t}[k - i(x-x_0)/2D_i t]$ so that the integral becomes

$$\begin{aligned} n_i(x,0) &= \frac{N_i}{2\pi\sqrt{D_i t}} e^{-(x-x_0)^2/4D_i t} \int_{-\infty}^{\infty} e^{-y^2} dy & (15) \\ &= \frac{N_i}{\sqrt{4\pi D_i t}} e^{-(x-x_0)^2/4D_i t}, & (16) \end{aligned}$$

since $\int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\pi}$.

(c) The semi-infinite constant-composition initial profile can be represented with the help of the δ function:

$$n_i(x,0) = \begin{cases} n_i^0, & x < 0 \\ 0, & x > 0 \end{cases} = n_i^0 \int_{-\infty}^{0} \delta(x-x') dx'. \tag{17}$$

By using the result of (b), we thus get

$$n_i(x,t) = \frac{n_i^0}{\sqrt{4\pi D_i t}} \int_{-\infty}^{0} e^{-(x-x')^2/4D_i t} dx'. \tag{18}$$

Let's make a change of variable $y \equiv (x-x')/\sqrt{4D_i t}$, so

$$\begin{aligned} n_i(x,t) &= \frac{n_i^0}{\sqrt{\pi}} \int_{x/\sqrt{4D_i t}}^{\infty} e^{-y^2} dy & (19) \\ &= \frac{n_i^0}{2} \operatorname{erfc}(x/\sqrt{4D_i t}), & (20) \end{aligned}$$

by the definition of complementary error function erfc.