

Calculating capillary pressures in frozen and ice-free soils below the melting temperature

Steven A. Grant¹ and Ronald S. Sletten²

¹ Cold Regions Research & Engineering Laboratory
Hanover, New Hampshire 03755, USA
steven.a.grant@usace.army.mil

² Quaternary Research Center
University of Washington
Seattle, Washington, USA
sletten@u.washington.edu

Received: date / Revised version: September 19, 2001

Abstract Approaches to calculating capillary pressure in frozen and ice-free soils below the melting temperature are surveyed. Three methods for calculating capillary pressure in frozen porous media are presented and compared. Except at very low temperatures all give comparable results. The effect of changes in the ice-melt interfacial tension on the soil freezing curves are expected to be trivial since the relative decrease in ice-melt interfacial tension becomes appreciable only at temperatures at which unfrozen water contents become vanishingly small. The thermodynamic relationships and formulae are presented to estimate the capillary pressure for unfrozen water in ice-free soils.

1 Introduction

While very little liquid water remains in soils at temperatures below $-1\text{ }^{\circ}\text{C}$, in certain situations the amount and thermophysical properties of liquid or liquid-like water in these soils is of interest. For example, accurate estimates of the liquid-water contents and enthalpies of fusion of frozen subsoils are needed for prediction of the global warming effects on permafrost distributions (Osterkamp and Romanovsky 1997, Romanovsky and Osterkamp 2000). The energy status of unfrozen water in the very dry surface soils of the dry valleys of Antarctica and the regolith of Mars is thought to control the sublimation rates from underlying perennial frozen ground (Clifford and Hillel 1983, Komarov 1983, McKay and others 1998).

Send offprint requests to: E-mail: steven.a.grant@usace.army.mil, Fax: +1-603-646-4561

The capillary pressure and energy status of the unfrozen water in frozen ground is specified if ice is present in the soil. This fact has been long used to deduce the liquid water contents of frozen soils at given temperatures. If the ice phase is lost from a frozen soil, by sublimation for example, the remaining unfrozen water can achieve chemical potentials well below that of ice at the same temperature (de Jong and Kachanoski 1988). Under these conditions the energy status of water is a function of both temperature and amount of unfrozen water. Accordingly, it is proper to consider the capillary pressures of ice-free soils at temperatures below the melting temperature with unsaturated, unfrozen soils. This article begins with a consideration of the correspondence between capillary-pressure saturation relations in unfrozen soils and soil freezing curves including a discussion of the two-junction model and a suggested modification. The capillary pressure in soils containing ice is then considered, in which three approaches to calculating capillary pressure as a function of temperature are compared. The article concludes with a discussion of an approach to calculating capillary pressures in ice-free soils at temperatures below the melting point.

2 Correspondence between capillary-pressure saturation relations and soil freezing curves

Capillary pressure is commonly defined for the liquid water in unsaturated unfrozen soils and in saturated unfrozen soils. Capillary pressure in an ice-free unsaturated soil p_c^{lg} (Pa) is the difference between the pressure in aqueous liquid and gas phases (p_l and p_g , respectively, both Pa) in the porous medium:

$$p_c^{lg} = p_g - p_l. \quad (1)$$

The corresponding relation for capillary pressure in a saturated, frozen soil (p_c^{sl} , Pa) is

$$p_c^{sl} = p_s - p_l \quad (2)$$

where p_s (Pa) is the pressure in the ice phase.

The strongest effects on p_c^{lg} are volumetric water content (θ , $\text{m}^3 \text{m}^{-3}$), solute molalities in the soil solution (m_B , m_C , ... mol kg^{-1} , where B, C, etc refer to individual solutes), and temperature (T , K). These relationships can be presented mathematically by representing p_c^{lg} as a function:

$$p_c^{lg} = p_c^{lg}(\theta, T, m_B, m_C, \dots) \quad (3)$$

For soils in which some ice remains, the capillary pressure is thought to be independent of the liquid-water content but determined entirely by the temperature and liquid-phase chemical composition, that is

$$p_c^{sl} = p_c^{sl}(T, m_B, m_C, \dots). \quad (4)$$

A number of researchers, beginning with Koopmans and Miller (1966) has assumed that there is a direct relationship between the liquid water contents in frozen

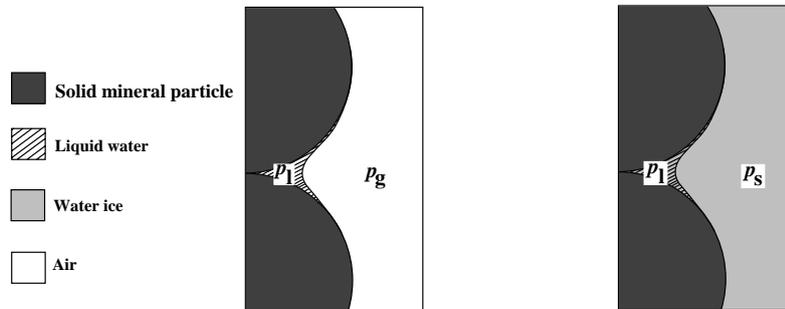


Fig. 1 Schematic drawing showing the assumed correspondence between gas-liquid capillary pressure in unsaturated porous media and liquid-capillary pressure in frozen porous media.

saturated granular soils and ice-free unsaturated granular soils via:

$$\theta(p_c^{sl}, T) = \frac{\gamma^{sl}}{\gamma^{lg}} \theta(p_c^{lg}, T) \quad (5)$$

where γ^{sl} is the hexagonal ice-melt water interfacial tension and γ^{lg} is the liquid-gas interfacial tension of water (both N m^{-1}) (Shvetsov and others 1978, Kinoshita and Ishizaki 1980, Spaans and Baker 1996). This correspondence at a microscopic level between p_c^{lg} and p_c^{sl} is presented schematically in Fig. 1.

To our knowledge no model of soil freezing curves consider the effect of changes in the ice-melt interfacial tension with temperature. The best available evidence indicates that the cubic ice-melt water interfacial tension is proportional to the 0.30 power of thermodynamic temperature (Huang and Bartell 1995, Wood and Walton 1970). Assuming reasonably that the proportional change for γ^{sl} is the same, we obtain

$$\gamma^{sl} = \frac{\gamma^{sl}(T_{mp})}{T_{mp}^{0.30}} T^{0.30}. \quad (6)$$

Fig. 2 presents the expected soil freezing curve for a Royal soil as predicted by the two-parameter junction model of Rossi and Nimmo (1994). Fig. 3 presents

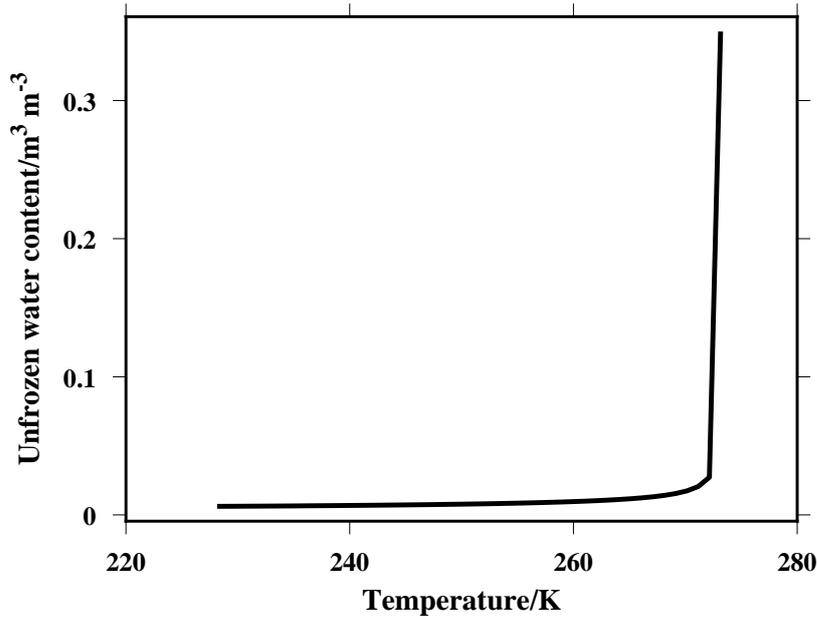


Fig. 2 Estimated unfrozen water content of a water-saturated Royal soil as a function of temperature.

the relative effect of a temperature-sensitive ice-melt interfacial tension on the predicted volumetric content—showing that the expected effect is trivial.

2.1 Capillary-pressure saturation relations

The constitutive relationship between liquid-water content and capillary pressure is central to the geophysical modeling of many processes in unsaturated soils and frozen ground. Conventional capillary pressure saturation relations rarely consider capillary pressures above 15 bars. Capillary pressures can be much higher below the melting temperature. For example, at $-5\text{ }^{\circ}\text{C}$, $p_c^{sl} = 82\text{ bar}$ (Kinosita and Ishizaki 1980). Accordingly capillary-pressure saturation relations appropriate for soils below the melting temperature must consider very high capillary pressures and very low liquid water contents. An appealing candidate capillary pressure saturation relation for describing soil freezing curves is the two-parameter junction model proposed by Rossi and Nimmo (1994)

2.1.1 Two-parameter junction model The two-parameter junction model developed by Rossi and Nimmo consists of three functions, which are continuous at the two points where the functions are joined:

$$\frac{\theta}{\theta_s} = \theta_I = 1 - c \left(\frac{p_c}{p_{c,0}} \right)^2 \quad 0 \leq p_c \leq p_{c,i}$$

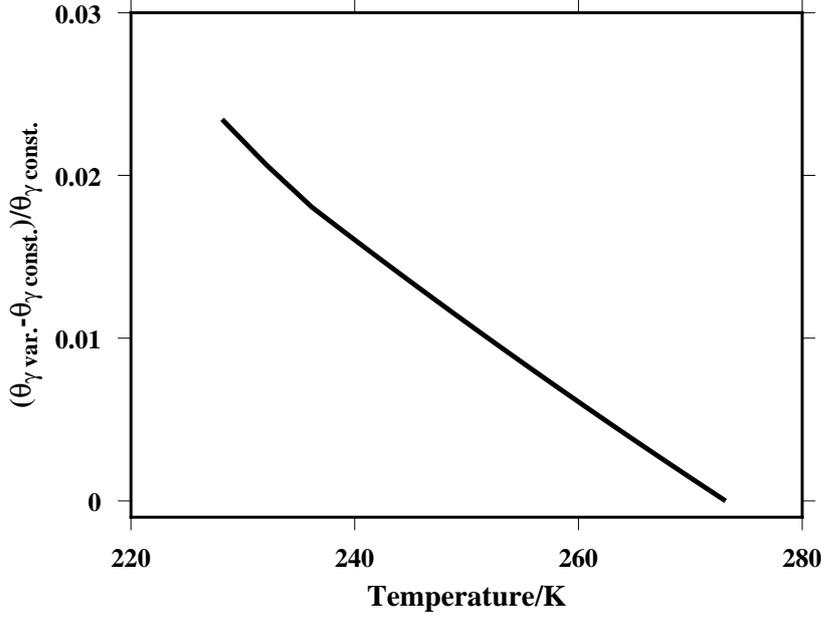


Fig. 3 Relative difference between unfrozen water contents of a Royal soil with a temperature-sensitive ice-melt interfacial tension to the same soil with a constant ice-melt interfacial tension.

$$\begin{aligned} \frac{\theta}{\theta_s} &= \theta_{II} = \left(\frac{p_c}{p_{c,0}} \right)^\lambda & p_{c,i} \leq p_c \leq p_{c,j} \\ \frac{\theta}{\theta_s} &= \theta_{III} = \alpha \ln\left(\frac{p_{c,d}}{p_c}\right) & p_{c,j} \leq p_c \leq p_{c,d} \end{aligned} \quad (7)$$

where θ_I , θ_{II} , and θ_{III} (dimension 1) are water-content segments of the capillary-pressure saturation relation normalized by the saturated water content, θ_s ($\text{m}^3 \text{m}^{-3}$). The two-parameter junction model has two fixed parameters, the capillary pressure at oven dryness, $p_{c,d}$, which is set arbitrarily at 980.665 MPa (equivalent to a hydraulic head of 10^7 cm) and θ_s . The two-parameter junction model has two fitted parameters, $p_{c,o}$ (Pa) and λ (dimension 1). The remaining four parameters $p_{c,i}$, $p_{c,j}$, c , and α are determined from $p_{c,o}$ and λ based on four continuity criteria:

$$\begin{aligned} \theta_I(p_{c,i}) &= \theta_{II}(p_{c,i}) \\ \frac{\partial \theta_I(p_{c,i})}{\partial p_c} &= \frac{\partial \theta_{II}(p_{c,i})}{\partial p_c} \\ \theta_{II}(p_{c,j}) &= \theta_{III}(p_{c,j}) \\ \frac{\partial \theta_{II}(p_{c,j})}{\partial p_c} &= \frac{\partial \theta_{III}(p_{c,j})}{\partial p_c}. \end{aligned} \quad (8)$$

Capillary pressure as a function of liquid water content may be calculated by

$$\begin{aligned} p_c &= p_{c,0} \left[\frac{1}{c(1-\theta_I)} \right]^{1/2} \\ p_c &= p_{c,0} (\theta_{III})^{1/\lambda} \\ p_c &= p_{c,0} \exp(-\alpha \theta_{III}). \end{aligned} \quad (9)$$

2.1.2 Modification to the Rossi-Nimmo equation Based on Eq. 7, one would expect that the driest segment of the capillary-pressure saturation relation (where $p_{c,j} \leq p_c \leq p_{c,d}$) that p_c would be an exponential function of water content. This is not the case for the soils studied by Campbell and Shiozawa (1992). In fact, for the soils they studied, water content was a exponential function of capillary pressure. Accordingly, a modification to the two-parameter junction model should be suggested. Fig. 4 presents the nominal thickness of water on six soils against the partial pressure of water (Campbell and Shiozawa 1992). The nominal adsorbed water thickness, δ (m) is calculated by dividing the soil's volumetric water content by the surface area

$$\delta = \frac{\theta r_s \rho_s}{3\rho_{\text{bulk}}}, \quad (10)$$

where r_s (m) the mean particle radius for a given particle size class, ρ_s (Mg m^{-3}), the particle density, and ρ_{bulk} , the soil's bulk density (Mg m^{-3}). The mean particle radius for a give particle-size class was calculated by:

$$r_s = (d_{\text{max}} + d_{\text{min}})/4 \quad (11)$$

where d_{max} and d_{min} are maximum and minimum effective particle diameter for the given size class (both m).

The graph indicates that there is a linear relationship between vapor pressure and the amount of adsorbed liquid water at nominal water film thicknesses smaller than 0.7 nm. The relationship appears to hold for granular soils over an order-of-magnitude range of specific surfaces. For very dry soils (and by extension very cold soils), the following equation appears to be appropriate:

$$p_{\text{soil}}/p^{1+g} = g + 10^9 h \delta \quad (12)$$

A linear regression of the data yielded parameter estimates of $g = 0.094656 (\pm 0.00992148)$ and $h = 0.598015 (\pm 0.01830185)$, respectively. This relation can be incorporated into the two-parameter junction model via

$$p_{\text{soil}}/p^{1+g} = g + \frac{10^9 h \theta_s}{A_s \rho_B} \frac{\theta}{\theta_s} \quad (13)$$

where A_s is the specific surface of the soil colloids ($\text{m}^2 \text{kg}^{-1}$) and ρ_B is the bulk density of the soil (kg m^{-3}). This yields the following modification to the driest segment of the two-parameter junction model:

$$\frac{\theta}{\theta_s} = \theta_{III} = \frac{A_s \rho_B}{10^9 h \theta_s} \left\{ \exp[-p_c^{\text{lg}} V_{\text{m,H}_2\text{O}(l)}^*/(RT)] - g \right\}. \quad (14)$$

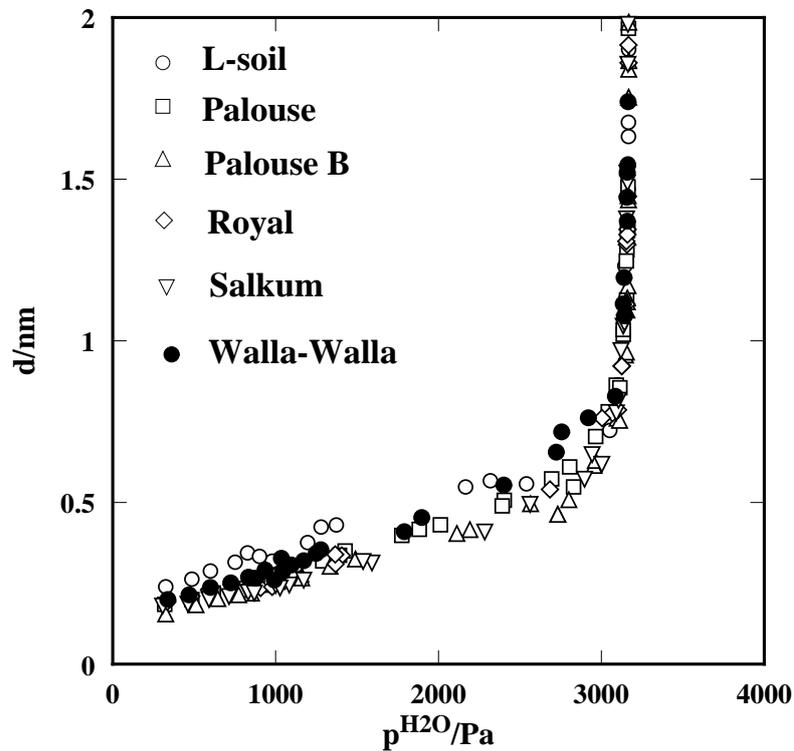


Fig. 4 Relation between water vapor pressure at 298 K and nominal adsorbed water thickness for six soils having specific surfaces from 25 to 200 m²/g.

The advantage of this modification is that all parameters of the driest segment of the model are experimentally accessible. The lower segment of the capillary-pressure saturation relations is “fixed” by the surface area, bulk density and saturated water content of the soil. The deficiency of this relation is that it calculates a minute (but nonzero) water content ($\theta \approx 0.000026 \text{ m}^3 \text{ m}^{-3}$) at infinite capillary pressure.

3 Capillary pressure in soils containing ice

Below we will compare three approaches to calculating capillary pressure in frozen porous media. While the calculated capillary pressures differ, the relative differences are not large. The development of Brun and others (1977) argues convincingly that capillary pressure in frozen porous media should be calculated based on the entropy differences between the ice and water phases. The approach of Brun

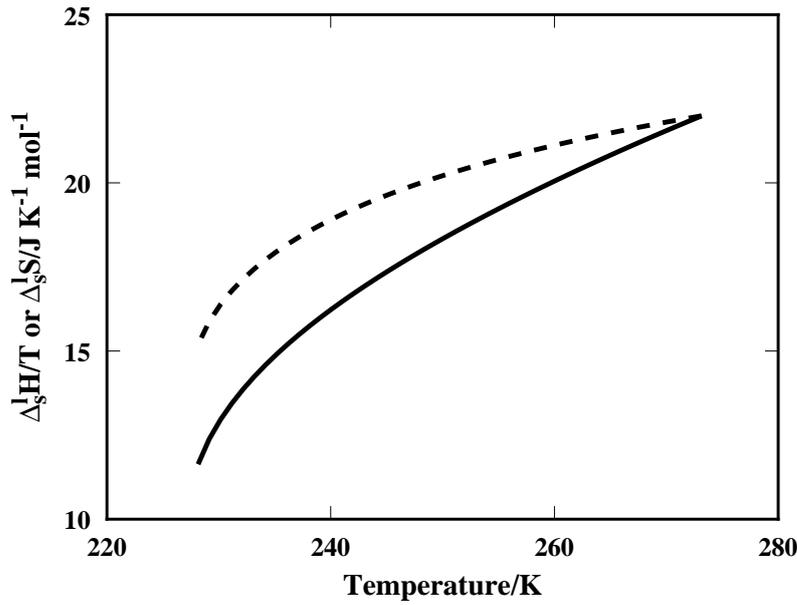


Fig. 5 Comparison of $\Delta_s^1 S_{\text{H}_2\text{O}}^*$ (solid line) and $\Delta_s^1 H_{\text{H}_2\text{O}}^*/T$ (dashed line).

and others (1977) has been applied successfully to calculate the effect of a dissolved electrolyte on the capillary pressures of frozen kaolinite pastes (Grant and others 1999). Most other approaches to calculating capillary pressure in frozen porous media rely on the enthalpy differences between the ice and water phases, that is they assumed implicitly that the enthalpy of fusion ($\Delta_s^1 H_{\text{m,H}_2\text{O}}^*$, J mol^{-1}) and entropy of fusion ($\Delta_s^1 S_{\text{m,H}_2\text{O}}^*$, $\text{J K}^{-1} \text{mol}^{-1}$) were related by: $\frac{\Delta_s^1 H_{\text{m,H}_2\text{O}}^*}{T} \equiv \Delta_s^1 S_{\text{m,H}_2\text{O}}^*$. This is true any substance only at its melting temperature, when the Gibbs energies of the two phases are equal. Fig. 5 shows the relative values of $\frac{\Delta_s^1 H_{\text{m,H}_2\text{O}}^*}{T}$ and $\Delta_s^1 S_{\text{m,H}_2\text{O}}^*$ as functions of temperature, showing that disparity between the two quantities becomes large at temperatures well below the melting temperature.

3.1 Approach of Brun and others (1977)

Building on previous earlier theoretical work, Brun and others (1977) developed a detailed thermodynamic analysis of capillary pressure in frozen porous media. Their relation is the most rigorously developed thus far and can be calculated precisely with thermophysical information available for supercooled water and ice. According to the derivation of Brun and others (1977), capillary pressure in a frozen porous medium is

$$p_c^{\text{sl}} \equiv \int_0^{p_c} dp_c^{\text{sl}}$$

Table 1 Coefficients to the empirical equation of Speedy (1987) with which the density and heat capacity of supercooled water can be calculated.

Parameter	value	parameter	value
C_ρ	-0.80	C_{C_p}	14.2
$B_\rho^{(0)}$	1.8021803	$B_{C_p}^{(0)}$	25.952
$B_\rho^{(1)}$	-0.9416980	$B_{C_p}^{(1)}$	128.281
$B_\rho^{(2)}$	0.9055070	$B_{C_p}^{(2)}$	14.2
$B_\rho^{(3)}$	-0.80	$B_{C_p}^{(3)}$	-221.405
		$B_{C_p}^{(4)}$	-64.812

$$= \int_{T_{mp}}^T \frac{S_{m,H_2O(l)}^* - S_{m,H_2O(cr,l)}^*}{V_{m,H_2O(l)}^*} dT. \quad (15)$$

Eq. (15) can be evaluated explicitly from 273 to 227 K with formulae describing the heat capacities of ice and supercooled water and the density of supercooled water. Speedy (1987) presented formulae by which the describe well the heat capacity ($C_{p,H_2O(l)}^*$, $J K^{-1} mol^{-1}$) and density ρ ($g cm^{-3}$) of supercooled water:

$$C_{p,H_2O(l)}^* = \sum_{n=0}^4 B_{C_p}^{(n)} \epsilon^n + 2C_{C_p} \epsilon^{-1/2} \quad (16)$$

and

$$\rho = \rho_s \exp \left(-T_s \left\{ \sum_{n=0}^4 \frac{1}{n+1} B_\rho^{(n)} \epsilon^{n+1} + 2C_\rho \epsilon^{1/2} \right\} \right) \quad (17)$$

where $T_s = 227.15$ K, $\epsilon = \frac{T-T_s}{T_s}$, ρ_s is a reference density $1.0 g cm^{-3}$ and $B_{C_p}^{(n)}$, C_{C_p} , $B_\rho^{(n)}$, C_ρ are empirical parameters, the values of which are presented in Table 1. Molar volume can be calculated from density by

$$V_{m,H_2O(cr,l)}^* = \frac{1000}{\rho M_{H_2O}} \quad (18)$$

where M_{H_2O} is the molecular weight of water ($kg mol^{-1}$). As with many solids, the heat capacity of ice can be described with the Maier-Kelly equation:

$$C_{p,H_2O(cr,l)}^* = \kappa + \nu T + \frac{\xi}{T^2}. \quad (19)$$

We fitted by non-linear regression (Marquardt procedure) the values of $C_{p,H_2O(cr,l)}^*$ between $T = 198.57$ K and 268.39 K reported by Haida and others (1974) to Eq. (19). The regression had a coefficient of determination (R^2) of 0.999997. The following parameter estimates (with parameter-estimate standard errors in parentheses) were obtained:

$$\begin{aligned} \kappa &= -10.6644 (1.5999) J K^{-1} mol^{-1} \\ \nu &= 0.1698 (0.0046) J K^{-2} mol^{-1} \\ \xi &= 198\ 148. (28\ 230.) J K mol^{-1}. \end{aligned}$$

The entropy of ice can be calculated via:

$$\begin{aligned}
S_{m,\text{H}_2\text{O}(\text{cr,I})}^*(T) &= S_{m,\text{H}_2\text{O}(\text{cr,I})}^*(T_{\text{mp}}) + \int_{T_{\text{mp}}}^T \frac{C_{p,\text{H}_2\text{O}(\text{cr,I})}^*}{T} dT \\
&= S_{m,\text{H}_2\text{O}(\text{cr,I})}^*(T_{\text{mp}}) + j [\ln(T) - \ln(T_{\text{mp}})] \\
&\quad + k(T - bT_{\text{mp}}) + \frac{\ell}{2(T_{\text{mp}}^2 - T^2)}. \tag{20}
\end{aligned}$$

The entropy of supercooled water can be calculated similarly:

$$\begin{aligned}
S_{m,\text{H}_2\text{O}(\text{l})}^*(T) &= \\
\int_{T_{\text{mp}}}^T \frac{C_{p,\text{H}_2\text{O}(\text{l})}^*}{T} dT &= \\
&\quad \frac{B_{C_p}^{(4)} (T^4 - T_{\text{mp}}^4)}{4 T_s^4} \\
&\quad + \frac{(B_{C_p}^{(3)} - 4 B_{C_p}^{(4)}) (T^3 - T_{\text{mp}}^3)}{3 T_s^3} \\
&\quad + \frac{(B_{C_p}^{(2)} - 3 B_{C_p}^{(3)} + 6 B_{C_p}^{(4)}) (T^2 - T_{\text{mp}}^2)}{2 T_s^2} \\
&\quad + \frac{(B_{C_p}^{(1)} - 2 B_{C_p}^{(2)} + 3 B_{C_p}^{(3)} - 4 B_{C_p}^{(4)}) (T - T_{\text{mp}})}{T_s} \\
&\quad + 2 C_{C_p} \arctan\left(\sqrt{\frac{T}{T_s}} - 1\right) \\
&\quad - 2 C_{C_p} \arctan\left(\sqrt{\frac{T_{\text{mp}}}{T_s}} - 1\right) \\
&\quad + (B_{C_p}^{(0)} - B_{C_p}^{(1)} + B_{C_p}^{(2)} - B_{C_p}^{(3)} + B_{C_p}^{(4)}) \times \\
&\quad [\ln(T) - \ln(T_{\text{mp}})] \tag{21}
\end{aligned}$$

The calculated capillary pressure as a function of temperature is presented in Fig. 6. We found that the relation is generally linear and can be approximated well by

$$p_c^{\text{sl}} = q[s_0 + s_1(T/T_{\text{mp}}) + s_2(T/T_{\text{mp}})^2 + s_3(T/T_{\text{mp}})^3] \tag{22}$$

where $s_0 = -46.485355$, $s_1 = 163.833545$, $s_2 = -171.794177$, $s_3 = 54.447607$, $q = 200$ bar, and $T_{\text{t}} = 273.15$ K.

3.2 Approach of Koopmans and Miller (1966)

Among the several approaches to approximating Eq. (15) are those by Koopmans and Miller (1966) and Spaans and Baker (1996). Koopmans and Miller (1966) considered capillary pressure over a very limited range of temperature. Accordingly,

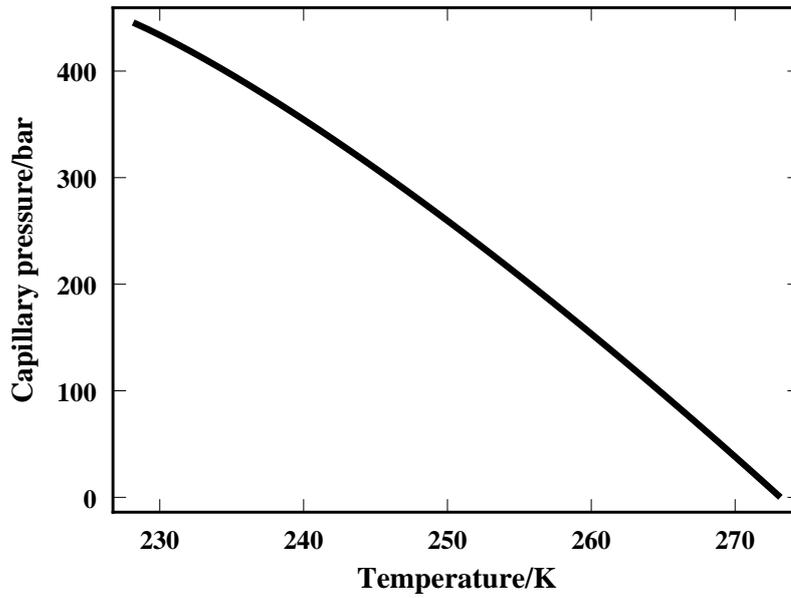


Fig. 6 Capillary pressure as a function of temperature as calculated by the approach of Brun and others (1977).

they derived

$$p_c^{sl} = -\frac{\Delta_s^1 H_{m,H_2O}^*(T_{mp})}{T_{mp} V_{m,H_2O(cr,I)}^*} (T - T_{mp}). \quad (23)$$

In this case, capillary pressure is referenced to the ice phase, so that the molar volume of ice ($V_{m,H_2O(cr,I)}^*$, $\text{m}^3 \text{mol}^{-1}$) is in the denominator. Additionally, no allowance for the decrease in enthalpy of fusion with temperature was made.

3.3 Spaans and Baker (1996)

Spaans and Baker (1996) chose to express capillary pressure as matric potential in units of specific energy (J mol^{-1}):

$$d(\Delta\mu_{\text{soil}} - \Delta\mu_{H_2O(cr,I)}) = \frac{\Delta_s^1 H_{m,H_2O}^*}{T} d(T) \quad (24)$$

where

$$\Delta_s^1 H_{m,H_2O}^* = \sigma + \tau T + \phi T^2 \quad (25)$$

where $\sigma = -12.8337 \text{ J mol}^{-1}$, $\tau = 0.09989 \text{ J mol}^{-1} \text{ K}^{-1}$, $\phi = -1.13146 \times 10^{-4} \text{ J mol}^{-1} \text{ K}^{-2}$.

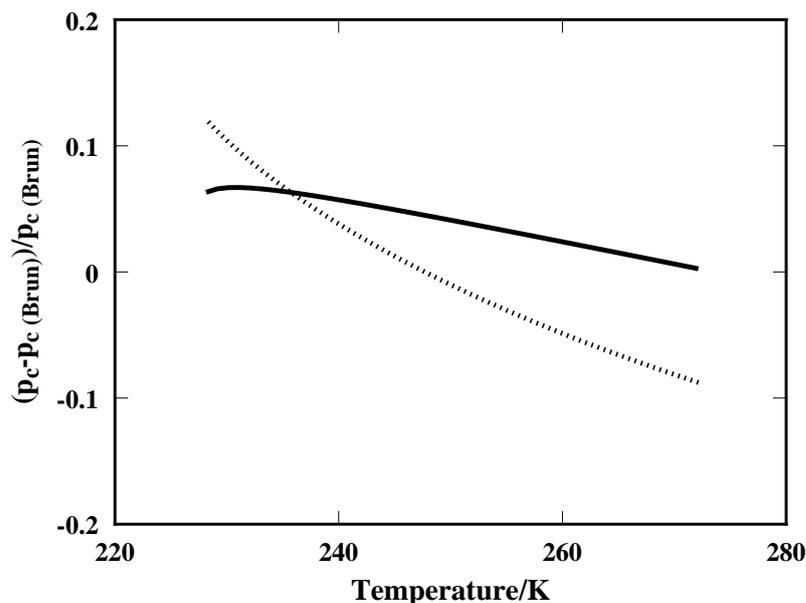


Fig. 7 Relative differences between p_c^{s1} as calculated via the approach of Koopmans and Miller (1966) (dashed line) and Spaans and Baker (1996) (solid line) to that of Brun and others (1977).

3.4 Comparison of the approaches

Fig. 7 presents the relative differences between the approaches of Koopmans and Miller (1966) and Spaans and Baker (1996) with that of Brun and others (1977). The relative difference of the Koopmans and Miller (1966) approach is the larger of the two—approximately 10 % at 273 and 230 K. The relative difference of the Spaans and Baker (1996) estimate is smaller but tracks the Gibbs energy of fusion for supercooled water.

4 Capillary pressure and chemical potential of soil water in ice-free unsaturated soils

Capillary pressure in an ice-free unsaturated soil can be related to the chemical potential of the soil water, relative to pure bulk water at the same temperature and under a saturated vapor pressure, $\Delta\mu_{\text{soil}}$ (J mol^{-1}) by (Taylor and Ashcroft 1972):

$$\Delta\mu_{\text{soil}} = -p_c^{1g} V_{m, \text{H}_2\text{O}(l)}^* \quad (26)$$

where $V_{m, \text{H}_2\text{O}(l)}^*$ is the molar volume of pure liquid water ($\text{m}^3 \text{mol}^{-1}$).

The corresponding vapor pressure of water at equilibrium with the soil water (p_{soil}) relative to the vapor pressure of water (p^{1+g}) is

$$p_{\text{soil}}/p^{1+g} = \exp[\Delta\mu_{\text{soil}}/(RT)] \quad (27)$$

where R is the gas constant ($\text{J K}^{-1} \text{mol}^{-1}$) and T is temperature (K). It is useful to refer to the sublimation pressure of ice and Gibbs energy of fusion for supercooled water to calculate the vapor pressure in ice-free soils below the melting temperature. The ratio of the vapor pressure of supercooled water to the sublimation pressure of ice (p^{s+g} , Pa) is related to the molar Gibbs energy of fusion ($\Delta_s^1\mu$, J mol^{-1}) by

$$p^{1+g}/p^{s+g} = \exp[\Delta_s^1\mu/(RT)]. \quad (28)$$

While not an equilibrium quantity, the molar Gibbs energy of fusion for supercooled water can be estimated from the heat capacities of ice and supercooled water below the melting point. Their values as functions of temperature have been measured precisely (Haida and others 1974, Speedy 1987). We found that the molar Gibbs energy of fusion for supercooled water could be well described by the function:

$$\Delta_s^1\mu = b[a_0 + a_1(T/T_{\text{mp}}) + a_2(T/T_{\text{mp}})^2 + a_3(T/T_{\text{mp}})^3] \quad (29)$$

where $a_0 = -33.689$, $a_1 = 122.232$, $a_2 = -128.55$, $a_3 = 40.0314$, $b = 400 \text{ J mol}^{-1}$, and $T_{\text{mp}} = 273.15 \text{ K}$. The ratio of vapor pressure of soil water to that of ice is therefore

$$p_{\text{soil}}/p^{s+g} = \exp[(\Delta\mu_{\text{soil}} + \Delta_s^1\mu)/(RT)], \quad (30)$$

in which the sublimation pressure of ice can be calculated via

$$\ln(p^{s+g}/p_t) = f_1[1 - (T/T_t)^{1.5}] + f_2[1 - (T/T_t)^{-1.25}] \quad (31)$$

where p_t ($= 611.657 \text{ Pa}$) and T_t ($= 273.16 \text{ K}$) are the triple-point pressure and triple-point temperature of water and f_1 ($= -13.9281690$) and f_2 ($= 34.7078238$) are fitted parameters (Wagner and others 1994).

5 Concluding remarks

Additional relevant thermophysical data and theoretical work have become available since the seminal papers on the thermodynamics of frozen ground appeared. While these new contributions do not alter the fundamental understanding of capillary pressure in frozen and ice-free soils, they do allow its calculation with greater precision.

The effect of temperature on interfacial properties has profound effects on the hydraulic properties of unsaturated, unfrozen soils. It is likely that these effects are even more pronounced in ice-free soils below the melting point since water transfers in the soils are dominated by diffusional flows of water vapor. The effect of temperature on interfacial properties in frozen soils, though not considered before, appears to be minimal.

Acknowledgements This work was supported by, the U.S. Army Engineer Research and Development Center, work unit 61102/AT24/129/EE005, Chemistry of Frozen Ground and the National Science Foundation project, Assessing the Risk and Dispersion Rate of Ionic Contaminants in Permafrost Terrain (OPP-99-79685).

References

1. Brun M, Lallemand A, Quinson J-F, and Eyraud C (1977) A new method for the simultaneous determination of the size and shape of pores, the thermoporometry. *Thermochim Acta* 21 : 59-88.
2. Campbell GS and Shiozawa S (1992) Prediction of hydraulic properties of soils using particle size distribution and bulk density data. pp. 317-328 in van Genuchten MTh, Leij F, and Lund LJ eds. *International workshop on indirect methods for estimating the hydraulic properties of unsaturated soils*, University of California Press, Riverside.
3. Clifford SM, and Hillel D (1983) *J Geophys Res* 88 : 2456-2474
4. de Jong E and Kachanoski RG (1988) Drying of frozen soils. *Can J Soil Sci* 68 : 807-811
5. Grant SA, Boitnott GE, and Tice AR, Effect of dissolved NaCl on freezing curves of kaolinite, montmorillonite, and sand pastes. *CRREL Special Report 99-2 Cold Regions Research and Engineering Laboratory*, Hanover NH USA
6. Haida O, Matsuo T, Suga H, and Seki S (1974) Calorimetric study of the glassy state, 10, Enthalpy relaxation at the glass transition temperature of hexagonal ice. *J Chem Thermodynamics* 6 : 815-825
7. Huang J. and Bartell LS (1995) Kinetics of homogeneous nucleation in the freezing of large water. *J Phys Chem* 99 : 3941-3931
8. Kinoshita S and Ishizaki T (1980) Freezing point depression in moist soil. pp. 640-646, in *2nd International Symposium on Ground Freezing*, Norwegian Institute of Technology, Trondheim, Norway
9. Komarov IA (1983) A theory of desiccation of unconsolidated rocks in areas with negative temperatures. pp. 236-241 *Permafrost*, 4th international conference. National Academy of Sciences, Washington DC
10. Koopmans RWR and Miller RD (1966) Soil freezing and soil water characteristic curves. *Soil Sci Soc Am Proc* 30 : 680-685
11. McKay CP, Mellon MT, and Friedmann EI (1998) Soil temperatures and stability of ice-cemented ground in the McMurdo dry valleys. *Antarctic Sci* 10 : 31-38
12. Osterkamp TE and Romanovsky VE (1997) Freezing of the active layer on the coastal plain in the Alaskan Arctic. *Permafrost Periglacial Proc* 8 : 23-44
13. Romanovsky VE and Osterkamp TE (2000) Effects of unfrozen water on heat and mass transport processes in the active layer and permafrost. *Permafrost Periglacial Proc* 11 : 219-239
14. Rossi C and Nimmo JR (1994) Modeling of soil water retention from saturation to oven dryness. *Water Resour Res* 30 : 701-708
15. Shvetsov PF, Grechishev SYe, and Chistotinov LV (1978) Basic laws of cryogenic processes in silt-clay and sandy formations. pp. 254-261 Sanger FJ ed *Permafrost*, 2nd international conference, USSR contribution. National Academy of Sciences, Washington DC
16. Spaans EJ and Baker JM (1996) The soil freezing characteristic, Its measurement and similarity to the soil moisture characteristic. *Soil Sci Soc Am J* 60 : 13-19
17. Speedy RJ (1987) Thermodynamic properties of supercooled water at 1 atm *J Phys Chem* 91 : 3354-3358
18. Taylor SA and Ashcroft GL (1972) *Physical edaphology*. Freeman, San Francisco, pg. 163
19. Wagner W, Saul A, and Pruß A (1994) International equations for the pressure along the melting and along the sublimation curve of ordinary water substance. *J Phys Chem Ref Data* 23 : 515-524
20. Wood GR and Walton AG (1970) Homogeneous nucleation kinetics of ice from water. *J Appl Phys* 41 : 3027-3036