On the use of the mixed-phase entropy potential temperature based on the Third law to understand moist atmospheric processes.

by Pascal Marquet (Météo-France/CNRM/GMAP)

GABLS4 Workshop (13 September 2018)

Outline

- 1) Motivations: the Third Law? (my papers from 2011)
- 2) The 3rd-Law moist-air entropy potential temperature θ_s
- 3) Impact for warm-clouds (FIRE-I, EUCLIPSE Sc $\rightarrow$ Cu)
- 4) Impacts for mixed-phase Polar clouds (M-PACE, SHEBA)
- 5) Impacts of the Lewis Number ?
- 6) Conclusions - Perspectives

Motivations: *what is the problem?*

- A fact: it is interesting to compute the moist-air entropy ($\boldsymbol{S}$)
- simply because it is one of the 4 basic quantities ($\boldsymbol{T}$, $\boldsymbol{U}$, $\boldsymbol{H}$, $\boldsymbol{S}$)
- So what's the problem with computing the moist-air entropy?

- A simple case: a parcel of moist but clear air with $\boldsymbol{q_d}$ **of dry air** and $\boldsymbol{q_v}$ **of water vapour** (specific contents $\boldsymbol{q_d + q_v = 1}$).
- The weighted sum of the specific entropies: $\boldsymbol{s = q_d\, s_d + q_v\, s_v}$

with $\quad s_d = c_{pd} \ln(T/T_0) + R_d \ln(p_d/p_0) + s_d^0$

and $\quad s_v = c_{pv} \ln(T/T_0) + R_v \ln(e/p_0) + s_v^0$

$$s = c_p \ln(T/T_0) + q_d\, R_d \ln(p_d/p_0) + q_v R_v \ln(e/p_0) + \left[\boldsymbol{q_d\, s_d^0 + q_v\, s_v^0}\right]$$

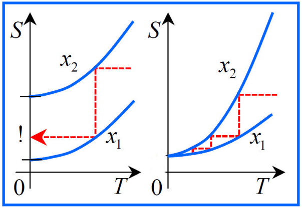
- The problem: terms in red are not constant if q_d and $q_v = 1 - q_d$ are not constant. Thus *both* $\boldsymbol{s_d^0}$ *and* $\boldsymbol{s_v^0}$ *must be determined*.
  Question: **arbitrary choices? or physically based ones?**

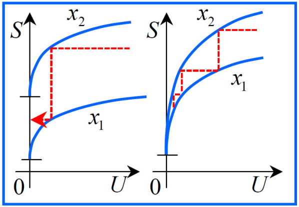
Motivations: *this is an old question!*

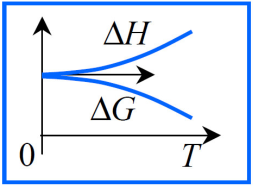
- **Massieu** (1869-76-77): "fonctions caractéristiques" $\psi = S - U/T$ and $\psi' = S - H/T$; values of $(U - U_0)/T$ and $(H - H_0)/T$?
- **Gibbs** (1875, with credit to Massieu): free energy $\psi = U - T\,S$ and the free enthalpy $\zeta = H - T\,S$; values of $T\,(S - S_0)$?
- **Le Chatelier** (1888): which is the impact of the **constant of integration** for the entropy "$S = S_0 + \ldots$" in the equilibrium of chemical reactions? (like s_d^0 and s_v^0 for computing the moist-air entropy. . .)

Motivations: *there is a physical solution!*

- **Nernst** (1906): impact of the **constant of integration** of the Helmholtz function $\boxed{A = \Delta H + T\, dA/dT = \Delta G}$ (maximum Available work / "maximale Arbeit"). Nernst's 1906 theorem: $[\,\Delta G \rightarrow \Delta H\,]$ and $[\,dA/dT \rightarrow A(T_0)/T_0 \rightarrow 0\,]$ as $T_0 \rightarrow 0$ K.







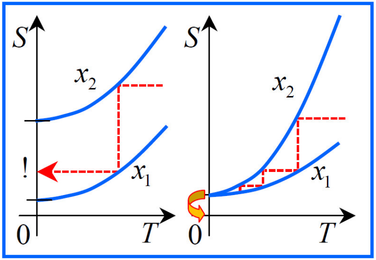
1st Solvay congress (1911) by Nernst + Einstein -> Nernst (1912): $C \propto T^3 \;\Rightarrow\; U \propto T^4$ and $S \propto T^3 \;\Rightarrow\; S \propto U^{3/4}$ / It is impossible to reach 0 K in a finite number of step and in a finite lapse of time (the principle of unattainability of $T = 0$ K; "*Unerreichbarkeit des absoluten Nullpunktes*")

Motivations: *the "Third Law" of thermodynamics?*

Planck (1911, 1917):

- 1) The entropy $S(T)$ tends to the **same universal value S_0** for the more stable form of all solids when $T \to 0$ K
- 2) It is possible to set $S_0 = 0$ without loss of generality
- 3) And this applies to the Boltzmann (Planck, 1900-1901) entropy: $\boxed{S = k \log(W)} + (S_0 = 0)$

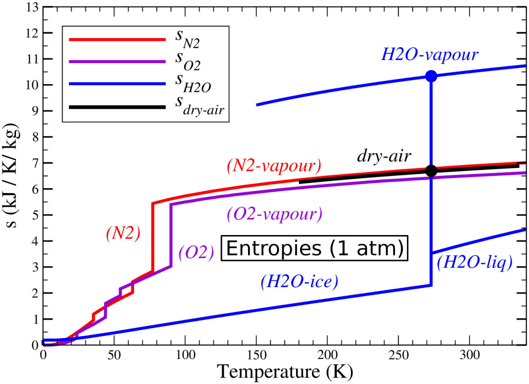
- Planck (1917): "The theorem has received abundant confirmation and may now be regarded as well established"
- And indeed: in agreement with all chemical reactions, otherwise possibly in the wrong direction!



The 3rd Law reference entropies (Marquet QJ-2015 / JAS-2017)

Entropy at (T_0, p_0) : *(1) calorimetry*

$$S(T_0, p_0) \;=\; \int_0^{T_0} \frac{C_p(T)}{T}\, dT \;+\; \sum_k \frac{L(T_k)}{T_k} \;+\; S(T\!=\!0, p_0) = 0 \qquad (1)$$



The 3rd Law reference entropies (Marquet JAS-2017)

Entropy at (T_0, p_0) : (1) calorimetry ; (2) Stat.-Phys. + Q.M.

(1) $$S(T_0,p_0) = \int_0^{T_0} \frac{C_p(T)}{T}\,dT + \sum_k \frac{L(T_k)}{T_k} + S(T=0,p_0)=0$$

(2) $$S(T_0,p_0) = R\left(\frac{\partial}{\partial T}\left[\,T\,\ln(Z)\,\right]_V\right)_{T_0} + S(T=0,p_0)=0$$; Z = partition fonction

Very good comparisons between theoretical and experimental values!

	C98/Sat.	GR96/Stat.	GR96/Cal.	M15/Cal.
Ar	37.000 ± 0.001	37.00	36.96 ± 0.2	
O_2	49.031 ± 0.008	49.02	49.12 ± 0.1	49.7 ± 0.4
N_2	45.796 ± 0.005	45.78	45.94 ± 0.2	46.0 ± 0.2
H_2O	45.132 ± 0.010	45.12	44.31	45.2 ± 0.1
CO_2	51.098 ± 0.029	51.09	51.13 ± 0.1	

C98 : Chase (1998) ; GR96 : Gokcen and Reddy (1996) ; M15 : Marquet (2015)
... Stat.Phys. values already available in Kelley (1932)
and Gordon and Barnes (1932, 1934, 1935)!

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The Third Law in Meteorology?

- **Richardson (book 1922)**: citations to Nernst's works, but cryogenic measurements not yet available, with the arbitrary choice $s = 0$ **at 180 K**, although: "*approximation are not here permissible*" ...
- **Hauf & Höller (JAS 1987)**: the first relevant computations of the moist-air entropy with $s_d^0 = 6775$ J/K/kg and $s_v^0 = 10320$ J/K/kg. However with a potential temperature θ_S that does not vary as the entropy expressed by $s = c_p^* \ln(\theta_S) + s^*$, since both c_p^* and s^* depend on the **varying** q_t ...
- **Marquet (QJ 1993)**: same issue as in Hauf & Höller (1987), though with a potential temperature θ^* better symmetrized in terms of (q_l, q_i) ...
- **Marquet (QJ 2011)**: a potential temperature θ_s valid for all case, even with varying q_t with $s = c_{pd} \ln(\theta_s) + s_{ref}$ and c_{pd} and s_{ref} constant
- **Rossby (1932), Normand (1921), Betts (1973), Tripoli and Cotton (1981), Emanuel (1994), Pauluis (2010)**: arbitrary zero entropies set at **273.15 ≠ 0 K** plus c_p^* and s^* $\Rightarrow$ θ_l, θ_{il} and $\theta_e \neq$ moist entropy ...

The moist-air entropy potential temperature θ_s?

The moist-air entropy is written in terms of a potential temperature :

- $\boxed{s = c_{pd}\ ln(\theta_s) + Cste}$ + 3rd Law / Marquet (2011 ... 2018)

$$\boxed{\theta_s} = \overbrace{\boxed{\theta\ \exp\left(-\frac{L_v\,q_l + L_s\,q_i}{c_{pd}\ T}\right)}}^{\approx\ \theta_{il}\ \text{(TC80) or}\ \approx\ \theta_l\ \text{(B73)}}\ \overbrace{\boxed{\exp(\Lambda_r\ q_t)}}^{\text{(varying } q_t \text{ "open")}}\ \left(\frac{T}{T_r}\right)^{\lambda\,q_t}\left(\frac{p}{p_r}\right)^{-\kappa\,\delta\,q_t}\left(\frac{r_r}{r_v}\right)^{\gamma\,q_t}$$

$$\frac{(1+\eta\,r_v)^{\kappa\,(1+\,\delta\,q_t)}}{(1+\eta\,r_r)^{\kappa\,\delta\,q_t}}\ \underbrace{(H_l)^{\gamma\,q_l}\ \ (H_i)^{\gamma\,q_i}}_{\text{mixed phases}}\ \underbrace{\left(\frac{T_l}{T}\right)^{(c_l\,q_l)/c_{pd}}\ \left(\frac{T_i}{T}\right)^{(c_i\,q_i)/c_{pd}}}_{\text{precip. at } T_l \neq T \text{ and/or } T_i \neq T}$$

- The boxed terms are the leading order ones; *other (black) ones are smaller...*
- Includes the Betts' potential temperature θ_l or TC80 liquid-ice value θ_{il} (in red)
- with a new factor $\boxed{\exp(\Lambda_r\ q_t)}$ depending on $\Lambda_r \approx 6$ (given by the Third law)
- Thus: θ_s is **conserved** for **isentropic** processes, **even if** q_t **is varying!**
  and θ_s is a special combination and generalisation of θ_{il} and q_t

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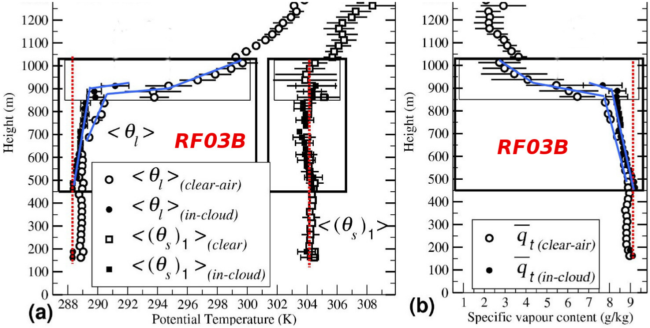
Entropy $s(\theta_s)$ in marine Sc (Marquet QJRMS 2011)



Observations FIRE-I

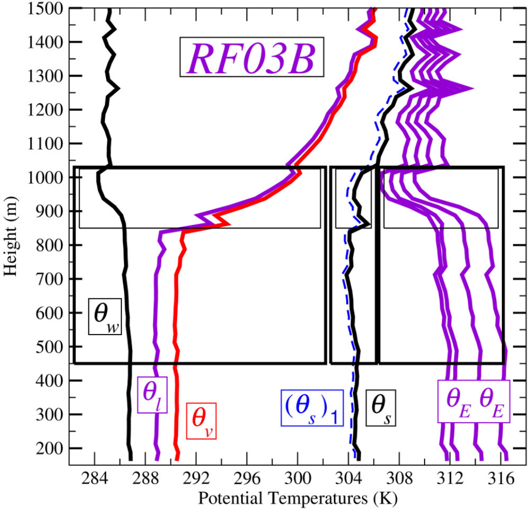
Radial-Flight RF03 (+02 04 08 10) raw datasets

- **Only θ_s is conserved!**

- The "conservative" Bett's variables (1973) (θ_l, q_t) are not-conserved;
- θ_l and q_t vary with height, are different within • and outside ○ clouds;
- large top-PBL jumps at the inversion ($\Delta\theta_l \approx 10$ K and $\Delta q_t \approx -5.5$ g/kg)

- Differently θ_s (entropy) almost constant along z (within error-bars), and for both cloud • and clear-air ○ values, and almost no top-PBL jumps!
- **⇒ a need to use θ_s in the turbulence! (Richardson, 1919)**

Entropy in marine Sc (Marquet QJRMS 2011)



$$s = c_{pd} \ln(\theta_s) + Cste$$

$\rightarrow \theta_l \approx \theta \ \exp(-9 \, q_l)$

$$\boldsymbol{\theta_{s1} \approx \theta_l \ \exp(6 \, q_t)}$$

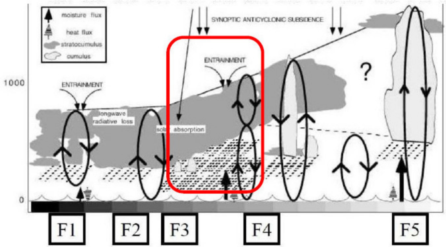
$\rightarrow \theta_e \approx \theta_l \ \exp(9 \, q_t)$

θ'_w and θ_e not constant:
$\searrow$ with z in the PBL;
<0 jumps at inversion

Moist turbulence Paradigm:

Richardson (1919) : *turbulence intends to homogenize the moist-air entropy*, and thus θ_s (thus neither θ_{il} nor θ_e): confirmed!

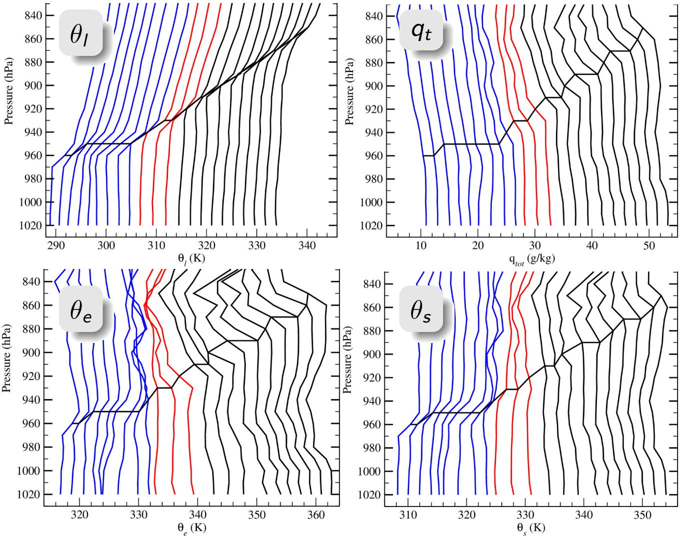
Transition Sc->Cu?



ASTEX-Lag. (43 RS ; Bretherton 1995)

- F1→F3 = St-Sc / F4→F5 = Cumulus
  F3↔F4 = Sc->Cu (box)
- different regimes based on some "CTEI" criteria and some threshold for either $\Delta\theta_e$ or $\Delta\theta_l$?

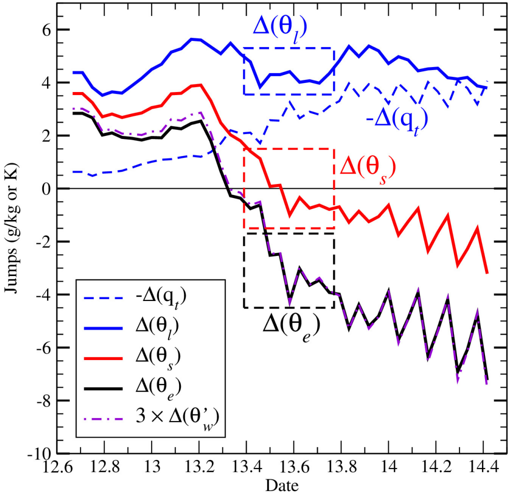
Transition Sc-> Cu: ASTEX-Lag1



22 vertical profiles

- 43 soundings forming the ASTEX-lagrangian transect (Bretherton and Pincus 95, Roode and Duynkerke 97)
- Only half of the soundings, with a shift of 2 K between these soundings
- A transition (in red) difficult to guess or understand with either θ_l and θ_e...
- whereas the transition is easily seen "by eye" with the "truly vertical" medium red plotted profile of θ_s!

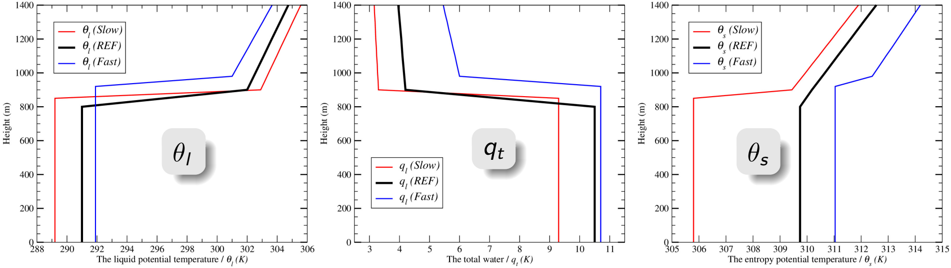
Transition Sc-> Cu: ASTEX-Lag1



Top-PBL jumps

- Jumps computed for the 43 soundings forming the ASTEX-lagrangian transect (Bretherton and Pincus 95, Roode and Duynkerke 97)
- The dashed boxes correspond to the known Sc/Cu (F3/F4) transition
- The (positive) threshold for $\Delta(\theta_l)$ cannot be really determined: does it exist?
- The (negative) thresholds for $\Delta(\theta_e)$ and for $3\,\Delta(\theta'_w)$ are about -3 K ...
- The curve for $\Delta(\theta_s)$ is, as expected, in a $9/6 = 2/3$ position between the curves for $\Delta(\theta_l)$ and $\Delta(\theta_e)$, ...
- ... and the threshold for $\Delta(\theta_s)$ is simply close to 0!

The EUCLIPSE “Slow/Ref/Fast” cases



Improvements for LES/CRM/SCM if vertical profiles of θ_s are considered?

- Large positive jump in θ_s for the “Slow” case: a relevant “very stable” case
- The zero jump in θ_s for the “Ref” case: a relevant “neutral” case
- Differently, positive jump in θ_s for the “fast” case: likely too “stable”?
- It would have been more relevant to ensure a more gradual sequence, like:
  [large positive / small positive / zero] jumps?
  or [positive / neutral / negative] jumps?
- The same for the Forcings: switch from advection for (θ_{il}, q_t) to those for (θ_s, q_t)?

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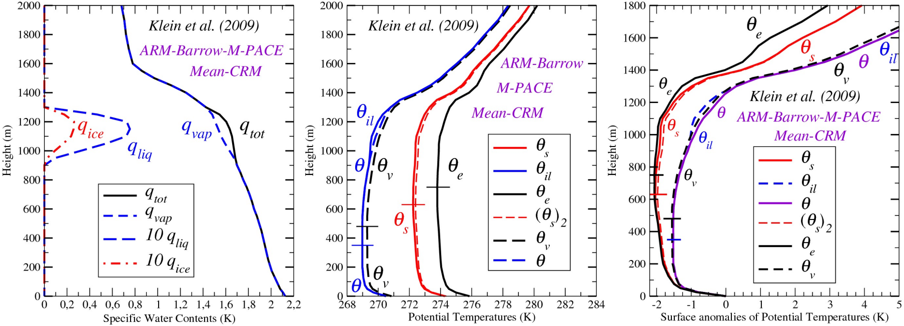
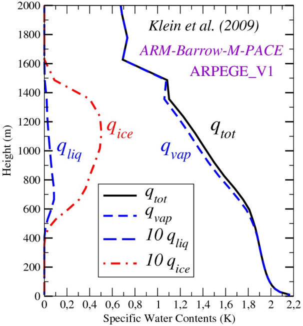
Klein *et al.* (2009) ARM/MPACE-B: the mean-CRM vertical profiles

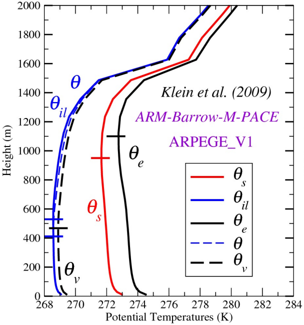


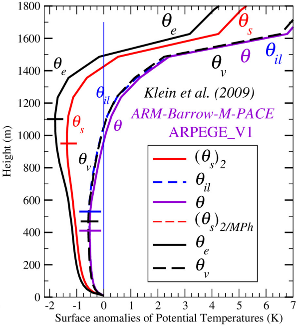
- $\theta_{il} = \theta \approx \theta_v$ conserved below the cloud: the impact of the parameterised turbulence?

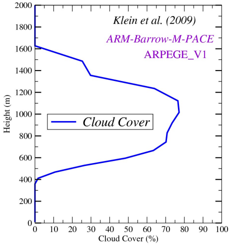
- The moist-air entropy and θ_s is in a 2/3 position in between θ_{il} and θ_e (like FIRE-I)
- The moist-air entropy and θ_s better conserved in the cloud
- An hypothesis: is θ_s to be well-mixed by the turbulence? (like FIRE-I, Richardson 1919)
- If so: possible different mean profiles for T, q_v, q_l, q_i?

ARM/MPACE-B: the ARPEGE-NWP SCM (MUSC) vertical profiles



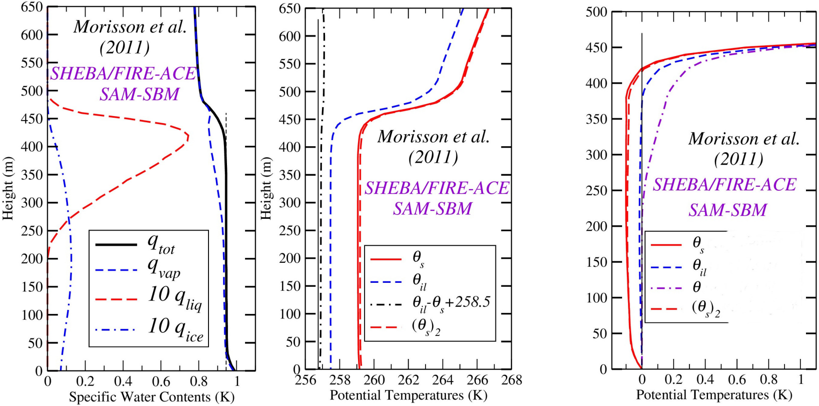






- The SCM cloud is thicker than for the CRM
- q_i larger and q_l smaller than for the CRM (impact of micro-phys.)
- A tiny impact of the mixed-phase terms $(H_l)^{\gamma\, q_l}$ and $(H_i)^{\gamma\, q_i}$:
  the red curves $(\theta_s)_2$ and $(\theta_s)_{2/MPh}$ superimposed!
- The same hypothesis: is θ_s to be well-mixed by the turbulence?
  with possible different mean profiles for T, q_v, q_l, q_i ...

Morisson *et al.* (2011): the FIRE-ACE SHEBA vertical profiles



Differences / similarities in comparison with the ARM/M-PACE-B case?

- Values of q_t and changes in q_t are smaller: leading to smaller impacts for θ_s
- The same well-mixed feature for θ_{il} in the BL, though θ_s with vertical gradients
- Not imposed by the actual turbulence scheme? (because SAM-SBM = "2D LES")
- Impacts of the forcings? balance of ω versus $\partial T/\partial t$ and $\partial q_v/\partial t$?

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Why studying the Lewis-number?

According to Richardson (1919), turbulence is acting on: $s(\theta_s)$, (u, v), q_t...

- $\overline{w' q_t'} \approx -K_w \dfrac{\partial \overline{q_t}}{\partial z}$ with $\overline{w' \theta_s'} \approx -K_s \dfrac{\partial \overline{\theta_s}}{\partial z}$ instead of $\overline{w' \theta_l'} \approx -K_h \dfrac{\partial \overline{\theta_l}}{\partial z}$?
- The use of $\overline{w' \theta_s'}$ leads to $\boldsymbol{\overline{w' \theta_l'} \approx -K_s \dfrac{\partial \overline{\theta_l}}{\partial z}} - \boldsymbol{(K_s - K_w)\, \Lambda_r\, \overline{\theta_l}\, \dfrac{\partial \overline{q_t}}{\partial z}}$
- If $K_s = K_h = K_w$, or equivalently $Le_t = K_h/K_w = 1$ or $Le_{ts} = K_s/K_w = 1$: the same as usual (ARPEGE / AROME / Monin-Obukov . . .)
- But a new (bold-red) term if $K_s \neq K_w$ or $K_h \neq K_w$, i.e. if $Le_t \neq 1$ or $Le_{ts} \neq 1$
- A counter-gradient (or over-gradient) expected term for the Betts variable θ_l!
- But with no counter-gradient term for the moist-air entropy θ_s!

Why studying the Lewis-number?

- Computation of the buoyancy flux: (e.x. thermal production in TKE prog. Equ.)

$$\overline{w'\theta'_v} \approx - K_w \left[\frac{\partial \overline{\theta_v}}{\partial z} + (\text{Le}_{ts} - 1) \frac{\partial \overline{\theta_s}}{\partial z} \right]$$

$$\overline{w'\theta'_v} \approx - K_w \left[\text{Le}_{ts} \frac{\partial \overline{\theta_s}}{\partial z} - 5.4 \; \overline{\theta} \; \frac{\partial \overline{q_v}}{\partial z} \right]$$

- with the two limit cases:

$$\boxed{\overline{w'\theta'_v} \approx - K_w \left[\frac{\partial \overline{\theta_v}}{\partial z} \right]} \quad \text{if Le}_{ts} \approx 1$$

$$\boxed{\overline{w'\theta'_v} \approx K_w \left[5.4 \; \overline{\theta} \; \frac{\partial \overline{q_v}}{\partial z} \right]} \quad \text{if Le}_{ts} \approx 0$$

- The second case would prevent the interpretation of the vertical gradients of θ_v as “stable” versus ‘instable” features, or “source” versus “sinks” of turbulence?
- The case $\text{Le}_{ts} \approx 0$ would imply a control of the turbulence by $\partial \overline{q_v} / \partial z$ only?

So, what about the hypothesis $Le_t = K_h/K_w \equiv 1$?

Dyer (1967) is one of the paradigm of $Le_t = K_h/K_w \equiv 1$

- What about the hypothesis: $\boxed{Le_t = K_h/K_w = 1}$?

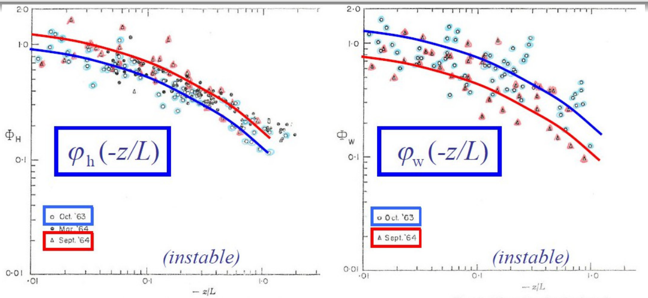


Figure 1. Values of ϕ_H plotted against z/L.

Figure 2. Values of ϕ_W plotted against z/L.

$$\frac{\partial \theta}{\partial z} = -\frac{H}{\rho c_p \, k u_* \, z} \phi_H$$

$$\frac{\partial q}{\partial z} = -\frac{E}{\rho L_W \, k u_* \, z} \phi_W$$

Dyer (QJRMS, 1967) : the paradigm of $\varphi_h \approx \varphi_w$?

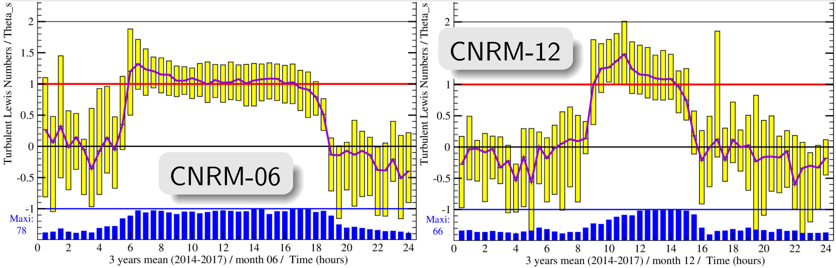
… in fact: a mixing of two different monthes with

$\varphi_h \neq \varphi_w$? ➔ $K_h \neq K_w$? ➔ $Le \neq 1$?

Lewis-number from observations: CNRM-Météopole-Flux?

Météopole-Flux / 3 years 2014-2017 (Marquet-Canut-Maurel WGNE 2015)

- What about the hypothesis: $\boxed{Le_{ts} = K_s/K_w = 1}$?



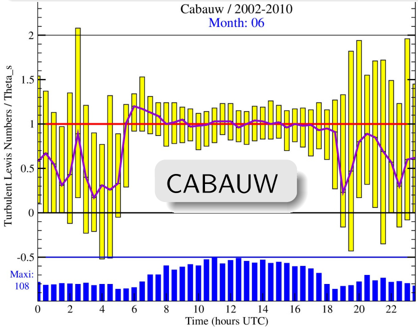
- $\boxed{Le_{ts} > 1}$ at daytime (unstable cases) $\boxed{Le_{ts} < 1}$ at night (stable cases)
- $\boxed{Le_{ts} = K_s/K_w \approx 0}$ means $\left(\overline{w'\theta'_v}\right)_{\mathrm{Le}_{ts}=0} \approx + K_w \; (\, 5.4 \;\, \overline{\theta}\,) \; \dfrac{\partial \overline{q_v}}{\partial z}$!

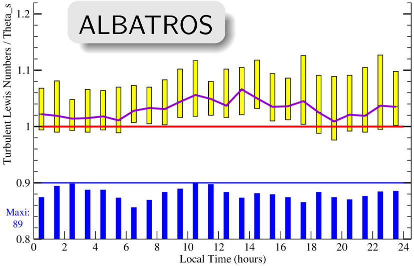
namely a control of buoyancy fluxes by gradients of q_t only...

Lewis-number from observations: Cabauw / Albatros?

Cabauw/KNMI and Albatros (ocean)

- What about the hypothesis: $\boxed{Le_{ts} = K_s / K_w = 1}$?



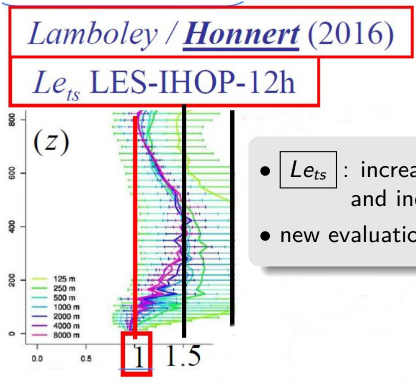


- $\boxed{Le_{ts} > 1}$ at daytime (unstable cases) $\boxed{Le_{ts} < 1}$ at night (stable cases)

Lewis-number from LES: IHOP (Honnert-Marquet)

The vertical profile of the Lewis-number?

- What about the hypothesis: $\boxed{Le_{ts} = K_s / K_w = 1}$?



- $\boxed{Le_{ts}}$: increasing with height from 1 to more than 1.5 and independent on the averaging scales!
- new evaluations of $\boxed{Le_{ts}(z)}$ to come during HIGH-Tune

Outline

- 1) Motivations: the Third Law? (my papers from 2011)
- 2) The 3rd-Law moist-air entropy potential temperature θ_s
- 3) Impact for warm-clouds (FIRE-I, EUCLIPSE Sc $\rightarrow$ Cu)
- 4) Impacts for mixed-phase Polar clouds (M-PACE, SHEBA)
- 5) Impacts of the Lewis Number ?
- **6) Conclusions - Perspectives**

Conclusions ?

- It is possible to compute a potential temperature $\boldsymbol{\theta_s}$ which fully represents the moist-air entropy $\boldsymbol{s = c_{pd}\ \ln(\theta_s)\ +\ Cste}$ in all cases.
- It is about the product of $\boldsymbol{\theta_{il}}$ and $\boldsymbol{\exp(\Lambda\ q_t)}$, with a special factor $\boldsymbol{\Lambda \approx 6}$ given by the Third Law.
- $\boldsymbol{\theta_s}$ reveals new conservative (isentropic) properties, and the turbulence is likely acting on $\boldsymbol{\theta_s}$ according to Richardson (1919, 1920, 1922).

- A wish to improve the understanding of **cold air** properties: **a need of in situ observations** of $(T,\ q_v,\ q_l,\ q_i)$? (drop-soundings, radial flights)
- A wish to improve the computations of the Lewis number for **cold air**: **a need of turbulent fluxes and vertical gradients** of $(T,\ q_v,\ q_l,\ q_i)$?

FAQ?

FAQ: examples of impacts of properties set at 0 K?

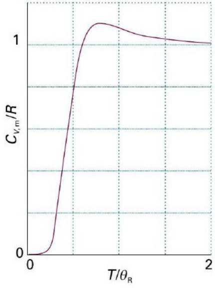
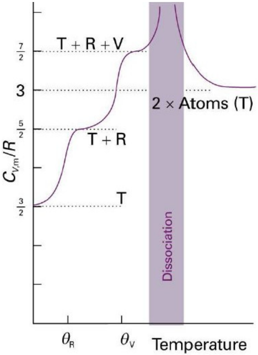


Fig. 17.10 The temperature dependence of the rotational contribution to the heat capacity of a linear molecule.

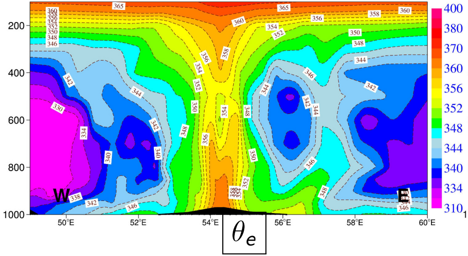


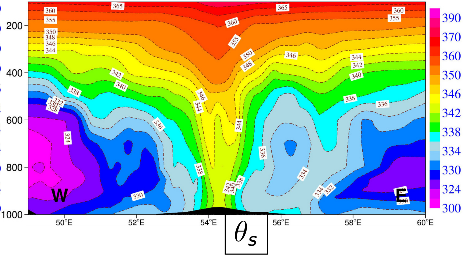
	O_2	N_2	H_2O
θ_R	2.1	2.9	13.4/40.1
θ_V	2239	3358	2290/5360

Figures from Atkins and Paula (Chapter 17):

- If the shape of $C_v(T)$ is given from quantum mechanics, values of θ_R and θ_V are only given by observations, and they continuously impact the value of $C_v(T)$ from 0 K to the atmospheric temperatures (180 K to 350 K).
- Only $(3+2+0) \Longrightarrow (5/2)\,R$ for N_2 and O_2, and $(3+3+0) \Longrightarrow (6/2)\,R$ for H_2O
- No choice / observed facts: to rely on observed values for $\theta_R \ll T \ll \theta_V$!

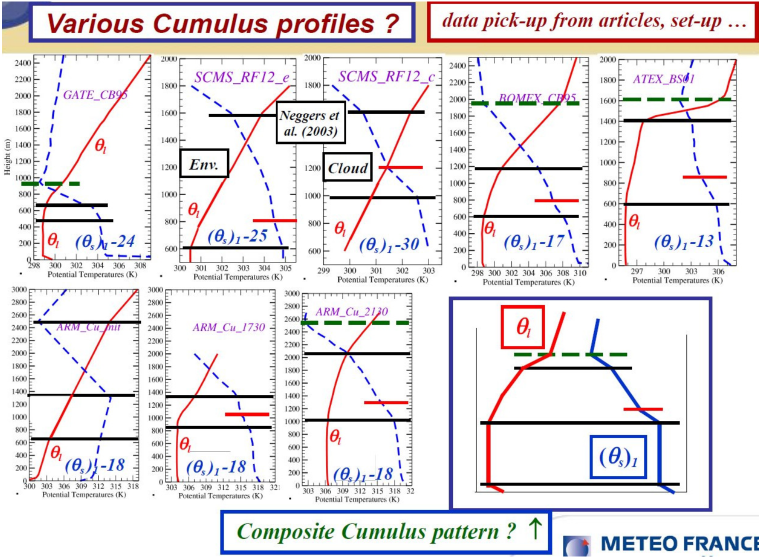
Entropy and cyclones? (JAS-2017)



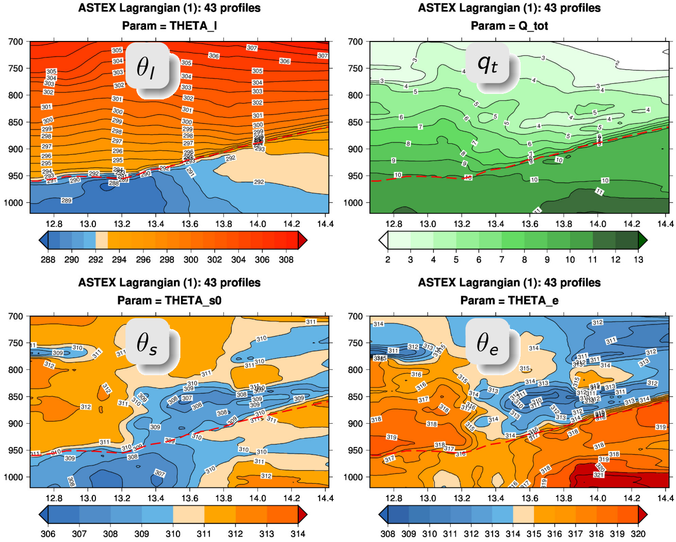


- Vertical Cross-sections for the Cyclone Dumilé (ALADIN-Réunion)
- $\theta_e \approx$ "constant" up to 200 hPa, but with a "warm foot" and $\theta_e \nearrow$ above 700 to 500 hPa ... thus **θ_e not really "constant"...** ;
- $\theta_s \approx$ constant in the PBL (turbulence), even in the core, then $\nearrow$ above 800 to 600 hPa, with a "pumping" of isentropes until 850 hPa in the core
- This "**pumping of the moist isentropes**" (θ_s) in the troposphere is the continuation (the pendant) of the pumping of $\theta \approx \theta_s$ at the tropopause...

Profils composite de $\theta_s(z)$ pour Cumulus (EUCLIPSE 2011, Exceter)



Transition Sc-> Cu: ASTEX-Lag1



The cross section

- The 43 profiles form a Lagrangian cross-section
- The positive jumps in θ_l are indicated by blue PBL versus orange Upper-Air colors
- The positive/negative jumps in θ_e are indicated by orange PBL versus reddish and then blue Upper-Air colors
- The positive/negative jumps in θ_s are indicated by blue/orange PBL versus orange/blue Upper-Air colors, with a Blue-Blue region between 13.4 and 13.6, where the jumps are very small (the transition regime from Sc to Cu)