Clausius-Clapeyron equation and saturation vapour pressure: simple theory reconciled with practice

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Abstract. While the Clausius-Clapeyron equation is very important as it determines the saturation vapour pressure, in practice it is replaced by empirical, typically Magnus type, equations which are more accurate. It is shown that the reduced accuracy reflects an inconsistent assumption that the latent heat of vaporization is constant. Not only is this assumption unnecessary and excessive, but it is also contradictory to entropy maximization. Removing this assumption and using a pure entropy maximization framework we obtain a simple closed solution, which is both theoretically consistent and accurate. Our discussion and derivation are relevant to students and specialists in statistical thermophysics and in geophysical sciences, and our results are ready for practical application in physics as well as in such disciplines as hydrology, meteorology and climatology.

Keywords: entropy, maximum entropy, saturation vapour pressure, Clausius-Clapeyron equation, Magnus equation.

1. Introduction

The Clausius–Clapeyron relationship characterizes the transition between two phases of matter. The importance of this equation cannot be overemphasized and transcends thermodynamics and physics. As it determines the saturation vapour pressure for water, it provides the physical basis of the hydrological cycle and becomes a principal equation in hydrology, meteorology, climatology, and other geophysical sciences. Specifically, the saturation vapour pressure, also known as equilibrium vapour pressure, is an upper limit of the quantity of vapour that the atmosphere can contain. When this limit is reached, no additional liquid water is evaporated, while below the limit more water evaporates. This limit is expressed in terms of the partial pressure of the vapour. At standard temperature and pressure (STP) conditions, i.e. at a temperature of 273.15 K (0°C) the saturation vapour pressure is 6.11 hPa, i.e. 0.611% of the total pressure of 1000 hPa. The saturation vapour pressure increases at higher temperatures, e.g. at 25°C it is over five times higher. Conversely, when moist air ascends and its temperature decreases, so does the saturation vapour pressure. Vapour in excess of the lower saturation pressure starts to condense, giving rise to the formation of clouds.

The Clausius-Clapeyron equation derives from entropy maximization, which determines the equilibrium between two phases of a substance. Mathematically it is expressed as the relationship between temperature, T, and pressure, p, at the equilibrium. Usually it is expressed in differential form [e.g. 1, 2; see also below]. However, in addition to the differential form, most texts [e.g. 3, p. 98; 4, p. 180; 5, p. 612; 6, p. 300] as well as electronic sources, provide an analytical equation written as

$$p = \mathrm{CT}_1 \, \exp\left(-\frac{L}{RT}\right) \tag{1}$$

where CT_1 is an integration constant (generally, we use the symbol CT_i to denote integration constants), L is the latent heat of vaporization and R is the specific gas constant. This is supposed to be the integration of the differential form under the assumption that L is constant. However, as will be shown, this assumption is inconsistent with the entropy maximization framework and, as a result, (1) is not an integration of the Clausius-Clapeyron equation.

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Furthermore, due to the inconsistent assumption, (1) is not accurate enough as an approximation to be used in practice. Therefore, more accurate empirical relationships are more often used to determine the saturation vapour pressure. The so-called Magnus-type equations are the most typical in application and the most recent version [7] for temperature range -40° to 50°C is

$$p = 6.1094 \exp\left(\frac{17.625T}{243.04 + T}\right) \quad [T \text{ in } ^{\circ}\text{C}, p \text{ in hPa}] \tag{2}$$

A theoretically consistent closed solution exists [8, p. 203; see also below] and is not much more complex than (1), but it is rarely mentioned (e.g. none of the above referenced books contains it). Even when it is mentioned, it is still presented along with (1), which may again be characterized as the best known approximation to calculate the liquid–vapour equilibrium pressure [9].

Here we demonstrate the inconsistency inherent in the assumptions that are made to derive (1) and we derive a theoretically consistent closed solution, which is in line with the aforementioned existing consistent solution, removing incorrect assumptions. We also determine its numerical constants for the phase change of water, thus providing an expression ready for use in practice, and we show that numerically its error with respect to standard reference data is negligible, smaller than that of (2) and spectacularly smaller than that of (1). In all this, the underpinning logic is that the principle of maximum entropy, which is a variational principle, is economic in assumptions needed: Mathematically, there is no limit to the number of unknowns that can be determined in a maximization problem (as compared to one formulated in terms of equations, where the number of unknowns should equal the number of equations). Thus, we should be able to determine any unknown quantity without assumptions.

2. The inconsistency

It is well known [e.g. 1, p. 143] that in two systems at equilibrium, entropy maximization constrained with the conditions that the total energy, volume and number of particles are constant, results, respectively, in temperature, T, pressure, p, and chemical potential, μ, that are equal in the two systems. In particular, the last equality is

$$\mu_{\mathrm{G}} = \mu_{\mathrm{L}} \tag{3}$$

where the subscripts G and L denote the gaseous and liquid phase, respectively. Classical and statistical thermodynamics texts do not use (3) directly; rather, they derive, as a consequence of (4), and use the equality of differentials [e.g. 2. p. 71],

$$\mathrm{d}\mu_{\mathrm{G}} = \mathrm{d}\mu_{\mathrm{L}} \tag{4}$$

The entropies per unit mass s_{G} and s_{L} at the gaseous and liquid phase, respectively, are given as

$$s_{\mathrm{G}} = \mathrm{CT}_2 + c_p \ln T - R \ln p \tag{5}$$

$$s_{\mathrm{L}} = \mathrm{CT}_3 + c_{\mathrm{L}} \ln T \tag{6}$$

where c_p is the specific heat at constant pressure of the vapour and c_{L} is the specific heat of the liquid. The liquid was regarded as incompressible and, for this reason, in (6) the entropy does not depend on pressure. The differentials of the chemical potentials are given by Gibbs-Duhem equations [e.g. 2] as

$$\mathrm{d}\mu_{\mathrm{G}} = v_{\mathrm{G}}\,\mathrm{d}p - s_{\mathrm{G}}\,\mathrm{d}T \tag{7}$$

$$\mathrm{d}\mu_{\mathrm{L}} = -\, s_{\mathrm{L}}\,\mathrm{d}T \tag{8}$$

where again in (8) we neglected the specific volume v_{L} of the liquid phase. Combining (4), (7) and (8) we obtain

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s_{\mathrm{G}} - s_{\mathrm{L}}}{v_{G}} \tag{9}$$

If we express the entropy difference in terms of the latent heat as

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$$s_G - s_L = \frac{L}{T} \tag{10}$$

then we obtain the following typical form of the Clausius-Clapeyron equation,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{Tv_G} \tag{11}$$

Furthermore, using the ideal gas law, $pv_G = RT$, we obtain the expression

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{Lp}{RT^2} \tag{12}$$

whose integration assuming constant L results in (1).

In fact, however, assuming a constant L renders the above derivation unnecessary. Indeed, we can express the difference of entropies from (5) and (6) as

$$s_G - s_L = (CT_2 - CT_3) + (c_p - c_L)\ln T - R\ln p \tag{13}$$

Substituting into (10) and solving for p we readily obtain

$$p = CT_4 \exp\left(-\frac{L}{RT}\right)T^{(c_p - c_L)/R} \tag{14}$$

where $CT_4 := \exp[(CT_2 - CT_3)/R]$. Equations (1) and (14) describe the same relationship of p and T, and were derived by precisely the same assumptions. However they are clearly inconsistent, which implies that at least one of the assumptions made is excessive and incorrect.

3. Alternative derivation using classical thermodynamics

In this section we will remove the assumption for constant L. We express the difference of entropies in (13) as an unknown function $g(T, p) := s_G - s_L$ and we write (13) in differential form as

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$$(c_p - c_L)\frac{\mathrm{d}T}{T} - R\frac{\mathrm{d}p}{p} = \mathrm{d}g \tag{15}$$

Using the law of ideal gases to eliminate v_G from (9), we obtain

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{p}{RT}(s_G - s_L) = \frac{pg}{RT} \tag{16}$$

Solving (16) for $\mathrm{d}p/p$ and substituting it in (15) we obtain

$$(c_p - c_L)\frac{\mathrm{d}T}{T} - g\frac{\mathrm{d}T}{T} = \mathrm{d}g \tag{17}$$

which can be written as

$$(c_p - c_L)\,\mathrm{d}T = \mathrm{d}(Tg) \tag{18}$$

and can be readily solved to give

$$g = s_G - s_L = \frac{\alpha}{T} - (c_L - c_p) \tag{19}$$

where α is an integration constant. Comparing (19) with (10), we conclude that L appears to be a linear function of temperature, rather than a constant:

$$L = \alpha - (c_L - c_p)T \tag{20}$$

Now, substituting g from (19) to (16) we obtain

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{p}{RT}(c_p - c_L) + \frac{\alpha p}{RT^2} \tag{21}$$

This is readily solved to give

$$p = CT_5 \exp\left(-\frac{\alpha}{RT}\right) T^{(c_p - c_L)/R} \tag{22}$$

Comparing (21) with the earlier results, we observe that it is functionally equivalent with (14) (both include a multiplicative factor that is a power function of T) whereas (1) proves to have an inappropriate functional form.

To eliminate CT_5 from (22) we assume a known saturation vapour pressure p_0 at a specific temperature T_0. We can then write (22) as

$$p = p_0 \exp\left[\frac{\alpha}{RT_0}\left(1 - \frac{T_0}{T}\right)\right]\left(\frac{T_0}{T}\right)^{(c_L - c_p)/R} \tag{23}$$

which is our final closed solution of the Clausius-Clapeyron equation.

4. Alternative derivation in a statistical mechanical framework

In this section we derive the phase transition equation in a purely statistical mechanical framework totally avoiding the assumptions about the equality of chemical potentials and temperatures; rather we will derive them by entropy maximization. For this maximization we assume that our system contains a total of N particles, N_G of which in the gaseous phase and N_L in the liquid phase, so that

$$N_G + N_L = N \tag{24}$$

If S denotes the total extensive entropy, and S_G and S_L denote the extensive entropy in the gaseous and liquid phase, respectively, then,

$$S = S_G + S_L = N_G s^*_G + N_L s^*_L \tag{25}$$

where s^*_G and s^*_L denote entropies per particle. From generalized Sackur-Tetrode equations [e.g. 2] we have

$$s^*_G/k = CT_6 + (c_v/R) \ln (E_G/N_G) + \ln (V/N_G), \quad s^*_L/k = CT_7 + (c_L/R) \ln (E_L/N_L) \tag{26}$$

where again we neglected the volume per particle in the liquid phase, which is by several orders of magnitude smaller than that of the gaseous phase. In (26) k is Boltzmann's constant and c_v is the specific heat at constant volume of the vapour. We recall that $c_v = c_p - R$ and that the quantity $2c_v/R$ represents the degrees of freedom available to the molecular (thermal) motion. In addition, E_G and E_L in (26) are the thermal energies in the two phases. If E is the total energy, then conservation of energy demands

$$E_G + E_L + N_G \xi = E \tag{27}$$

where ξ is the amount of energy per molecule required to break the bonds between molecules of the liquid phase in order for the molecule to move to the gaseous phase, which we assume constant.

We wish to find the conditions which maximize the entropy S in (25) under constraints (24) and (27) with unknowns E_G, E_L, N_G, N_L. We form the function Ψ incorporating the total entropy S as well as the two constraints with Langrage multipliers κ and λ:

$$\Psi = (S_G + S_L)/k + \kappa (E_G + E_L + N_G \xi - E) + \lambda (N_G + N_L - N) \tag{28}$$

To maximize Ψ, we first take the derivatives with respect to E_G and E_L and equate them to 0 to obtain

$$\frac{\partial \Psi}{\partial E_G} = \frac{1}{k}\frac{\partial S_G}{\partial E_G} + \kappa = 0, \quad \frac{\partial \Psi}{\partial E_L} = \frac{1}{k}\frac{\partial S_L}{\partial E_L} + \kappa = 0 \tag{29}$$

We recall that in statistical thermodynamics the temperature is defined as

$$\frac{1}{T} := \frac{\partial S}{\partial E} \tag{30}$$

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Thus, (29) results in

$$\kappa = -\frac{1}{kT_G} = -\frac{1}{kT_L} = -\frac{1}{kT} \qquad (31)$$

In other words, it was proved that the temperatures in the two phases are equal.

Furthermore, taking the derivatives of Ψ with respect to N_G and N_L, and equating them to 0 we obtain

$$\frac{\partial \Psi}{\partial N_G} = \frac{s_G^*}{k} - \frac{c_v}{R} - 1 + \kappa\xi + \lambda = 0, \quad \frac{\partial \Psi}{\partial N_L} = \frac{s_L^*}{k} - \frac{c_L}{R} + \lambda = 0 \qquad (32)$$

Eliminating λ, substituting κ from (31) and c_v from $c_v = c_p - R$, and making algebraic manipulations, we find:

$$\frac{s_G^* - s_L^*}{k} = \frac{\xi}{kT} - \frac{c_L - c_p}{R} \qquad (33)$$

On the other hand, from (26), observing that E_G/N_G and E_L/N_L are both proportional to T, while V/N_G is proportional to T/p, we also obtain the difference of entropies per particle as:

$$\frac{s_G^* - s_L^*}{k} = CT_8 - \frac{c_L - c_p}{R} \ln T - \ln p \qquad (34)$$

Combining (33) and (34), eliminating $s_G^* - s_L^*$, and solving for p we find

$$\ln p = CT_9 - \frac{\xi}{kT} - \frac{c_L - c_p}{R} \ln T \qquad (35)$$

Now if we introduce $\alpha = \xi R/k$ ($= \xi N_a$, where N_a is the Avogadro constant) and take antilogarithms, then we obtain (22) again, which was our desideratum.

To finish this analysis, we will show the equality of chemical potentials (although the chemical potential was not involved at all in the above proof). We recall that the chemical potential is by definition:

$$-\frac{\mu}{T} := \frac{\partial S}{\partial N} = s^* + N\frac{\partial s^*}{\partial N} \qquad (36)$$

where the partial derivative applies for constant internal energy. Applying this definition in the two phases and using (26) we find,

$$-\frac{\mu_G}{T} = s_G^* - \frac{kc_v}{R} - k, \quad -\frac{\mu_L}{T} = s_L^* - \frac{kc_L}{R} + \frac{\xi}{T} \qquad (37)$$

where the last term (ξ/T) in the second equation represents the conversion from constant thermal energy E_L to constant internal energy $U_L = E_L - N_L\xi$. Specifically, this term represents the quantity $(\partial S_L/\partial E_L)(\partial E_L/\partial N_L) = (1/T)\,\xi$. This gives the difference of chemical potentials as

$$\frac{\mu_L - \mu_G}{T} = s_G^* - s_L^* + \frac{k(c_L - c_p)}{R} - \frac{\xi}{T} \qquad (38)$$

Combining (33) and (38) we find

$$\mu_L - \mu_G = 0 \qquad (39)$$

5. Application to water vapour

We choose as reference point the triple point of water, for which it is known with accuracy that $T_0 = 273.16$ K ($= 0.01$°C) and $p_0 = 6.11657$ hPa [10]. The specific gas constant of water vapour is $R = 461.5$ J kg^{-1} K^{-1}. The specific heat of water vapour at constant pressure, again determined at the triple

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point, is $c_p = 1884.4$ J kg^{-1} K^{-1} and that of liquid water is $c_L = 4219.9$ J kg^{-1} K^{-1} [10], so that $c_L - c_p = 2335.5$ J kg^{-1} K^{-1} and $(c_L - c_p)/R = 5.06$.

The latent heat at T_0 is $L_0 = 2.501 \times 10^6$ J kg^{-1} so that $\alpha = L_0 + (c_L - c_p)T_0 = 3.139 \times 10^6$ J kg^{-1} and $\xi / kT_0 = \alpha / RT_0 = 24.9$. According to (20), this results in the functional form

$$L \text{ [J kg}^{-1}] = \alpha - (c_L - c_p)T = 3.139 \times 10^6 - 2336\, T \text{ [K]} \tag{40}$$

It can be readily verified that this is very close to a commonly suggested (e.g. [11]) empirical linear equation for latent heat, i.e.,

$$L \text{ [J kg}^{-1}] = 3.146 \times 10^6 - 2361\, T \text{ [K]} \; (= 2.501 \times 10^6 - 2361\, T_C \text{ [}^\circ\text{C]}) \tag{41}$$

Figure 1 provides a graphical comparison of equation (40) with (41), as well as with tabulated data from Smithsonian Meteorological Tables [12], which agree with the equations. Furthermore, it is important to know that the entropic framework which gives the saturation vapour pressure is the same framework that predicts the relationship of the latent heat of vaporization with temperature.
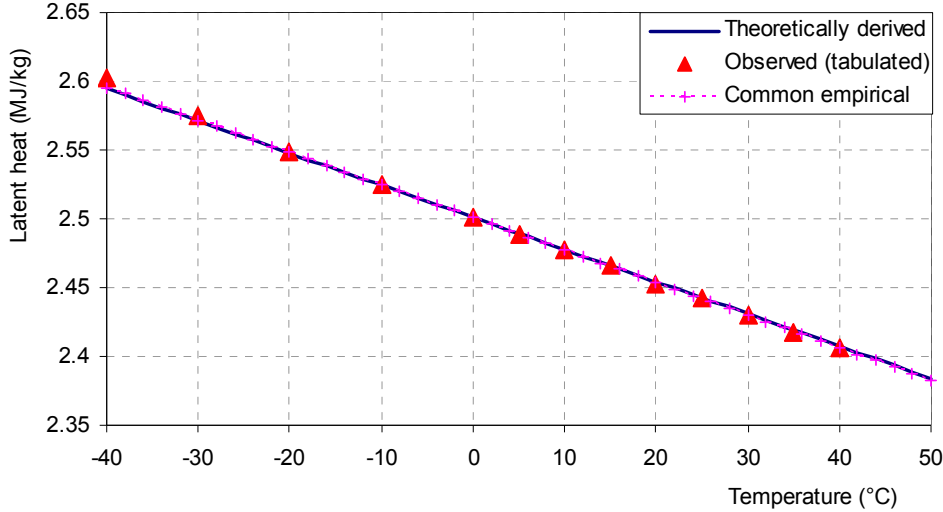
Figure 1. Comparison of latent heat of water as given by equation (40) proposed in this study with the empirical equation (41) and with standard tabulated data from ref. [12].

Now, according to (23), the saturation vapour pressure will be

$$p = p_0 \, \exp\left[24.921\left(1 - \frac{T_0}{T}\right)\right]\left(\frac{T_0}{T}\right)^{5.06}, \text{ with } T_0 = 273.16 \text{ K}, \, p_0 = 6.11657 \text{ hPa}. \tag{42}$$

where we have slightly modified the last two decimal digits of the constant α / RT_0 to optimize its fit to the data (see below). For comparison, the inconsistent version (1) for constant $L = L_0$ is

$$p = p_0 \, \exp\left[19.84\left(1 - \frac{T_0}{T}\right)\right], \text{ with } T_0 = 273.16 \text{ K}, \, p_0 = 6.11657 \text{ hPa}. \tag{43}$$

Equations (42) and (43), if plotted on a p vs. T graph, seem indistinguishable from each other as well as from the Magnus-type equation (2) (Figure 2). However, because p ranges at several orders of magnitude, the plot of Figure 2 is misleadingly hiding the differences between the different equations. The maximum relative difference of the proposed equation (42) with respect to (43) exceeds 7%, while that with respect to (2) is much lower, 0.29%. It is thus more informative to compare the three equations in terms of relative differences and also to compare them to data rather than to intercompare to each other.
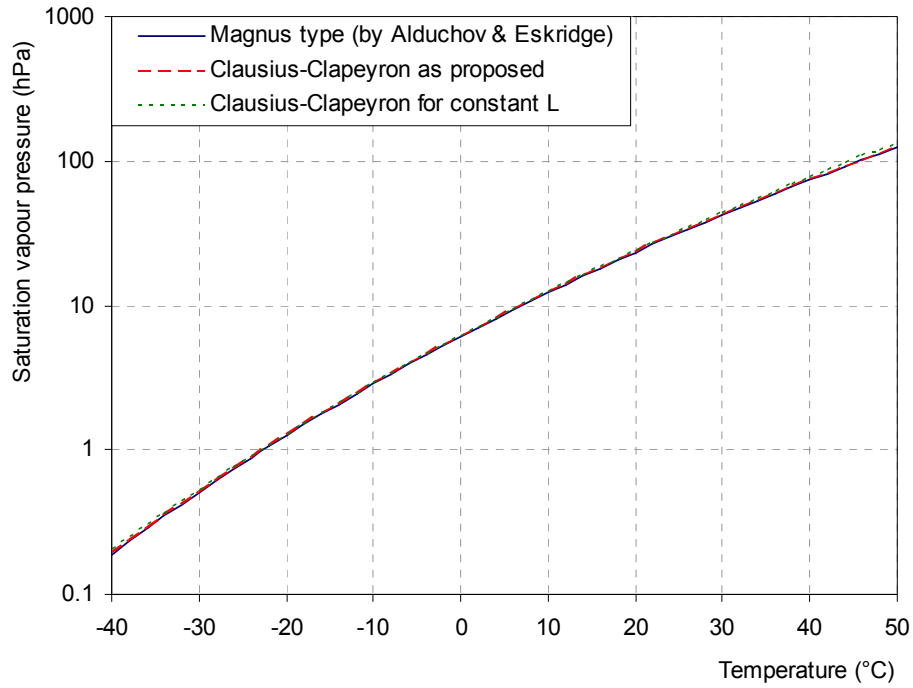
Figure 2. Comparison of saturation vapour pressure obtained by the proposed equation (42), by the Magnus-type equation (2) from ref. [7], and by the standard but inconsistent equation (43) for constant L.
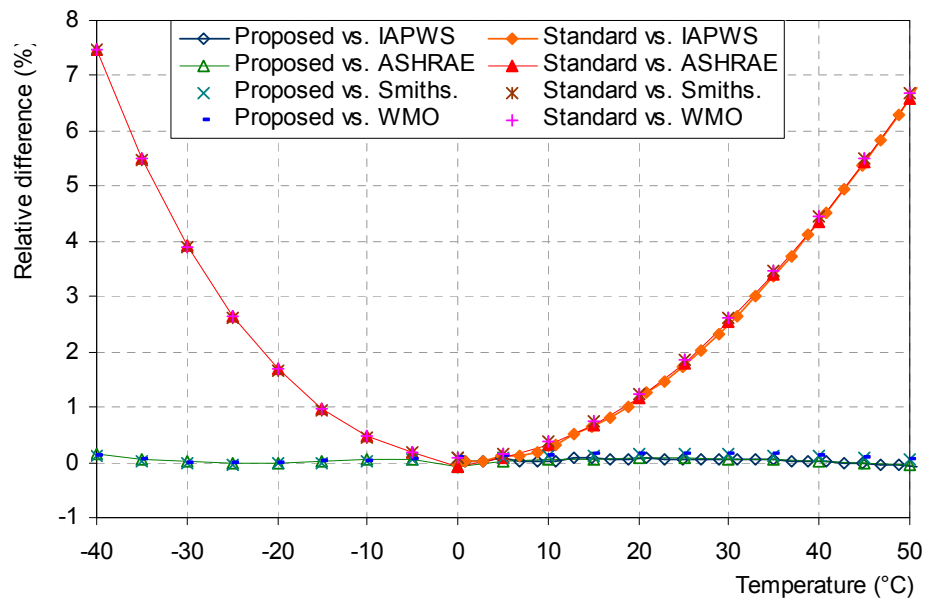
Figure 3. Comparison of relative differences of the saturation vapour pressure obtained by the proposed equation (42), as well as by the standard but inconsistent equation (43), with data of different origins (see text).

Table 1 Maximum values of the relative differences from data of the saturation vapour pressure obtained by three different equations (see text).

	Standard (inconsistent) equation (43)	Magnus-type equation (2)	Proposed equation (42)
Difference from IAPWS data	6.8%	0.27%	0.07%
Difference from all data	7.6%	0.39%	0.15%

For the comparisons four reference data sets have been used, which are given in tabulated form from different origins: (a) the International Association for the Properties of Water and Steam (IAPWS), (b) the Smithsonian Meteorological Tables (Smiths.), (c) the World Meteorological Organization (WMO) meteorological tables, and (d) the American Society of Heating, Refrigerating and Air-conditioning Engineers (ASHRAE). The temperature domain of the comparison extends from –40° to 50°C, that is the typical range used in hydrometeorological applications. The data set (a), taken from ref. [10], contains values of saturation vapour pressure for temperatures higher than the water triple point (273.16 K). The other three data sets, all taken from ref. [13], contain values also below triple point; such temperatures prevail in the upper air and the saturation vapour pressure in such temperatures is necessary in order to estimate the relative humidity of the atmosphere. It is clarified that the values for $T < 0°C$ are for water vapour over a surface of liquid water (not over ice), and thus are relevant to our study. Nonetheless, it is reasonable to expect that the values for $T \geq 0°C$ are more accurate and that the IAPWS data set, which is newer, is the most accurate among the four. The different data sets display small differences between each other for the same temperature value, up to 0.16%.

Figure 3 provides a graphical comparison of equations (42) and (43) with the reference data. Clearly, the common inconsistent equation (43), derived for constant L, proves to be inappropriate, as its relative error exceeds 7%. In contrast, the derived closed solution (42) has negligible relative errors. The maximum relative errors of the two equations, as well as those of the Magnus-type equation (2), with respect to the data are given in Table 1. It can be seen that the differences of the proposed equation (42) from the data is negligible, smaller that the deviations among the values of different data sets. The error of Magnus-type equation (2) is four times larger than that of (42) for the most accurate IAPWS data set and 2.5 times larger for all data sets. The error of the standard equation (43) is too high, 1.5-2 orders of magnitude higher that that of the proposed equation (42).

The simplicity of (42) makes numerical calculations easy. For known T, (42) provides p directly. The inverse problem (to calculate T, i.e. the saturation temperature, also known as dew point, for a given partial vapour pressure p) cannot be solved algebraically. However, the Newton-Raphson numerical method at an origin $T_0/T = 1$ gives a first approximation T' of temperature by

$$\frac{T_0}{T'} = 1 + \frac{1}{24.921 - 5.06} \ln\left(\frac{p_0}{p}\right) \tag{44}$$

Notably, this is virtually equivalent to solving (43) for T_0/T. This first approximation can be improved by re-applying (42) solved for the term T_0/T contained within the exponentiation, to give

$$\frac{T_0}{T} = 1 + \frac{1}{24.921} \ln\left(\frac{p_0}{p}\right) + \frac{5.06}{24.921} \ln\left(\frac{T_0}{T'}\right) \tag{45}$$

A systematic numerical investigation showed that a single application of (45) suffices to provide a value of T with a numerical error in T_0/T less than 0.1%, while a second iteration (setting the calculated T as T') reduces the error to 0.02%.

6. Summary and concluding remarks

Evidently, theoretically consistent relationships are preferable over purely empirical ones as far as the former agree with empirical evidence and their use is convenient. The Clausius-Clapeyron equation is a nice theoretical relationship, but the analytical solution typically contained in books, while it is

simple and easy to use, proves to be flawed and also a bad approximation of reality. It is, thus, reasonable that in calculations of saturation vapour pressure, empirical, typically Magnus-type, equations are preferred over this theoretical equation. By removing an unnecessary, excessive and inconsistent assumption that is made within the common derivation, we obtain a closed solution that is still very simple and combines both theoretical consistency and accuracy. With reference to water vapour saturation, the proposed solution is by orders of magnitude more accurate than the standard equation of the literature and also better than the more accurate Magnus-type equation. Compared to standard tabulated data of saturation vapour pressure for temperature range -40° to 50°C, which is relevant to hydrometeorological applications, the derived equation has negligible error. These facts may allow recommending the use of the derived equation (42) as one combining theoretical consistency and accuracy.

The alternative theoretical framework proposed, which is based on entropy maximization avoiding unnecessary assumptions, provides a better understanding and intuition development for the phase transition. Such understating and intuition development can help to recognize, particularly within the university education, the power of variational principles and the extremization (maximization/minimization) approach over the more common approach that the physical laws are mathematically expressed only by equations, as well as to recognize the fundamental character of entropy maximization as a powerful physical principle, contrary to a common perception that physical laws are only deterministic and mechanistic.

As first indicated by Boltzmann and Gibbs, later succeeded by Shannon who used essentially the same entropy definition to describe the information content, entropy is none other than a measure of uncertainty [e.g. 14, 15, 16]. Thus, the interpretation of the framework proposed is that the quantification of the phase change relies on maximization of uncertainty. In particular, the entropy in equations (25) and (26) represents the combined uncertainty as to (a) whether a molecule is in the liquid or gaseous phase, (b) the molecule's position in space and (c) the molecule's kinetic state expressed by its velocity. This combined uncertainty is maximal at the microscopic (molecular) level. It is amazing that the entropy maximization represents a principle so powerful as to fully explain and accurately quantify the phase transition determining its latent heat (equations (20) and (40)) and the resulting equilibrium vapour pressure (equations (23) and (42)). It is even more amazing that, while at the microscopic level the uncertainty is maximized, at the macroscopic level all the resulting laws express near certainties, verified by measurements. This is not a surprise, though, because, given the probabilistic meaning of entropy, the negligible macroscopic uncertainty can be predicted by application of probability theory for systems with large number of elements, as the typical thermodynamic systems are.

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