

On Maximum Entropy Profiles

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ABSTRACT

A column of dry air in hydrostatic equilibrium is considered, bounded by two fixed values of the pressure, and the question is asked, what vertical temperature profile maximizes the total entropy of the column? Using an elementary variational calculation, it is shown how the result depends on what is kept fixed in the maximization process. If one assumes that there is no net heat exchange between the column and its surroundings—implying that the vertical integral of the absolute temperature remains constant—an isothermal profile is obtained in accordance with classical thermodynamics and the kinetic theory of gases. If instead the vertical integral of the potential temperature is kept fixed—as argued by several authors to be appropriate in the case of convective mixing—an isentropic profile results. It is argued that, if one wishes to apply the latter constraint, it should be used as an additional, rather than as an alternative, constraint. The variational problem with both constraints leads to a profile in between the isothermal and the isentropic extremes. This profile has the merit of reproducing very accurately the tropospheric part of the *U.S. Standard Atmosphere, 1976*.

1. Introduction

The question of what vertical temperature profile corresponds to the state of maximal entropy was posed more than a century ago. At first, the discussion took place within the framework of classical thermodynamics; one considers an ideal gas in a gravitational field and seeks the state of maximum entropy under the constraints of 1) a constant mass and 2) a constant energy (internal plus potential). The answer—the profile will be isothermal—was rigorously proven by Gibbs (in 1876, see Gibbs 1961, p. 144ff) for arbitrary types of fluids. In the framework of the kinetic theory of gases, Boltzmann (1896, p. 136) arrived at the same conclusion by using his H theorem. Despite these proofs, the issue remained a source of contention and confusion; for example, a common misconception was that gravity would change the nature of thermodynamic equilibrium so as to create a vertical temperature gradient. Traces of this debate can be found in the older literature on dynamic meteorology, for example, in the textbooks by Exner (1925, 60–62) and Ertel (1938, 72–73). Exner pointed out that the confusion arose from defining the problem in an inconsistent way, such as by considering a moving

parcel in a pressure field without taking into account the effect that its movement will have on the ambient field. Emden (1926) attempted to end the ongoing confusion in a section that he gave the pessimistic title “Periodisch wiederkehrende Irrtümer” (which translates to “Periodically recurring errors, or misconceptions”).

In the discussion presented by Maxwell (1888, p. 320), one observes a shift toward a broader framework. First he discusses the classical formulation of the problem and its answer (the profile will be isothermal), but then he argues that, in the actual atmosphere, convective motions rather than molecular diffusion will be important, which he presumes would lead to an isentropic profile. This idea, plausible though it is, still awaits rigorous proof. In a recent textbook, Bohren and Albrecht (1998, 164–171) discuss this problem in much detail. They consider an ideal gas in a gravitational field, and seek the state of maximal entropy under constraint 1 as above, but as a second constraint they choose 3) a constant integrated potential temperature. Bohren and Albrecht show that constraints 1 and 3 result in an isentropic profile. This can be regarded as a confirmation of Maxwell’s idea, if one accepts constraint 3 as valid.

Constraint 2 manifests itself as the requirement that the vertically integrated (absolute) temperature be constant. As we will show below, the same requirement is found if one relaxes 2 by allowing neighboring layers

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to do work on the layer under consideration; constraint 2 is then to be replaced by $2'$, a constant enthalpy. As a result, here too the outcome is that of an isothermal profile. Bohren and Albrecht arrive at their constraint 3 by starting with a constraint similar to $2'$, and then modify it in an approximate way, which in fact amounts to replacing $2'$ by 3. This way of obtaining 3 can be criticized on the grounds that, had no approximation been made, one would have found an isothermal instead of an isentropic profile, which in itself shows that the approximation is problematic. A different way of justifying constraint 3 was suggested by Ball (1956), who argued that the integrated potential temperature will be constant when convective mixing dominates molecular diffusion. It is the purpose of this article to suggest a way of incorporating 3 in the maximization problem without sacrificing the constraint $2'$, which after all stems from the first law of thermodynamics. We will, in other words, pose 3 as an additional constraint to 1 and $2'$. This brings us outside the domain of classical thermodynamics, and hence one can expect that the temperature profile will no longer be isothermal; we will derive below what profile forms the outcome.

2. Maximum entropy profiles

We consider an atmosphere consisting of dry air of which the temperature T , density ρ , and pressure p obey the ideal gas law $p = \rho RT$ with R the gas constant. For an atmosphere in local thermodynamic equilibrium, the total entropy of a given amount of air is the mass integral of the specific entropy $s = c_p \ln \theta$, where θ is the potential temperature. The potential temperature of an ideal gas is defined by $\theta = T(p_r/p)^\kappa$, where $\kappa = R/c_p$, with c_p the specific heat at constant pressure, and p_r a reference pressure taken to be 1000 hPa. We disregard the arbitrary constant that can be added to the definition of specific entropy, as it will play no role in the following.

We next consider a vertical column of air with unit horizontal area, assumed to be in hydrostatic equilibrium, $\partial p/\partial z = -\rho g$, between the heights z_1 and z_2 and corresponding pressures p_1 and p_2 (see Fig. 1). Because of hydrostatic equilibrium, the total entropy of the air in this column can be written as

$$S = \int_{z_1}^{z_2} \rho s \, dz = \frac{c_p}{g} \int_{p_2}^{p_1} \ln \theta \, dp. \quad (1)$$

One of the constraints under which we will maximize the entropy is that the total mass M of the column is fixed. This mass is given by

$$M = \int_{z_1}^{z_2} \rho \, dz = \frac{1}{g} \int_{p_2}^{p_1} dp = \frac{1}{g} (p_1 - p_2). \quad (2)$$

For a variation δM , we therefore have

$$\delta M = \frac{1}{g} (\delta p_1 - \delta p_2), \quad (3)$$

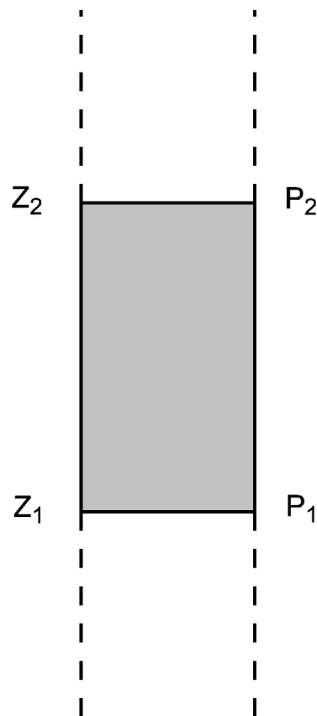


FIG. 1. Schematic representation of a midair atmospheric column, bounded by the heights z_1 and z_2 . These heights are variable in the variational process, but the corresponding pressures p_1 and p_2 are kept fixed. The column is assumed to exchange no net heat with its surroundings but may perform work on the air above and below the column.

where δp_1 and δp_2 are the variations in the lower and upper pressure. We will impose that no mass flows in or out of the column by keeping both p_1 and p_2 at fixed values.

Fixing p_1 and p_2 means that we deal with a closed system: a system that is not allowed to exchange mass with its surroundings, although it may exchange heat and work. However, we will assume that the net exchange of heat with the column's surroundings is zero. This means that changes in the internal, kinetic plus potential energy are equal and of opposite sign to the work performed by the system. We ignore the kinetic contribution; the internal plus potential energy is given by [see Dutton 1973, Eq. (2.3)]

$$\begin{aligned} E &= \int_{z_1}^{z_2} \rho (c_v T + gz) \, dz \\ &= p_1 z_1 - p_2 z_2 + \frac{c_p}{g} \int_{p_2}^{p_1} T \, dp. \end{aligned} \quad (4)$$

In addition to hydrostatic equilibrium, use is made of the ideal gas law, the relation $c_v + R = c_p$ between the specific heats at constant volume and constant pressure, as well as the rule $z \, dp = d(pz) - p \, dz$. The work performed by the system as a result of variations δz_1 and δz_2 is given by $\delta W = p_2 \delta z_2 - p_1 \delta z_1$. Using our

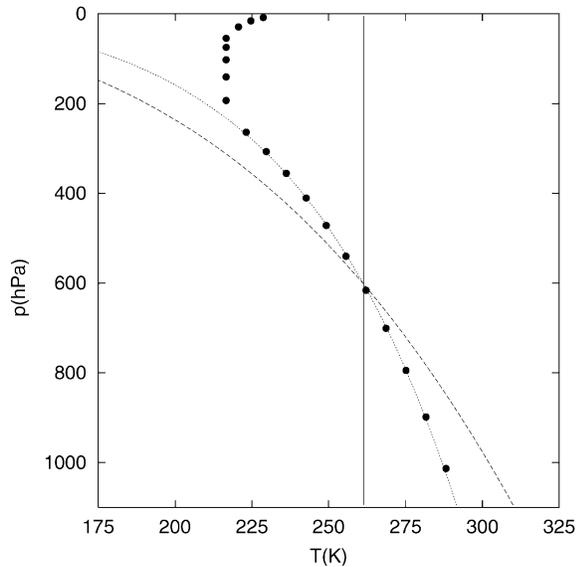


FIG. 2. Pressure (hPa) vs temperature (K). The Standard Atmosphere is represented by the dots. The vertical solid line is the isothermal profile given by (12), with $T_r = 261.36$ K. The dashed line is the isentropic profile (18), with $T_r = 302.04$ K. The dotted line is the intermediate profile (22) with $T_r = 286.90$ K and $\alpha = 1.6868$. The value of p_r , at which the temperature is T_r , is 1000 hPa.

assumption that δp_1 and δp_2 are 0, we can derive from (4)

$$\delta E + \delta W = \frac{c_p}{g} \int_{p_2}^{p_1} \delta T dp. \quad (5)$$

Now, $\delta E + \delta W = \delta Q$, where δQ is the net amount of heat added to the column. If in the variational process no net heat is to be transferred to or from the column, the enthalpy

$$H = \frac{c_p}{g} \int_{p_2}^{p_1} T dp \quad (6)$$

is to remain constant. We note that the form of this constraint is holonomic in the sense that a state function H is kept fixed. The holonomic form is due to the fact that we have fixed p_1 and p_2 in the variational process.

In the rest of this paper we shall consider three distinct types of variational problems: the classical one, the one proposed by Bohren and Albrecht (1998), and a new one. It will be interesting to compare the results of each with empirical values, which we base on a representative atmospheric profile: the *U.S. Standard Atmosphere, 1976* [hereafter Standard Atmosphere, (U.S. Committee on Extension to the Standard Atmosphere) COESA 1976], as given by Holton (1992, Table E.2). In Fig. 2, the dots represent the pressure–temperature distribution of the 19 entries of Holton’s table. We restrict ourselves to the tropospheric part of the Standard Atmosphere and consider the data between the pressures $p_1 = 1013.25$ hPa and $p_2 = 264.36$ hPa (the 1st and 11th entry of the

TABLE 1. The values of H , L , and S for the Standard Atmosphere, the isothermal profile, the isentropic profile, and the intermediate profile.

Profile	H (10^9 J m $^{-2}$)	L (10^9 J m $^{-2}$)	S (10^7 J K $^{-1}$ m $^{-2}$)
Observed	2.0032	2.3150	4.3764
Isothermal	2.0032	2.3326	4.3783
Isentropic	2.0106	2.3150	4.3769
Intermediate	2.0032	2.3150	4.3764

table). We use $R = 287$ J K $^{-1}$ kg $^{-1}$, $c_p = 1004$ J K $^{-1}$ kg $^{-1}$, and $g = 9.81$ m s $^{-2}$, which are also taken from Holton (1992, appendix A). The mass M of the column is then found to be 7.6339×10^3 kg m $^{-2}$. The corresponding values of enthalpy H and entropy S (as well as of L , defined below) are gathered in Table 1. To calculate these integrals, the profile was first cubically interpolated. Then the integral was performed numerically with the pressure interval (p_2, p_1) divided into 10 000 equal subintervals and using the trapezoidal rule. The same method was used for the integrals considered below (some of which can be checked analytically).

a. Isothermal profile

The classical variational problem for a midair atmospheric column is to maximize S , the mass M and the enthalpy H being kept fixed. For S we can write, using the definition of potential temperature,

$$S = \frac{c_p}{g} \int_{p_2}^{p_1} \ln T dp + \frac{c_p}{g} \int_{p_2}^{p_1} \ln \left(\frac{p_r}{p} \right)^\kappa dp. \quad (7)$$

The second term does not contribute to the variation so that δS can be written, with $\delta \ln T = \delta T/T$,

$$\delta S = \frac{c_p}{g} \int_{p_2}^{p_1} \frac{\delta T}{T} dp. \quad (8)$$

Using a Lagrange multiplier λ , we can write the variational problem as

$$\delta S + \lambda \delta H = 0, \quad (9)$$

which leads to

$$\int_{p_2}^{p_1} \left(\frac{\delta T}{T} + \lambda \delta T \right) dp = 0. \quad (10)$$

Since this should be true for all variations δT , we must have

$$\frac{1}{T} + \lambda = 0; \quad (11)$$

that is, $T = -\lambda^{-1}$ is constant, thus, the profile is *isothermal*. This is the well-known result of classical thermodynamics and the kinetic theory of gases. If we denote the temperature at pressure p_r by T_r , we may write

$$T(p) = T_r. \quad (12)$$

TABLE 2. The parameters α and T_r for the three profiles discussed in section 2.

Profile	α	T_r (K)
Isothermal	0	261.36
Isentropic	∞	302.04
Intermediate	1.6868	286.90

The temperature T_r is an arbitrary constant; its most appropriate value can be determined on the basis of the empirical profile. In line with how we posed the variational problem (fixed H), we must require that H , obtained from using (12) in (6), be equal to the empirical value of H ; this requirement yields T_r (see Table 2 and the vertical line in Fig. 2). The value of T_r , being known, we can calculate the isothermal value of the entropy S from (1) (see Table 1). As expected, it exceeds the empirical value of S .

b. Isentropic profile

Now, in Ball [1956, Eq. (4)] it is argued that for convective motions that mix potential temperature, molecular effects being neglected, it is to be expected that the quantity

$$L = \frac{c_p}{g} \int_{p_2}^{p_1} \theta dp \quad (13)$$

remains constant. This had led Bohren and Albrecht (1998) to the formulation of an alternative variational problem in which S is maximized under the constraints of fixed M and L .

Their procedure perhaps requires some comment. First of all, notice that the requirement of a fixed value of L does *not* imply that $D\theta/Dt = 0$ (which, in turn, would imply constancy of S , and hence would render the maximization problem meaningless); it only means that the potential temperature is allowed to be redistributed such that its vertical integral remains constant. This indeed brings us to the broader framework discussed by Maxwell, in the sense that convective turbulent motions are now taken into account, albeit implicitly. Their role is to mix the potential temperature field, to strive to homogenize it. We should now interpret the state variables as averages over volumes that are large compared to the size of the turbulent motions. In particular, the first law of thermodynamics expressed in terms of potential temperature:

$$\frac{D\theta}{Dt} = \frac{\theta}{c_p T} J, \quad (14)$$

now refers to volume elements of this larger scale. Even when on the scale of the turbulence the heating rate J would be zero, this now needs not to be the case. Indeed, (14) is expected to have a nonvanishing right-hand side that includes the result of convective turbulent mixing.

For this particular form of heating it makes sense to assume that the integrated potential temperature θ remains constant as its main effect is to redistribute θ . The value of the integrated entropy may thus increase despite the fact that the integrated potential temperature remains constant. This is what the variational problem posed by Bohren and Albrecht (1998)—maximize S for fixed M and L —is intended to express, even though a proper foundation of the latter constraint would require further scrutiny.

We use a Lagrange multiplier μ ; the variational problem then leads to the condition

$$\delta S + \mu \delta L = 0 \quad (15)$$

and gives

$$\int_{p_2}^{p_1} \left[\frac{\delta T}{T} + \mu \left(\frac{p_r}{p} \right)^\kappa \delta T \right] dp = 0. \quad (16)$$

This implies that

$$\frac{1}{T} + \mu \left(\frac{p_r}{p} \right)^\kappa = 0; \quad (17)$$

that is, $\theta = -\mu^{-1}$ is constant, therefore, the profile is *isentropic*. Thus, the result by Bohren and Albrecht (1998) is reproduced. Denoting again the temperature at pressure p_r by T_r , we may write

$$T(p) = T_r \left(\frac{p}{p_r} \right)^\kappa. \quad (18)$$

A comparison with the empirical profile should now be based on the constancy of L ; that is, we must require that (13) calculated with (18) reproduces the empirical value of L [obtained by numerically integrating (13) for the interpolated empirical profile]. This requirement yields T_r , see Table 2; the corresponding profile of $T(p)$, given by (18), is shown in Fig. 2. We see that the temperature gradient is considerably larger than in the empirical profile.

c. Intermediate profile

The above calculations show that the result of the maximization process depends on the constraints that are used. Keeping M and H fixed leads to a uniform absolute temperature (isothermal profile); keeping M and L fixed leads to a uniform potential temperature (isentropic profile). The principal difference between the two is as follows: in the former, the vertically integrated absolute temperature is kept constant (classical thermodynamic approach); in the latter, the vertically integrated potential temperature is kept constant (Bohren and Albrecht 1998).

At this point one might wonder—taking for granted that constancy of L is appropriate—whether it should not be used as an *additional*, rather than as an *alternative*, constraint. Indeed, it seems more natural to use

constancy of L as an additional constraint because the assumption of no net heat exchange, which is the essence of keeping H fixed, remains a sensible constraint in the variational process. The problem of maximizing S , now for fixed M , H , and L , leads to

$$\delta S + \lambda \delta H + \mu \delta L = 0. \quad (19)$$

This gives, if we express both the entropy and the potential temperature in terms of T ,

$$\int_{p_2}^{p_1} \left[\frac{\delta T}{T} + \lambda \delta T + \mu \left(\frac{p_r}{p} \right)^\kappa \delta T \right] dp = 0, \quad (20)$$

so that we should have

$$\frac{1}{T} + \lambda + \mu \left(\frac{p_r}{p} \right)^\kappa = 0. \quad (21)$$

Introducing $\alpha = \mu/\lambda$, and (as before) denoting the temperature at p_r by T_r , we can write the requirement (21) more conveniently as

$$T(p) = T_r \frac{1 + \alpha}{1 + \alpha(p_r/p)^\kappa}. \quad (22)$$

This profile lies between the isothermal and the isentropic profile: the isothermal profile (12) is recovered in the limit $\alpha \rightarrow 0$; the isentropic profile (18) in the limit $\alpha \rightarrow \infty$.

We shall compare the result (22) with the empirical profile. There are now *two* constants to be determined: T_r and α , in accordance with the fact that we required H and L to be constant. The task of finding them is less trivial than in the previous two cases (where only T_r was to be determined), because of the more complicated integrals involved. Fortunately, the two problems can be separated because for (22), H/L depends only on α , not on T_r . Moreover, the functional dependence is single valued and monotonic (see Fig. 3); this figure is based on numerical integration of H and L for (22), T_r being immaterial. Thus, we can find α by requiring H/L to be equal to its empirical value. Having determined α , we can now simply obtain T_r by requiring H (or L) to be equal to its empirical value as well. The resulting values are given in Table 2, and the corresponding curve is shown in Fig. 2. The profile agrees almost perfectly with the tropospheric part of the Standard Atmosphere.

3. Concluding remarks

We reiterate that the entropy maximization problem in its pure classical setting—that is, imposing the constraints of 1) a constant total mass, as well as one of the two following constraints: 2) a constant energy E or 2') a constant enthalpy H —will result in an isothermal profile, corresponding to the state of thermodynamic equilibrium. This is the established classical result, despite all the confusion that existed already a century ago and that persists to the present day.

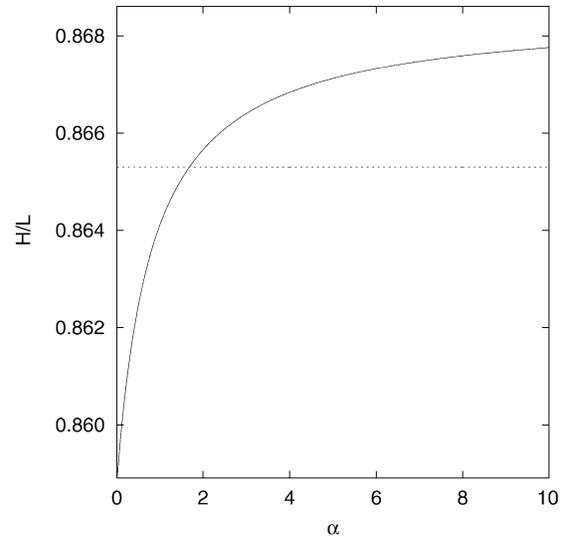


FIG. 3. The fraction H/L , calculated using the profile (22), as a function of α . The lower and upper limits of the vertical axis are 0.858 79 and 0.868 51, respectively, and correspond to the isothermal and isentropic limits. The horizontal line denotes the observed value 0.865 31, calculated from the Standard Atmosphere. The figure illustrates that there is a unique value of α that reproduces the observed value of H/L . This value is $\alpha = 1.6868$.

Of course, the actual atmosphere is subject to processes like convective mixing. They prevent the atmosphere from ever coming close to thermodynamic equilibrium, that is, the ultimate state of maximal entropy. In this sense, these processes lower the maximum value that the entropy is allowed to attain. It thus seems natural that one should represent them by posing certain *additional* constraints in the maximization problem, considering that constraints 1 and 2' will continue to be valid. This is the key idea of this article.

The question then arises what these constraints should be. Here, we have taken, following Ball (1956) and Bohren and Albrecht (1998), constancy of the integrated potential temperature as a single additional constraint 3, but this choice is of course open for debate. In our view, this particular constraint still lacks a solid physical basis; yet, the above results give reason to expect that the construction of such a basis may be possible because the three constraints 1, 2', and 3 together lead to a temperature profile that corresponds remarkably well to the tropospheric part of the Standard Atmosphere.

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