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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:

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

where,

\[
P_{not,k} = \exp(-J_s(T_k)A\delta t_r)
\]

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

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

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 \( \delta t \), steps this can be expanded:

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

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

\[
J_s(T_{k=2}) = \exp(-\lambda(T_0 + \delta T + \delta T) + c)
\begin{align*}
&= \exp(-\lambda(T_0 + c) \cdot \exp(-\lambda \delta T) \cdot \exp(-\lambda \delta T) \\
&= \exp(-\lambda(T_0 + c) \cdot \exp(-\lambda \delta T)^2
\end{align*}
\]

\[
J_s(T_{k=3}) = \exp(-\lambda(T_0 + \delta T + \delta T + \delta T) + c)
\begin{align*}
&= \exp(-\lambda T_0 + c) \cdot \exp(-\lambda \delta T) \cdot \exp(-\lambda \delta T) \cdot \exp(-\lambda \delta T) \\
&= \exp(-\lambda T_0 + c) \cdot \exp(-\lambda \delta T)^3
\end{align*}
\]

Therefore it can be seen that:
\[ J_s(T_k) = \exp(-\lambda T_0 + c) \cdot [\exp(-\lambda \delta T)]^k = J_s(T_0) \cdot [\exp(-\lambda \delta T)]^k \] (4)

Incorporating into Eq. (3):

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

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

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

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

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

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

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

\[ n_r = \ln \left[ 1 - \left[ \frac{-\ln(1 - f(n_r)) \cdot (1 - \exp(-\lambda \delta T))}{A \cdot \delta t_r \cdot J_s(T_0)} \right] \right] \frac{1}{-\lambda \delta T} - 1 \] (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 \( f = f(n_{r1}) = f(n_{r2}) \):
\[
\begin{align*}
n_{r_2} - n_{r_1} &= \ln \left[ 1 - \frac{1 - \ln(1 - f) \cdot (1 - \exp(-\lambda \delta T)) \cdot \frac{1}{A \cdot \delta t_{r_2} \cdot j_s(T_0)}}{1 - \ln(1 - f) \cdot (1 - \exp(-\lambda \delta T)) \cdot \frac{1}{A \cdot \delta t_{r_1} \cdot j_s(T_0)}} \right] \cdot \frac{1}{-\lambda \delta T} \tag{12}
\end{align*}
\]

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

\[
\begin{align*}
n_{r_2} - n_{r_1} &= \ln \left[ 1 - \frac{C}{A \cdot \delta t_{r_2} \cdot j_s(T_0)} \right] \cdot \frac{1}{-\lambda \delta T} \tag{13}
\end{align*}
\]

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

\[
\begin{align*}
n_{r_2} - n_{r_1} &= \ln \left[ \frac{C \cdot A \cdot \delta t_{r_1} \cdot j_s(T_0)}{C \cdot A \cdot \delta t_{r_2} \cdot j_s(T_0)} \right] \cdot \frac{1}{-\lambda \delta T} \tag{14}
\end{align*}
\]

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:

\[
\begin{align*}
n_{r_2} - n_{r_1} &= \ln \left[ \frac{\delta t_{r_1}}{\delta t_{r_2}} \right] \cdot \frac{1}{-\lambda \delta T} \tag{15}
\end{align*}
\]

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

\[
\begin{align*}
\Delta T = (n_{r_2} - n_{r_1}) \delta T = \ln \left[ \frac{\delta t_{r_1}}{\delta t_{r_2}} \right] \cdot \frac{1}{-\lambda} \tag{16}
\end{align*}
\]

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:

\[
\begin{align*}
\Delta T = \ln \left[ \frac{r_1}{r_2} \right] \cdot \frac{1}{\lambda} \tag{17}
\end{align*}
\]

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 \(\ln(t_2 / t_1)\):

\[
\begin{align*}
\Delta T = \ln \left[ \frac{t_2}{t_1} \right] \cdot \frac{1}{\lambda} \tag{18}
\end{align*}
\]
where \( \lambda \) describes the temperature dependence of \( J_s \): \(-d\ln(J_s)/dT\).

**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 \( f_{\text{cool}}(T) = f_{\text{iso}}(T) \).

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 \((1 - P_{\text{f}}} \cdot A \cdot \delta t_{\text{iso}} \cdot n_{\text{iso}})\)

For the cooling experiment, from Eq. (3), we have:

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

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

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

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 \( t_{\text{total,iso}} = n_{\text{iso}} \cdot \delta t_{\text{iso}} \). Incorporating this into Eq. (20) gives:

\[
f_{\text{iso}}(T) = 1 - \exp(-J_s(T) \cdot A \cdot t_{\text{total,iso}}). \tag{21}
\]

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

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

where the LHS represents the cooling experiment simulation and the RHS, the isothermal experiment simulation. Solving for \( t_{\text{total,iso}} \) gives:
\[ t_{\text{total,iso}} = \frac{1}{f_s(T_{n_{\text{cool}}})} \sum_{k=0}^{n_{\text{cool}}} f_s(T_k) \cdot \delta t_{\text{cool}} \]  

(23)

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

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

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

(24)

Cancelling out terms gives:

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

(25)

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

(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

\[ \sum_{k=0}^{n_{\text{cool}}} a^{(k-n_{\text{cool}})} = \sum_{k=0}^{n_{\text{cool}}} a^{(-k)} \]

so that:

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

(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:

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

(28)
Substituting $\gamma = (\lambda \cdot \delta T_{\text{cool}} \cdot (n_{\text{cool}} + 1))$ we can see that where $\gamma \gg 1$, $\left[\exp(\lambda \cdot \delta T_{\text{cool}})^{n_{\text{cool}}+1}\right] \rightarrow 0$. Rearranging so that $\gamma = \frac{\delta T_{\text{cool}} n_{\text{cool}} + \delta T_{\text{cool}}}{-\lambda^{-1}} - T_{\text{iso}} + \delta T_{\text{cool}} \cdot \frac{1}{-\lambda^{-1}}$, we can see that this limit is reached for all cases except when, together, $T_{\text{iso}}$ is very high ($> -5 ^\circ\text{C}$) and $-\lambda$ is very shallow ($\lambda < 1$).

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

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

(29)

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

$$t_{\text{total iso}}(T_{\text{n cool}}) = \frac{\delta t_{\text{cool}}}{\lambda \cdot \delta T_{\text{cool}}}$$

(30)

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

$$t_{\text{total iso}}(T_{\text{n cool}}) = \frac{\delta t_{\text{cool}}}{\lambda \cdot r_{\text{cool}} \cdot \delta T_{\text{cool}}} = \frac{1}{\lambda \cdot r_{\text{cool}}}$$

(31)

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

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

(32)

For isothermal experiments, replacing $r_{\text{cool}}$ with $r_{\text{standard}}$ 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 $t_{\text{total}}$ in Eq. (31), and $t_2$ with the experimental residence time $t$, in seconds, gives $\beta$ as a function of residence time:

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

(33)

Where, again, $\lambda$ describes the temperature dependence of $J_s$; $-\ln(J_s)/d\bar{T}$. 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.