Supplementary Note 1

Derivation of specific volumes of water and ice-1h as a function of absolute ice nucleus volume.
The goal of this derivation is to enable determination of the specific volume of each phase as function of ice nucleus growth, which in turn enables calculation of the specific Helmholtz free energies of each phase as a function of ice nucleus growth, $F_{\mathrm{water}}(v_{\mathrm{water}}(V_{\mathrm{ice}}))$ and $F_{\mathrm{ice}}(v_{\mathrm{ice}}(V_{\mathrm{ice}}))$. These parameters are employed in the main text in the derivation of the isochoric nucleation barrier.

In the following text, subscripts function as follows:

$X_{\mathrm{s}} = property\ of\ whole\ system$
$X_{\mathrm{w}} = property\ of\ water\ phase$
$X_{\mathrm{i}} = property\ of\ ice\ phase$

As described in the main text section entitled "Mathematical formulation of the system", the four constraints that govern an isochoric system comprised of supercooled water and an emergent ice nucleus are:

Conservation of mass, absolute system volume, and specific system volume:

$$V_{\mathrm{s}} = V_{\mathrm{i}} + V_{\mathrm{w}} \tag{1}$$

$$m_{\mathrm{s}} = m_{\mathrm{i}} + m_{\mathrm{w}} \tag{2}$$

$$v_{\mathrm{s}} = \frac{V_{\mathrm{s}}}{m_{\mathrm{s}}} = \frac{V_{\mathrm{i}}+V_{\mathrm{w}}}{m_{\mathrm{i}}+m_{\mathrm{w}}} \tag{3}$$

Continuity of pressure between phases:

$$-\left(\frac{dF_{\mathrm{w}}}{dv}\right)\Big|_{v_{\mathrm{w}}} = -\left(\frac{dF_{\mathrm{i}}}{dv}\right)\Big|_{v_{\mathrm{i}}} \tag{4}$$

Using the continuity of pressure, the specific volumes of the water and ice phases may be related. For the purposes of this analysis, we assume a parabolic form for each of the *F(v)* curves relating specific free energy to specific volume:

$$F_{\mathrm{i}}(v) = Av^2 + Bv + C \tag{5}$$

$$F_{\mathrm{w}}(v) = Dv^2 + Ev + F \tag{6}$$

and thus

$$\left(\frac{dF_{\mathrm{i}}}{dv}\right) = 2Av + B \tag{7}$$

$$\left(\frac{dF_{\mathrm{w}}}{dv}\right) = 2Dv + E \tag{8}$$

Now substituting into Eq. 4, an expression for v_{w} in terms of v_{i} is achieved:

$$-\left(\frac{dF_{\mathrm{w}}}{dv}\right)\Big|_{v_{\mathrm{w}}} = -\left(\frac{dF_{\mathrm{i}}}{dv}\right)\Big|_{v_{\mathrm{i}}} \tag{4}$$

$$-(2Av_{\mathrm{i}}+B)=-(2Dv_{\mathrm{w}}+E) \tag{9}$$

$$v_{\mathrm{w}}=\frac{A}{D}\,v_{\mathrm{i}}+(\frac{B-E}{2C}) \tag{10}$$

$$C_1=\left(\frac{B-E}{2C}\right) \tag{11}$$

$$v_{\mathrm{w}}=\frac{A}{D}\,v_{\mathrm{i}}+C_1 \tag{12}$$

This relatability of the specific volumes is an essential product of the pressure continuity requirement, and a unique fundamental feature of isochoric systems.

Now, using eqs. 1-3 and eq. 12, we may derive the functions $v_{\mathrm{w}}(V_{\mathrm{i}})$ and $v_{\mathrm{i}}(V_{\mathrm{i}})$ (eqs. 22 and 23), which give the specific volume of each phase as a function of the absolute volume of the ice nucleus:

$$V_{\mathrm{i}}=V_{\mathrm{s}}-V_{\mathrm{w}} \tag{13}$$

$$V_{\mathrm{i}}=v_{\mathrm{s}}m_{\mathrm{s}}-v_{\mathrm{w}}m_{\mathrm{w}} \tag{14}$$

$$V_{\mathrm{i}}=v_{\mathrm{s}}m_{\mathrm{s}}-\left(\frac{A}{D}\,v_{\mathrm{i}}+C_1\right)(m_{\mathrm{s}}-m_{\mathrm{i}}) \tag{15}$$

$$V_{\mathrm{i}}=v_{\mathrm{s}}m_{\mathrm{s}}-\frac{A}{D}v_{\mathrm{i}}m_{\mathrm{s}}+\frac{A}{D}v_{\mathrm{i}}m_{\mathrm{i}}-C_1m_{\mathrm{s}}+C_1m_{\mathrm{i}} \tag{16}$$

$$V_{\mathrm{i}}=v_{\mathrm{s}}m_{\mathrm{s}}-\frac{A}{D}v_{\mathrm{i}}m_{\mathrm{s}}+\frac{A}{D}V_{\mathrm{i}}-C_1m_{\mathrm{s}}+C_1\frac{V_{\mathrm{i}}}{v_{\mathrm{i}}} \tag{17}$$

$$\frac{V_{\mathrm{i}}\left(1-\frac{A}{D}\right)}{m_{\mathrm{s}}}=\frac{V_{\mathrm{s}}}{m_{\mathrm{s}}}-\frac{A}{D}v_{\mathrm{i}}-C_1+\frac{C_1}{m_{\mathrm{s}}}\frac{V_{\mathrm{i}}}{v_{\mathrm{i}}} \tag{18}$$

$$\frac{V_{\mathrm{i}}\left(1-\frac{A}{D}\right)-V_{\mathrm{s}}}{m_{\mathrm{s}}}+C_1=-\frac{A}{D}v_{\mathrm{i}}+\frac{C_1}{m_{\mathrm{s}}}\frac{V_{\mathrm{i}}}{v_{\mathrm{i}}} \tag{19}$$

$$\left(\frac{V_{\mathrm{i}}\left(1-\frac{A}{D}\right)-V_{\mathrm{s}}}{m_{\mathrm{s}}}+C_1\right)v_{\mathrm{i}}=-\frac{A}{D}v_{\mathrm{i}}^2+\frac{C_1V_{\mathrm{i}}}{m_{\mathrm{s}}} \tag{20}$$

$$\frac{A}{D}v_{\mathrm{i}}^2+\left(\frac{V_{\mathrm{i}}\left(1-\frac{A}{D}\right)-V_{\mathrm{s}}}{m_{\mathrm{s}}}+C_1\right)v_{\mathrm{i}}-\frac{C_1V_{\mathrm{i}}}{m_{\mathrm{s}}}=0 \tag{21}$$

$$v_{\mathrm{i}}=-\frac{\left(\frac{V_{\mathrm{i}}\left(1-\frac{A}{D}\right)-V_{\mathrm{s}}}{m_{\mathrm{s}}}+C_1\right)\pm\sqrt{\left(\frac{V_{\mathrm{i}}\left(1-\frac{A}{D}\right)-V_{\mathrm{s}}}{m_{\mathrm{s}}}+C_1\right)^2-4\left(\frac{A}{D}\right)\left(-\frac{C_1V_{\mathrm{i}}}{m_{\mathrm{s}}}\right)}}{2\left(\frac{A}{D}\right)} \tag{22}$$

$$v_{\mathrm{w}}=\frac{A}{D}\,v_{\mathrm{i}}+C_1 \tag{23}$$

These expressions may now be used to determine the specific free energy of each phase as a function of the absolute ice nucleus volume, $F_{\mathrm{w}}(v_{\mathrm{w}}(V_{\mathrm{i}}))\ and\ F_{\mathrm{i}}(v_{\mathrm{i}}(V_{\mathrm{i}}))$, in the derivation of the isochoric nucleation barrier in the main text.

Supplementary Note 2

Parameters used in the calculation of the free energy curve in main text Figure 3A:

System absolute volume $V_{\mathrm{s}} = 2\ x\ 10^{-22}\ m^3$

System specific volume $v_{\mathrm{s}} = 0.001\ m^3\ kg^{-1}$

System mass $m_{\mathrm{s}} = 2\ x\ 10^{-19}\ kg$

Temperature $T = -4.15\ °C$

For all calculations plotted in Figure 3, the same system specific volume was retained, and the interfacial free energy gamma was calculated using the following relation from (1):

$$\gamma = (28.0 + 0.25T)\ mJ\ m^{-2}$$

in which the units of temperature are degrees Celsius.

For the purposes of relating the radius of the ice nucleus to its volume and surface area, the nucleus was assumed spherical.

Supplementary References

1. H.R. Pruppacher, J.D. Klett, Microphysics of Clouds and Precipitation, second ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997.