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Crossover Equation and the Vapor Pressure of Supercooled Water

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Abstract Recently, Fuentevilla and Anisimov have published a scaled parametric equation of state that is universal in terms of theoretical variables and belongs to the three-dimensional Ising-model class of universality. The equation can be used for description and prediction of properties of supercooled water. The main advantage of the scaled equation mentioned above is the possibility to predict some properties of supercooled water below the limit of homogenous nucleation, where it is very difficult to obtain experimental data. This equation has been used to predict the behavior of the isobaric heat capacity in the range 150 K to 233 K, and from a knowledge of the isobaric heat capacity, calculations of the vapor pressure in the range from 123 K to 273 K have been carried out.

Keywords Clausius–Clapeyron equation · Heat capacity · Scaled equation · Supercooled water · Vapor pressure

1 Introduction

Vapor–pressure equations are often used in atmospheric applications. Also properties of water at temperatures below the triple point are needed for calculating the saturation pressure in clouds, because clouds are often composed of deeply supercooled water. There are many equations used in meteorology that describe the saturation pressure of H_2O also below the triple point. Most of them are based on the Clapeyron equation, because experimental data are not of high quality. Measurements are restricted to

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temperatures above approximately 233 K, which is the limit of homogenous nucleation. But meteorologists are interested in the vapor pressure of water at temperatures down to 160 K. Minimum temperatures in the Antarctic winter stratosphere could be below 175 K [1]. How does one predict vapor pressures of supercooled water below the limit of homogenous nucleation?

Murphy and Koop [1] carried out an evaluation of many vapor–pressure equations. They used the knowledge of the isobaric heat capacity, c_p, above 233 K (where experimental data exist) and the asymptotic behavior of c_p at the temperature limit of amorphous ice (130 K to 150 K) to develop an equation for the vapor pressure of supercooled liquid water. They made detailed comparisons of the new equation with other vapor–pressure equations and with existing experimental data. The crucial area is the range of temperatures between 150 K and 232 K, referred to as a "no-man's land" where experimental data are missing.

The general approach to the "no-man's land" area is based on an extrapolation of thermophysical properties. Experimental data are known in the region above 233 K [2–4], and experimental data on amorphous ice can be used to constrain the thermodynamic functions at ∼155 K [5,6]. The problem is that some properties (isobaric heat capacity, thermal expansivity, isothermal compressibility) change dramatically [7] (but we suppose continuously) in the vicinity of the Widom line, the line of maxima of the order-parameter fluctuations [8], when the water is cooled isobarically at ambient pressure. A new idea is needed to solve the difficult task of extrapolation.

There are three theories to explain the properties of water in this temperature range: the theory of the spinodal curve, the theory of a second critical point, and a singularity-free hypothesis [9]. Recent molecular simulations and some experiments support the theory of a second critical point, a critical point of liquid–liquid phase transition. Water exhibits a well-known (first) critical point near 647 K and 22 MPa. The predicted second critical point in supercooled water describes the pressure and temperature where two distinct liquid phases—the low-density liquid and high-density liquid—become identical. If there is a second critical point, it is possible to describe the thermodynamic properties near the critical point with a scaled parametric equation, which can explain the divergent behavior of many thermodynamic properties.

Fuentevilla and Anisimov [8] proposed a scaled equation based on only a few adjustable parameters. To obtain values far from the critical point, it is necessary to use some "background" functions. The description of some properties far from the critical point consists of two parts. The first part describes the critical behavior, and the second is a background function which balances the values far from the critical point. It is possible to use the scientific IAPWS-95 formulation [10] and existing experimental data to find the background functions at ambient pressure and then to calculate some thermodynamic properties from the scaled equation [11].

There is a very accurate equation for the vapor pressure of water, namely, the Wagner and Pruss equation [12]:

$$\ln(p) = \ln(p_\mathrm{c}) + \left(\frac{T_\mathrm{c}}{T}\right) \times \Big(-7.85951783\tau + 1.84408259\tau^{1.5} - 11.7866497\tau^{3} + 22.6807411\tau^{3.5} - 15.9618719\tau^{4} + 1.80122502\tau^{7.5}\Big), \quad (1)$$

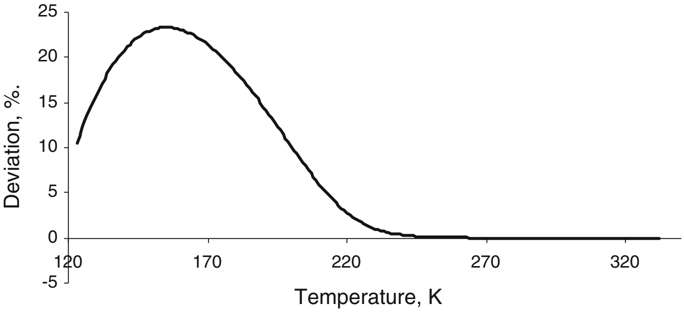

Fig. 1 Comparison of Eqs. 2 and 1 for the saturation pressure of water vapor over liquid water; Deviation $= \frac{p_{\text{Wagner,Pruss}} - p_{\text{Murphy,Koop}}}{p_{\text{Murphy,Koop}}} \times 100$

$p_c = 2.2064 \times 10^7$ Pa, $\tau = 1 - \frac{T}{T_c}$, $T_c = 647.096$ K, with p in Pa. This equation is declared to be valid in the range $273.16\,\text{K} \leq T \leq 647\,\text{K}$.

Murphy and Koop [1] have derived

$$\ln(p) = 54.842763 - \frac{6763.22}{T} - 4.210\ln(T) + 0.000367T + \tanh$$
$$\{0.0415(T - 218.8)\} \times \left(53.878 - \frac{1331.22}{T} - 9.44523\ln(T) + 0.014025T\right), \tag{2}$$

with p in Pa. Equation 2 is valid in the temperature interval $123\,\text{K} < T < 332$ K.

If the Wagner and Pruss equation is extrapolated down to the temperature 123 K, it is possible to calculate the differences between Eqs. 2 and 1. The pressure deviations are shown in Fig. 1.

The Wagner and Pruss equation can be extrapolated below the triple point (to temperatures near 233 K). In this region, experimental data exist [2,4].

2 Clausius–Clapeyron Equation

The Clausius–Clapeyron equation can be used to calculate vapor pressures for temperatures below the triple point, and a knowledge of $c_{p,\text{liq}}$ is useful for this purpose.

The Clausius–Clapeyron equation extrapolated to the ideal-gas limit can be written as

$$\frac{\mathrm{d}\ln(p)}{\mathrm{d}T} = \frac{L_{\text{liq}}(T)}{RT^2}, \tag{3}$$

where $L_{\text{liq}}(T)$ is the enthalpy of vaporization as a function of temperature and $R = 8.314472\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ is the molar gas constant. A starting point is needed for the integration of Eq. 3. The integration can start at the triple-point (pressure $p_t = (611.657 \pm 0.01)$ Pa, temperature $T_t = 273.16$ K).

It is necessary to know the temperature dependence of $L_{\text{liq}}(T)$ to integrate Eq. 3. An equation for $L_{\text{liq}}(T)$ was published in [13];

$$L_{\text{liq}}(T) = L_{\text{liq,t}} + \int_{T_t}^{T} \Delta c_p(T')\mathrm{d}T' + \int_{T_t}^{T} \frac{\mathrm{d}p}{\mathrm{d}T'}\left[(v_{\text{vap}} - v_{\text{liq}}) - T'\left(\frac{\partial\left(v_{\text{vap}} - v_{\text{liq}}\right)}{\partial T'}\right)_p\right]\mathrm{d}T', \tag{4}$$

where $L_{\text{liq,t}}$ is the enthalpy of vaporization at the triple-point temperature T_t, Δc_p, is the difference in isobaric molar heat capacities $\left(\Delta c_p = c_{p,\text{liq}} - c_{\text{p,vap}}\right)$, and v_{vap} and v_{liq} are the molar volumes of the vapor and liquid, respectively. The second integral is very small compared to the first. For example, if $v_{\text{vap}} \gg v_{\text{liq}}$ and the behavior of the vapor is approximated by an ideal-gas equation, the second integral is zero. The enthalpy of vaporization at the triple point is $L_{\text{liq,t}} = 45054.7\,\text{J}\cdot\text{mol}^{-1}$ [10] (IAPWS-95). Equation 4 can be written as

$$L_{\text{liq}}(T) = 45054.7 + \int_{T_t}^{T} \Delta c_p(T')\mathrm{d}T'. \tag{5}$$

From [1], one can obtain a relation for $c_{p,\text{vap}}$ (in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$):

$$c_{p,\text{vap}} = 33.2618 + 0.00187T - 0.06165T\exp(-(T/129.85)^2) + 0.06163T\exp(-(T/125.1)^2). \tag{6}$$

Therefore, it is necessary to know only $c_{p,\text{liq}}$ at atmospheric pressure to be able to calculate $L_{\text{liq}}(T)$. It is assumed that at temperatures near 155 K, the heat capacity of the liquid is close to the heat capacity of ice [1,5], namely, $c_{p,\text{liq}}$ is equal to $c_{p,\text{ice}}$ of hexagonal ice plus $2\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Murphy and Koop [1] obtained the equation for $c_{p,\text{ice}}$ (in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$):

$$c_{p,\text{ice}} = -2.0572 + 0.14644T + 0.06163T\exp\left(-(T/125.1)^2\right). \tag{7}$$

It is therefore possible to write in the temperature range between 123 K and 167 K (in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$):

$$c_{p,\text{liq}} = -0.0572 + 0.14644T + 0.06163T\exp(-(T/125.1)^2). \tag{8}$$

One can obtain from Eqs. 6 and 8:

$$\Delta c_p = -33.319 + 0.14457T + 0.06165T\exp(-(T/129.86)^2). \tag{9}$$

There are several ways to get $c_{p,\text{liq}}$ for temperatures between 236 K and 273 K. The data for $c_{p,\text{liq}}$ from [4,14] are used in this temperature interval.

3 Scaled Equation

In the vicinity of the critical point, Ψ_{cr}, the critical part of the Gibbs thermodynamic potential, Ψ is the universal function of two scaling fields, h_1 and h_2 [15,16]:

$$\Psi_{\mathrm{cr}} \cong h_2^{2-\alpha} f\left(\frac{h_1}{h_2^{\beta+\gamma}}\right), \tag{10}$$

where $\alpha = 0.109$, $\beta = 0.326$, and $\gamma = 1.239$ are universal exponents (with relation $\alpha + 2\beta + \gamma = 2$). The first derivatives of the thermodynamic potential define two scaling densities:

$$\Phi_1 = -\frac{\partial \Psi_{\mathrm{cr}}}{\partial h_1}, \tag{11}$$

$$\Phi_2 = -\frac{\partial \Psi_{\mathrm{cr}}}{\partial h_2}. \tag{12}$$

The second derivatives define three scaling susceptibilities:

$$\chi_1 = \left(\frac{\partial \Phi_1}{\partial h_1}\right)_{h_2}, \tag{13}$$

$$\chi_2 = \left(\frac{\partial \Phi_2}{\partial h_2}\right)_{h_1}, \tag{14}$$

$$\chi_{12} = \left(\frac{\partial \Phi_1}{\partial h_2}\right)_{h_1} = \left(\frac{\partial \Phi_2}{\partial h_1}\right)_{h_2}. \tag{15}$$

In the mean-field approximation ($\alpha = 0, \beta = 0.5, \gamma = 1$), it is possible to write the thermodynamic potential in a Landau expansion,

$$\Psi_{\mathrm{cr}} = \frac{1}{2} a_0 h_2 \Phi_1^2 + \frac{1}{4} u_0 \Phi_1^4 - h_1 \Phi_1 \tag{16}$$

with system-dependent coefficients a_0 and u_0. If one assumes [8]

$$h_1 = a_1 \Delta \hat{P} + a_2 \Delta \hat{T} + a_3 \Delta \hat{P}^2, \tag{17}$$

and

$$h_2 = b_1 \Delta \hat{T} + b_2 \Delta \hat{P}, \tag{18}$$

where $\Delta\hat{P} = \frac{P-P_c}{\rho_c R T_c}$ and $\Delta\hat{T} = \frac{T-T_c}{T_c}$, subscript "c" indicates critical parameters, a_i and b_i are system-dependent coefficients, and (in the linear approximation [8]),

$$\Phi_1 = \frac{b_1 \Delta\hat{V} + b_2 \Delta\hat{S}}{a_2 b_2 - (a_1)_{\text{eff}} b_1}, \tag{19}$$

$$\Phi_2 = \frac{a_2 \Delta\hat{V} + (a_1)_{\text{eff}} \Delta\hat{S}}{(a_1)_{\text{eff}} b_1 - a_2 b_2}, \tag{20}$$

where $\Delta\hat{S} = \frac{S-S_c}{R}$, $\Delta\hat{V} = \frac{V-V_c}{V_c}$, and $(a_1)_{\text{eff}} = \left(\frac{\partial h_1}{\partial \hat{P}}\right)_{\hat{T}} = a_1 + 2a_3\Delta\hat{P}$. It is then possible to calculate thermodynamic properties:

$$\Delta\hat{V} = -(a_1)_{\text{eff}}\,\Phi_1 - b_2\Phi_2, \tag{21}$$

$$\Delta\hat{S} = a_2\Phi_1 + b_1\Phi_2 \tag{22}$$

and

$$\left(\hat{C}_P\right)_{\text{cr}} = \hat{T}\left(\frac{\partial\hat{S}}{\partial\hat{T}}\right)_{\hat{P}} - \left(\hat{C}_P\right)_{\text{b}} = \hat{T}\left(a_2^2\chi_1 + 2a_2 b_1\chi_{12} + b_1^2\chi_2\right), \tag{23}$$

where $\hat{T} = \frac{T}{T_c}$, $\hat{P} = \frac{P}{\rho_c R T_c}$, $\hat{S} = \frac{S}{S_c}$, $\hat{V} = \frac{V}{V_c}$, and the subscript "b" indicates background property.

Fuentevilla and Anisimov [8] presented the following constants obtained from a fit to the existing experimental values:

$P_c = 27\,\text{MPa}, T_c = 232\,\text{K}$
$u_0 = 2.2634676$
$a_0 = 1$
$a_1 = 0.0078$
$a_2 = 1$
$a_3 = 0.062$
$b_1 = 0.0078$
$b_2 = -1$

4 Isobaric Heat Capacity

From Eq. 23 (c_p in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$),

$$c_p = c_{p\text{cr}} + c_{p\text{b}} = R\frac{T}{T_c}\left(a_2^2\chi_1 + 2a_2 b_1\chi_{12} + b_1^2\chi_2\right) + c_{p\text{b}}. \tag{24}$$

We have used the following steps to obtain the background function $c_{p\text{b}}$:

(A) It is assumed in the region of temperatures between 123 K and 167 K, that c_p is equal to $c_{p,\mathrm{ice}}$ of hexagonal ice plus $2\,\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. We use Eq. 8.
(B) Patek et al. [14] developed equations for the properties of water at ambient pressure for temperatures between 253 K and 383 K. The properties are based on IAPWS-95 (within tolerances). We use c_p from this study in this temperature interval.
(C) The data of Archer and Carter [4] are used for temperatures between 236 K and 250 K.
(D) The critical part of c_p is calculated from Eq. 24 for all temperature intervals.
(E) The critical part is subtracted from values obtained in steps (A)–(C). As a result, the $c_{p\mathrm{b}}$ values are obtained in the temperature intervals. It is possible to fit the values with some analytical function—the least-squares method was used.
(F) The background $c_{p\mathrm{b}}$ is fitted with some analytical functions, and we suppose that the background function is valid in the entire temperature interval between 130 K and 383 K. One can calculate the critical part of Eq. 24 and obtain $c_p = c_{p\mathrm{cr}} + c_{p\mathrm{b}}$.

Changing the value of coefficient a_2 from 1 to 1.25 [17] was suggested to eliminate the undesirable behavior of the background function.

For the background function $c_{p\mathrm{b}}$ ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$), the behavior is displayed in Fig. 2,

$$\begin{aligned} c_{p\mathrm{b}} &= 6725.474 + 6462.0717\tau - 552.53268\mathrm{e}^{-(\tau)3} \\ &\quad + 88.473461\mathrm{e}^{-(4-\tau)^4} - 12454.046\tau^{1/2} - 500.781\tau^2, \end{aligned} \tag{25}$$

where $\tau = \frac{T}{100}$. The values of c_p together with the background function are shown in Fig. 3.

We can use the Murphy and Koop equation to get values of c_p. From Eqs. 3 and 5, it is possible to express

$$c_{p,\mathrm{liq}} = c_{p,\mathrm{vap}} - \frac{\mathrm{d}}{\mathrm{d}T}\left(RT^2 \frac{\mathrm{d}\ln p}{\mathrm{d}T}\right). \tag{26}$$

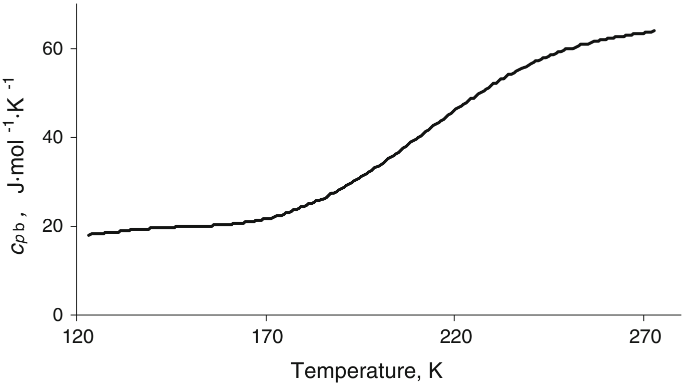

Fig. 2 Background function $c_{p\mathrm{b}}$ (Eq. 25) with $a_2 = 1.25$

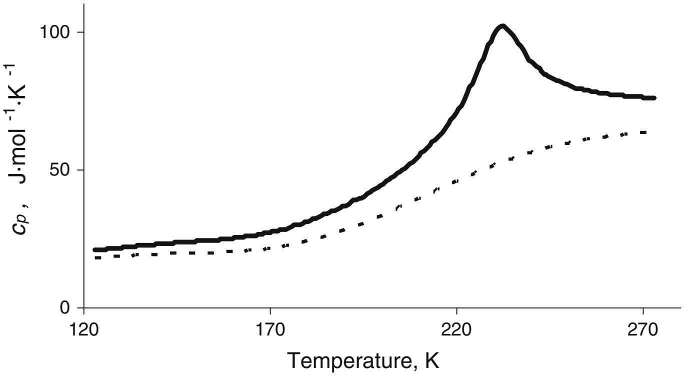

Fig. 3 Isobaric heat capacity calculated with Eq. 24 in the interval 123 K to 273 K (*solid line*) and the background function from Eq. 25 (*dashed line*)

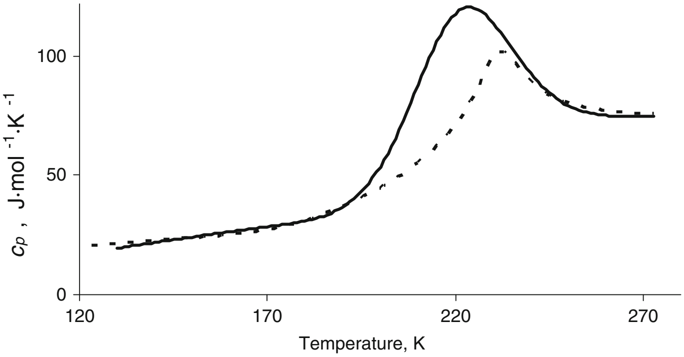

Fig. 4 Isobaric heat capacity in the interval 123 K to 273 K (the *dashed line* for c_p calculated from the scaled equation Eq. 24 and the *solid line* for calculated values from Eq. 26)

From Eqs. 2 and 26, one can calculate the values of c_p and compare them. The comparison is displayed in Fig. 4.

We can see differences in extrapolation into the "no-man's land" region between c_p from Eq. 26 and values gained by using the scaled equation. We believe that our extrapolation gives more accurate results, because only the background function is extrapolated while the critical part of c_p is given by a scaled equation.

5 Calculation of Vapor Pressure

The values of $c_{p,\text{liq}}$ and $c_{p,\text{vap}}$ can be substituted in Eq. 5 for a calculation of L_{liq}. A numerical integration has been performed. Obtained values are displayed in Fig. 5.

If the Clausius–Clapeyron equation is integrated (numerically), then the values for the vapor pressure are obtained. Comparison of the calculated values with Eqs. 1,2 is displayed in Fig. 6.

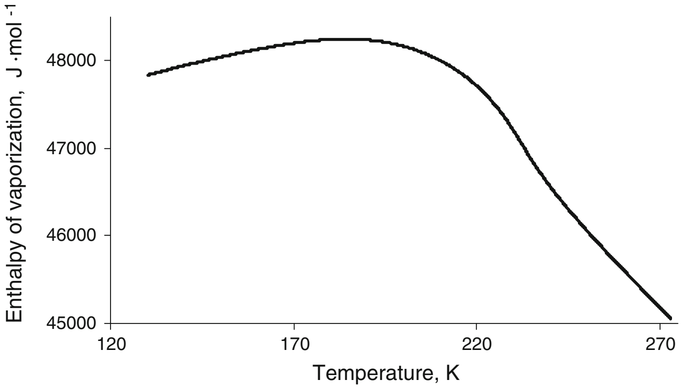

Fig. 5 Enthalpy of vaporization as a function of temperature–values obtained from numerical integration of Eq. 5

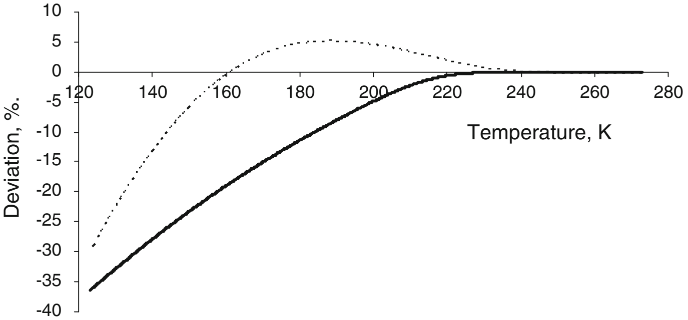

Fig. 6 Deviations of Eq. 2 (*dashed line*) and Eq. 1 (*solid line*) from Eq. 27; $Deviation = \frac{p-p_{\text{Eq.27}}}{p_{\text{Eq.27}}} \times 100$

We use the fact that the Wagner–Pruss equation describes the calculated vapor–pressure data very well in the region below the triple point to temperatures near −30 °C (Fig. 1). We added correction terms to the Wagner–Pruss equation. The terms are significant only in the region from 130 K to 250 K. The resulting equation is

$$\begin{aligned}\ln(p) = {} & \ln\left(2.2064\times10^{7}\right) + \left(\frac{T_c}{T}\right) \\ & \times \left(-7.85951783\tau + 1.84408259\tau^{1.5} - 11.7866497\tau^{3}\right. \\ & \left. + 22.6807411\tau^{3.5} - 15.9618719\tau^{4} + 1.80122502\tau^{7.5}\right) \\ & -0.05611e^{-\tau_2^4} - 14.2133\tau_1^{-8} + 46.174\tau_1^{-9} - 32.52\tau_1^{-10},\end{aligned} \tag{27}$$

where $\tau = 1 - \frac{T}{T_c}$, $T_c = 647.096\,\text{K}$, $\tau_1 = \frac{T}{100\,\text{K}}$, $\tau_2 = \frac{T-182\,\text{K}}{35\,\text{K}}$, with p in Pa.

6 Conclusion

In this article, we have constructed non-critical background functions for the isobaric heat capacity and have used this knowledge to calculate vapor–pressure data in the wide interval of temperatures from 123 K to 273.16 K. We have used the Murphy and Koop vapor pressure equation to calculate values of the isobaric heat capacity, and we have compared them with isobaric heat capacities calculated from the scaled equation. We believe that our extrapolation gives more accurate results, because only the background function is extrapolated. We have shown that the Wagner–Pruss equation can be used down to $-30\,^{\circ}\mathrm{C}$, and we have developed some additional terms to the equation to describe the behavior of the vapor pressure down to 123 K. Equation 27 describes the vapor pressure of water in the interval of temperatures from 123 K to 647 K.

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References

1. D.M. Murphy, T. Koop, Q.J.R. Meteorol. Soc. **131**, 1539 (2005)
2. C.A. Angell, M. Oguni, W.J. Sichina, J. Phys. Chem. **86**, 998 (1982)
3. E. Tombari, C. Ferrari, G. Salvetti, Chem. Phys. Lett. **300**, 749 (1999)
4. D.G. Archer, R.W. Carter, J. Phys. Chem. **104**, 8563 (2000)
5. F.W. Starr, C.A. Angell, H.E. Stanley, Physica A **323**, 51 (2003)
6. O. Mishima, H.E. Stanley, Nature **396**, 329 (1998)
7. L. Xu, P. Kumar, S.V. Buldyrev, S.-H. Chen, P.H. Poole, F. Sciortino, H.E. Stanley, Proc. Natl. Acad. Sci. USA **102**, 16558 (2005)
8. D.A. Fuentevilla, M.A. Anisimov, Phys. Rev. Lett. **97**, 195702 (2006)
9. P.G. Debenedetti, *Metastable Liquids. Concepts and Principles* (Princeton University Press, Princeton, NJ, 1996)
10. W. Wagner, A. Pruss, J. Phys. Chem. Ref. Data **31**, 387 (2002)
11. J. Kalova, R. Mares, Scaled equation of state for supercooled water—comparison with wxperimental sata and IAPWS-95, in *Proceedings of the 15th International Conference on the Properties of Water and Steam*, Berlin/Germany, 7–11 September 2008
12. W. Wagner, A. Pruss, J. Phys. Chem. Ref. Data **16**, 893 (1987)
13. H.R. Pruppacher, J.D. Klett, *Microphysics of Clouds and Precipitation*, 2nd edn. (Kluwer, Dordrecht, The Netherlands, 1997)
14. J. Patek, J. Hruby, J. Klomfar, M. Souckova, A.H. Harvey, J. Phys. Chem. Ref. Data **38**, 21 (2009)
15. M.E. Fisher, in *Critical Phenomena*, ed. by F.J.W. Hahne (Springer, Berlin, 1982), p. 186
16. D.A. Fuentevilla, A scaled parametric equation of state for the liquid-liquid critical point in supercooled water. Ph.D. Thesis, Department of Chemical and Biomolecular Engineering, University of Maryland, 2007
17. J. Kalova, R. Mares, Equations for the thermodynamic properties at the saturation line in the supercooled water region, in *Proceedings of the 15th International Conference on the Properties of Water and Steam*, Berlin/Germany, 7–11 September 2008