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Supplement of

Representing time-dependent freezing behaviour in immersion mode ice nucleation

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Supplementary Information

1 FROST framework derivations

1.1 Normalising cooling-rate dependence

In this derivation we want to know the temperature required in order to attain a specific fraction frozen in a cooling experiment, and how this changes with the cooling rate. For a population of droplets containing a specific INP species, starting at a temperature T_0 – upon cooling the fraction of droplets frozen (f) after n_r steps (of time or temperature) can be calculated with the product of the probability for an event not happening (P_{not}) at each consecutive step. Once we have this then the probability of an event happening is $(1 - P_{not})$ so that:

$$f(n_r) = 1 - \prod_{k=0}^{n_r} P_{not,k} \quad (1)$$

where,

$$P_{not,k} = \exp(-J_s(T_k) A \delta t_r) \quad (2)$$

$J_s(T_k)$ is the nucleation rate coefficient at time step k , A is the surface area of INP and δt_r is the time step of the cooling experiment. Incorporating Eq. (2) into Eq. (1) gives:

$$f(n_r) = 1 - \prod_{k=0}^{n_r} \exp(-J_s(T_k) A \delta t_r) = 1 - \exp\left(-\sum_{k=0}^{n_r} J_s(T_k) A \delta t_r\right) \quad (3)$$

Over a small change in temperature the nucleation rate coefficient, $J_s(T_k)$, can be approximated by a linear relationship: $\ln J_s(T_k) = -\lambda T_k + c$. To calculate $J_s(T_k)$ for any number of δt_r steps this can be expanded:

$$J_s(T_{k=0}) = \exp(-\lambda T_0 + c)$$

$$J_s(T_{k=1}) = \exp(-\lambda(T_0 + \delta T) + c) = \exp(-\lambda T_0 + c) \cdot \exp(-\lambda \delta T)$$

$$\begin{aligned} J_s(T_{k=2}) &= \exp(-\lambda(T_0 + \delta T + \delta T) + c) \\ &= \exp(-\lambda(T_0) + c) \cdot \exp(-\lambda \delta T) \cdot \exp(-\lambda \delta T) \\ &= \exp(-\lambda(T_0) + c) \cdot \exp(-\lambda \delta T)^2 \end{aligned}$$

$$\begin{aligned} J_s(T_{k=3}) &= \exp(-\lambda(T_0 + \delta T + \delta T + \delta T) + c) \\ &= \exp(-\lambda T_0 + c) \cdot \exp(-\lambda \delta T) \cdot \exp(-\lambda \delta T) \cdot \exp(-\lambda \delta T) \\ &= \exp(-\lambda T_0 + c) \cdot \exp(-\lambda \delta T)^3 \end{aligned}$$

Therefore it can be seen that:

$$J_s(T_k) = \exp(-\lambda T_0 + c) \cdot [\exp(-\lambda \delta T)]^k = J_s(T_0) \cdot [\exp(-\lambda \delta T)]^k \quad (4)$$

Incorporating into Eq. (3):

$$f(n_r) = 1 - \exp\left(-A \cdot \delta t_r \cdot J_s(T_0) \sum_{k=0}^{n_r} [\exp(-\lambda \delta T)]^k\right) \quad (5)$$

The summation term can be removed using a geometric summation of series where

$$\sum_{k=0}^{n-1} ar^k = a \frac{1 - r^n}{1 - r}.$$

Rearranging Eq. (5) identifies the series:

$$\frac{-\ln(1 - f(n_r))}{A \cdot \delta t_r \cdot J_s(T_0)} = \sum_{k=0}^{n_r} [\exp(-\lambda \delta T)]^k \quad (6)$$

Substituting the RHS into the geometric summation of series formula where $a = 1$; $r = \exp(-\lambda \delta T)$; and $n - 1 = n_r$ (therefore $n = n_r + 1$) gives:

$$\frac{-\ln(1 - f(n_r))}{A \cdot \delta t_r \cdot J_s(T_0)} = \frac{1 - [\exp(-\lambda \delta T)]^{n_r+1}}{1 - \exp(-\lambda \delta T)} \quad (7)$$

This now needs to be rearranged and solved for the number of steps n_r :

$$\frac{-\ln(1 - f(n_r)) \cdot (1 - \exp(-\lambda \delta T))}{A \cdot \delta t_r \cdot J_s(T_0)} = 1 - \exp(-\lambda \delta T(n_r + 1)) \quad (8)$$

$$1 - \left[\frac{-\ln(1 - f(n_r)) \cdot (1 - \exp(-\lambda \delta T))}{A \cdot \delta t_r \cdot J_s(T_0)} \right] = \exp(-\lambda \delta T(n_r + 1)) \quad (9)$$

$$\ln \left[1 - \left[\frac{-\ln(1 - f(n_r)) \cdot (1 - \exp(-\lambda \delta T))}{A \cdot \delta t_r \cdot J_s(T_0)} \right] \right] \frac{1}{-\lambda \delta T} = n_r + 1 \quad (10)$$

$$n_r = \ln \left[1 - \left[\frac{-\ln(1 - f(n_r)) \cdot (1 - \exp(-\lambda \delta T))}{A \cdot \delta t_r \cdot J_s(T_0)} \right] \right] \frac{1}{-\lambda \delta T} - 1 \quad (11)$$

A change in the cooling rate from r_1 to r_2 results in a change in the number of steps required to reach fraction f , so that $f = f(n_{r1}) = f(n_{r2})$:

$$n_{r_2} - n_{r_1} = \ln \left[\frac{1 - \left[-\ln(1-f) \cdot (1 - \exp(-\lambda\delta T)) \cdot \frac{1}{A \cdot \delta t_{r_2} \cdot J_s(T_0)} \right]}{1 - \left[-\ln(1-f) \cdot (1 - \exp(-\lambda\delta T)) \cdot \frac{1}{A \cdot \delta t_{r_1} \cdot J_s(T_0)} \right]} \right] \cdot \frac{1}{-\lambda\delta T} \quad (12)$$

where δT is constant in both simulations, and δt is dependent on the cooling rate. Introducing the constant $C = -\ln(1-f) \cdot (1 - \exp(-\lambda\delta T))$ gives:

$$n_{r_2} - n_{r_1} = \ln \left[\frac{1 - \left[\frac{C}{A \cdot \delta t_{r_2} \cdot J_s(T_0)} \right]}{1 - \left[\frac{C}{A \cdot \delta t_{r_1} \cdot J_s(T_0)} \right]} \right] \cdot \frac{1}{-\lambda\delta T} \quad (13)$$

When $(A \cdot \delta t \cdot J_s(T_0)) \ll C$, Eq. (13) is approximated by the following equation:

$$n_{r_2} - n_{r_1} = \ln \left[\frac{C \cdot A \cdot \delta t_{r_1} \cdot J_s(T_0)}{C \cdot A \cdot \delta t_{r_2} \cdot J_s(T_0)} \right] \cdot \frac{1}{-\lambda\delta T} \quad (14)$$

This condition breaks down when the temperature T_0 (for $J_s(T_0)$) is close to the temperature at which a cooling experiment simulation (cooled from 273.15 K) exceeds a cumulative fraction frozen of 0.9.

Cancelling terms in Eq. (14) provides:

$$n_{r_2} - n_{r_1} = \ln \left[\frac{\delta t_{r_1}}{\delta t_{r_2}} \right] \cdot \frac{1}{-\lambda\delta T} \quad (15)$$

Multiplying the change in n_r by the temperature step δT (constant in both cases) provides a formula for the change in temperature:

$$\Delta T = (n_{r_2} - n_{r_1})\delta T = \ln \left[\frac{\delta t_{r_1}}{\delta t_{r_2}} \right] \cdot \frac{1}{-\lambda} \quad (16)$$

Substituting $r_1 = \frac{\delta T}{\delta t_{r_1}}$ and $r_2 = \frac{\delta T}{\delta t_{r_2}}$ into Eq. (16) provides us with a formula that can be used to calculate the change in temperature observed at a fraction f upon a change in cooling rate:

$$\Delta T = \ln \left[\frac{r_1}{r_2} \right] \cdot \frac{1}{\lambda} \quad (17)$$

Using $r = \Delta T/t$ the relative change in cooling rate described by $\ln(r_1/r_2)$ can also be expressed as a relative change in time $\ln(t_2/t_1)$:

$$\Delta T = \ln \left[\frac{t_2}{t_1} \right] \cdot \frac{1}{\lambda} \quad (18)$$

where λ describes the temperature dependence of J_s ; $-\ln(J_s)/dT$.

Reconciling isothermal experiments with cooling experiments

For the framework to be consistent between all experiments the residence-time dependence and the cooling-rate dependence need to be reconciled. The aim is to derive a formula that can be used to describe the entire stochastic dependence (cooling-rate and residence-time dependence) of an INP species. The cooling-rate dependence manifests because the time-step at each temperature increases, or decreases, therefore we hypothesise that there is a similar dependence for changes in residence time in isothermal experiments.

In order to reconcile the two experimental we need to understand how the change in cooling rate corresponds to a change in residence time for an isothermal simulation. To start off we need to equate the fraction frozen in a cooling experiment simulation (denoted as 'cool') to that of an isothermal experiment simulation (denoted as 'iso'), so that $f_{cool}(T) = f_{iso}(T)$.

As per the section above, the number of droplets frozen at a specific temperature (upon cooling from $T_0 = 273.15$ K) can be determined by calculating the product of the probability that an event does not occur between T_0 and T , with the probability of an event occurring per droplet as $(1 - P_{not})$. For the cooling experiment, from Eq. (3), we have:

$$f_{cool}(T) = 1 - \exp\left(-\sum_{k=0}^{n_{cool}} J_s(T_k) A \delta t_r\right) \quad (19)$$

The probability of a freezing event occurring in an isothermal experiment follows Eq. (19) but temperature T_k is constant so that $J_s(T_k) = J_s(T)$:

$$f_{iso}(T) = 1 - \exp\left(-\sum_{k=0}^{n_{iso}} J_s(T) A \delta t_{iso}\right) = \exp(-J_s(T) \cdot A \cdot \delta t_{iso} \cdot n_{iso}) \quad (20)$$

In the isothermal simulation, the total time for a fraction to be reached is simply a product of the time step and number of steps where $t_{total,iso} = n_{iso} \cdot \delta t_{iso}$. Incorporating this into Eq. (20) gives:

$$f_{iso}(T) = 1 - \exp(-J_s(T) \cdot A \cdot t_{total,iso}). \quad (21)$$

For a specific fraction frozen, Eq. (21) can be equated to Eq. (19) so that $f_{cool}(T) = f_{iso}(T)$. Realising that $J_s(T)$ for the isothermal simulation equals $J_s(T)$ in the cooling experiment after n_{cool} steps gives:

$$1 - \exp\left(-\sum_{k=0}^{n_{cool}} J_s(T_k) A \delta t_r\right) = 1 - \exp(J_s(T_{n_{cool}}) \cdot A \cdot t_{total,iso}) \quad (22)$$

where the LHS represents the cooling experiment simulation and the RHS, the isothermal experiment simulation. Solving for $t_{total,iso}$ gives:

$$t_{\text{total,iso}} = \frac{1}{J_s(T_{n_{\text{cool}}})} \sum_{k=0}^{n_{\text{cool}}} J_s(T_k) \cdot \delta t_{\text{cool}} \quad (23)$$

From Eq. (4) we know that for a nucleation rate coefficient represented by $\ln J_s(T_k) = -\lambda T_k + c$, in a cooling experiment simulation $J_s(T_k) = \exp(-\lambda T_0 + c) \cdot [\exp(-\lambda \delta T)]^k$ and in an isothermal simulation $J_s(T_{n_{\text{cool}}}) = \exp(-\lambda T_{n_{\text{cool}}} + c) = \exp(-\lambda T_0 + c) \cdot [\exp(-\lambda \delta T)]^{n_{\text{cool}}}$.

Replacing $J_s(T_k)$ and $J_s(T_{n_{\text{cool}}})$ in Eq. (23) gives:

$$t_{\text{total,iso}}(T_{n_{\text{cool}}}) = \frac{\delta t_{\text{cool}} \cdot \exp(-\lambda T_0 + c) \cdot \left(\sum_{k=0}^{n_{\text{cool}}} [\exp(-\lambda \cdot \delta T_{\text{cool}})]^k \right)}{\exp(-\lambda T_0 + c) \cdot [\exp(-\lambda \cdot \delta T_{\text{cool}})]^{n_{\text{cool}}}} \quad (24)$$

Cancelling out terms gives:

$$t_{\text{total,iso}}(T_{n_{\text{cool}}}) = \delta t_{\text{cool}} \cdot \left(\sum_{k=0}^{n_{\text{cool}}} [\exp(-\lambda \cdot \delta T_{\text{cool}})]^k [\exp(-\lambda \cdot \delta T_{\text{cool}})]^{-n_{\text{cool}}} \right) \quad (25)$$

$$t_{\text{total,iso}}(T_{n_{\text{cool}}}) = \delta t_{\text{cool}} \cdot \left(\sum_{k=0}^{n_{\text{cool}}} [\exp(-\lambda \cdot \delta T_{\text{cool}})]^{(k-n_{\text{cool}})} \right) \quad (26)$$

We can remove the summation term using a geometric summation of series, in order to do this we need to reverse the summation sequence using

$$\sum_{k=0}^{n_{\text{cool}}} a^{(k-n_{\text{cool}})} \equiv \sum_{k=0}^{n_{\text{cool}}} a^{(-k)},$$

so that:

$$t_{\text{total,iso}}(T_{n_{\text{cool}}}) = \delta t_{\text{cool}} \cdot \left(\sum_{k=0}^{n_{\text{cool}}} [\exp(-\lambda \cdot \delta T_{\text{cool}})]^{-k} \right) \quad (27)$$

The Summation of series can be performed using the following formula:

$$\sum_{k=0}^n ar^k = a \frac{1 - r^{n+1}}{1 - r},$$

which gives:

$$t_{\text{total,iso}}(T_{n_{\text{cool}}}) = \delta t_{\text{cool}} \cdot \frac{1 - [\exp(\lambda \cdot \delta T_{\text{cool}})]^{n_{\text{cool}}+1}}{1 - \exp(\lambda \cdot \delta T_{\text{cool}})} \quad (28)$$

Substituting $\gamma = (\lambda \cdot \delta T_{\text{cool}} \cdot (n_{\text{cool}} + 1))$ we can see that where $\gamma \gg 1$, $[\exp(\lambda \cdot \delta T_{\text{cool}})]^{n_{\text{cool}}+1} \rightarrow 0$. Rearranging so that $\gamma = \frac{\delta T_{\text{cool}} n_{\text{cool}} + \delta T_{\text{cool}}}{-\lambda^{-1}} = \frac{T_{\text{iso}} + \delta T_{\text{cool}}}{-\lambda^{-1}}$, we can see that this limit is reached for all cases except when, together, T_{iso} is very high (> -5 °C) and $-\lambda$ is very shallow ($\lambda < 1$).

So, assuming that the isothermal experiment is below this temperature:

$$t_{\text{total,iso}}(T_{n_{\text{cool}}}) = \frac{\delta t_{\text{cool}}}{1 - \exp(\lambda \cdot \delta T_{\text{cool}})} \quad (29)$$

A Taylor expansion of $\exp(\lambda \cdot \delta T_{\text{cool}})$ will result in $\left[1 + \lambda \delta T_{\text{cool}} - \frac{(\lambda \delta T_{\text{cool}})^2}{2!} + \frac{(\lambda \delta T_{\text{cool}})^3}{3!} \dots\right]$. When $\lambda \delta T_{\text{cool}} \gg \frac{1}{2} (\lambda \delta T_{\text{cool}})^2$, $\exp(\lambda \delta T_{\text{cool}}) \cong 1 + \lambda \delta T_{\text{cool}}$. This is satisfied when the simulation temperature step $\delta T_{\text{cool}} \ll 1$.

$$t_{\text{total,iso}}(T_{n_{\text{cool}}}) = \frac{\delta t_{\text{cool}}}{\lambda \cdot \delta T_{\text{cool}}} \quad (30)$$

Substituting $r_{\text{cool}} = -\frac{\delta T_{\text{cool}}}{\delta t_{\text{cool}}}$, where $r_{\text{cool}} > 0$

$$t_{\text{total,iso}}(T_{n_{\text{cool}}}) = \frac{\delta t_{\text{cool}}}{\lambda \cdot r_{\text{cool}} \cdot \delta t_{\text{cool}}} = \frac{1}{\lambda \cdot r_{\text{cool}}} \quad (31)$$

Using a standard cooling rate r_{standard} , for which we have chosen 1 K min^{-1} , allows us to reconcile the isothermal and cooling rate experiment simulations. For cooling rate experiments, replacing r_1 in Eq. (17) with r_{standard} and r_2 with the experimental cooling rate r , in K min^{-1} , gives the shift in temperature (named β) as a function of cooling rate:

$$\beta(r) = \Delta T = \frac{1}{\lambda} \ln\left(\frac{1}{|r|}\right) \quad (32)$$

For isothermal experiments, replacing r_{cool} with r_{standard} in Eq. (31) gives the time required for an isothermal experiment to be comparable to a normalised cooling experiment.

Substituting t_1 in Eq. (18) with t_{total} in Eq. (31), and t_2 with the experimental residence time t , in seconds, gives β as a function of residence time:

$$\beta(t) = \Delta T = \frac{1}{\lambda} \ln\left(\frac{\lambda \cdot t}{60}\right) \quad (33)$$

Where, again, λ describes the temperature dependence of J_s ; $-\ln(J_s)/dT$. Experimental data can now be modified and normalised using $T' = T_{\text{experiment}} - \beta$, where T' is the normalised temperature, and $T_{\text{experiment}}$ the temperature of the experiment data point.

