Supplementary Material for

Fast dynamics of water droplets freezing from the outside-in

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I. STEFAN PROBLEM OF A RADIALLY INWARDS FREEZING WATER DROP

To estimate the thickness of the ice shell at a particular time t after nucleation, we solve the heat transfer problem of a water droplet that slowly freezes radially inwards. Consider a spherical droplet of outer radius R_o which at time t has reached an ice shell of thickness $R_o - R_i(t)$, where $R_i(t)$ is the radius of the liquid inclusion. The quasi-steady heat flow through a spherical shell held at a temperature difference of $\Delta T = T_i - T_o$ is given by (see e.g. [1])

$$q_s = 4\pi k \Delta T \frac{R_o R_i(t)}{R_o - R_i(t)}, \tag{S1}$$

where $k \approx 2\,\mathrm{W/(m\,K)}$ is the thermal conductivity of the ice shell. In our experiment the estimation of q_s is greatly facilitated by the fact that the temperature at both the inner and outer shell surface is determined by a well defined phase equilibrium, ice-liquid and ice-vapor, respectively. The ice-vapor buffer on the bottom of the chamber ensures that the vapor pressure in the chamber stays approximately constant during the whole experiment (even when the vacuum pump is kept on) so that ΔT is constant and equal to $\Delta T = T_{il} - T_{iv} \approx 7\mathrm{K}$.

This heat flow through the shell sets the rate at which latent heat $L_m \approx 330\,\mathrm{kJ/kg}$ is released as the freezing front advances inwards ($dR_i/dt < 0$):

$$q_f = -4\pi\rho L_m R_i^2 \frac{dR_i}{dt}, \tag{S2}$$

where $\rho \approx 1000\ \mathrm{kg/m^3}$ is the density of water. For simplicity we neglected the 9% decrease in density associated with the liquid to ice phase transition and the slight decrease in outer radius due to evaporation (to keep $T_o = T_{iv}$ we have $dR_o/dR_i = (R_i/R_o)^2(L_m/L_s) \approx 0.12(R_i/R_o)^2$, where $L_s \approx 2840\,\mathrm{kJ/kg}$ is the latent heat of sublimation of ice). Setting $q_s = q_f$, we find the following differential equation for $R_i(t)$:

$$R_i \frac{dR_i}{dt} = -\frac{k\Delta T}{\rho L_m}\frac{R_o}{R_o - R_i}. \tag{S3}$$

By introducing $\tilde{R}_i = R_i/R_o$ and $\tilde{t} = t/\tau_f$, with the timescale

$$\tau_f = \frac{\rho L_m R_o^2}{k\Delta T}, \tag{S4}$$

this expression can be recast in an universal dimensionless form as:

$$\tilde{R}_i \frac{d\tilde{R}_i}{d\tilde{t}} = -\frac{1}{1 - \tilde{R}_i}. \tag{S5}$$

Using separation of variables and integrating once the solution to equation (S5) is readily obtained as:

$$\frac{1}{3}\tilde{R}_i^3 - \frac{1}{2}\tilde{R}_i^2 + \frac{1}{6} = \tilde{t}. \tag{S6}$$

It is clear from this relation that the droplet will be completely frozen ($\tilde{R}_i = 0$) at $\tilde{t} = 1/6$.

II. ESTIMATION OF THE TIME TO EXPLOSION

The model for the thickening of the ice shell can be combined with the criteria for explosion (as derived in the main text) to obtain an estimate of the time it takes for droplet to explode. A lower bound on the explosion time can be obtained by (numerically) finding the ratio R_i/R_o for which the stored elastic energy, $E_e = (1/2)V_i P_i^2/K$, at the moment of crack formation exceeds the energy, $E_\gamma = 2\pi\gamma R_i^2$, required to create the fresh liquid-vapor interface (for a given droplet size R_o). This minimum shell thickness then serves as input for the freezing model to obtain the corresponding minimal time to explosion. An upper bound is given by the time $t = \tau_f/6$ for the droplet to freeze completely.

In Fig. S1 the results of this calculation are compared to experimental explosion times. Although the precise explosion time for each drop is random in nature, it is clear that the droplets did indeed always explode within the predicted time frame. In fact, with a few exceptions the explosions occur before or near the time for which the stored elastic energy reaches an optimum, i.e. when $R_i/R_o \approx 0.57$ (dashed line in Fig. S1).

[1] A. Bejan, *Heat transfer* (Wiley, 1993).

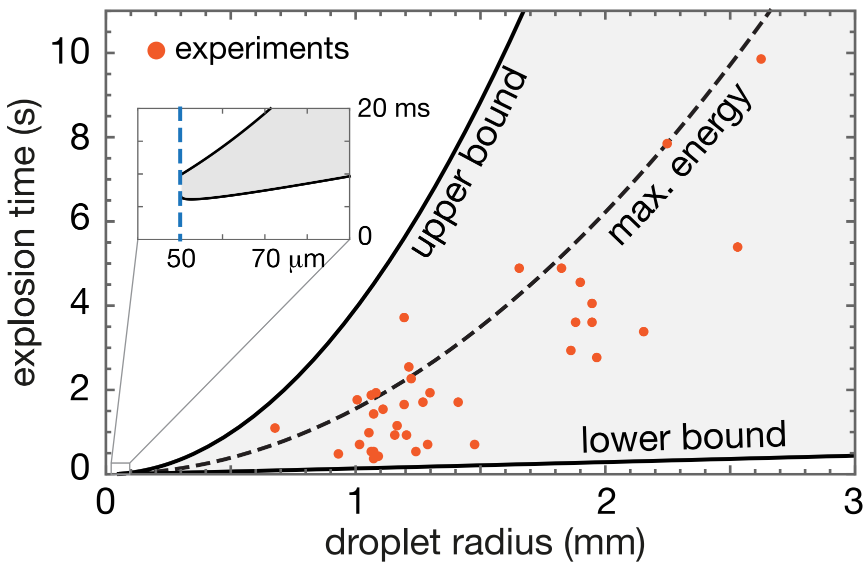

FIG. S1. Explosion time as a function of the outer droplet radius R_o. The upper solid line shows the theoretical upper bound given by the total freezing time $\tau_f/6$. The lower solid line represents the theoretical lower bound given by the time it takes for the shell to reach a thickness for which sufficient internal pressure can build up. The dashed line indicates the time at which the bursting is expected to be the most energetic. Orange dots represent our experimental observations. The inset shows a zoomed in-region near the origin, highlighting the predicted inhibition of ice drop explosions below a critical radius of about 50 micron (vertical dashed line).