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The generalized Clapeyron equation and its application to confined ice growth

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Abstract

Most theoretical descriptions of stresses induced by freezing are rooted in the (generalized) Clapeyron equation, which predicts the pressure that a solid can exert as it cools below its melting temperature. This equation is central for topics ranging beyond glaciology to geomorphology, civil engineering, food storage and cryopreservation. However, it has inherent limitations, requiring isotropic solid stresses and conditions near bulk equilibrium. Here, we examine when the Clapeyron equation is applicable by providing a rigorous derivation that details all assumptions. We demonstrate the natural extension for anisotropic stress states, and we show how the temperature and pressure ranges for validity depend on well-defined material properties. Finally, we demonstrate how the range of applicability of the (linear) Clapeyron equation can be extended by adding higher-order terms, yielding results that are in good agreement with experimental data for the pressure melting of ice.

1. Introduction

When water freezes in confined spaces, it can generate large stresses, often resulting in material damage. This is important across fields ranging from glaciology to geomorphology, food science, civil engineering and cryopreservation (Walder and Hallet, 1985; Karlsson and Toner, 1996; Dash and others, 2006; Petzold and Aguilera, 2009; Rempel, 2010; Vlahou and Worster, 2015; Jha and others, 2019). Broadly speaking, ice can generate stresses via two different mechanisms (Wettlaufer and Worster, 2006; Peppin and Style, 2013). The first is due to the expansion of water as it freezes: in a closed cavity, freezing will generate pressure (Fig. 1a). The second is unrelated to the expansion of water and often dominates in porous materials – for example, in the process of frost heave (Peppin and Style, 2013). Here, ice can form in open pores of a wet material (Fig. 1b), but no pressure builds up during the initial ice-formation process (any pressure is relieved by water flow away from the growing ice). However, after the initial ice formation, unfrozen water is sucked back toward the ice crystals. When this water freezes onto the existing ice, it can cause the ice to expand its confining pore. This *cryosuction* process is aided by the presence of thin, mobile layers of water at the surface of ice (known as premelted films) (Slater and Michaelides, 2019). These allow growth of the ice, not just at the pore throat, but also along the pore/ice interface. In both cases, ice will continue to grow, building up pressure, until the pressure reaches a maximum value given by a temperature-dependent stall pressure, P_{st} (Peppin and Style, 2013; Gerber and others, 2022). P_{st} is very similar to the concept of crystallization pressure, found when confined crystals grow from supersaturated solutions (Flatt, 2002; Steiger, 2005; Desarnaud and others, 2016) and to the concept of condensation pressure, when phase separation occurs in confinement (Style and others, 2018; Fernández-Rico and others, 2021).

Theoretical descriptions of these stress-generation mechanisms are rooted in the (generalized) Clapeyron equation, a fundamental equation that describes static equilibrium between a solid (ice) at pressure P_s, and a reservoir of liquid (water) at a different pressure P_l, but at the same temperature, T (Black, 1995; Henry, 2000; Wettlaufer and Worster, 2006):

$$(P_s - P_l) + (P_l - P_0)\left(1 - \frac{\rho_s}{\rho_l}\right) = \rho_s q_m \frac{(T_m - T)}{T_m}. \quad (1)$$

Here, ρ_l and ρ_s are the densities of water and ice respectively, q_m is the specific latent heat of freezing of ice and T_m is the melting temperature at a reference pressure, P_0 (often taken as atmospheric pressure). For the freezing mechanisms described above, this equation can be used to predict P_{st} as a function of the temperature, T. For case (i) with ice growing in a closed cavity, the ice and water are both at the same pressure ($P_s = P_l = P_{st}$) (ignoring capillary effects), so

$$(P_{st} - P_0)\left(\frac{1}{\rho_s} - \frac{1}{\rho_l}\right) = \frac{q_m (T_m - T)}{T_m}. \quad (2)$$

Using values from Table 1, we find that ice can exert pressures of ~11 MPa per degree of undercooling ($T_m - T$).

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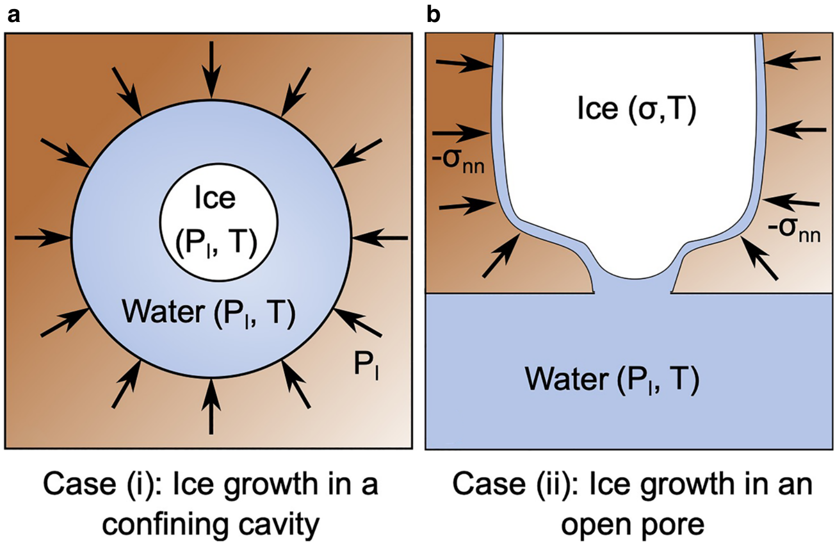

Figure 1. (a) Ice generates pressure as it grows in a closed cavity, due to the expansion of water upon freezing. (b) Ice growing in an open pore is fed by nearby water, and this growth wedges open the cavity, generating stresses.

For case (ii), the ice and water need no longer have the same pressure. If the water reservoir is held at the reference pressure $P_l = P_0$, then $P_{st} = P_s$ and

$$\frac{(P_{st} - P_0)}{\rho_s} = \frac{q_m(T_m - T)}{T_m}. \tag{3}$$

In this case, ice can exert pressures of ∼1 MPa per degree of undercooling.

Even when ice is not in equilibrium (e.g. it is growing), the Clapeyron equation gives us useful information. During growth, there is no macroscopic equilibrium, but water immediately adjacent to an ice surface can often be considered to be in equilibrium with the ice (Wettlaufer and Worster, 2006). Then, the Clapeyron equation relates the local hydrodynamic pressure in the water, P_l, to the local pressure that has been built up in the ice (P_l is the pressure that would exist in a bulk reservoir of water that was connected to, and in thermodynamic equilibrium with water at the ice interface – note that this definition works even for water in premelted films). Water flows along non-hydrostatic gradients in P_l, so the Clapeyron equation allows us to predict how water is transported toward (or away from) ice, and thus gives ice growth/melting rates (Derjaguin and Churaev, 1986; Wettlaufer and Worster, 1995; Rempel and others, 2004; Style and Worster, 2005; Wettlaufer and Worster, 2006).

The various applications of the Clapeyron equation make it a key tool for understanding freezing processes (e.g. Dash and others, 2006; Wettlaufer and Worster, 2006; Vlahou and Worster, 2015; Gerber and others, 2022). However, it makes a number of assumptions. For example, it assumes that ice can be described by an isotropic pressure, whereas ice is often characterized by an anisotropic stress state, σ_{ij} (Budd and Jacka, 1989) – for example, in glacier flow (Glen, 1955), or because anisotropic stresses arise spontaneously in a temperature gradient (Gerber and others, 2022). It also uses linear approximations that are valid only near the bulk melting point of ice (see later). Thus, several key questions arise. In particular: What is the appropriate extension of the Clapeyron equation for anisotropically stressed ice? Over what range of conditions should the Clapeyron equation be applicable?

Surprisingly, we are not aware of a systematic derivation of the Clapeyron equation that would allow us to address these questions. However, there are several related works. For example, several authors have established the thermodynamic relations that govern the dissolution of anisotropically stressed solids into adjacent fluids (Gibbs, 1879; Kamb, 1959, 1961), with notable applications to recrystallization and pressure solution processes (e.g. Paterson, 1973). Although melting was not a focus of these works, some of the consequences for ice melting were recognized by Nye (1967). He argued that the phenomenon of wire regelation requires a generalization of Eqn (2). For this case, P_s should be replaced by the normal stress $-\sigma_{nn}$, and not by the mean of the principal stresses $-\mathrm{Tr}(\sigma)/3$, as had been argued by others. Finally, Sekerka and Cahn (2004) examined the special case of a solid with $\sigma_{nn} = -P_l$, to show that anisotropically stressed solids in equilibrium with their melt will recrystallize to form an isotropically stressed state.

Here, we provide a first-principles derivation of the generalized Clapeyron equation, along similar lines to Paterson (1973). We clearly lay out all the underlying assumptions, and present the appropriate extension for the melting behavior of anisotropically stressed ice.

Table 1. Ice/water parameter values at atmospheric pressure and 273.15 K (Hobbs, 2010)

Density of ice	ρ_s	917 kg m^{-3}
Density of water	ρ_l	997 kg m^{-3}
Latent heat of fusion	q_m	334 kJ kg^{-1}
Melting temperature	T_m	273.15 K
Heat capacity of ice	c_s^p	2093 J (kg K)$^{-1}$
Heat capacity of water	c_l^p	4184 J (kg K)$^{-1}$
Bulk modulus of ice	K_s	11.33 GPa
Bulk modulus of water	K_l	1.96 GPa
Coeff. thermal expansion, ice	α_s	51×10^{-6} K^{-1}.
Coeff. thermal expansion, water	α_l	-50×10^{-6} K^{-1}

2. Deriving the generalized Clapeyron equation

We consider thermodynamic equilibrium for the two scenarios shown in Figure 1, in both of which the temperature is held fixed at $T < T_m$. In case (i), water freezes in a closed cavity, so that the ice and and water both have the same pressure, $P_s = P_l$. In case (ii), ice has frozen in an open cavity, and is in equilibrium with neighboring bulk water, which has pressure P_l. At the same time, the ice exerts a normal stress, $-\sigma_{nn}$, on the walls of the cavity, but is assumed to exert negligible shear forces, due to the presence of premelted films which lubricate the ice/cavity interface (Gerber and others, 2022). The ice cannot grow through the small, connecting pore throat into the neighboring water due to capillarity (i.e. the Gibbs–Thomson effect (Hardy, 1977; Schollick and others, 2016)).

For each scenario, we establish equilibrium behavior by minimizing the relevant free energy of the ice/water system. The relevant free energy, G_{sys} satisfies $\Delta G_{sys} = \Delta U_{sys} - T\Delta S_{sys} + W$, where U_{sys} is the internal energy of the ice/water system, S_{sys} is its entropy and W is the work done by the system on its surroundings. For case (i), $\Delta G_{sys} = \Delta U_{sys} - T\Delta S_{sys} + P_l(\Delta V_s + \Delta V_l)$, while for case (ii), $\Delta G_{sys} = \Delta U_{sys} - T\Delta S_{sys} - \sigma_{nn}\Delta V_s + P_l\Delta V_l$ where V_s and V_l are the volumes of ice and water, respectively. The first case is just a specialized version of the second, where $-\sigma_{nn} = P_l$. Thus, without loss of generality, we can proceed with the case (ii) expression, and the result will describe both cases.

We consider a perturbation to the system in Figure 1b, where a small mass of ice, Δm, melts and flows into the reservoir. Thus, the volumes of ice and water change as $\Delta V_s = -v_s\Delta m$, and $\Delta V_l = v_l\Delta m$, where $v_s(\boldsymbol{\sigma}_{ij}, T)$ and $v_l(P_l, T)$ are the specific volumes of the ice and water, respectively. At equilibrium, this perturbation must not change the free energy, so $\Delta G_{sys} = 0$, which becomes

$$u_l\Delta m - u_s\Delta m - T(s_l - s_s)\Delta m + \sigma_{nn}v_s\Delta m + P_l v_l\Delta m = 0. \quad (4)$$

Here, $u_s(\boldsymbol{\sigma}_{ij}, T)$ and $u_l(P_l, T)$ are the specific internal energies of the ice and water, respectively, and $s_s(\boldsymbol{\sigma}_{ij}, T)$ and $s_l(P_l, T)$ are the respective specific entropies. Dividing through by Δm, we obtain

$$-(\sigma_{nn}v_s + P_l v_l) = (u_l - u_s) - T(s_l - s_s). \quad (5)$$

In principle, Eqn (5) completely describes equilibrium between ice and water – i.e. one could use tabulated values of u, v, and s to find $-\sigma_{nn}(P_l, T)$. However, a more convenient form is found by expressing the equation relative to the pressure and temperature under bulk melting reference conditions, (P_0, T_m). With $-\sigma_{nn} = P_l = P_0$ Eqn (5) becomes

$$P_0(v_s^o - v_l^o) = (u_l^o - u_s^o) - T_m(s_l^o - s_s^o), \quad (6)$$

where the superscript ° indicates reference conditions. Subtracting Eqns (5) and (6), we find

$$g_l - g_l^o = g_s - g_s^o, \quad (7)$$

where the specific free energies $g_l(T, P_l) = u_l - Ts_l + P_l v_l$, and $g_s(T, \sigma_{ij}) = u_s - Ts_s - \sigma_{nn} v_s$. These can be Taylor-expanded to obtain the Clapeyron equation (e.g. Dash and others, 2006; Hütter and Tervoort, 2008):

$$g_l(T, v) = g_l^o(T_m, P_0) + \left(\frac{\partial g_l}{\partial T}\right)_{P_l}(T - T_m) + \left(\frac{\partial g_l}{\partial P_l}\right)_T(P_l - P_0) \quad (8)$$

and

$$g_s(T, \sigma_{ij}) = g_s^o(T_m, P_0) + \left(\frac{\partial g_s}{\partial T}\right)_{\sigma_{ij}}(T - T_m) + \left(\frac{\partial g_s}{\partial \sigma_{ij}}\right)_T(\sigma_{ij} + P_0\delta_{ij}), \quad (9)$$

where δ_{ij} is the identity matrix. To evaluate the derivatives, we note that $\Delta g_l = -s_l\Delta T + v_l\Delta P_l$. Thus, at reference conditions,

$$\left(\frac{\partial g_l}{\partial T}\right)_{P_l} = -s_l^o, \quad \left(\frac{\partial g_l}{\partial P_l}\right)_T = v_l^o, \quad (10)$$

and similarly in the solid at reference conditions $(\sigma_{ij} = -P_0\delta_{ij})$

$$\left(\frac{\partial g_s}{\partial T}\right)_{\sigma_{ij}} = -s_s^o. \quad (11)$$

To calculate the final derivative, we notice that $g_s = (f_s + P_0 v_s) - \bar{\sigma}_{nn}v_s$, where f_s is the specific Helmholtz free energy of the solid, and $\bar{\sigma}_{ij} = \sigma_{ij} + P_0\delta_{ij}$. Here, $(f_s + P_0 v_s)/v_s^o$ is the free-energy per unit volume for deformations in an atmosphere at constant pressure, P_0, and thus is the elastic energy per volume of ice in the reference state. Assuming that ice has linear-elastic behavior, we can write

$$g_s = \frac{1}{2}\bar{\sigma}_{ij}\epsilon_{ij}v_s^o - \bar{\sigma}_{nn}v_s^o\left(1 + \frac{\mathrm{Tr}(\bar{\sigma})}{3K_s}\right), \quad (12)$$

where K_s is now the bulk modulus of the solid. ϵ_{ij} is the strain of the ice relative to its shape in the reference state (T_m, P_0), and satisfies the linear-elastic constitutive relationship:

$$\epsilon_{ij} = \frac{1}{E_s}\left[(1 + \nu_s)\bar{\sigma}_{ij} - \nu_s\delta_{ij}\mathrm{Tr}(\bar{\sigma})\right], \quad (13)$$

where $E_s = 3K_s(1 - 2\nu_s)$ is the Young's modulus of the ice and ν_s is its Poisson ratio. For small strains, $v_s = v_s^o(1 + \mathrm{Tr}(\epsilon))$, and we use this in the second term of Eqn (12).

With the two equations above, we can evaluate the remaining derivative at (P_0, T_m):

$$\left(\frac{\partial g_s}{\partial \sigma_{ij}}\right)_T(\bar{\sigma}_{ij} = 0) = -n_i n_j v_s^o. \quad (14)$$

Here, n_i is the normal vector to the surface of the ice, so that $\bar{\sigma}_{nn} = n_i\bar{\sigma}_{ij}n_j$.

Finally, we can insert these first-derivative expressions into Eqns (7)–(9) to obtain the Clapeyron equation for anisotropically stressed solids:

$$-\frac{(\sigma_{nn} + P_0)}{\rho_s^o} - \frac{(P_l - P_0)}{\rho_l^o} = \frac{q_m(T_m - T)}{T_m}. \quad (15)$$

Here, $\rho_l^o = 1/v_l^o$, and $\rho_s^o = 1/v_s^o$ are the densities of water and ice respectively at the bulk melting point, and $q_m \equiv (s_l^o - s_s^o)T_m$. Consistent with the regelation analysis of Nye (1967), this version of the Clapeyron equation is identical to Eqn (1), but with P_s replaced by $-\sigma_{nn}$, and not $-\mathrm{Tr}(\sigma)/3$, as some might assume (Verhoogen, 1951).

3. Field data supporting the anisotropic Clapeyron equation

While Nye (1967) has presented arguments supporting the form of Eqn (15) in the context of regelation, further evidence comes from simultaneous measurements of temperatures and liquid pressures in glacier boreholes. These measurements show that temperatures increase when changes in the hydrologic system cause borehole pressures, P_l, to decrease (e.g. Andrews and others, 2014).

The anisotropic Clapeyron equation indeed recovers this correlation. Along borehole walls, $\sigma_{nn} = -P_l$. Inserting this into Eqn (15), we find that changes in temperature are correlated with changes in borehole pressure by:

$$\Delta T = -\frac{T_m}{q_m}\left(\frac{1}{\rho_s^0} - \frac{1}{\rho_l^0}\right)\Delta P_l$$
$$\approx \left(-7.16 \times 10^{-8}\,\mathrm{K\,Pa^{-1}}\right)\Delta P_l\,, \quad (16)$$

in agreement with the field data.

By contrast, extending the isotropic Clapeyron Eqn (1), by replacing $-P_s = \mathrm{Tr}(\sigma)/3$, does not match the experimental data. The classic analysis of Nye (1953) gives the complete stress tensor at the surface of an idealized cylindrical borehole containing liquid at pressure P_l. Far from the borehole, the ice has a far-field isotropic ice pressure P_∞, and creeps according to Glen's flow law with exponent $n = 3$ (Glen, 1955; Hewitt and Creyts, 2019). In this case, $-\mathrm{Tr}(\sigma)/3 = P_l + (P_\infty - P_l)/n$. Substituting $P_s = -\mathrm{Tr}(\sigma)/3$ into the isotropic Clapeyron Eqn (1) and treating the far-field ice pressure as constant leads to

$$\Delta T = -\frac{T_m}{q_m}\left(\frac{1}{\rho_s^0} - \frac{1}{\rho_l^0} - \frac{1}{n\rho_s^0}\right)\Delta P_l$$
$$\approx \left(2.26 \times 10^{-7}\,\mathrm{K\,Pa^{-1}}\right)\Delta P_l\,. \quad (17)$$

This predicts the opposite of the correlation seen in the field data.

4. Errors in the Clapeyron equation

In deriving this version of the Clapeyron equation, we have had to make two main assumptions. Firstly, strains in the ice are small, so we can use linear elasticity (Sekerka and Cahn, 2004). This is reasonable as the stresses in the ice (which are O(MPa) – see introduction) are much less than the ice's elastic moduli E_s, $K_s = O$(GPa), so strains will be small.

Secondly, we assume that higher-order terms in the expansions of g_l and g_s are negligible. We can test this by reverting to the case of isotropically stressed ice ($\sigma_{ij} = -P_s\delta_{ij}$). Then, we Taylor-expand Eqn (7) in T, P_l and P_s to obtain the second-order version of the Clapeyron equation:

$$\frac{(P_s - P_0)}{\rho_s^o} - \frac{(P_l - P_0)}{\rho_l^o} = \frac{q_m(T_m - T)}{T_m}$$
$$- \frac{c_l^P - c_s^P}{2T_m}(T_m - T)^2 - \frac{1}{2\rho_l^o K_l}(P_l - P_0)^2 + \frac{1}{2\rho_s^o K_s}(P_s - P_0)^2$$
$$- \frac{\alpha_l}{\rho_l^o}(T_m - T)(P_l - P_0) + \frac{\alpha_s}{\rho_s^o}(T_m - T)(P_s - P_0). \quad (18)$$

Here, we use the following identities (e.g. Venerus and Öttinger, 2018): $\partial^2 g/\partial T^2 = c^P/T_m$, $\partial^2 g/\partial P^2 = 1/(K\rho^o)$ and $\partial^2 g/\partial T\partial P = \alpha/\rho^o$, where c^P is the heat capacity at constant pressure, K is again the isothermal bulk modulus and α is the coefficient of thermal expansion.

We can now predict the pressure-melting curve for different freezing scenarios. For bulk ice/water equilibrium (Fig. 1a), $P_s = P_l$, and we take atmospheric pressure, P_a, as the reference pressure, and $T_m = 273.15$ K. Figure 2a compares the isotropic Clapeyron Eqn (1) (red, dashed) with experimental data (black, dotted) (Dunaeva and others, 2010). There is a significant error between the two results for an undercooling of more than ~3 °C. However, when we use the full, second-order Clapeyron Eqn (18) (blue), we find good agreement down to an undercooling of at least 15 °C. In this situation, the terms that are quadratic in pressure dominate the error, and to excellent approximation (Fig. 1a, orange dash-dotted):

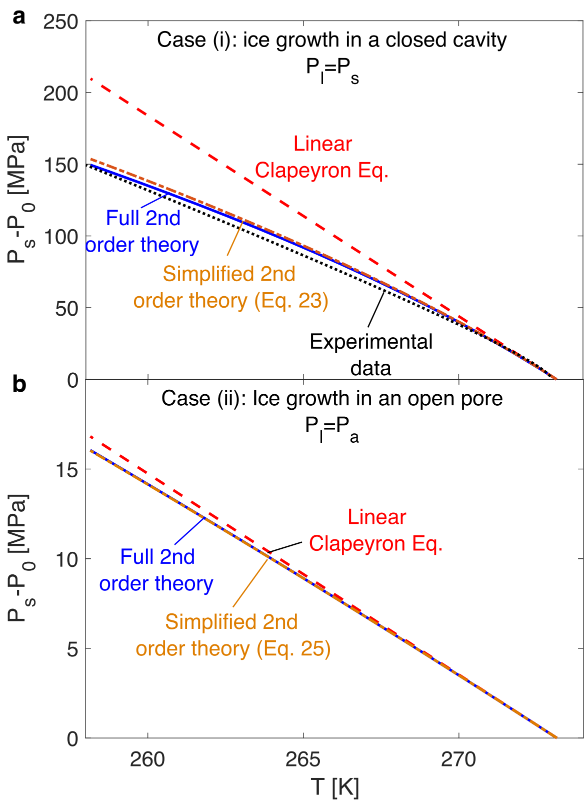

Figure 2. Evaluating the accuracy of the Clapeyron Equation. (a) The pressure of ice in bulk ice/water equilibrium in a closed cavity ($P_l = P_s = -\sigma_{nn}$), as a function of undercooling. The black, dotted curve shows experimental data (Dunaeva and others, 2010). (b) The stress exerted by ice in an open pore, as a function of undercooling. Both figures show the linear Clapeyron equation (dashed red), full second-order theory (Eqn (18), blue) and simplified second-order theory (Eqns (19) and (21), orange dash-dotted).

$$\left(\frac{1}{\rho_s^o} - \frac{1}{\rho_l^o}\right)(P_s - P_0) + \left(\frac{1}{2\rho_l^o K_l} - \frac{1}{2\rho_s^o K_s}\right)(P_s - P_0)^2$$
$$= \frac{q_m(T_m - T)}{T_m}. \quad (19)$$

Note this equation offers a way to extract information about material properties from a pressure/temperature phase diagram, as the curvature of the liquidus is controlled by the quadratic term's prefactor. Comparing the first two terms in the equation, we see that the linear Eqn (15) is only appropriate when:

$$|P_s - P_a| \ll \Delta P^* = \left|\left(\frac{1}{\rho_s^o} - \frac{1}{\rho_l^o}\right)\left(\frac{1}{2\rho_s^o K_s} - \frac{1}{2\rho_l^o K_l}\right)^{-1}\right|$$
$$\approx 420\,\mathrm{MPa}. \quad (20)$$

Typically, a factor of 10 suffices for such inequalities to hold. Thus, we expect the linear theory to hold when $|P_s - P_a| < \Delta P^*/10 = 42$ MPa: in good agreement with the data.

We can perform a similar analysis for freezing in an open system (Fig. 1b). We let $P_l = P_0 = P_a$, and assume that the ice is in an isotropic state of stress, with pressure, P_s. Figure 2b compares the prediction of the Clapeyron Eqn (1) (red, dashed) with that obtained when we keep the extra quadratic terms (18) (blue). We are not aware of any experimental data precise enough to validate the theory (Gerber and others, 2022). However, here, the higher-order theory agrees well with the linear Clapeyron equation down to large undercoolings. The difference is dominated by the term in Eqn (18) that is quadratic in undercooling. Thus, to excellent approximation (Fig. 1a, orange dash-dotted):

$$P_\mathrm{s} - P_\mathrm{a} = \frac{\rho_\mathrm{s}^\mathrm{o} q_\mathrm{m}(T_\mathrm{m} - T)}{T_\mathrm{m}} - \frac{\rho_\mathrm{s}^\mathrm{o}(c_\mathrm{l}^\mathrm{P} - c_\mathrm{s}^\mathrm{P})}{2T_\mathrm{m}}(T_\mathrm{m} - T)^2. \qquad (21)$$

Comparing terms on the right-hand side shows that we only recover the linear Clapeyron Eqn (1) if

$$|T_\mathrm{m} - T| \ll \Delta T^* = \left|\frac{2q_\mathrm{m}}{c_\mathrm{l}^\mathrm{P} - c_\mathrm{s}^\mathrm{P}}\right| \approx 320\,\mathrm{K}. \qquad (22)$$

Again, assuming a factor of 10 for the inequality to hold, we find that linear theory should work when $|T_\mathrm{m} - T| \ll \Delta T^*/10 = 32$ K. This requirement is certainly reasonable for many terrestrial temperatures. Thus, there is some justification for use of the linear Clapeyron equation down to relatively large undercoolings to model this type of freezing scenario.

To summarize, our results suggest that the linearized Clapeyron equation will be valid, provided that $|P_\mathrm{l} - P_0|$ and $|P_\mathrm{s} - P_0|$ are both less than $\Delta P^*/10$, while $|T_\mathrm{m} - T| < \Delta T^*/10$. At larger pressures/undercoolings, the quadratic terms in Eqn (18) should be included.

5. Conclusions

In conclusion, we have derived the linear Clapeyron equation describing equilibrium between water and ice, clearly laying out all the assumptions involved. In particular, this equation is derived using a Taylor expansion around a reference temperature and pressure, and ignoring higher-order terms. Thus, it is only valid for a range of pressures and temperatures around the reference conditions. Fortunately, for most naturally occurring terrestrial freezing scenarios, the linear form of the Clapeyron equation should be adequate. For example, at the base of a glacier, pressures are typically close to hydrostatic, and thus O(MPa) (Sugiyama and Gudmundsson, 2004) – this is small enough to lie within the range of applicability of the Clapeyron equation. However, more extreme conditions are expected in extraterrestrial settings (e.g. Dunaeva and others, 2010; McCarthy and Cooper, 2016). There, the linearized Clapeyron equation will not accurately predict melting temperatures, which could lead to significant errors in models of ice dynamics (as predicted flow rates are typically based on the departure from bulk melting conditions (Budd and Jacka, 1989)). In this case, the accuracy of the Clapeyron equation can be improved by retaining higher-order terms in the Taylor expansion.

We have also demonstrated the correct form of the Clapeyron equation for the case where ice is anisotropically stressed. This is identical to the isotropic form of the Clapeyron equation, but with ice pressure, P_s replaced by the normal stress exerted by ice on its surroundings, $-\sigma_{nn}$. One consequence of this is that differently stressed faces of ice (e.g. in a polycrystal) will have different melting temperatures.

While our analysis has focused on ice and water, the results should apply to any processes involving solid/liquid equilibrium, for example, in the melting and deformation of rocks in geological processes (e.g. Katz and others, 2006). Note however, that there are two key further effects that will likely be important to include in real-world applications. Firstly, we have neglected the presence of solutes, which are known to strongly affect the solid/liquid equilibrium (Zhang and others, 2021; Wettlaufer, 1999; Zhou and others, 2018; Dedovets and others, 2018). Secondly, we have ignored the surface energy of the ice (Wettlaufer and Worster, 2006; Wilen and Dash, 1995). We anticipate that both of these effects can be incorporated into the results presented here, by including colligative and capillary effects in the analysis above. In the case of capillary effects, we expect that the anisotropic Clapeyron equation will continue to hold, with capillarity just causing a jump between P_l and $-\sigma_{nn}$ at curved interfaces (e.g. Style and Worster, 2005).

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