Solution to Assignment 04: Supersaturation and crystal growth
October 17, 2019

Exercise 01: Estimation of growth kinetics by desupersaturation of a solution
Supersaturation

1. It is assumed that sample 7 is fully equilibrated. Hence, the solubility of the given compound at the given temperature corresponds to the concentration of sample 7. Hence, the concentration of the compound (g/g), c_i and hence the supersaturation can be calculated as follows:

$$c_i = \frac{M_{2,i}}{M_{1,i} - M_{2,i}} \tag{1a}$$

$$S_i = \frac{c_i}{c_i^*} \tag{1b}$$

The summary of the experimental data and the results is given in Table 1.

Table 1: Summary of the experimental data and the results.

t [s]	m_1 **[g]**	m_2 **[g]**	**c [g/g solvent]**	**S [-]**	m_{cry} **[kg]**	**L [m]**	**G [m/s]**
0	12.4815	5.8143	0.872	1.015	0.075	0.00055	5.20E-07
60	12.4532	5.7841	0.867	1.010	0.088	0.00058	2.77E-07
120	12.5106	5.8006	0.864	1.007	0.095	0.00060	1.65E-07
180	12.4251	5.7546	0.863	1.005	0.100	0.00061	1.41E-07
240	12.4805	5.7746	0.861	1.003	0.104	0.00061	3.65E-08
300	12.4857	5.7755	0.861	1.002	0.105	0.00062	1.10E-08
1200	12.4700	5.7614	0.859	1.000	0.110	0.00063	-

Mass balance

2. The mass balance for the system with the solute and the solvent and its differential form are given as follows:

$$m_{\text{cry}} + c_i m_{\text{sol}} = k \tag{2a}$$

$$\frac{dm_{\text{cry}}}{dt} = -m_{\text{sol}}\frac{dc}{dt} \tag{2b}$$

3. With the assumption that all crystals are cubes of identical size, the surface area, A and mass, M of a single crystal can be written as functions of L, as follows:

$$A = k_A L^2 \tag{3a}$$

$$M = \rho_C k_{\text{V}} L^3 \tag{3b}$$

For crystals which are cubic, the surface (k_{A}) and volume (k_{V}) shape factors are 6 and 1, respectively.

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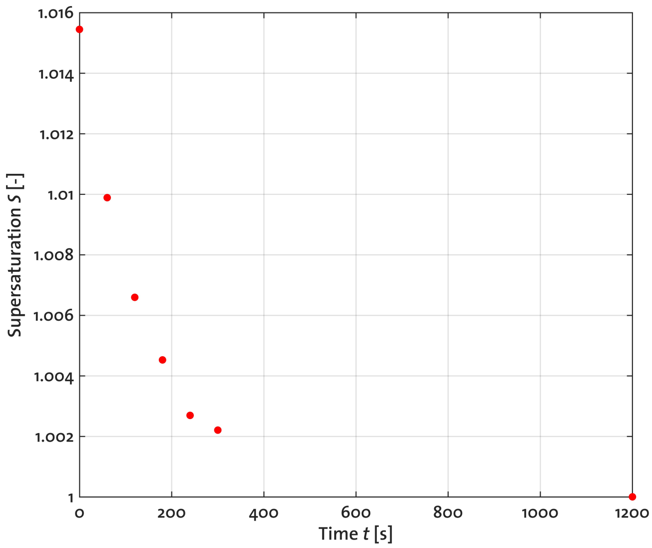

Figure 1: Time-resolved evolution of supersaturation.

4. From Equation 3b, the number of crystals can be calculated as follows.

$$m_{\text{cry}}(L) = N\rho_c k_{\text{V}} L^3$$

$$N = \frac{m_{\text{cry}}(L)}{\rho_c k_{\text{V}} L^3} = \frac{0.075\text{kg}}{1769\frac{\text{kg}}{\text{m}^3}.1.(0.00055\text{m})^3} = 254827$$

By using the mass balance given in Equation 2a, the length of the average length of the crystals for each sample can be calculated as follows

$$L_i = \left(\frac{m_{\text{cry},i}}{N\rho_c k_{\text{V}}}\right)^{\frac{1}{3}} \tag{5}$$

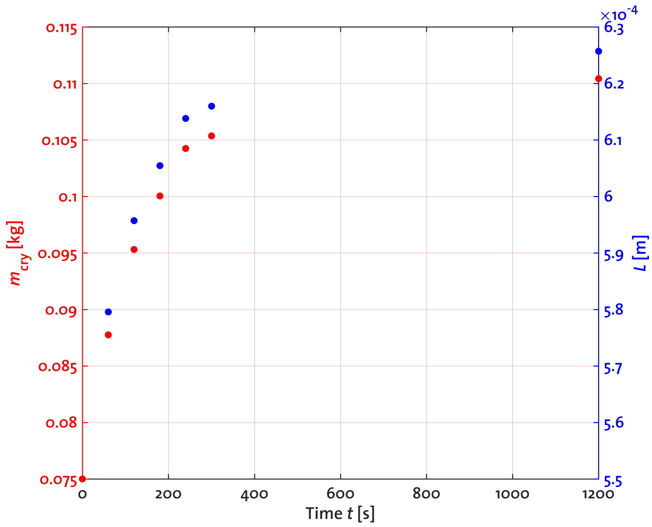

Figure 2: Time-resolved evolution of mass of crystals and average length of crystals.

Growth rate

5. The expression for growth rate can be derived as follows:

$$\frac{dm_{\text{cry}}}{dt} = -m_{\text{sol}}\frac{dc}{dt} = \frac{dm_{\text{cry}}}{dL}\frac{dL}{dt} = 3N\rho_c k_{\text{V}} L^2 \frac{dL}{dt}$$

$$G = \frac{dL}{dt} = -\frac{m_{\text{sol}}}{3N\rho_c k_{\text{V}} L^2}\frac{dc}{dt}$$

$$G = \frac{dL}{dt} \approx \frac{m_{\text{sol}}}{3N\rho_c k_{\text{V}} L^2}\frac{c_i - c_{i+1}}{t_{i+1} - t_i}$$

6. The growth rate G can be expressed as a function of the supersaturation S as follows:

$$G\left(S\right) = k_G\left(S-1\right)^g \tag{7}$$

Upon linearizing the equation by taking the logarithm, the following equation is obtained,

$$\log G(S) = \log k_G + g\log(S-1) \tag{8}$$

Upon performing a linear fit on the growth rate and the supersaturation, we obtain

$$g = 1.79 \qquad k_G = 1.19\times10^{-3}\text{ms}^{-1}$$

Hence, the growth rate equation for the given compound is given as follows,

$$G(S) = 1.19\times10^{-3}(S-1)^{1.79}\text{ms}^{-1}$$

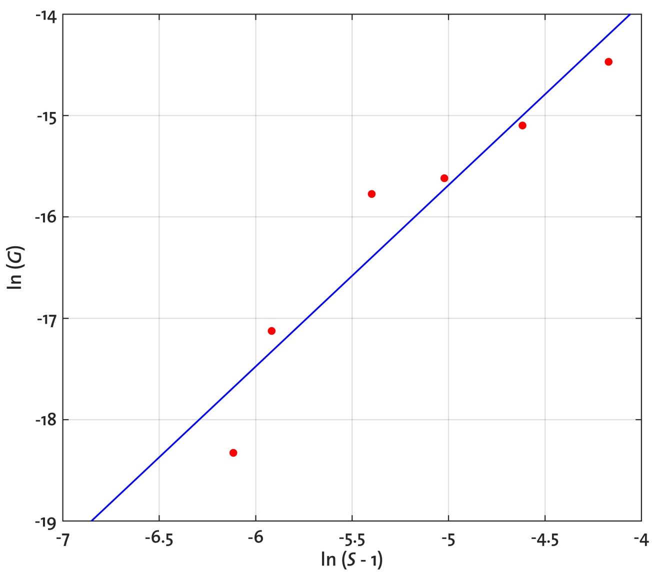

Figure 3: Growth rate vs. supersaturation for the estimation of growth rate parameters.

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