A summary of several meteorological properties of the moist-air entropy variables $\theta_s$ and $PV(\theta_s)$.

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1 Introduction - Motivations

The aim of this note is to describe several meteorological properties shown in Marquet (2022) for the moist-air specific entropy, the associated potential temperature ($\theta_s$) defined in Marquet (2011) and the associated potential vorticity $PV(\theta_s)$ defined in Marquet (2014).

The three Tables 1 to 3 provide the numerical values of all thermodynamic constants used in this note.

### Table 1: Dry- and moist-air thermodynamic constants

| $R_d$ | $R_v$ | $c_{pd}$ | $c_{pv}$ | $c_l$ | $c_i$ | $L_v(T_0)$ | $L_s(T_0)$ |
|-------|-------|----------|----------|-------|-------|------------|------------|
| J/K/kg | J/K/kg | J/K/kg | J/K/kg | J/K/kg | kJ/kg | kJ/kg |
| 287.06 | 461.52 | 1004.7 | 1846.1 | 4218 | 2106 | 2501 | 2835 |

### Table 2: Standard and reference values

| $T_0$ | $p_0$ | $s_{d0}(T_0,p_0)$ | $s_{s0}(T_0,p_0)$ | $e_r$ | $e_s(T_r)$ | $p_{dr}$ | $p_r$ | $e_r$ | $s_{dr}(T_r,p_{dr})$ | $s_{vr}(T_r,e_r)$ | $r_r$ |
|-------|-------|-----------------|-----------------|-------|----------|--------|-------|-------|----------------|----------------|-------|
| K     | hPa   | J/K/kg          | J/K/kg          | hPa   | hPa      | J/K/kg | J/K/kg | hPa   | g/kg            | g/kg            | 3.82 |
| 273.15| 1000  | 6775            | 10320           | 6.1064| 993.89   | 6777   | 12673 | 3.82 |

### Table 3: Non-dimensional derived constants

| $\eta$ | $\varepsilon$ | $\gamma$ | $\kappa$ | $\lambda$ | $\delta$ | $\Lambda_r$ |
|--------|---------------|---------|----------|-----------|---------|-------------|
| 1.608  | 0.622         | 0.4594  | 0.2857   | 0.8375    | 0.6078  | 5.869 ± 0.03 |

The way the old dry-air potential temperature ($\theta$) was defined in the nineteenth century is recalled in section 2. The definitions of other moist-air potential temperatures ($\theta$, $\theta'_w$, $\theta_e$, $\theta_v$, $\theta_t$, $\theta_{es}$, $\theta_{st}$, $\theta'_e$) are provided in section 3. The definition of the new moist-air entropy potential temperature ($\theta_s$) published in Marquet (2011) is recalled in section 4 before to be compared to the other potential temperatures in section 5.

The moist-air entropy potential vorticity $PV(\theta_s)$ published in Marquet (2014) is recalled in section 6 together with the other previous definitions $PV(\psi)$ with $\psi = \theta$, $\theta'_w$, $\theta_e$, $\theta_v$ or $\theta_{es}$. The section 7 shows comparisons between the potential vorticity functions $PV(\theta) \approx PV(\theta_e)$, $PV(\theta_s)$ and $PV(\theta_v)$, with in particular regions of negative values of $PV(\theta_s)$ close to the cold fronts that seems to indicate regions of symmetric instability.

General conclusions are provided in section 8.
2 The old dry-air potential temperature ($\theta$)

With von Helmholtz (1888) coined the term “potential temperature” for the dry-air quantity:

$$\theta(T, p) = T \left( \frac{p_0}{p} \right)^{R_d/c_{pd}} = T \left( \frac{p_0}{p} \right)^{\kappa},$$

(1)

where $T$ is the absolute temperature, $p$ the pressure, $p_0 = 1000$ hPa a standard value, $R_d$ the dry-air gas constant, $c_{pd}$ the dry-air specific heat at constant pressure and $\kappa = R_d/c_{pd}$.

The link between the dry-air potential temperature ($\theta$) and the dry-air specific entropy ($s_d$) was derived by Bauer (1908, 1910), through a relationship which can be written as

$$s_d = c_{pd} \ln \left( \theta \right) + [s_{d0}(T_0, p_0) - c_{pd} \ln (T_0)] = c_{pd} \ln \left( \frac{\theta}{T_0} \right) + s_{d0}(T_0, p_0) \quad (2)$$

and thus $s_d = c_{pd} \ln \left( \theta \right) + s_0(p_0)$, where $s_0(p_0) = s_{d0}(T_0, p_0) - c_{pd} \ln (T_0)$.

The dry-air specific heat $c_{pd}$, the reference (standard) temperature $T_0 = \theta_0 = \theta(T_0, p_0)$ and the standard dry-air entropy $s_{d0}(T_0, p_0)$ are all constant terms. Moreover, the quantity $s_0(p_0)$ in (3) only depends on the reference standard pressure $p_0 = 1000$ hPa, because the changes of $s_{d0}(T_0, p_0)$ with $T_0$ are balanced (and cancelled) by the second term $-c_{pd} \ln (T_0)$.

3 The old moist-air potential temperatures ($\theta'_w$, $\theta_v$, $\theta_e$, $\theta_l$, $\theta_{es}$, $\theta_{il}$, $\theta'_e$)

With von Bezold (1888a) coined the definition of the “pseudo-adiabatic” processes, corresponding to the wet-bulb potential temperature ($\theta'_w$) and defined by integration of saturation moist-air differential equations, without analytic expression for $\theta'_w$.

$$\theta'_w = \theta \left[ 1 + \left( \frac{R_v}{R_d} - 1 \right) q_v - (q_l + q_i) \right],$$

(5)

where $R_v$ is the water-vapor gas constant and $q_v$, $q_l$ and $q_i$ are the specific content for water vapor, liquid water and ice species, respectively.

The difference between the wet-bulb ($\theta'_w$) and equivalent ($\theta_e$) potential temperatures was studied by Normand (1921), von Stüve (1927), Robitzsch (1928), Rossby (1932), Bleeker (1939), among others, with the equivalent potential temperature defined by quantities close to the first-order approximation

$$\theta_e \approx \theta \exp \left( \frac{L_v q_v}{c_{pd} T} \right),$$

(6)

where $L_v$ is the latent heat of vaporization.

Hewson (1936, 1938) studied the application of the wet-bulb potential temperature ($\theta'_w$) to air mass analysis, with its meaning and significance studied in Hewson (1946a,b).

The same differential equations derived in von Bezold (1888a) are used in Saunders (1957) to define the adiabatic and pseudo-adiabatic equations.
The three quantities $\theta'_w$, $\theta_v$ and $\theta_e$ were considered in Lilly (1968).

As a companion of $\theta_e$, the “liquid-water potential temperature” ($\theta_l$) was defined and studied in Betts (1973), with the first-order approximation relationship

$$\theta_l \approx \theta \exp \left( - \frac{L_v \ q_l}{c_{pd} \ T} \right).$$  \hfill (7)

Similar values of $\theta_l$ and/or $\theta_e$ were derived and studied by Emanuel (1994); Pauluis et al. (2008, 2010); Laliberté et al. (2013); Pauluis and Mrowiec (2013); Pauluis (2016); Mrowiec et al. (2016); Pauluis and Zhang (2017); Fang et al. (2017); Dauhut et al. (2017); Fang et al. (2019).

Empirical formula for the saturation pseudo-adiabats and the “saturation equivalent potential temperature” ($\theta_{es}$) were derived in Betts and Dugan (1973), leading to the first-order approximation relationship

$$\theta_{es} \approx \theta \exp \left( \frac{L_v \ r_{sw}}{c_{pd} \ T} \right),$$  \hfill (8)

where $r_{sw}$ is the saturation water-vapor mixing ratio.

The “ice-liquid water potential temperature” ($\theta_{il}$) defined in Tripoli and Cotton (1981) can be considered as a generalization of the Betts (1973) “liquid-water potential temperature” ($\theta_l$) to the case of ice ($q_i \neq 0$), with the relationship

$$\theta_{il} \approx \theta \exp \left( - \frac{L_v \ q_l + L_s \ q_i}{c_{pd} \ T} \right),$$  \hfill (9)

where $L_s$ is the latent heat of sublimation.

The Betts (1973) conservative quantity $\theta_l$ is nowadays used in most of parameterization of atmospheric turbulence (ex. based on: Deardorff, 1980; Mellor and Yamada, 1982; Cuxart et al., 2000, etc), and to study the subgrid-condensation schemes (ex. those based on: Deardorff and Sommeria, 1977; Bougeault, 1982, etc), with both $\theta_l$ and $\theta_e$ usually considered to study the cloud-top entrainment instability (ex. those based on: Deardorff, 1980; MacVean and Mason, 1990; Lock, 2004, etc).

The equivalent potential temperature computed in Bolton (1980), Bryan (2008) and Davies-Jones (2009), among others, are different from the “adiabatic” version $\theta_e$ approximated by Eq. (6), and rather corresponds to the “pseudo-adiabatic” value $\theta'_w$, which is not analytically defined in Eq. (4). As an example, the (adjusted up to about 0.03 K?) approximation derived in Eqs. (21), (22), (24) and (39) of Bolton (1980) correspond to

$$T_L \approx \frac{2840}{3.5 \ \ln(T) - \ln(e/100) - 4.805} \approx \frac{1}{T - 55 - \frac{1}{2840} \ \ln(H_l)},$$  \hfill (10)

$$\theta_{DL} \approx T \left( \frac{p_0}{p - e} \right)^{0.2854} \left( \frac{T}{T_L} \right)^{0.28 \ r_v},$$  \hfill (11)

$$\theta'_w \approx \theta_{DL} \ \exp \left[ \left( \frac{3036}{T_L} - 1.78 \right) \left( 1 + 0.448 \ r_v \right) \right],$$  \hfill (12)

where $T$ is the absolute temperature (K), $p$ the total pressure (Pa), $e$ the water-vapor partial pressure (Pa), $H_l = e/e_{sw}$ the relative humidity (Pa/Pa), and $r_v = q_v/(1 - q_w)$ the water-vapor mixing ratio (kg/kg).
This formulation of Bolton (1980) is different from \( \theta_e \) given by (5), and especially in non-saturated regions where \( H_i \neq 1 \) and \( T_L \neq T \), since:

- \( \theta_{DL} \neq \theta = T \left( \frac{p_0}{p} \right)^\kappa \approx T \left( \frac{p_0}{p} \right)^{0.2857} \), because \( T_L \neq T \), \( p - e \neq p \) and 0.2854 \( \neq \) 0.2857 in (11);
- \( 3036/T_L - 1.78 \neq \left[ L_v(T_0) + (c_{pv} - c_l)(T - T_0) \right]/(c_{pd} T) \approx 3134/T - 2.36 \) in (12);
- even if \( (1 + 0.448 r_v) \approx [ q_v ] \) because \( r_v = q_v/(1 - q_v) \approx q_v \) and \( (1 + 0.448 r_v) \approx 1 \).

4 The moist-air entropy potential temperature (\( \theta_s \))

The more recent “moist-air entropy potential temperature” (\( \theta_s \)) published in Marquet (2011) can be considered as an improvement of the quantity \( \theta_s \) already derived in Hauf and Hölter (1987) and Marquet (1993).

The relationship between the moist-air specific entropy (\( s \)) and the corresponding potential temperature (\( \theta_s \)) was assumed in Marquet (2011) to be the same as the one derived by Bauer (1980, 1987) or Pauluis et al. (2010).

The specific heat capacity (at constant pressure) \( c_{pd} \), the reference (standard) temperature \( T_0 = \theta_0 = \theta(T_0, p_0) \) and the reference dry-air entropy \( s_{d0}(T_0, p_0) \) are all constant. Moreover, the quantity \( s_0(p_0) \) in (14) only depends on the same reference standard pressure \( p_0 = 1000 \) hPa as the one introduced to define the dry-air potential temperature \( \theta \) in (3), because the changes of \( s_{d0}(T_0, p_0) \) with \( T_0 \) are balanced (and cancelled) by the second term \( - c_{pd} \ln(T_0) \).

These properties (13) and (14) show that \( \theta_s \) becomes a true synonym for the specific moist-air entropy \( s \). This property did not hold in the previous formulations of \( \theta_s \) and \( \theta^* \) derived in Hauf and Hölter (1987) and Marquet (1993), nor in those of \( \theta_l \) and \( \theta_e \) derived in Betts (1973), Emanuel (1994) or Pauluis et al. (2010).

A general version of \( \theta_s \), which generalizes those of Marquet (2011, 2017), can be written from (51) as:

\[
\theta_s = \theta \exp \left[ - \frac{L_v(q_i + q_{rain}) + L_s(q_i + q_{snow})}{c_{pd} T} \right] \exp(\Lambda_\gamma q_t) \\
\times \left( \frac{T}{T_r} \right)^{\lambda q_t} \left( \frac{p_r}{p} \right)^{\kappa \delta q_t} \left( \frac{r_r}{r_v} \right)^{\gamma q_t} \left( \frac{1 + \eta r_v}{1 + \eta r_r} \right)^{\kappa (1 + \delta q_t)} \\
\times \left( H_i \right)^{\gamma (q_i + q_{rain})} \left( H_s \right)^{\gamma (q_i + q_{snow})} \left( \frac{T_{rain}}{T} \right)^{c_l q_{rain}/c_{pd}} \left( \frac{T_{snow}}{T} \right)^{c_l q_{snow}/c_{pd}}
\]

where \( \theta = T \left( \frac{p_0}{p} \right)^{R_d/c_{pd}} \) is the dry-air potential temperature. The relative humidities are noted \( H_i = e/e_{sw} \) and \( H_s = e/e_{si} \). The temperatures of precipitations (rain and snow) are noted \( T_{rain} \) and \( T_{snow} \). See the Tables 1 to 3 for the other thermodynamic constants.

Differently, the potential temperature \( \theta_{s/HH87} \) defined in Hauf and Hölter (1987) see Eqs. 3.23
to 3.25 page 2893) was linked to the specific entropy through the relationship

$$s = q_d c^*_pe \ln \left( \frac{\theta_{s/HH87}}{T_0} \right) + q_d s^*,$$

(16)

with $\theta_{s/HH87} = T \left( \frac{p - e}{p_0} \right)^{-R_d/c^*_pe} \exp \left( \frac{L_v r_v - L_s r_i}{c^*_pe T} \right) (H_t)^{-R_v r_v/c^*_pe} (H_i)^{R_v r_v/c^*_pe}$. 

Hauf and Höller (1987, p.2890) explained that, in (16) and (17): “$T_0$ and $p_0$ denote reference values of $T$ and $p$, and $s_d(T_0, p_0)$, $s_v(T_0, p_0)$, $s_i(T_0)$ and $s_i(T_0)$ are the values of dry-air and water entropies at this reference point.” This means that we must consider that $T_r = T_0$ and $p_r = p_0$ in Hauf and Höller (1987), without justification.

In (16) both $q_d c^*_pe = (1 - q_t) c_{pd} + q_t c_l$ and $q_d s^* = [(1 - q_t) s_d(T_0, p_0) + q_t s_i(T_0)]$ depend on $q_t$. Therefore, the first drawback is that $\theta_{s/HH87}$ cannot represent the moist-air entropy ($s$) unless the total-water specific content $q_t = r_t/(1 + r_t)$ is a constant. The words of Hauf and Höller (1987, p.2893) were: “The entropy temperature $\theta_{s/HH87}$ is related to entropy ($s$) by the functional relationship (16), and thus can be considered as a measure of entropy. However, Eq. (16) involved, beside entropy, the concentration of dry air $q_d = 1 - q_t$ and the total water mixing ratio $r_t = q_t/(1 - q_t)$. Therefore, a constant entropy does not generally imply that the entropy temperature $\theta_{s/HH87}$ is also a constant.”

The other drawback is the term $(H_t)^{-R_v r_v/c^*_pe}$ in (17) that is different from 1 in unsaturated regions, where the relative humidity $H_t = e/e_{sw} < 1$ but $r_v > 0$ is different from 0. The last term $(H_i)^{R_v r_v/c^*_pe}$ is most often equal to 1 for both unsaturated ($r_i = 0$) and saturated regions ($H_i = 1$). This issue (see Hauf and Höller 1987, p.2893) is due to “the definition of entropy temperature which presumes a system of cloudy air and especially the existence of liquid water, as can be seen from $q_d c^*_pe = (1 - q_t) c_{pd} + q_t c_l$ and $q_d s^* = [(1 - q_t) s_d(T_0, p_0) + q_t s_i(T_0)]”, which both depend on $c_l$ and $s_i(T_0)”. Problems arise if no liquid water is present, either locally or in principle.”

The potential temperature $\theta_{M93}$, defined in Marquet (1993) before Eq.42 and Eq.43 partially solved the issues of Hauf and Höller (1987), with $\theta_{M93}$ linked to the specific entropy through the relationship

$$s = q_d c^*_{pl} \ln \left( \frac{\theta_{M93}}{\theta_0^*} \right) + [(1 - q_t) s_d(T_0, p_0 - e_0) + q_t s_v(T_0, e_0)],$$

(18)

with $e_0 = e_{sat}(T_0)$ and

$$\theta_{M93} = T \left( \frac{p - e}{p_0} \right)^{-R_d/c^*_{pl}} \exp \left( -\frac{L_v r_v + L_s r_i}{c^*_{pl} T} \right) \left( \frac{e}{p_0} \right)^{-R_v r_v/c^*_{pl}} (H_t)^{R_v r_v/c^*_{pl}} (H_i)^{R_v r_v/c^*_{pl}}.$$ 

(19)

Like in (16), both $q_d c^*_{pl} = (1 - q_t) c_{pd} + q_t c_{pv}$ and the bracketed terms (with the reference entropies) depend on $q_t$ in (18), and therefore $\theta_{s}^*$ cannot always represent the moist-air entropy ($s$) in (18) unless the total-water specific content $q_t = r_t/(1 + r_t)$ is a constant.

However, the first advantage is the term $c_l$ used in Hauf and Höller (1987) that is replaced by $c_{pv}$ in $\theta_{M93}$, with the more comfortable idea that there is always some water-vapor content in real parcels of moist air, whereas there was no guaranty of existing liquid water in the formulation of Hauf and Höller (1987).
The other advantage is the symmetric use of the two mixing ratios \((r_t, r_i)\) in the exponential, instead of the use of \((r_v, r_i)\) with two different signs in \cite{HH87}, with also the possibility to neglect the last two terms \((H_l)^{R_v r_i/c_p^*}\) and \((H_i)^{R_v r_i/c_p^*}\) in \eqref{eq:19} for both unsaturated (since \(r_l = r_i = 0\)) and saturated regions (if \(H_l = H_i = 1\)).

In fact, the formulation (17) of \cite{HH87} corresponds to the equivalent potential temperature derived in \cite{EN94} and \cite{P10}, but with the ice content included. Therefore : \(\theta_{s/HH87} \approx \theta_{e/EN94} \approx \theta_{e/P10}\), but with no citation to the JAS paper of \cite{HH87} by K. Emanuel nor by O. Pauluis.

The words of \cite{HH87} (p.2895) were: “The equivalent potential temperature is a constant in a closed adiabatic system where water vapor is saturated. If in a rising parcel of cloudy air the liquid water remains in the parcel and does not fall out, then \(\theta_e\) is a constant.” And then (Hauf and H¨oller 1987 p.2896): “As a result, we see that for a saturated warm cloud the entropy temperature” \(\theta_{s/HH87}\) “is identical with the equivalent potential temperature \(\theta_e\)” (i.e. this equivalence is valid only if \(q_t\) is a constant).

Moreover \(\theta_{s/HH87} = \theta_{e/HH87}\) can be approximated by \(\theta_e\) of \cite{B73} given by (6), which can be considered as a first-order approximation of the more general formulations of \cite{HH87}, \cite{EN94} and \cite{P10}. This is the reason why the “first-order approximation” \(\theta_e\) of \cite{B73} given by (6) is used in almost all practical applications to study convection and is considered as a “conservative variable” in almost all moist-air turbulence schemes. The words of \cite{HH87} (p.2895) were: “other definitions of equivalent potential temperature exist (e.g. Betts [1973], which arise from approximations of the definition of” \(\theta_{s/HH87}\). “The present one” (i.e. \(\theta_{s/HH87} \approx \theta_{e/HH87}\) for constant \(q_t\) “is the most general definition, as no further approximations or assumptions have been made.”

The main result is that the equivalent potential temperatures \(\theta_e\) derived in \cite{B73}, \cite{HH87}, \cite{EN94} and \cite{P10} cannot represent the moist-air entropy (s) unless the total-water specific content \(q_t = r_i/(1 + r_i)\) and the mixing ratio \(r_t = q_t/(1 - q_t)\) are constant. Only \(\theta_s\) given by \eqref{eq:13} is really synonymous with the specific moist-air entropy, due to the relationship \eqref{eq:15} where both \(c_{pd}\) and \(s_{d0}(T_0, p_0)\) are constant.

The same is true for the liquid-water potential entropy \(\theta_l\) that can be written, following the same method described in \cite{HH87}, as

\[
\theta_l = T \left( \frac{p - e}{p_0} \right)^{-R_d/c_p^*} \exp \left( - \frac{L_v r_l + L_s r_i}{c_p^* T} \right) \left( \frac{e}{e_0} \right)^{-r_l R_v/c_p^*} (H_l)^{R_v r_i/c_p^*} \left( H_i \right)^{R_v r_i/c_p^*} .
\]

Both \((1 - q_t) c_p^* = (1 - q_l) c_d + q_l c_{pd}\) and the bracketed terms of \eqref{eq:20} depend on \(q_t\), and both prevent \(\theta_l\) to represent the moist-air entropy in all conditions if \(q_t\) and \(r_t\) are not constant.

The last terms of \eqref{eq:20} \((H_l)^{R_v r_i/c_p^*}\) and \((H_i)^{R_v r_i/c_p^*}\) are most often equal to 1 for both unsaturated (because \(r_l = r_i = 0\)) and saturated regions (if either \(H_l = 1\) or \(H_i = 1\)).
However, the term \((e/e_0)^{−r_1 R_e/c_{pl}}\) may be significantly different from unity and was missing in the formulation of Betts (1973).

The only difference between \(θ_i\) defined by (21) and \(θ_{M93}\) defined by (19) is the term \((e/e_0)^{−r_1 R_e/c_{pl}}\) in (21) replaced by \((e/p_0)^{−r_1 R_e/c_{pl}}\) in (19), with a ratio of these terms \((e_0/p_0)^{−r_1 R_e/c_{pl}}\) that is constant if \(r_1\) is a constant. However, \(e/e_0\) with \(e_0 = 6\) hPa is likely more often closer to unity than \(e/p_0\) with \(p_0 = 1000\) hPa, and for this reason (21) is likely more relevant than (19).

### 4.1 Establishment/demonstration of the formulation for \(θ_s\)

The formulation (13) can be derived starting from the Appendix B of Marquet (2011), but:

- with a more direct method;
- with all computations shown;
- with the additional hypotheses of \(T_i\) and \(T_{li}\) different from \(T\) for condensed species (precipitations at the wet-bulb temperature?); and
- with the possibility that \(H_i = 1\) and \(H_{li} = 1\) where \(q_i \neq 0\) and \(q_{li} \neq 0\) (unsaturated conditions with condensed species), or the possibility that \(H_i > 1\) or \(H_{li} > 1\) (super-saturation or mixed-phase conditions).

The specific moist-air entropy is first assumed to be a weighted sum of the partial entropies for dry air \(s_d(T, p - e)\), water vapor \(s_v(T, e)\), liquid water \(s_l(T)\), ice \(s_{li}(T)\), rain \(s_{rain}(T_{rain})\) and snow \(s_{snow}(T_{snow})\) species, with \(q_d + q_v + q_l + q_{i} + q_{rain} + q_{snow} = q_d + q_i = 1\) the specific contents of these species (i.e. the mass concentrations \(q_x = M_x/m\) with \(m = m_d + m_v + m_l + m_i + m_{rain} + m_{snow} = m_d + m_i\) the total mass of a small and homogeneous parcel of the moist-air fluid), leading to

\[
\begin{align*}
\Delta s &= q_d s_d(T, p - e) + q_v s_v(T, e) + q_l s_l(T) + q_i s_{li}(T) \\
&\quad + q_{rain} s_{rain}(T_{rain}) + q_{snow} s_{snow}(T_{snow}).
\end{align*}
\]  

(22)

The moist-air entropy formulation (22) depends on the partial pressure of dry air \((p - e)\) and water vapor \((e)\). This formulation (22) can then be transformed by using \(q_v = q_l - q_i - q_{rain} - q_{snow}\) in the first line, and by inserting/removing \(s_l(T)\) and \(s_{li}(T)\) in the second line, leading to

\[
\begin{align*}
\Delta s &= q_d s_d(T, p - e) + q_l s_v(T, e) + q_i \left[ s_l(T) - s_v(T, e) \right] + q_i \left[ s_{li}(T) - s_v(T, e) \right] \\
&\quad + q_{rain} \left[ s_{rain}(T_{rain}) - s_l(T) \right] + q_{rain} \left[ s_{li}(T) - s_v(T, e) \right] \\
&\quad + q_{snow} \left[ s_{snow}(T_{snow}) - s_l(T) \right] + q_{snow} \left[ s_{li}(T) - s_v(T, e) \right],
\end{align*}
\]

(23)

\[
\begin{align*}
\Delta s &= q_d s_d(T, p - e) + q_l s_v(T, e) \\
&\quad + q_{rain} \left[ s_{rain}(T_{rain}) - s_l(T) \right] - \left( q_l + q_{rain} \right) \left[ s_v(T, e) - s_l(T) \right] \\
&\quad + q_{snow} \left[ s_{snow}(T_{snow}) - s_l(T) \right] - \left( q_l + q_{snow} \right) \left[ s_v(T, e) - s_l(T) \right].
\end{align*}
\]

(24)

If the “gas constants” \((R_d\) and \(R_v\)) and the “specific heat at constant pressure” \((c_{pd}, c_{pv}, c_l, c_i)\) are assumed to be constant within the range of atmospheric temperatures, the partial entropies can be computed from the relationships

\[
\begin{align*}
s_d(T, p - e) &= c_{pd} \ln \left( \frac{T}{T_r} \right) - R_d \ln \left( \frac{p - e}{p_r - e_r} \right) + s_{dr}(T_r, p_r - e_r), \\
s_v(T, e) &= c_{pv} \ln \left( \frac{T}{T_r} \right) - R_v \ln \left( \frac{e}{e_r} \right) + s_{vr}(T_r, e_r), \\
s_l(T) &= c_l \ln \left( \frac{T}{T_r} \right) + s_{lr}(T_r), \\
s_{li}(T) &= c_i \ln \left( \frac{T}{T_r} \right) + s_{ir}(T_r),
\end{align*}
\]

(25-28)
where, at this stage, the reference temperature $T_r \neq T_0$ and the reference total pressure $p_r \neq p_0$ are, a priori, different from the standard values $T_0 = 273.15 \text{ K}$ and $p_0 = 1000 \text{ hPa}$. The reference partial pressure for water vapor is assumed to be the saturation water-vapor pressure $e_r = e_s(T_r)$, which is the only possible value different from 0 and depending on the reference temperature $T_r$.

The differences in entropy $s_l(T_{\text{rain}}) - s_l(T)$ and $s_l(T_{\text{snow}}) - s_l(T)$ in (23) can be computed from (29) and (30), yielding

$$s_l(T_{\text{rain}}) - s_l(T) = c_l \ln \left( \frac{T_{\text{rain}}}{T} \right)$$

and

$$s_l(T_{\text{snow}}) - s_l(T) = c_l \ln \left( \frac{T_{\text{snow}}}{T} \right),$$

whereas the other differences in entropy can be computed in terms of the latent heats $L_v(T)$ and $L_s(T)$ and the relative humidities $H_l = e/e_{sw}$ and $H_i = e/e_{si}$ according to Hauf and Höller (1987, Eqs. 3.10 to 3.12, p. 2891), yielding

$$s_v(T,e) - s_l(T) = \frac{L_v(T)}{T} - R_v \ln (H_i),$$

and

$$s_v(T,e) - s_l(T) = \frac{L_s(T)}{T} - R_v \ln (H_i).$$

These differences in water-species entropy (29)-(32) can be inserted into (24), together with $s_d(T,p-e)$ and $s_v(T,e)$ given by (25)-(26), to give

$$s = q_d s_{dr}(T_r, p_r - e_r) + q_t s_{vr}(T_r, e_r) - \left( q_l + q_{\text{rain}} \right) \frac{L_v(T)}{T} + \left( q_l + q_{\text{snow}} \right) \frac{L_s(T)}{T} + q_d c_{pd} + q_t c_{pv} \ln \left( \frac{T}{T_r} \right) - q_d R_d \ln \left( \frac{p - e}{p_r - e_r} \right) - q_t R_v \ln \left( \frac{e}{e_r} \right) + q_{\text{rain}} c_l \ln \left( \frac{T_{\text{rain}}}{T} \right) + q_{\text{snow}} c_i \ln \left( \frac{T_{\text{snow}}}{T} \right) + (q_l + q_{\text{rain}}) R_v \ln (H_i) + (q_l + q_{\text{snow}}) R_v \ln (H_i).$$

The property $q_d = 1 - q_t$ can be used to rewrite the first two terms of (33) as

$$q_d s_{dr}(T_r, p_r - e_r) + q_t s_{vr}(T_r, e_r) = s_{dr}(T_r, p_r - e_r) + c_{pd} \Lambda_r q_t,$$

where the non-dimensional term $\Lambda_r = [s_{vr}(T_r, e_r) - s_{dr}(T_r, p_r - e_r)]/c_{pd}$ depends on the reference entropies for water vapor and dry air, to be computed for the reference temperature $T_r$ and partial pressures $p_r$ and $e_r$. Similarly, the term in factor of the logarithm of $T$ can be rewritten as

$$q_d c_{pd} + q_t c_{pv} = c_{pd} + c_{pd} \Lambda q_t,$$

where $\Lambda = (c_{pv} - c_{pd})/c_{pd}$.

The dry-air and water species reference entropies can be computed for any set of reference values $(T_r, p_r, e_r)$ according to

$$s_{dr}(T_r, p_r - e_r) = s_{d0}(T_0, p_0) + c_{pd} \ln \left( \frac{T_r}{T_0} \right) - R_d \ln \left( \frac{p_r - e_r}{p_0} \right),$$

$$s_{vr}(T_r, e_r) = s_{v0}(T_0, p_0) + c_{pv} \ln \left( \frac{T_r}{T_0} \right) - R_v \ln \left( \frac{e_r}{p_0} \right),$$

$$s_{dr}(T_r) = s_{d0}(T_0) + c_l \ln \left( \frac{T_r}{T_0} \right),$$

$$s_{vr}(T_r) = s_{v0}(T_0) + c_i \ln \left( \frac{T_r}{T_0} \right).$$
Eqs. (34), (35) and (36) can be inserted into (33), also with the term “$R_d \ln(p_0/p)$” added and removed in the first line, to give

$$s = s_{d0}(T_0, p_0) + c_{pd} \ln \left( \frac{T}{T_0} \right) + R_d \ln \left( \frac{p_0}{p} \right) - \frac{(q_t + q_{rain}) L_v(T) + (q_t + q_{snow}) L_s(T)}{T}$$

$$+ c_{pd} \Lambda_r q_t + c_{pd} \lambda q_t \ln \left( \frac{T}{T_r} \right) - R_d \ln \left( \frac{p - e_r}{p} \right) - q_d R_d \ln \left( \frac{p - e_r}{p - e_r} \right) - q_t R_v \ln \left( \frac{e}{e_r} \right)$$

$$+ q_{rain} c_l \ln \left( \frac{T_{rain}}{T} \right) + q_{snow} c_i \ln \left( \frac{T_{snow}}{T} \right) + (q_t + q_{rain}) R_v \ln(H_t) + (q_t + q_{snow}) R_v \ln(H_i). \quad (40)$$

An important property can be deduced from (40): because the first and third lines do not depend on the reference values $T_r$, $p_r$ and $e_r(T_r)$, the second line cannot depend on, and is thus independent on, these reference value. This means that any changes in $T_r$, $p_r$ and $e_r(T_r)$ corresponds to changes in all terms that leave the whole second line unchanged.

The next step is to write the equations for the dry air, water vapor and moist air

$$p_d = p - e = \rho_d R_d T = \rho q_d R_d T, \quad (41)$$

$$e = \rho_v R_v T = \rho q_v R_v T, \quad (42)$$

$$p = p_d + e_r = \rho R T = \rho (q_d R_d + q_v R_v) T = \rho q_d R_d (1 + \eta r_v) T, \quad (43)$$

and thus with $p = (1 + \eta r_v) (p - e)$, \quad (44)

$$e = \rho q_d R_d \eta r_v T = \eta r_v (p - e), \quad (45)$$

where $r_v = q_v/q_d = \rho_v/\rho_d$ and $\eta = R_v/R_d$, leading to

$$p - e = \frac{1}{1 + \eta r_v} p, \quad (46)$$

$$e = \frac{\eta r_v}{1 + \eta r_v} p. \quad (47)$$

The same relationship exist for the “just saturated” (i.e. with $q_{tr} = q_{ir} = 0$ and thus $q_{tr} = q_{ir} = q_{sat}(T_r, p_r) = q_r$) reference state

$$p_r - e_r = \frac{1}{1 + \eta r_r} p_r, \quad (48)$$

$$e_r = \frac{\eta r_r}{1 + \eta r_r} p_r = \eta r_r (p_r - e_r), \quad (49)$$

and thus with $r_r = \frac{e_r}{\eta (p_r - e_r)}$ and $q_r = \frac{r_r}{1 + r_r}$. \quad (50)

The partial pressures relationships (46), (47), (48) and (49), can then be inserted into (40) with

\footnote{Many thanks to Almut Gassman who see a typo in the version 1 of the arXiv note for the term $-q_t R_v \ln(e/e_r)$ at the end of the second line of (40), which was badly written $c_{pd} \gamma q_t \ln(r_r/r_v)$, in that wrongly anticipating the end of the third line of (51) and via a bad LaTeX copy/paste... sorry!}
The numerical values listed in (52)-(55) show that the uncertainties on dry-air and water-vapour standard entropies \( s_{d0} \) and \( s_v \) are small: about 1 and 2 J/K/kg, respectively.

It is worthwhile to remember that the standard entropies computed at 298.15 K and 1000 hPa (or 1013.25 hPa) for \( \text{N}_2, \text{O}_2, \text{Ar}, \text{CO}_2 \) and \( \text{H}_2\text{O} \) were already fully available since \textit{Kelley} (1932), and
then in the Thermodynamic Tables of Rossini et al. (1952), Lewis and Randall (1961), Wagman et al. (1965) and Robie et al. (1978), thus long before the computations made in atmospheric science by Betts (1973), Iribarne and Godson (1973, 1981), Emanuel (1994), Pauluis et al. (2010) and others, with (very) little changes in comparison to the more modern computations available in the Thermodynamic Tables and book of Gokcen and Reddy (1996), Chase (1998) and Atkins and de Paula (2014).

Figure 1 summarizes the way all absolute entropies can be computed with either the calorimetric or statistical-physics methods, leading to the same values at 273.15 K. The third law must be applied to the “more stable crystalline states” at 0 K (and not to the gases as wrongly stated in the Appendix of Pauluis et al., 2010, where criticisms of the third law of thermodynamics were unfounded). It is also needed to take into account the special residual entropy of 189 J/K/kg for ice-Ih, according to Pauling (1935) and Nagle (1966).

Similarly, IAPWS and TEOS10 computations of the entropies of ocean and moist-air (Wagner and Pruss, 2002; Feistel et al., 2008; IAPWS, 2010; Feistel et al., 2010; Feistel, 2012, 2019; Feistel and Hellmuth, 2020) may have use the values of Millero (1983) for sea water and Lemmon et al. (2000) for dry air, which are moreover available (but commented and unused) in the TEOS10 FORTRAN software. Differently, IAPWS and TEOS10 computations are made by canceling some standard entropies of dry air and water species at 273.15 K, in that being in contradiction with the third law of thermodynamics and with statistical physics principles, like in Iribarne and Godson (1973, 1981), Emanuel (1994), Pauluis et al. (2010) and others.

It was similarly assumed by Emanuel (1994), Pauluis et al. (2010) and many others that $s_d(T_0, p_0)$ and either $s_v(T_0, p_0)$ for $\theta_t$ or $s_l(T_0)$ for $\theta_e$ can be freely set to zero, in clear disagreement with the third law of thermodynamics and differently from Hauf and Hölzer (1987), Millero (1983), Lemmon et al. (2000) and Marquet (2011, 2017), where the third law is fully taken into account for the solid states of all dry-air and water species ($N_2$, $O_2$, Ar, CO$_2$, H$_2$O).

Moreover, in fact, there is no need to set to zero these standard values $s_d(T_0, p_0)$, $s_v(T_0, p_0)$ or $s_l(T_0)$ to defined $\theta_t$ and $\theta_e$ from the formulation $\theta_{t/HH87}$ of Hauf and Hölzer (1987), and the same should have been for Emanuel (1994), Pauluis et al. (2010) and others.

The only (however big) price to pay for leaving terms depending on the variable water content $q_t$ outside the logarithm in (16) and (18), including the terms depending on the non-zero entropies $s_d(T_0, p_0)$, $s_v(T_0, p_0)$ and $s_l(T_0)$, is that none of $\theta_t$, $\theta_e$, $\theta_{s/HH87}$ and $\theta_{s/M93}$ can represent the moist-air entropy in the real world, where $q_t$ is neither a constant due to evaporation, precipitations, entrainment, detrainment and turbulent-mixing processes.

Anyhow, since the entropy is a state function, there is only one definition of it, and only $\theta_s$ can represent the moist-air entropy in all conditions. In order to understand more precisely this property, let us imagine two parcels of the moist-air fluid labeled by $A$ and $B$, with the thermodynamic conditions $(T_A, p_A, q_{vA}, q_{mA}, q_{rA}, \ldots)$ and $(T_B, p_B, q_{vB}, q_{mA}, q_{rB}, \ldots)$, respectively. The total water contents $q_{tA} = q_{vA} + q_{mA} + \ldots$ and $q_{tB} = q_{vB} + q_{rB} + \ldots$ are thus different. In that case, according to (16), (18) or (20), the difference in specific entropy $\Delta s = s_B - s_A$ between the two points $A$ and $B$ depends on differences like $\left[ s_l(T_0) - s_d(T_0, p_0) \right] \Delta q_t$ for (16), where $\Delta q_t = q_{tB} - q_{tA}$.
Figure 1: Entropies for dry-air ($N_2$, $O_2$, Ar, $CO_2$ and water $H_2O$) species plotted against the absolute temperature and computed at 1000 hPa. The calorimetric method \( \int_0^T c_p(T') \, d\ln(T') + \sum_j L(T_j)/T_j \) corresponds to the coloured solid lines. The third-law hypothesis is applied at 0 K with zero entropies for all the solid phases, but with the residual entropy of 189 J/K/kg for ice-Ih. The vertical jumps correspond to phase changes at $T_j$ with the phase-change enthalpies $L(T_j)$ between solids phases (for $N_2$ and $O_2$), then from solid to liquid phases, then from liquid to vapour phases. The statistical-physics values (black dashed lines) are computed from $S = k \ln(W)$ and $F = -kT \ln(Z)$ for the vapour phases according to the method described in Chase (1998) for translational, rotational, vibrational and electronic partition functions ($Z$).
Therefore, since the specific entropy “s” is a state function, then the difference between two points $\Delta s = s_B - s_A$ must have a unique (non-arbitrary) value independent on any thermodynamic path leading from $A$ to $B$, and then it is not possible to modify at will and arbitrarily the difference $[s_l(T_0) - s_d(T_0, p_0)]$, because it is in factor of the variable term $\Delta q_l$ and any arbitrarily change in $s_l(T_0)$ or $s_d(T_0, p_0)$ would generate arbitrary changes in $\Delta s$ associated with $\Delta q_l$. This would be in contradiction with the second law of thermodynamics and the need to know precisely if the (moist-air) entropy decreases, increases or remain constant. It is therefore needed to rely on the third law of thermodynamics (applied at 0 K for the more stable crystalline states) and the absolute definitions of the entropies for dry-air and water species ($N_2$, $O_2$, $Ar$, $CO_2$, $H_2O$).

Another way to avoid arbitrarily canceling the reference entropies is to keep the terms depending on $q_t$ and the reference entropies in [16], [18] or [20] as they are, in order to define $\theta_l$ and $\theta_e$ without trying to make them synonymous with the specific entropy $s$.

This approach was chosen in Marquet and Stevens (2022), where $\theta_l$, $\theta_s$ and $\theta_e$ are defined (for ice-free conditions $q_t = q_{snow} = 0$) in a similar way without canceling any of the reference partial entropies. The new method is the one previously described in Stevens and Siebesma (2020, from a course with the same name given at MPI) for deriving both $\theta_l$ and $\theta_e$, but generalizes in Marquet and Stevens (2022) to the definition of $\theta_s$.

Stevens and Siebesma (2020, after Eq. 2.30) reinterpret entropy equations like [16] in the following way: “Given a completely specified reference state it provides an expression for the entropy. This was the sense in which it was derived. Alternatively, one can use this equation to ask what would the reference state temperature need to be, for the system in the reference state configuration (as specified through the pressure, amount and distribution of water mass) to have the same entropy as in the given state.”

Accordingly, the three equations

$$s(T, p, q_v, q_t) = c_{pe} \ln \left( \frac{\theta_e}{T_r} \right) + [ (1 - q_t) s_d(T_r, p_0) + q_t s_l(T_r) ] ,$$

$$s(T, p, q_v, q_t) = c_{pd} \ln \left( \frac{\theta_l}{T_r} \right) + [ (1 - q_t) s_d(T_r, p_0 - e_0) + q_t s_v(T_r, e_0) ] ,$$

and

$$s(T, p, q_v, q_t) = c_{pd} \ln \left( \frac{\theta_s}{T_r} \right) + [ s_d(T_r, p_0) ] = c_{pd} \ln \left( \frac{\theta_s}{T_0} \right) + [ s_d(T_0, p_0) ]$$

provide the new definitions:

$\theta_e$, $\theta_l$ and $\theta_s$ are the reference temperature $T_r$ for which the actual entropy $s(T, p, q_v, q_t)$ on the left-hand-sides of [56]-[58] is equal to the reference entropies into brackets on the right-hand-sides of [56]-[58].

These definitions avoid canceling any of the reference partial entropies $s_d(T_r, p_0)$, $s_d(T_r, p_0 - e_0)$, $s_v(T_r, e_0)$ or $s_l(T_r)$ for arbitrary values of $T_r$, as done in Libbarne and Godson (1973, 1981), Emanuel (1994), Pauluis et al. (2010) and others.

The peculiar feature valid for $\theta_s$ only is that the second part of [58] is also valid for $T_r$ replaced by the standard value $T_0 = 273.15$ K. This is simply due to the dry-air equation [30] and the corresponding property $s_d(T_0, p_0) - c_{pd} \ln (T_0) = s_d(T_r, p_0) - c_{pd} \ln (T_r)$, whatever $T_r$ may be. This is precisely why $\theta_s$ given by [15] is independent on any value of $T_r$. 

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The method of Stevens and Siebesma (2020) corresponding to (56)-(58) is used in Marquet and Stevens (2022) to define and compute the three potential temperatures, leading to

$$\theta_e = T \left( \frac{p_0}{p} \right)^{\kappa_e} \exp \left( \frac{q_v L_v}{c_{pe} T} \right) \Omega_e, \text{ where } \Omega_e = \left( \frac{R}{R_i} \right)^{\kappa_e} \left( \frac{H_i}{q_v R_e} \right)_{q_v R_e/c_{pe}},$$

(59)

$$\theta_{\ell} = T \left( \frac{p_0}{p} \right)^{\kappa_{\ell}} \exp \left( -\frac{q_l L_v}{c_{pd} T} \right) \Omega_{\ell}, \text{ where } \Omega_{\ell} = \left( \frac{R}{R_i} \right)^{\kappa_{\ell}} \left( \frac{q_l R_v}{q_v} \right)_{q_l R_v/c_{pd}},$$

(60)

$$\theta_s = \theta \exp \left( -\frac{q_l L_v}{c_{pd} T} + \Lambda_r q_l \right) \Omega_s, \text{ where } \Omega_s = \left( \frac{R}{R_i} \right)^{\kappa_s} \left( \frac{p - e}{p_0 - e_0} \right)_{q_l R_v/c_{pd}} \left( \frac{e_0}{e} \right)_{q_l R_v/c_{pd}} \left( \frac{T}{T_0} \right)_{q_l R_v/c_{pd}}^{\kappa_s},$$

(61)

and with $\theta = T \left( \frac{p_0}{p} \right)^{\kappa_s}$ the usual dry-air potential temperature.

The moist-air exponent terms appearing in (59)-(61) are $R = R_d (1 - q_t) + R_v q_v$ (i.e; the moist-air gas constant), $R_e = R_d (1 - q_t) + c_t q_t$, $c_{pe} = c_{pd} (1 - q_t) + c_t q_t$, $\kappa_e = R_e/c_{pe}$, $R_{\ell} = R_d (1 - q_t) + R_v q_t$, $c_{pd} = c_{pl} (1 - q_t) + c_{pw} q_t$ and $\kappa_{\ell} = R_{\ell}/c_{pd}$.

The hope is that the Omega terms ($\Omega_e$, $\Omega_{\ell}$, $\Omega_s$) in (59)-(61) may remain close to unity in all atmospheric conditions, with therefore the “first-order approximations” of $\theta_e$, $\theta_{\ell}$ and $\theta_s$ given by the other terms depending on $T$, ($p_0/p$) and the exponentials. In particular, we can recognize for $\theta_s$ in (61) the first line of (15) with $q_t = q_{snow} = 0$, this first line being interpreted as the “first-order approximation of $\theta_s$” hereafter.

Indeed, the vertical profiles of the FIRE-I (RF03B) observed radial flight studied in Marquet (2011) plotted between 0 and 1.5 km are shown in the Fig. (8) below, together with the vertical profiles plotted between 0 and 4 km in the Fig 1 of Marquet and Stevens (2022), which are the average for 757 drop-sounds observed during the EUREC 4A-Circle. It is possible to check with these vertical profiles that the dashed or dotted lines (first-order approximations) remain close to the solid lines (exact formulations), up to about 0.6 K for $\theta_e$ and $\theta_s$ and better than 0.1 K for $\theta_{\ell}$. Moreover, these differences are by far smaller than the differences between $\theta_{\ell}$, $\theta_s$ and $\theta_e$, this comforting the status of “first-order approximations”.

A rigorous method is described in Marquet (2015, 2019a) to derive not only the first-order approximation ($\theta_s)_1$, but also a second-order approximation ($\theta_s)_2$.

The relationship already suggested in Marquet (2011) is indeed a first-order approximation: it corresponds to the first line of (15)

$$\theta_s \approx (\theta_s)_1 = \theta \exp \left[ -\frac{L_v (q_t + q_{rain}) + L_s (q_t + q_{snow})}{c_{pd} T} \right] \exp(\Lambda_r q_t) \approx \theta_{il} \exp(\Lambda_r q_t),$$

(62)

where

$$\theta_{il} = \theta \exp \left[ -\frac{L_v (q_t + q_{rain}) + L_s (q_t + q_{snow})}{c_{pd} T} \right]$$

(63)

is close to the ice-liquid formulation of Tripoli and Cotton (1981), except the constant values $T_0$, $L_v(T_0)$ and $L_v(T_0)$ are replaced by the variable values $T$, $L_v(T)$ and $L_v(T)$ that depend on $T$ in the exponential of (63), and with the rain and snow contents added from (9). The second-order relationship derived in Marquet (2015, 2019a) corresponds to:
\[ \theta_s \approx (\theta_s)_2 = (\theta_s)_1 \exp \left[ -\gamma \, q_t \, \ln \left( \frac{r_v}{r_s} \right) - \gamma \, (q_t + q_{\text{rain}} + q_i + q_{\text{snow}}) \right], \quad (64) \]

where \( r_s \approx 12.4 \, \text{g/kg} \) is a tuning parameter.

The reference entropies are computed with the standard temperature \( T_r = T_0 = 273.15 \, \text{K} \) and pressures \( p_r = p_0 = 1000 \, \text{hPa} \) and \( e_r = e_{\text{sw}}(T_r) \approx 6.11 \, \text{hPa} \), with Eq. \( (36) \) and \( (37) \) leading to \( s_{dr}(T_r, p_r - e_r) \approx 6777 \, \text{J/K/kg}, \ s_{vr}(T_r, e_r) \approx 12673 \, \text{J/K/kg}, \ r_r = e_r / (p_r - e_r) \approx 3.8214 \, \text{g/kg} \), and \( q_r = r_r / (1 + r_r) \approx 3.8068 \, \text{g/kg} \).

These values of the dry air and water vapor reference entropies lead to

\[ \Lambda_r = \frac{s_{vr}(T_r, e_r) - s_{dr}(T_r, p_r - e_r)}{c_{pd}} \approx 5.869 \pm 0.003. \quad (65) \]

The accuracy of \( \Lambda_r \) can be computed from \( \Delta s_{vr} \approx 2 \, \text{J/K/kg} \) and \( \Delta s_{dr} \approx 1 \, \text{J/K/kg} \), leading to \( \Delta \Lambda_r \approx 3/1000 = 0.003 \).

Furthermore, for ice-free conditions \( (q_i = 0), \ \theta_s \) can be expressed in terms of the “conservative variables” \( (q_t, \theta_t \text{ and } \theta_e) \), according to

\[ \theta_{s1} \approx \theta_t \exp(\Lambda q_t) \approx \theta_e \exp \left[ -\left( \frac{L_v}{c_{pd} T} - \Lambda_r \right) q_t \right], \quad (66) \]

and thus \( \theta_{s1} \approx \theta_t \exp(6 \, q_t) \approx \theta_e \exp(-3 \, q_t) \quad (67) \)
because \( L_v / (c_{pd} T) \approx 9 \) and \( \Lambda_r \approx 6 \).

This result shows that \( \theta_s \) is different from both \( \theta_t \) and \( \theta_e \) if \( q_t \neq 0 \), and is in a two-third position in between these two variables, a property indeed valid in Fig. \( (8) \):

(i) for the FIRE-I (RF03B) observed radial flight \( \text{[Marquet, 2011]} \);
(ii) for drop-sounds observed during the EUREC \( 4 \) - Circle \( \text{[Marquet and Stevens, 2022]} \);
(iii) for \( (2.5 \, \text{km}) \) DYAMOND simulation outputs \( \text{[Marquet and Stevens, 2022]} \); and
(iv) for all studied undergone since December 2008 \( \text{(the date of the discovery of } \theta_s) \).

An important question is now to explain and justify the choices \( T_r = T_0 = 273.15 \, \text{K} \) and \( p_r = p_0 = 1000 \, \text{hPa} \) for the reference values equal to the standard values for temperature and pressure. Indeed, if \( \theta_s \) given by \( (15) \) is independent on any values of \( T_r \) and \( p_r \), both \( (\theta_s)_1 \) and \( (\theta_s)_2 \) given by \( (62) \) and \( (64) \) do depend on \( \Lambda_r \) given by \( (65) \), and thus on \( T_r \) and \( p_r \).

Fig. \( 2 \) shows that \( \Lambda(T_r, p_r) \) varies relatively little with the reference pressure \( p_r \). Also, why not choose the standard value \( p_r = p_0 = 1000 \, \text{hPa} \)? And among all the possible values of \( T_r \), the zero Celcius seems relevant since it represents a kind of average value according to the variations of \( T \). Also, why choose another value than \( 273.15 \, \text{K} \)?

Moreover, it is the product of \( \Lambda_r \) with \( q_t \) that influences \( \theta_s \), and therefore with a maximum impact in the lower layers and temperatures and pressures close to \( p_0 = 1000 \, \text{hPa} \) and \( T_0 = 273.15 \, \text{K} \).

In any case, if the aim is to go beyond the first order to the second order, the impact of humidity must be taken into account. Indeed, let us first define (without approximation) the more general variable \( \Lambda_s \) by the formula \( \theta_s = \theta_{il} \exp(\Lambda_s \, q_t) \), where \( \theta_{il}, \ q_t \) and \( \theta_s \) given by \( (15) \) are three known
Figure 2: An unpublished plot of $\Lambda(T_r, p_r)$ for $T_r$ from 220 K to 315 K and $p_r$ from 1000 hPa to 200 hPa. quantities, and thus with $\Lambda_s$ given by the reciprocal relationship valid for the liquid case (with $q_i = 0$ and $\theta_{il} = \theta_l$):

$$\Lambda_s(T, p, q_v, q_l) = \frac{1}{q_t \ln\left(\frac{\theta_s}{\theta_l}\right)}.$$  \hfill (68)

Fig. 3 (top) shows that, as a first guess, the term $\Lambda_s$ varies from about 5.7 to 7.6 for 16 vertical profiles of cumulus and stratocumulus (FIRE-I RF02/03/04/08/10, EPIC, DYCOMS-II, ARM-Cu, ASTEX, ATEX, GATE, BOMEX, SCMS-RF12). A detailed study indicates that $\Lambda_s$ is:
- smaller for the moister (solid-red) cumulus ($q_t$ and $q_v$ from 9 to 23 g/kg);
- larger for the moderate (dashed-blue) stratocumulus ($q_t$ and $q_v$ from 1 to 15 g/kg); and
- even larger for the dryer (solid-black) ASTEX case ($q_t$ and $q_v$ from 0.3 to 11 g/kg).
Figure 3: Top: an unpublished plot of $\Lambda(T_r, p_r)$ for $T_r$ from 220 K to 315 K and $p_r$ from 1000 hPa to 200 hPa. Bottom: a plot from Marquet (2019a) showing $\Lambda_s$ a function of $\ln(r_v)$. 

$\Lambda_s = \frac{\ln(\theta_s/\theta_t)}{q_t}$
As a consequence, we are encouraged to seek for a value of $\Lambda_s$ which would decrease with $q_t$ or $q_v$. To do so, according to the second-order formulations derived in [Marquet (2015)] and [Marquet (2019a)] and leading to (64), the dependence of $\Lambda_s$ with moisture variables could be of the form

$$\Lambda_s = \frac{1}{q_t} \ln \left( \frac{\theta_s}{\theta_l} \right) \approx \Lambda_r - \gamma \ln (r_v) - \gamma \frac{q_t}{q_t} + Cste,$$  

(69)

where $\Lambda_r = 5.87$ and $\gamma \approx 0.46$. Fig. 3 (bottom) clearly shows that, for the same 16 vertical profiles of cumulus and stratocumulus as in the top figure, the term $\Lambda_s$ indeed varies like $-\gamma \ln (r_v) = -0.46 \ln (r_v)$. This linear law appears to be valid for a large range of $r_v$ (from 0.2 to 24 g kg$^{-1}$).

This corresponds to a linear decrease of

$$\Lambda_s + \gamma \frac{q_t}{q_t} = \frac{1}{q_t} \left[ \ln \left( \frac{\theta_s}{\theta_l} \right) + \gamma q_t \right] \approx \Lambda_r - \gamma \ln \left( \frac{r_v}{r_*} \right),$$  

(70)

with $\ln (r_v)$, where the constant in (69) is written without loss of generality as $-\gamma \ln (r_*)$ in (70) in terms of a tuning parameter $r_*$ to be determined.

It is then possible to plot in Fig. 4 (top) the vertical profiles of this tuning parameter $r_*$ for the same 16 vertical profiles of cumulus and stratocumulus as in the Figs. 3 with $r_*$ obtained from (70) and written as

$$r_* \approx r_v \exp \left\{ \frac{1}{\gamma q_t} \left[ \ln \left( \frac{\theta_s}{\theta_l} \right) + \gamma q_t \right] - \frac{\Lambda_r}{\gamma} \right\}. \tag{71}$$

A first-guess value for $r_*$ derived in [Marquet (2015)] and [Marquet (2019a)] is $r_r \times \exp (1) \approx 3.82 \times 2.718 \approx 10.4$ g/kg.

According to the second-order formulation derived in [Marquet (2019a)], it is then possible to find the tuning mixing ratio $r_*$ for which hold true, where $r_*$ will play the role of positioning the dashed-dotted thick black line of slope $-\gamma \approx -0.46$ in between the cumulus and stratocumulus profiles. This corresponds to a linear fitting of $r_v$ against $\exp \left[ (\Lambda_r - \Lambda_s)/\gamma + \gamma q_t \right]$, $r_*$ being the average slope of the scattered data points. It is shown in Fig. 4 (top) that the value $r_* \approx 12.4$ g kg$^{-1}$ corresponds to a relevant fitting of all cumulus and stratocumulus vertical profiles for a range of $r_v$ from 0.2 up to 24 g kg$^{-1}$.

It is finally shown in Fig. 4 (bottom) that $\Lambda_s$ can indeed be approximated by $\Lambda_*(r_v, r_*)$ given by (69), with a clear improved accuracy in comparison with the constant value $\Lambda_r \approx 5.87$ for a range of $r_v$ between 0.2 and 24 g kg$^{-1}$. Curves of $\Lambda_*(r_v, r_*)$ with $r_* = 10.4$ and 12.4 g kg$^{-1}$ (solid black lines) both simulate with a good accuracy the non-linear variation of $\Lambda_s$ with $r_v$, and both simulate the rapid increase of $\Lambda_s$ for $r_v < 2$ g kg$^{-1}$.
Figure 4: Top: Bottom:
Figure 5: Top: Bottom:
All definitions of $\theta_s$/HH87 or $\theta_l$ by Hauf and Höller (1987), $\theta_e$ by Betts (1973) recalled in (16), (6).

Previously, the relationship (16) for $\theta_s$/HH87 is usually approximated by the first-order approximation $\theta_e$ of Betts (1973) given by (6). Similarly, $\theta_l$ defined by (21) is usually approximated by the first-order approximation of Betts (1973) given by (7).

By doing this, the first-order approximation neglects the impact of the ratio $e/e_0$ for $\theta_l$ defined by (21), and also the impact of the choice of $T_0$ and $e_0$ in the additional terms left outside the logarithms in (16) and (21), which depends on the reference values $s_d(T_0, p_0)$, $s_v(T_0, e_0)$ and $s_l(T_0)$.

The moist-air entropy variables $\theta_s$, $\theta_{s1}$ and $\theta_{s2}$ have been studied in several papers since 2011:

- for computing the moist-air Brunt-Väisälä frequency (Marquet and Geleyn, 2013);
- for computing and studying the associated Potential Vorticity $PV(\theta_s)$ (Marquet, 2014);
- in a synthetic chapter about moist-air thermodynamics (Marquet and Geleyn, 2015);
- for computing improved adjustment of marine bulk formulas (Marquet and Belamari, 2017);
- for computing the work- and stream-functions for the hurricane Dumilé (Marquet, 2017);
- to answers O. Pauluis’s criticisms with Hector-the-Convector (Marquet and Dauhut, 2018);
- to explain in French and English the third-law of thermodynamics (Marquet, 2019b,c);
- to improve a $\theta_s$-based E.I.S. in the IFS-ECMWF model (Marquet and Bechtold, 2020);
- to compare the H2O pathways with lines of constant $\theta_e$ or $\theta_s$ (Marquet and Bailey, 2021);
- to provide a common method to derive $\theta_l$, $\theta_e$ and $\theta_s$ (Marquet and Stevens, 2022);
- to use $\theta_s$ and $q_t$ in a 1D-Var assimilation scheme (Marquet et al., 2022).
5 Comparison of dry and moist-air potential temperature

All previous dry- and moist-air potential temperatures ($\theta'_w$, $\theta_v$, $\theta_l$, $\theta_{st}$, $\theta$, $\theta_s$, $\theta_e$, $\theta_{es}$ and $\theta'_e$) have been computed for a realistic updraft based on (a slightly modified version of) the vertical profile of the Hurricane “Season” described in Table 5 of [Jordan (1958)], with precipitating and entrainment processes and with liquid water, ice and mixed phases. Figs [6] shows that:

- a clear-air region extends from the surface up to about 820 hPa;
- a mixed-phase exists between about 500 hPa and 300 hPa;
- $\theta_l$ and $\theta_{st}$ (in orange) remain close to $\theta$ (dashed black), with differences (in the cloud region between 850 and 200 hPa) of the same order of magnitude than the difference between $\theta$ and $\theta_v$ (dashed grey);
- the four versions of $\theta_e$ (in blue) are not so different from each others (they all increases with height with discrepancies of less than 1 to 2 K);
- the vertical changes in $\theta'_w$ (in violet) and $\theta_e$ (in blue) are very different ($\theta'_w$ is almost conservative whereas the four $\theta_e$ increase with height);
- the first- and second-order approximations $\theta_{s1}$ and $\theta_{s2}$ (dashed and dotted-dashed red) remain very close to the exact version $\theta_s$ (solid red), up to less than 0.6 K for $\theta_{s1}$ and 0.05 K for $\theta_{s2}$;
- the entropy potential temperature $\theta_s$ (in red) is indeed in a two-third position in between $\theta$ or $\theta_l$ (dashed black or orange) and $\theta_e$ (in blue), and is significantly different from all the other potential temperatures;
- the saturated-equivalent temperature $\theta_{es}$ (in black) is very different from the four $\theta_e$ (in blue) in the unsaturated low-levels region below the cloud ($\theta_{es}$ is much larger by more than 50 K);
- the pseudo-adiabatic equivalent potential temperature $\theta'_e$ (in green) computed from Eqs. (10)-(12), which looks like $\theta'_w$ but with enhanced variations close to those of the (about 6 times) enhanced (dashed violet) vertical profile of $299.5 + 6 \times (\theta'_w - 299.5)$.

Figure 6: Vertical profiles for an updraft based on the Hurricane “Season” [Jordan (1958)]. Left: water vapor ($q_v$), liquid water ($10 \times q_l$) and ice ($10 \times q_i$) specific contents (in g/kg). Right: potential temperatures (in K).
After more than 30 years of work, and looking ahead to 2022:

→ The more general formulation for $\theta_s$ (Marquet, JAS, 2017):

$$
\theta_s = \theta \exp \left( - \frac{L_v q_t + L_s q_i}{c_{pd} T} \right) \exp [\Lambda_t q_t] \\
\times \left( \frac{T}{T_r} \right)^{\frac{\gamma}{\kappa} \frac{\theta_s q_i}{c_{pd}}} \left( \frac{T_r}{T} \right)^{\gamma - \frac{\kappa \theta_s q_i}{1 + \eta r_e^{\gamma} \delta q_i}} \\
\times \left( H_t \right)^{\gamma q_i} \left( H_i \right)^{q_i} \left( \frac{T_i}{T} \right)^{c_z q_i / c_{pd}} \left( \frac{T}{T} \right)^{c_z q_i / c_{pd}}
$$

→ With a relevant first-order formulation (Marquet, 2011, 2015, 2019) made by the first line only:

$$
\theta_{s1} = \theta \exp \left( - \frac{L_v q_t + L_s q_i}{c_{pd} T} \right) \exp [\Lambda_t q_t] \approx \theta \exp [\Lambda_t q_t]
$$

→ Impact of the Third Law:

$$\Lambda_r \approx 5.869 \pm 0.003$$

→ And with even more relevant simple formulations (if needed):

$$
\theta_s \approx \theta_{il} \times \exp (\theta \ g_t) \approx \theta \times (1 + \theta \ g_v)
$$

!! not used hereafter (just for pedagogy)

Figure 7: Two slides from Marquet (2022), where the main properties of the moist-air specific entropy $s = c_{pd} \ln(\theta_s) + s_0$, the associated potential temperature $\theta_s$ and the potential vorticity $PV(\theta_s)$ are summarized.
Figure 8: From Marquet (2022). Top: vertical profiles of potential temperatures from the Radial-Flight 03B of FIRE-I (Marquet, 2011). Bottom: vertical profiles of potential temperatures from dropsondes along the EUREC\textsuperscript{A}-Circle and from tropical simulated composite soundings (Marquet and Stevens, 2022).

→ $\theta_s$ was indeed in a 2/3 position between $\theta_l$ and $\theta_e$.
→ Only moist-air entropy ($\theta_s$) is well-mixed (constant) from the surface up to 1050 m including the entrainment region!

$\theta_l \approx \theta_l \times (1 + 0 q_t)$
$\theta_s \approx \theta_l \times (1 + 6 q_t)$
$\theta_e \approx \theta_l \times (1 + 9 q_t)$

Observations & Simulation: Marquet and Stevens (JAS 2022)

Average for 757 drop-sounds during the EUREC\textsuperscript{A}-Circle campaign

Stevens et al. (2021); George et al. (2021)

Figure 1: Mean profiles of the liquid water, $\theta_l$, entropy, $\theta_s$, equivalent $\theta_e$, potential temperatures from 757 dropsondes launched along the EUREC\textsuperscript{A}-Circle.

→ This implies that $\theta_s$ is in a 2/3 position between $\theta_l$ and $\theta_e$.
**Observations**: Marquet (La Météorologie, 2019a,b) Marquet and Stevens (JAS, 2022)

Figure 9: From Marquet (2022). **Top**: half of the ASTEX Lagrangien vertical profiles for $\theta_l$, $q_t$ and $\theta_s$ computed from the radio-sounding dataset for $T$, $q_v$, $q_l$ (Marquet, 2019b,c; Marquet and Stevens, 2022). The special property $\partial \theta_s / \partial p \approx 0$ at the transition between Stratocumulus and Cumulus regimes has been used to built a new Estimated-Inversion-Strength in the IFS model at ECWF (Marquet and Bechtold, 2020). **Bottom**: diagnostic outputs from the Meso-NH models (Ricard, 2018, unpublished), where the moist-air entropy (and $\theta_s$) entering the plumes of convective cells are more similar to mid-tropospheric values at 6 to 8 km (differently from colder PBL values for $\theta_l$ and warmer PBL values for $\theta_e$).
Figure 10: From Marquet (2022).

Top: the surface of equal values of $\theta$, $\theta_s$, and $\theta_e$ do not coincide in annual and zonal average, with a 2/3 position of $\theta_s$ in between $\theta$ and $\theta_e$ (unpublished result; from a 2019 course at the ENM / French School of Meteorology). Only $\theta_s$ represents the moist-air entropy and generates the true moist-air isentropes. One of the consequence is an impact on the definition of moist-air baroclinic waves in mid-latitudes (different slopes of “isentropic” surfaces).

Bottom: the $H_2O$ pathways originating from a certain band of latitude seems to preferentially follow the moist-air isentropes labeled with $\theta_s$ (Marquet and Bailey, 2021).

- Moist-air Entropy ($\theta_s$):
  - Dry stratosphere $\approx$ horizontal
  - Tropics: more homogeneous ... $\approx$ an “isentrope” region!
  - Baroclines: a 2/3 position for $\theta_s$!

- Have these differences in $\theta_s$ any meteorological impact?
- Especially in moist low levels?

Figure 2: The moisture plane evaporating from the latitude band 30°S to 30°S with the isentropes computed using either $\theta$, (solid lines) or with the new absolute moist-air entropy potential temperature $\theta_s$ (dashed lines).
Figure 11: From Marquet (2022). Top: It is possible to plot air-mass charts (here at 850 hPa) by replacing the pseudo-adiabatic variable \( \theta'_w \) (or \( \theta_e \)) by the moist-air entropy variable \( \theta_s \) (Blot, 2013). It is just necessary to change the color scale. Bottom: Vertical cross-sections published in Marquet (2014) showing how a front can be described with the variables \( \theta, \theta'_w, \theta_s \) and \( \theta_e \). The moist-air entropy variable \( \theta_s \) allows a better view of the air masses in the lower layers in relation to the frontal surfaces, with a boundary layer that is better mixed (homogeneous) in \( \theta_s \), and with the convective regions associated with some sort of “aspiration of moist-air isentropes”.

\[ \theta_s \approx \theta \times (1 + 6 q_v) \]

\[ \theta_e \approx \theta \times (1 + 9 q_v) \]
Figure 12: From Marquet (2022) and BLOT (2013). Top: the structure of a split cold front can be represented by the moist-air entropy variable $\theta_s$, as relevant as with the $\theta'_w$ variable. Bottom: the same is true for a squall-line line, which is clearly visible in terms of $\theta_s$, with the convective regions associated with some sort of "aspiration of moist-air isentropes".
Figure 13: From Marquet (2022) and Blot (2013). Top: the structure of a hurricane (here Dumilé, simulated by the Aladin 8 km model) can be equally represented by the pseudo-adiabatic variables $\theta_w'$ and $\theta_e$ (thanks to different color scales). Bottom: the moist-air entropy variable $\theta_s$ is as relevant as $\theta_w'$ and $\theta_s$ variable to see the core, the eye-walls and the spiral bands, with more homogeneous boundary layers and with the convective regions associated with some sort of “aspiration of mid-troposphere moist-air isentropes” labeled with $\theta_s$.

- Eye-walls (solid black lines) + Spiral bands (dashed black lines) plotted from a cross-section for RH (not shown)

- Almost the « same visions » for $\theta_w'$ & $\theta_e$

- A severe test for the entropy ($\theta_s$), because the more intense/moist atmospheric phenomena!

- Eye-walls (solid black) and spiral bands (dashed black) lines are clearly visible with the entropy ($\theta_s$)

- … like an "aspiration" of the (true) isentropes ($\theta_s$)

- No more “warm region” close to the surface with $\theta_s$

- (better) well-mixed (constant) $\theta_s$ in the boundary layer

$\theta_s \approx \theta \times (1 + 0.6 q_v)$
Figure 14: From Marquet (2022). **Top:** The surface fronts for the storm “Barra” are clearly located with the MSLP simulated with the Arome 1.3 km model. **Bottom:** The cross-sections at 46 N allow the plot of cold (solid blue) and warm (solid red) fronts up to 700 to 400 hPa.
Figure 15: From [Marquet (2022)]. **Top:** The cold (solid blue) and warm (solid red) fronts seems to be better associated with “air masses” labeled with the moist-air entropy variable $\theta_s$ for the cross section at 46 N (no more marked minimum at 850 or 800 hPa as for $\theta'_w$). This result is valid for the Arome 1.3 km model and the Arpege 8 km models as well. **Bottom:** The same is true for the cross section at 45 N.
Figure 16: From Marquet (2022). Historical examples justifying the plot of fronts with limited vertical extension on the previous cross-sections.
6 The dry- and moist-air potential vorticity formulations $PV(\theta)$

The original formulation of “potential vorticity” by [Ertel 1942a]

$$PV(\psi) = \frac{1}{\rho} \, \zeta_a \cdot \nabla(\psi) \tag{72}$$

was suitable for any “hydrodynamical invariant” (i.e. “conservative variable”) $\psi$, with $\rho$ the density, $\zeta_a$ the 3D absolute vorticity vector and $\nabla$ the 3D gradient operator (see the English translations of all Ertel’s papers in [Schubert et al. 2004]).

Ertel suggested different kinds of such “conservative variable” $\psi$:

- the “polytropic temperature under polytropic conditions” (for which the solenoidal term $N(p, \rho, \psi)$ cancels out), and thus the (dry-air) “potential temperature” $\psi = \theta$, or the “total water content” $\psi = q_t = q_v + q_l + q_i$ under conditions of no precipitation and without moisture input (Ertel, 1942a);
- the (dry-air) potential temperature $\psi = \theta$, i.e. a special case of the polytropic temperature $\psi = \Theta_x$ with $\Theta_x = T(p_0/\rho)^{1/x}$ and with $x = c_v/(c_p - c_v)$ (Ertel, 1942b);
- the (dry-air) polytropic temperature or the (dry-air) entropy $\psi = s_d$ (Ertel, 1942c), due to the Bauer (1908, 1910) relationship $s_d = c_{pd} \ln(\theta) + \text{cste}$, and thus with $PV(s_d) = PV[c_{pd} \ln(\theta)] = (c_{pd}/\theta) \, PV(\theta)$ indeed proportional to $PV(\theta)$.

After Ertel’s papers, different dry- and moist-air “(more or less) conservative” quantities have been studied:

- $PV(\theta)$ in [Hoskins and Bretherton 1972; Hoskins 1974; Hoskins et al. 1985], [Hoskins and Berrisford 1988; Hoskins 1991, 1997; Hoskins et al. 2003], (...) [Hoskins 2015];
- $PV(\theta'w)$ in [Bennetts and Hoskins 1979];
- $PV(\theta_e)$ in [Rotunno and Klemp 1985], [Cao and Cho 1995], [Persson 1995], [Gao et al. 2002], [Deng and Gao 2009];
- $PV(\theta_{es})$ in [Emanuel et al. 1987];
- $PV(\theta_s)$ in [Rivas Soriano and García Díez 1997] / for $\theta_s$ defined in [Hauf and Höller 1987];
- $PV(\theta_e)$ in [Schubert et al. 2001] and [Schubert 2004];
- $PV(q_v), PV(\theta)$ and $PV(\theta_e)$ in [Gao and Zhou 2008];
- $PV(\theta_s), PV(\theta_v)$ and $PV(q_t)$ in [Marquet 2014] / for $\theta_s$ defined in [Marquet 2011].
Comparison of dry and moist-air Potential Vorticity

Figure 17: From Marquet (2022). **Top:** It is recalled in this figure of R.A. Houze that regions with negative values of $PV(\theta_e)$ are associated with symmetric instability and slantwise convection. The first-order formulations for $PV(\theta_s)$ and $PV(\theta_e)$ show that the impact of the moisture part $PV(q_v)$ in $PV(\theta_s)$ is about $2/3$ of the moisture part in $PV(\theta_e)$. **Bottom** (from Marquet, 2014): Average low-level values seems too positive for $PV(\theta) \approx PV(\theta_v)$, too negative for $PV(\theta_e)$ and well-balanced for $PV(\theta_s)$. 
Figure 18: From Marquet (2022) and Marquet (2014). Top: the low-level (850 hPa) cold fronts seems to be associated with the negative values of $\text{PV}(\theta_s)$, whereas PV($\theta$) is positive everywhere and PV($\theta_e$) negative almost everywhere. Bottom: the negative values of PV($\theta$) seems clearly correspond to (are located with) the cold fronts in these cross-sections (same fronts as in Fig. 11), and possibly to symmetric instability and slantwise convection. On the one hand there is no negative values for PV($\theta$), whereas on the other hand there are negative values of PV($\theta_e$) almost everywhere in the low-level boundary layer.
Figure 19: From Marquet (2022). Top: The potential vorticity $PV(\theta)$ and $PV(\theta_s)$ for the storm “Barra” simulated with the global Arpege NWP (8 km) model (cross-sections at 46 N). Some negative values of the moist-air entropy variable $PV(\theta_s)$ appears close to the cold front (they already exist and are the same between the warm fronts), with almost unchanged upper-levels dynamic-meteorology signals above 500 hPa in the dry regions (tropospheric intrusion of high stratospheric values). Bottom: The same is true for the Arome 1.3 km (NH) model.
Conclusions

This note is a mere synthesis of the most important results I have discovered since 2009, with the aim to mainly show Figures instead of formulas (which can be found in my papers published since 2011 and available on arXiv).

However, I am now I am in retirement (since May, 2022) from the CNRM and Météo-France, and I am preparing a (huge) book showing in detail why it is needed, and how it is possible to defined and compute the third-law (absolute) definitions of not only the moist-air entropy for the atmosphere, but also the sea-salt entropy for the ocean.

In this book I will recall (and show) almost all the bibliography I have studied since 1988 about the atmosphere and ocean thermodynamics (even though many of them, but not all of them, have been recalled in my papers published between 2011 and 2022).
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