

Supplementary Information

1. The capillary length

Diffusion-limited crystal growth from solution can be described in two equivalent ways: by expressing supersaturation in terms of mole fractions or in terms of concentrations. In the former case mass transport is naturally given by Maxwell-Stefan diffusion, in the latter case by Fick diffusion. Maxwell-Stefan diffusion is diffusion driven by a chemical potential gradient and Fick diffusion is diffusion driven by a concentration gradient. In general, the chemical potential of the ice phase depends on the curvature of the crystal surface. This is comparable to the Laplace pressure in a droplet. The shift is inversely proportional to the radius of curvature; the constant of proportionality is the capillary length, defined in Eq. S1.

Because the numerical value of the supersaturation Δ in the two methods is different, so is the value of the capillary length, because the *relative* change in growth rate is the same in both formulations. In the formulation based on concentration, the capillary length is generally denoted by d_0 , and in the mole fraction formulation it is denoted by l_c . The former capillary length was derived by Langer as ¹

$$d_0 = \frac{\gamma_{wi} T^{abs}}{\rho_{ice} L_m} \cdot \left| \frac{d \ln C_{eq}}{dT} \right| \quad S1$$

Here, $\gamma_{wi} = (29 - 0.4T)$ mJ m⁻² is the ice-sucrose solution interfacial energy ². T^{abs} is the temperature in Kelvin; $\rho_{ice} = 917$ kg m⁻³ is the density of ice; and $L_m = (333 + 2.21T)$ kJ kg⁻¹ is the *effective* temperature-dependent latent heat of melting in a concentrated sucrose solution. The factor 2.21 is the difference of the specific heats of water and ice.

In the second formulation, the capillary length l_c was derived by Van Westen and Groot as ²

$$l_c = \frac{\gamma_{wi} V_m (1 - x)}{x^2 (\partial \mu / \partial x)_{p,T}} \quad S2$$

Here, V_m is the molar volume of ice, μ is the molar chemical potential and x is the molar fraction of sucrose in the matrix. In this expression we used the approximation that the sucrose molar fraction *vanishes* in the ice phase, otherwise one factor x in the denominator should be replaced by the molar miscibility gap. Van Westen and Groot used experimental data for the water activity of sucrose solutions to obtain the thermodynamic factor $x(\partial \mu / \partial x)_{p,T} / RT$, whereas Langer used the liquidus line.

In either case the concentration, or mole fraction, at a curved interface with a radius of curvature a , is given by

$$\begin{cases} x_a = x_{eq} (1 - l_c/a) \\ C_a = C_{eq} (1 - d_0/a) \end{cases} \quad S3$$

Hence the shifts in concentration or mole fraction are $\Delta C = -C_{eq} d_0/a$ and $\Delta x = -x_{eq} l_c/a$. The ratio of these is important to find a relation between the two definitions of the capillary length,

$$\frac{\Delta C}{\Delta x} = \frac{C_{eq} d_0}{x_{eq} l_c} \approx \frac{dC}{dx} \quad S4$$

To calculate the right-hand side of this equation, we consider a weight fraction w sucrose in aqueous solution. To a high degree of accuracy, the density of this solution is given by

$$\rho = \frac{1}{w/\rho_s + (1-w)/\rho_w} = \frac{\rho_w}{1 + w(\rho_w/\rho_s - 1)} \quad S5$$

where ρ_s and ρ_w are the densities of sucrose and water respectively. Thus, the total liquid volume is the sum of the water and sucrose volumes. The (mass) concentrations of sucrose and water are now found as $C = w\rho$ and $C_w = (1-w)\rho$, and the molar concentrations follow as $n_s = C/M_s$ and $n_w = C_w/M_w$. The molar fraction is now obtained as

$$x = \frac{n_s}{n_s + n_w} = \frac{1}{1 + \frac{M_s}{M_w} \cdot \frac{1-w}{w}} \quad S6$$

A straightforward calculation gives the sucrose concentration as

$$C = \frac{\rho_w}{1/w + (\rho_w/\rho_s - 1)} = \frac{\rho_w}{\rho_w/\rho_s + (1/x - 1) \cdot M_w/M_s} \quad S7$$

Combining S6 and S7 we find the derivative in A4 as

$$\frac{dC}{dx} = \frac{1}{\rho_w} \cdot \frac{M_w}{M_s} \cdot \frac{C^2}{x^2} \quad S8$$

Thus, from Eq. S4 and Eq. S8 we find the relation between d_0 and l_c as:

$$d_0 = l_c \cdot \frac{M_w}{M_s} \cdot \frac{C}{\rho_w x} = l_c \cdot \frac{1 + w(M_w/M_s - 1)}{1 + w(\rho_w/\rho_s - 1)} \quad S9$$

The capillary length d_0 can now be calculated in two ways: directly from the liquidus (Eq. S1), or from the thermodynamic relation Eq. S2 using a fit model for the thermodynamic factor ². From these *independent* methods we find at $T = -2$ °C from Eq. S1: $d_0 = 10.45$ nm, and from Eq. S2/S9: $d_0 = 10.59$ nm. The two methods agree to within 1%. At $T = -10$ °C, we find from Eq. S1: $d_0 = 1.26$ nm, and from Eq. S2/S9: $d_0 = 1.52$ nm. At this temperature, the two methods differ by some 17%. This may be caused by an uncertainty in temperature-dependence of the thermodynamic factor. Using the known liquidus for sucrose solutions (Eq. S11), we find from Eq. S1 the numerical result for d_0 in a sucrose solution as:

$$d_0 = -\frac{25.9}{T} \cdot \frac{(1 - 0.017T)}{(1 - 0.142T)} \quad [\text{nm}] \quad S10$$

where T is the temperature in °C and d_0 is expressed in nm. Note that the correspondence between d_0 and l_c (Eq. S9) can be used to obtain the thermodynamic factor along the melting line.

2. Calculation of ice phase volume fraction $\phi(T)$

The equilibrium ice phase mass fraction, $f(T)$, in a product containing mass fractions f_s of sucrose, f_w of pure water and f_{other} of additives is calculated as function of temperature using the Lever Rule from the equilibrium sucrose mass fraction in the aqueous phase, $w_{eq}(T)$.

Firstly, $w_{eq}(T)$ is given by equation (26) in reference as ²

$$w_{eq}(T) \approx \frac{1}{1.195 - 5.781/T} \quad S11$$

The numerical values in the equation for $w_{eq}(T)$ give a good fit to all available experimental data for $T > -14$ °C.

The equilibrium ice phase mass fraction as a function of temperature is thus obtained as

$$f(T) = 1 - f_{other} - \frac{f_s}{w_{eq}(T)} = f_w - f_s(1.195 - 5.781/T) \quad S12$$

The ice phase volume fraction, $\phi(T)$, follows straightforwardly as

$$\phi(T) = \left(\frac{f}{\rho_{ice}}\right) / \left(\frac{f}{\rho_{ice}} + \frac{1-f}{\rho_M}\right) \quad S13$$

where $\rho_{ice} = 0.917$ g/cm³ is the density of ice, and $\rho_M = 1.14$ g/cm³ is the density of the unfrozen matrix. For the numerical calculations we used the water and sucrose mass fractions of the experimental ice cream formulation which are $f_w = 0.5512$ and $f_s = 0.2883$.

3. Update scheme and consistency check

To find the mean cubed crystal size as function of time, we decrease the temperature by a small step δT (< 0) and calculate the corresponding time step from a chosen cooling rate $B = -dT/dt$. The cubed crystal size does not follow proportionally to the ice fraction but has to be integrated in steps because of the Ostwald ripening term in Eq. 6. For a stable result we use a Crank-Nicholson scheme:

$$\langle a^3 \rangle_{t+\delta t} = \langle a^3 \rangle_t + \frac{(\langle a^3 \rangle_t + \langle a^3 \rangle_{t+\delta t})}{(f_t + f_{t+\delta t})} \delta f + \frac{1}{2}((hK)_t + (hK)_{t+\delta t}) \delta t \quad S13$$

Since the mass fraction and weight fraction in the next time step depend only on temperature, the functions $h(\phi)$ and $K(\phi, T)$ in the next time step are known. Hence, the mean cubed crystal size in the next time step is solved as

$$\langle a^3 \rangle_{t+\delta t} = \frac{(1 + \delta f / (f_t + f_{t+\delta t})) \langle a^3 \rangle_t + \frac{1}{2}((hK)_t + (hK)_{t+\delta t}) \delta t}{(1 - \delta f / (f_t + f_{t+\delta t}))} \quad S14$$

In this scheme we use the equilibrium ice fraction explicitly in the calculation of the ice volume fraction which appears in g and h , and implicitly through using the equilibrium Ostwald ripening theory.

The update scheme above is essentially based on the *equilibrium* ice fraction, whereas we should use the *actual* ice fraction for the crystal size evolution. Moreover, we assumed that quasi-equilibrium conditions apply, so that we can use the equilibrium result for Ostwald ripening.

However, if temperature continually drops the actual ice fraction will lag behind. Here we check if this quasi-equilibrium assumption is justified.

When the ice mass fraction has non-equilibrium value f , it will generally move towards the equilibrium fraction f_{ice} as $df/dt = (f_{ice}-f)/\tau$, where τ is a relaxation time. For sufficiently slow, continuous cooling we will have $df/dt \approx df_{ice}/dt$ hence the deviation from equilibrium follows as

$$\delta f = f_{ice} - f \approx \tau \dot{f}_{ice} \quad S15$$

The relaxation time is calculated from the slowest relaxation mode of the diffusion field around a sphere of radius a , enclosed by an outer sphere of radius R_s , where $a^3/R_s^3 = \phi$. This mode is given by $C(r, t) = C_{eq} + A \sin(k(r - a)) \exp(-t/\tau) / r$, where k is a wave number that should satisfy the boundary condition $dC/dr = 0$ at the outer radius. Defining $\delta = k(R_s - a)$, we find this boundary condition to be satisfied for $\tan(\delta) = \delta/(1-\phi^{1/3})$, or $\phi = (1-\delta/\tan(\delta))^3$. A reasonable approximation to the inverse of this function is found by matching the solutions for low and high volume fractions. This leads to $\delta \approx \sqrt{3}\phi^{1/6}/(1 + \alpha\phi^\beta)$, where $\alpha = 2\sqrt{3}/\pi - 1 \approx 0.1027$ and $\beta = (1 - 8/\pi^2)/(6 - \pi\sqrt{3}) \approx 0.3391$. This approximation is accurate to 4 decimal places. The relaxation time is now obtained as

$$\tau = \frac{(R - a)^2}{D^{Fick} \delta^2} = \frac{a^2}{D^{Fick}} \frac{(\phi^{-1/3} - 1)^2 (1 + \alpha\phi^\beta)}{3\phi^{1/3}} \quad S16$$

Here, D^{Fick} is the Fick diffusivity at equilibrium, which is given by ²

$$D^{Fick} = \exp(-21.97 + \Omega T + \Psi T^2) \quad [\text{m}^2/\text{s}] \quad S17$$

where $\Omega=0.4157 \text{ K}^{-1}$ and $\Psi=0.0046 \text{ K}^{-2}$. The relaxation time depends on the starting radius, on the cooling rate and on temperature, but generally the relaxation time is in the order of 1 to 10 seconds. Multiplied by the growth rate of the equilibrium ice fraction, allows an estimate of how far the ice fraction is off equilibrium. For cooling rates of 0.01 to 0.1 K min^{-1} and crystals to start at a radius of $5 \text{ }\mu\text{m}$, the relative deviation from the equilibrium ice fraction is of the order $\delta f/f_{ice} \sim 10^{-5}$ - 10^{-3} , depending on temperature. Hence, for the calculation of the ice volume fraction the quasi-equilibrium assumption is justified.

Next, we check if the quasi-equilibrium assumption is justified for the Ostwald ripening rate. Generally, Ostwald ripening starts when the overall supersaturation is small compared to curvature effects, see Eq. 1 of the main text. For this estimate we will use the formulation in terms of the sucrose concentration. The supersaturation $\Delta = 1 - C_s/C_{s,eq}$ can be related to the ice fraction as $\Delta = \delta f/(1 - 0.375f_s - f_{ice})$. We substituted the densities of water and sucrose, to obtain $1 - \rho_w/\rho_s \approx 0.375$. The critical radius is now found as

$$a^* = 2d_0/\Delta = 2d_0(1 - 0.375f_s - f_{ice})/\delta f \quad S18$$

where d_0 is the capillary length. A detailed calculation of d_0 is given above. a_c is calculated from the supersaturation that is caused by fast cooling, whereas a^* is the actual mean radius of curvature which causes its own supersaturation due to curvature effects.

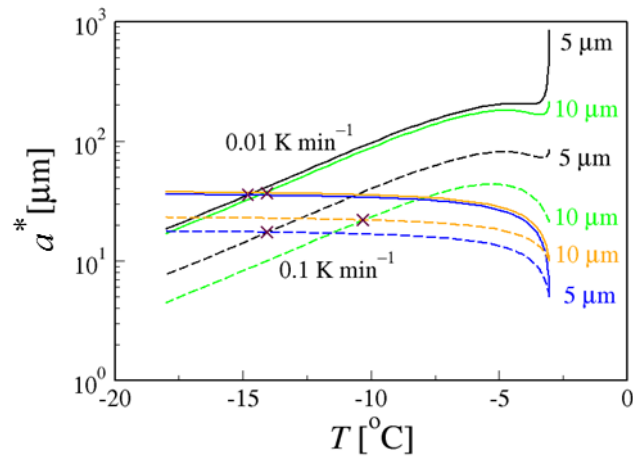


Figure S1. Critical radius, a^* , calculated for growing ice crystals in 30% sucrose solution, cooled at a rate of 0.01 K min^{-1} (full curves) and for 0.1 K min^{-1} (dashed curves), starting at 5 (black) and 10 (green) μm radius. The blue and orange curves show the actual mean radius; the crosses give the intersection points with the critical radius.

The question if quasi-equilibrium conditions apply depends on the size of the crystals. If the mean radius of curvature is smaller than the critical radius a^* , curvature effects will dominate over the overall supersaturation, and equilibrium Ostwald ripening applies. If the crystals are similar or larger in size than a^* we may expect distortions to the crystal size distribution and equilibrium Ostwald ripening can no longer be used. The critical radius a^* is shown in S1. Also shown is the actual cubed root of the mean cubed radius, $\langle a^3 \rangle^{1/3}$ as function of temperature. The blue curves correspond to the black curves, and orange corresponds to green. The intersection points have been marked by crosses. This shows that equilibrium conditions apply above a temperature between $-15 \text{ }^\circ\text{C}$ to $-14 \text{ }^\circ\text{C}$ if the cooling rate is $0.01 \text{ }^\circ\text{C/min}$, depending on the initial crystal radius. For a cooling rate of 0.1 K min^{-1} , equilibrium conditions apply above a temperature between $-14 \text{ }^\circ\text{C}$ to $-10 \text{ }^\circ\text{C}$. For lower temperatures we can expect strong deviations from the equilibrium Ostwald ripening theory. For conditions far from equilibrium, Ostwald ripening may not occur at all. This is the basis for the dashed curves in Figure S1.

References

- 1 Langer, J. S. Instabilities and pattern formation in crystal growth. *Reviews of Modern Physics* **52**, 1 (1980).
- 2 van Westen, T. & Groot, R. D. Predicting the Kinetics of Ice Recrystallization in Aqueous Sugar Solutions. *Crystal growth & design* **18**, 2405-2416 (2018).