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Thermodynamics of Planetary Atmospheres

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Thermodynamique des Atmosphères Planétaires

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Contents

Préface

Souvent, le plus dur à expliquer, c'est ce qui va de soi.

Ecrire son habilitation est souvent un exercice fastidieux. Aujourd'hui — où la compétition dès l'entrée dans la vie académique est devenue tellement forte que la capacité à encadrer s'est imposée petit à petit comme un critère de recrutement de plus — l'exercice parait anachronique. Plutôt un rite de passage obligé. Décrire ses recherches depuis la thèse comme un nième rapport d'activité, décrire les travaux des étudiants encadrés comme si c'était un gage que l'on savaient *bien* encadrer, décrire ses projets, enfin, comme si l'on cherchaient une fois de plus à être financé... Pas très enthousiasmant.

Mais puisqu'il faut vivre, autant le faire avec le sourire comme dirait l'autre. Alors faisant fi de la multitudes de conseils qui m'enjoignaient à *évacuer* cette formalité au plus vite et avec le moins d'efforts possible — éventualité si attrayante qu'elle aurait sans doute repoussé ce manuscrit aux calendes grecques — j'ai décidé de me ré approprier l'exercice. Point de rapport d'activité, point de description de projet. Si vous trouvé ici ces éléments, c'est à l'insu de mon plein gré. Quit à prendre du temps pour écrire ce manuscrit, autant qu'il soit utile. À qui me direz vous, et bien à moi pour commencer.

Au début de cette aventure, j'avais l'impression diffuse d'avoir accumulé tout un tas de petits boulets à mes chevilles. Depuis mon entrée dans le domaine des atmosphères planétaires avec mon premier postdoc au Laboratoire de Météorologie Dynamique (LMD) avec François Forget, un de mes fils rouges a été l'étude d'atmosphères (très) riches en vapeurs condensables. Cela a commencé par l'une des premières études de l'effet de serre divergeant[1] sur terre dans un modèle de climat tridimensionnel (Leconte et al. 2013). Dès cette première étude, il m'a fallut repenser un certain nombre de paramétrisations physiques du modèle de climat global générique du LMD qui venait juste de voir le jour pour que la vapeur d'eau — qui devient progressivement le composant majoritaire

[1] The so-called Runaway greenhouse.

de l'atmosphère lorsque l'atmosphère se réchauffe — ne soit plus traitée comme un gaz trace, avec toutes les approximations qui s'en suivent. Incidemment, cela a rendu le modèle extrêmement robuste et nous a permis, avec différents étudiants et collaborateurs, de nous attaquer à toutes sortes de questions sur les limites à la présence d'océans sur une planète (Leconte et al. 2013 ; Turbet et al. 2021 ; Chaverot et al. 2022 ; Turbet et al. 2023 ; Selsis et al. 2023 ; Leconte et al. 2024)

Mais au delà de la problématique scientifique de l'effet de serre divergeant, ce thème des atmosphères riches en "éléments lourds" a très vite résonné avec une autre thématique scientifique démarrée vers la fin de ma thèse visant à comprendre comment une hétérogénéité dans la composition de l'enveloppe gazeuse des planètes géantes du système solaire pouvait affecter leur structure thermique en affectant la convection à travers des phénomènes de convection double-diffusive, aussi appelée semi-convection (Leconte and Chabrier 2012, 2013). Effectivement, dans ce cas, prendre en compte la masse des espèces condensables et la différence de masse molaire avec le gaz de fond est primordial pour observer ce processus physique, et l'approximation de gaz trace devient vite obsolète. Dans notre Neptune ou dans les exo-Neptunes tempérées, c'est potentiellement plus d'un tier de la masse de l'atmosphère qui est condensable (Leconte et al. 2017 ; Cavalié et al. 2017 ; Charnay et al. 2021 ; Clément et al. 2024 ; Leconte et al. 2024) !

Cette nécessité de simuler des atmosphère où le gaz condensable peut être majoritaire m'a souvent amené à devoir questionner certaines equations bien établies des modèles terrestres, où la masse de vapeur est plutôt de l'ordre du pour-cent, pour savoir si elles ne reposaient pas implicitement sur des hypothèses qui ne tenaient plus.

À cela s'est ajouté une reflexion au long court sur les critères de déclenchement de la convection qui sont souvent exprimés en termes de gradient d'entropie, mais aussi justement parce que l'hypothèse d'une atmosphère homogène est souvent implicitement faite (Leconte 2018).

Tout cela pour dire que ces quelques volets de mes recherches m'ont amené à de nombreuses questions dont les réponses semblaient si évidentes qu'elles se trouvaient dans de nombreux textbooks sans qu'aucune des argumentations ne m'ait vraiment satisfait. Se sont ajoutés les questions des étudiants auxquelles je n'avais souvent à répondre qu'un "parce que tout le monde dit que c'est comme ça"[2] sans pour autant pouvoir les pointer vers une démonstration rigoureuse. À toutes ces questions, et à celles qui me sont venues en cours de route, vous trouverez les réponses ici — du moins à toutes celles auxquelles j'ai pu apporter une démonstration suffisamment robuste:

- Pourquoi est-ce l'enthalpie qui est conservée dans de nombreux modèles atmosphériques et pas l'énergie ? (§ 5)
- L'est-elle vraiment ? (§ 5.2)
- Pourquoi n'utilise-t-on jamais les potentiels chimiques dans les équations décrivant l'énergétique d'une atmosphère de composition chimique variable ? (§ 2.4.4)
- Comment interpréter le terme de travail chimique dans l'équation de l'énergie ? (§ 2.3)
- Pourquoi le chauffage par chaleur latente apparait-il souvent comme une source de chauffage externe dans les équations alors qu'il est dû à une transformation interne ? (§ 2.5)
- D'où vient réellement l'énergie hydroélectrique ? (§ 5.4.2)
- Comment savoir si différentes approximations sur la thermodynamique et l'énergétique d'une atmosphère sont cohérentes entre elles ? (§ 5.5)

[2] Éventuellement remplacé par le "Il faudrait que je prenne le temps de regarder en détail..."

- Est-il vraiment possible d'enlever le terme d'enthalpie de référence des espèces pures dans l'expression de l'enthalpie d'un mélange ? (§ 3.4)
- Une atmosphère qui est convectivement neutre est elle toujours isentropique ? (§ 4)
- Pourquoi mélanger une atmosphère change-t-il son enthalpie totale et ne fait pas que la redistribuer ? (§ 6.1.2)

Sans doute les réponses à certaines de ces questions vous sembleront évidentes. Pour moi elles ne l'étaient pas, mais le sont aujourd'hui. Et en cela, ce manuscrit a déjà pleinement rempli son objectif premier. Mais j'ose croire que les réponses élaborées au cours de ce manuscrit sont souvent plus subtiles qu'il n'y parait à première vue et que certaines pourraient vous surprendre. En tout cas, si j'ai sélectionné ces questions, c'est aussi parce que j'ai pu lire des livres et articles de références qui, sur ces sujets subtils, donnaient des explications qui me paraissaient au mieux absconses et trompeuses et au pire complètement fausses.

Et de là émerge le deuxième but de ce document : fournir aux étudiants et aux lecteurs intéressés un point de vue un peu complémentaire à la littérature existante sur la thermodynamique des atmosphères planétaires. Plus global que les articles où il faut souvent compiler de nombreuses références mais plus profond qu'un livre de cours qui lui se doit d'être exhaustif sur un sujet si vaste qu'il ne peut souvent pas faire l'impasse de certains raccourcis. C'est aussi pour cela que l'anglais a été choisi comme langue pour le corps du texte. Ici, les chapitres peuvent se lire ensemble et forment un tout aussi cohérent que possible, mais certaines démonstrations de bases sont éludées pour pouvoir approfondir les zones d'ombre. Aussi, dans les rares cas où j'ai choisi de développer certaines démonstrations de base, je me suis attaché à proposer des approches alternatives pour offrir un point de vue complémentaire à la littérature existante.

En tout cas, je vous souhaite d'avoir autant de plaisir à lire ce manuscrit que j'en ai eu à l'écrire.

Abstract

In this manuscript we give an overview of the various concepts and equations needed to model the thermodynamics of planetary atmospheres with compositional heterogeneities, with a particular focus on atmospheres with a condensible component, whether this component is in trace quantities or the main constituent. Along the way, we try to provide in-depth discussions and demonstrations correcting some subtle imprecisions or errors in the literature. The role of these discussions is to provide the curious reader with an alternative point of view compared to what is available in many textbooks to get a more intuitive understanding of the matter at hand.

The first chapter describes the equations for a homogeneous atmosphere and serves as an introduction to the notations and most basic quantities and concepts in planetary atmosphere modeling. Interestingly, the basic equations are derived using a generic approach that allows anyone to derive a local equation from the conservation of any extensive quantity.

In the second chapter, we delve a little deeper into the thermodynamics of heterogeneous atmospheres and discuss why *chemical potentials* — which are the key quantities describing the thermodynamical equilibrium of mixtures — or the fundamental relation of thermodynamics are generally not used in the set of equations for hydrodynamical systems. As we will see, this fundamentally comes down to the fact that hydrodynamical systems are locally "open". We therefore take the opportunity to formally derive energy and entropy equations for hydrodynamical systems that are valid for a volume moving arbitrarily. To complete our set of equations, Chapter 3 specifies the equation of state needed to describe moist air in our set of hydrodynamical equations, along with the various humidity variables that can be used to describe such a system. The pros and cons of the various variables are discussed. Along the way, we discuss in which context it is possible (or not) to remove the reference terms of the various pure gases in the expression for the enthalpy of our atmosphere, as is often done in the literature.

Now that we have all the thermodynamics prerequisite at hand, Chapter 4 discusses in depth whether or not the usual entropy criterion for convection in an homogeneous atmosphere, the so-called *Schwarzschild criterion*, can be extended to heterogeneous atmospheres. We will show that — contrary to some claims in the literature — an isentropic atmosphere can never be *Ledoux neutral*, i.e. marginally (un)stable to convection, if the atmosphere is compositionally heterogeneous. In other words, the Ledoux criterion can never be reduced to a criterion on the entropy alone.

Then we finally tackle one of the main subjects of this manuscript: dealing with energy (or rather enthalpy) conservation in a condensible atmosphere. This subject is made subtle by the fact that such atmospheres are open systems due to exchanges of condensible species with surface reservoirs and many implementations just invoke *ad hoc* terms to deal with such exchanges without properly demonstrating whether or why they lead to global energy conservation (in the instances where they actually do). In the first part of Chapter 5, we revisit why this is the enthalpy that is used as a conserved quantity in many models and, most importantly, when this approximation — which is often taken for granted in most textbooks — fails.

Next we use our energy equations for open systems derived in *chemical potentials* to formulate an equation for the total enthalpy conservation of an open atmosphere where condensible species can be exchanged with surface reservoirs through evaporation, condensation and precipitation. In doing so, we properly demonstrate that this is the total specific enthalpy — the sum of the enthalpy and kinetic and potential energies — of the matter entering or leaving the atmosphere that needs to be added or removed from the global enthalpy budget. Incidentally, this framework also makes the choice of when to add or remove some matter from the atmosphere — for example whether we want to treat evaporation as a surface process and later incorporate the vapor to the atmosphere, or directly count the liquid to be evaporated as a part of the atmosphere and treating the evaporation as an atmospheric process — more transparent enthalpy-wise.

This general conservation framework is then used to shed light on some conservation issues where a given contribution is added to the equations without taking care of adding its counterpart, thus breaking energy balance. We take the example of the dissipation of the potential energy of precipitations and take this opportunity to provide a rather counter intuitive explanation for the origin of hydro power that, to the best of our knowledge, we have never seen discussed elsewhere.

We further discuss how some common approximations on the energetics of a condensible atmosphere can break enthalpy conservation if they are not made in a thermodynamically consistent way and give a practical guide for the most common systems.

Finally, in Chapter 6, we dive deep into another example of potential energy loss that can arise when turbulent diffusion is treated solely as a diffusion of potential temperature without any correcting term. We demonstrate that this equation can be written as a conservative equation on the enthalpy that can be directly used in a numerical model. Finally we quantify numerically the impact that this effect can have on thick atmospheres.

Chapter 1

(Thermo)dynamics of homogeneous atmospheres

What we ever hope to do with ease,
we must first learn to do with diligence

Samuel Johnson

Contents

Atmospheric physics has always struck me as the poster child for interdisciplinarity. While it would seem that a good knowledge of fluid dynamics would suffice to tackle the problem, it very rapidly occurs to anyone trying that they will not get far without a good grasp on thermodynamics, chemistry, and radiative transfer.

Of course, many outstanding textbooks exist on the matter. But I always felt that many of them, too earth-centric, were making some simplifying assumptions that will not be valid in the cases we will be looking at. In particular, they often assume that any condensible component is only present in trace amounts and do not account for its effect on the thermodynamic properties of the atmosphere (e.g. its heat capacity), for its weight and the gravitational energy carried with it, or simply by the density change induced by a difference in molecular weight with the background non-condensible atmosphere.

While these points have been sometimes treated in isolation here and there in the literature, in the following chapters, I make a personal attempt at deriving the most general equations with a particular focus on noting where composition plays an interesting role. I will try to introduce new approximations only when necessary, but being very explicit about the approximations made and their effect so the reader may more easily know where to start when wanting to dive deeper.

But before doing the deep dive, I could not resist summarizing here the fundamental equations necessary to model planetary atmospheres in the case of a homogeneous, dry atmosphere. This will serve as an introduction of the notations and concepts for the following chapters. To keep things a bit interesting, I tried to offer a slightly different view of the derivation of the basic equations from general conservation principles (in particular, §1.1.1 and §1.1.2 present mathematical results that we will use throughout). But except for that, the expert reader will probably want to go directly to the next chapter.

1.1 The basics of dynamics

As in every problem of compressible fluid mechanics, the solution consists in finding expressions for the density (ρ) or specific volume ($\upsilon \equiv 1/\rho$), pressure (p), temperature (T), composition (that we loosely encompass in a single parameter χ for the moment) and velocity ($\mathbf{v}$) as a function of both the radius vector, $\mathbf{r}$, and time t. To solve the problem, we thus need six scalar equations plus one per compositional parameter that we want to follow. Usually, the first ones will be provided by the conservation of mass of every constituent. This yields one equation for the total conservation of mass and one additional equation per additional compositional parameter. However, in this first chapter, we will focus only on single-component, homogeneous atmospheres. The will allow us to introduce the key variables and equations in a simple way. So our first equation is just the conservation of total mass. Then, the conservation of momentum will bring us 3 scalar relations. The first principle of thermodynamics, a.k.a. the conservation of energy, will bring us an additional relation, but along

with it comes a new variable which can often be the specific internal energy, enthalpy, or entropy. So this is why we need a *fundamental relation* for the fluid constituting our object which encompasses two relations, one for the pressure (the famous *equation of state*) and one that will link the energy to the temperature (also called caloric equation of state).

Let us now review them in turn. As I will try to remain relatively concise, I refer the reader to the excellent book by Goeff Vallis (2006) for an in depth derivation of those equations and details about the mathematical operators.

1.1.1 Transport theorem

Generally, our conservation principles are inherited from classical mechanics and are thus valid for a closed system that does not exchange matter with the environment. This is why it is often easier to derive conservation equations following a small parcel of fluid enclosed in a moving volume.

To carry this out in practice, we must however recall some mathematical relations.

Let us consider any scalar field φ. For any moving volume $V(t)$ enclosed by a surface $A(t)$ whose outward normal vector is $\mathbf{n}$ and which is moving at an arbitrary velocity $\mathbf{w}$, Leibniz's rule states that

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V(t)} \varphi \,\mathrm{d}V = \underbrace{\int_{V(t)} \partial_t \varphi \,\mathrm{d}V}_{\text{Local variation}} + \underbrace{\int_{A(t)} \varphi\, \mathbf{w}\cdot\mathbf{n}\,\mathrm{d}A}_{\text{Flux trough surface}}, \tag{1.1}$$

where $\partial_t \equiv \partial/\partial_t$ is the Eulerian partial time derivative. This simply translates the fact that the variation of the integral in a volume is either due to the local variation of the field inside the volume or to the net capture by the moving volume (the first and second term on the left hand side, respectively).

In parallel, the divergence theorem allows us to change a surface integral into a volume one such that for any vector field $\mathbf{w}$,

$$\int_A \mathbf{w}\cdot\mathbf{n}\,\mathrm{d}A = \int_V \nabla\cdot\mathbf{w}\,\mathrm{d}V, \tag{1.2}$$

where ∇ is the classic nabla operator, and $\nabla\cdot\mathbf{w}$ is the divergence of $\mathbf{w}$. We can combine the two and take the arbitrary vector field ($\mathbf{w}$) to be the fluid velocity ($\mathbf{v}$) to get what is sometimes called the transport theorem

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_m(t)} \varphi \,\mathrm{d}V = \int_{V_m(t)} \left[\partial_t\varphi + \nabla\cdot(\varphi\mathbf{v})\right]\mathrm{d}V.} \tag{1.3}$$

Interestingly, in this case, because the volume follows the fluid, it always encompasses the same system, which can be considered closed. The volume is therefore called a material volume, V_m, and the surface a material surface, A_m.

This equation is fundamental as it relates the variation of a macroscopic quantity (on the left) to the variations of a local quantity and to the velocity field (on the right). It will be central hereafter as it will allow us to extend properties derived for closed systems to open ones.

Sometimes, it is easier think of how a given intensive property changes *along* the motion of the fluid. This Lagrangian, or material, derivative is linked to the Eulerian, or local, derivative by adding a term due to the advection of the property by the velocity field and writes

$$\boxed{D_t\varphi \equiv \partial_t\varphi + (\mathbf{v}\cdot\nabla)\varphi.} \tag{1.4}$$

Therefore, using some vector calculus identities, the transport theorem can also be written

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_m(t)}\varphi\,\mathrm{d}V=\int_{V_m(t)}\left[D_t\varphi+\varphi\nabla\cdot\mathbf{v}\right]\mathrm{d}V.} \tag{1.5}$$

1.1.2 General conservation principles

As discussed above, our conservation principles are often stated for a closed macroscopic system and state that a given *extensive* property of this system, Φ, changes due to an external forcing (that we will call $\dot{\Phi}$) or is purely conserved ($\dot{\Phi}=0$). Good examples, as we will see afterwards, are the mass of a closed system, which does not change, or its momentum, which can change if external forces are applied. In any case, this writes

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi=\dot{\Phi}. \tag{1.6}$$

In fluid mechanics, because of the continuous nature of the fluid, we are more interested in *intensive* properties that can be locally defined everywhere. These can be truly local variables such as temperature and pressure, but we can also manufacture them as the ratio of two extensive properties of an arbitrary system when it becomes smaller and smaller. The two most common types of such intensive properties are the volumic and specific variables that are respectively defined as

$$\varphi_V=\lim_{\delta V\to 0}\frac{\Phi}{\delta V}\quad\text{and}\quad\varphi_M=\lim_{\delta M\to 0}\frac{\Phi}{\delta M}, \tag{1.7}$$

which implies

$$\Phi=\int_{V_m}\varphi_V\,\mathrm{d}V=\int_{M}\varphi_M\,\mathrm{d}M \tag{1.8}$$

Two well-known examples are the volumic mass and the specific volume

$$\rho=\lim_{\delta V\to 0}\frac{\delta M}{\delta V}\quad\text{and}\quad\upsilon=\lim_{\delta M\to 0}\frac{\delta V}{\delta M}. \tag{1.9}$$

By definition, this yields

$$\varphi_V=\rho\varphi_M\quad\text{and}\quad\varphi_M=\upsilon\varphi_V. \tag{1.10}$$

With the help of the transport theorem and thanks to our intensive variables, we can now state any macroscopic conservation principle, Eq. (1.6), in local terms as follows.

If we are interested in the evolution of a volumic property, φ_V, this simply writes

$$\begin{aligned}\dot{\Phi}=\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_m}\varphi_V\,\mathrm{d}V&=\int_{V_m}\left[\partial_t\varphi_V+\nabla\cdot(\varphi_V\mathbf{v})\right]\mathrm{d}V\\&=\int_{V_m}\left[D_t\varphi_V+\varphi_V\nabla\cdot\mathbf{v}\right]\mathrm{d}V.\end{aligned} \tag{1.11}$$

Then, dividing by the volume of the system and taking the limit for a vanishing volume we get the local conservation equation in either its Eulerian or flux form

$$\boxed{\partial_t\varphi_V+\nabla\cdot(\varphi_V\mathbf{v})=\dot{\varphi}_V,} \tag{1.12}$$

or in its material or Lagrangian form

$$\boxed{D_t\varphi_V = \dot{\varphi}_V - \varphi_V \nabla\cdot\mathbf{v},} \tag{1.13}$$

where $\dot{\varphi}_V \equiv \lim_{\delta V\to 0} \dot{\Phi}/\delta V$ is the volumic forcing. The first version interprets the local variation of φ_V as the sum of the contributions of the local forcing and of the flux of matter bringing some amount of φ_V with it. The second interprets the variation of φ_V along the motion of the fluid as being due to the forcing inside the material volume minus the potential dilution of φ_V when the volume changes. But both predict the exact same behavior.

If we are interested in a specific property, φ_M, we will simply get back to a volumic property using $\varphi_V = \rho\varphi_M$ and use the above — although now we will be dividing by the vanishingly small mass of the system and defining the specific forcing $\dot{\varphi}_M \equiv \lim_{\delta M\to 0} \dot{\Phi}/\delta M$. This writes

$$\begin{aligned}\dot{\varphi}_M = \lim_{\delta M\to 0} \frac{1}{\delta M}\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_m} \rho\varphi_M \,\mathrm{d}V &= \lim_{\delta M\to 0} \frac{\delta V}{\delta M}\left[\partial_t\rho\varphi_V + \nabla\cdot(\rho\varphi_V\mathbf{v})\right]\\ &= \frac{1}{\rho}\left[\partial_t\rho\varphi_M + \nabla\cdot(\rho\varphi_M\mathbf{v})\right]\\ &= \frac{1}{\rho}\left[D_t\rho\varphi_M + \rho\varphi_M\nabla\cdot\mathbf{v}\right].\end{aligned} \tag{1.14}$$

The penultimate line yields the regular flux form equation

$$\boxed{\partial_t\rho\varphi_M + \nabla\cdot(\rho\varphi_M\mathbf{v}) = \rho\dot{\varphi}_M,} \tag{1.15}$$

which has exactly the same interpretation as before. The Lagrangian equation, however, is often presented differently to look more like the equation for a point mass. This formulation can simply be obtained by noting that the infinitesimal mass of the system is always independent of time so that is can transparently enter or leave the derivative on the first line of Eq. (1.14). This yields

$$\begin{aligned}\lim_{\delta M\to 0} \frac{1}{\delta M}\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_m} \rho\varphi_M \,\mathrm{d}V &= \frac{\mathrm{d}}{\mathrm{d}t}\lim_{\delta M\to 0} \frac{1}{\delta M}\int_{V_m} \rho\varphi_M \,\mathrm{d}V\\ &= \frac{\mathrm{d}}{\mathrm{d}t}\lim_{\delta M\to 0} \frac{1}{\delta M}\int_{\delta M} \varphi_M \,\mathrm{d}M\\ &= \frac{\mathrm{d}}{\mathrm{d}t}\varphi_M \equiv D_t\varphi_M.\end{aligned} \tag{1.16}$$

This leaves us with the very intuitive

$$\boxed{D_t\varphi_M = \dot{\varphi}_M \quad \text{or} \quad \rho D_t\varphi_M = \dot{\varphi}_V} \tag{1.17}$$

which is actually often the starting point in many presentations of fluid mechanics. The reason that we wanted to take this alternative approach is that it highlights how laws for a macroscopic, closed system can be applied to continuous open systems, a key feature in Chapter 2.

Finally, let us just combine Eqs. (1.15) and (1.17) to derive a very handy equation that can be used to rapidly transform an equation from its Lagrangian form to its flux form

$$\boxed{\rho D_t\varphi = \partial_t\rho\varphi + \nabla\cdot(\rho\varphi\mathbf{v}).} \tag{1.18}$$

Note that we have removed the subscript because the above equation is actually valid for any intensive property, even if it is neither volumic nor specific. The reason that we have made a difference between the two kind of variables is because this is the only way that we can properly define and give a physical meaning to the forcing term.

Now that we have the general equations, let us apply them to our conserved quantities.

1.1.3 Mass conservation

A first example of this approach is the conservation of mass where we will use the density or volumic mass (ρ) as our volumic scalar field. Just saying that the mass contained in a material volume

$$M = \int_{V_m(t)} \rho \, \mathrm{d}V, \tag{1.19}$$

does not change (by definition of the material volume) trivially entails that

$$\dot{M} = 0. \tag{1.20}$$

This is the same as saying that the local forcing is nil for the mass so that we get the two equation for the density from Eqs. (1.12) and (1.13):

$$\boxed{\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0,} \tag{1.21}$$

and

$$\boxed{D_t \rho = -\rho \, \nabla \cdot \mathbf{v}.} \tag{1.22}$$

The equation for the specific volume can be obtained either by using $\upsilon = 1/\rho$ and using differential identities. But funnily enough, we can just use $\varphi = 1$ in Eq. (1.3) which yields

$$\frac{\mathrm{d}}{\mathrm{d}t} V_m = \int_{V_m} \nabla \cdot \mathbf{v} \, \mathrm{d}V. \tag{1.23}$$

Because this relation is valid whatever the mass enclosed in the material volume, the integrand must vanish at any location in space, and we can derive the equation for the evolution of the specific volume

$$D_t \upsilon = \upsilon \nabla \cdot \mathbf{v}. \tag{1.24}$$

1.1.4 Momentum conservation

To express the conservation of linear momentum locally, we can see that the velocity of the fluid can be identified as the specific linear momentum of the fluid. The forcings are thus external forces per unit mass, whether it is due to gravity ($\mathbf{g}$), pressure ($-(1/\rho)\nabla p$) or other external forces ($\mathbf{F}_{\text{ext}}$). Using Eq. (1.17) for each scalar component of the momentum and collapsing all the equations in vectorial form thus leads to the well-known Euler equation

$$\boxed{\rho D_t \mathbf{v} = -\nabla p + \rho \mathbf{g} + \rho \mathbf{F}_{\text{ext}}.} \tag{1.25}$$

Other external body forces (per unit mass) can include Coriolis, friction or viscosity forces. Because gravity derives from a potential, called the geopotential in atmospheric sciences (ϕ), we can also write

$$\mathbf{g} = -\nabla \phi. \tag{1.26}$$

Taking each component along the direction of the unitary vectors $\hat{\mathbf{i}}$ yields

$$\rho D_t v_i = -\partial_i p + \rho \mathbf{g} \cdot \hat{\mathbf{i}} + \rho \mathbf{F}_{\text{ext}} \cdot \hat{\mathbf{i}}. \tag{1.27}$$

Using Eq. (1.18) yields the flux form

$$\partial_t \rho v_i + \nabla \cdot (\rho v_i \mathbf{v}) = -\partial_i p + \rho \mathbf{g} \cdot \hat{\mathbf{i}} + \rho \mathbf{F}_{\text{ext}} \cdot \hat{\mathbf{i}}, \tag{1.28}$$

which can be written in vectorial form with the tensorial notation

$$\boxed{\partial_t \rho \mathbf{v} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v} + p) = \rho \mathbf{g} + \rho \mathbf{F}_{\text{ext}}.} \tag{1.29}$$

1.1.5 Hydrostatic balance and the hypsometric relation

Before going further, it is often useful to rapidly have a look at what happens when the atmosphere is in hydrostatic equilibrium, i.e. when there is no motion and that the pressure gradient compensates exactly the gravity. In this case, the equilibrium writes

$$\nabla p = \rho \mathbf{g} = -\rho \nabla \phi. \tag{1.30}$$

Using the geopotential as the vertical coordinate, this simply writes

$$\partial_\phi p = -\rho, \tag{1.31}$$

but if we align the z-axis with the vertical defined by the potential, then we recover a more recognizable form

$$\partial_z p = -\rho g, \tag{1.32}$$

which allows the often useful change of variable

$$\frac{\mathrm{d}p}{g} = -\rho \mathrm{d}z \qquad \text{or} \qquad \mathrm{d}p = -\rho \mathrm{d}\phi. \tag{1.33}$$

These formulae are very useful because even when there is large scale motion in the atmosphere, the pressure and gravity terms are often so large that they still dominate the vertical balance. It is therefore acceptable to use these formulae when large scale motions are present such as in a global climate model. Alternatively, even for convection resolving models, it turns out that it is still useful to define a *hydrostatic pressure* coordinate system even though the motion is far from hydrostatic (Laprise 1992).

1.1.6 Energy conservation: the first law

While the momentum equation deals with the macroscopic forms of energy, the kinetic and potential energy, one needs to account for the energy contained in the fluid at the microscopic level. The first law is there to do exactly that. It postulates that there is a macroscopic property of the fluid called the *internal energy* (U ; or its specific counterpart, u) that accounts for these microscopic forms of energy. An important feature of this quantity is that it is a *state functions* that depends only on the macroscopic state of the fluid.

The first law further postulates that energy be conserved so that any variation of internal energy of an open system is due to an exchange of heat (δQ), work (δW), or matter (also called chemical work ; δC) with the environment, so that

$$\mathrm{d}U = \delta Q + \delta W + \delta C. \tag{1.34}$$

It is rather unusual to see this chemical work term presented like this. But it is a crucial term when considering an atmosphere with a condensable species. In order to have an intuitive feeling about the *raison d'être* for this term, consider, for example, a system consisting of a parcel of air on top of liquid water that is evaporating. While the parcel's water vapor content increases, its internal energy must increase as well. This is this reservoir that we will tap to release latent heat when saturation occurs.

However, the right expression for this term is not obvious either and depends on how we express the other terms. This will be the subject of Chapter 2. For the moment we will keep considering only single-component atmospheres for which $\delta C = 0$.

With this simplification, the first principle simply writes

$$\mathrm{d}U = \delta Q + \delta W. \tag{1.35}$$

Notice the well-known difference between the exact differential on the left, which translates the fact that the internal energy is a state function and the δ's on the right that translate the fact that many different combinations of heating and work can lead a system from a state to another. The reader that would not be familiar with this subtlety is referred to any thermodynamics textbook (Bruhat 1968 ; Callen 1985).

Although this formula is very general, for the matter at hand, there is little loss in assuming that the processes we will be interested in occur in a quasi-static fashion and that the only mechanical work that will affect the internal energy will be due to (de)compression. This entails

$$\delta W = -p\mathrm{d}V. \tag{1.36}$$

But because we are interested in intensive variables, we can define the work applied per unit mass ($\tilde{}$) and time ($\dot{}$) as discussed in § 1.1.2 as

$$\dot{\tilde{W}} = -pD_t\upsilon = -p\, D_t\frac{1}{\rho} = -\frac{p}{\rho}\nabla\cdot\mathbf{v}. \tag{1.37}$$

Using Eq. (1.17) for the specific internal energy thus directly yields the Lagrangian internal energy equation

$$\boxed{D_t u = -pD_t\upsilon + \dot{\tilde{Q}},} \tag{1.38}$$

where $\dot{\tilde{Q}}$ is the specific heating powers due to diabatic processes that we will discuss in greater detail later on. Using Eq. (1.24), this can be transformed in

$$\rho D_t u = -p\nabla\cdot\mathbf{v} + \rho\dot{\tilde{Q}}, \tag{1.39}$$

or, with the help of Eq. (1.18), its flux version

$$\boxed{\partial_t\rho u + \nabla\cdot(\rho u\mathbf{v}) = -p\nabla\cdot\mathbf{v} + \rho\dot{\tilde{Q}},} \tag{1.40}$$

or

$$\boxed{\partial_t\rho u + \nabla\cdot(\rho\,(u+p\upsilon)\,\mathbf{v}) = -\mathbf{v}\cdot\nabla p + \rho\dot{\tilde{Q}},} \tag{1.41}$$

For further reference, it is important to mention here that there are several ways to quantify and keep track of the microscopic energy of the fluid, i.e. several available *state functions*, which all have their own strengths. The most used in atmospheric science is probably the *specific enthalpy*

$$h \equiv u + p\upsilon \equiv u + p/\rho, \tag{1.42}$$

because it transforms the work term in Eq. (1.38) to give

$$\boxed{D_t h = \frac{1}{\rho}D_t p + \dot{\tilde{Q}},} \tag{1.43}$$

and we see that there is no change of enthalpy for an isolated system that undergoes an isobaric transformation. The reason why this is particularly helpful will be discussed in detail in § 5.2.

1.2 Global conservation of energy

Before doing the deep dive into the nasty description of the thermodynamic properties of the materials we will be studying, a description that will necessitate more approximations, it is interesting to stop and try deriving some general conservation laws that should apply no matter what.

We can start by taking the dot product of the momentum equation, Eq. (1.25), with the velocity, which yields

$$\frac{1}{2}\rho D_t \mathbf{v}^2 = -\mathbf{v}\cdot\nabla p - \rho\mathbf{v}\cdot\nabla\phi + \rho\mathbf{v}\cdot\mathbf{F}_{\text{ext}}. \tag{1.44}$$

On can notice that, since the gravitational potential does not vary explicitly in time, the geopotential of a parcel only varies following

$$\rho D_t \phi = \rho\mathbf{v}\cdot\nabla\phi, \tag{1.45}$$

so that we can write an equation for the conservation of *mechanical* energy

$$\boxed{\rho D_t\left(\frac{1}{2}\mathbf{v}^2 + \phi\right) = -\mathbf{v}\cdot\nabla p + \rho\mathbf{v}\cdot\mathbf{F}_{\text{ext}}.} \tag{1.46}$$

Finally, adding our equation for the mechanical energy to Eq. (1.39) for the internal energy we find

$$\rho D_t\left(\frac{1}{2}\mathbf{v}^2 + u + \phi\right) = -p\nabla\mathbf{v} - \mathbf{v}\cdot\nabla p + \rho\mathbf{v}\cdot\mathbf{F}_{\text{ext}} + \rho\dot{\tilde{Q}} \tag{1.47}$$

$$= -\nabla\cdot(p\mathbf{v}) + \rho\mathbf{v}\cdot\mathbf{F}_{\text{ext}} + \rho\dot{\tilde{Q}}. \tag{1.48}$$

Interestingly, we see that there is a connection between the macro and micro form of energy through the pressure term in the momentum equation and the compression term in the statement of the first law. This equation also illustrates the rather reassuring fact that in order to change the total energy of our parcel, one must either heat it or apply some work due to either pressure or external forces (like friction[1]). As we will see in latter chapters, energy can also be transferred by changing the composition of the parcel through either diffusion or sedimentation/precipitation of condensates.

A different perspective can be drawn by looking at the flux form of this equation using Eq. (1.18)

$$\boxed{\partial_t\left[\rho\left(\frac{1}{2}\mathbf{v}^2 + u + \phi\right)\right] + \nabla\left[\rho\mathbf{v}\left(\frac{1}{2}\mathbf{v}^2 + u + \phi + \frac{p}{\rho}\right)\right] = \rho\mathbf{v}\cdot\mathbf{F}_{\text{ext}} + \rho\dot{\tilde{Q}}.} \tag{1.49}$$

Integrating this equation over an isolated column of atmosphere shows that the specific total energy

$$\boxed{e = \mathbf{v}^2/2 + u + \phi} \tag{1.50}$$

is the right conserved quantity for the column.

[1] We are talking here about external friction at a boundary, for example. Indeed, any friction due to viscosity inside the volume would appear as a heating term in the internal energy equation, therefore leaving the total energy unchanged.

1.3 Thermodynamics of the dry atmosphere in a nutshell

While we will have a deeper discussion of the thermodynamics of a general atmosphere (e.g. one where part of the gas can condense or chemically react) later on, it is rather useful to have a look at the simple case of a dry atmosphere made of an ideal gas. This will allow us to introduce some general concepts and derive some order of magnitude estimates that will often remain a good approximations when more complex processes are at play.

At the beginning of the chapter, we mentioned that we would need 6 scalar equations to solve for the our 6 scalar variables (ρ, p, T, and v). Conservation of mass, momentum and energy have brought us 5 equations, but we have been forced to add another unknown in the process, the internal energy. We thus need 2 other equations to have a closed set. Thanks to the power of the principles of thermodynamics, we in fact only need to find the *fundamental relation* describing our gas, i.e. an expression for the internal energy as a function of its canonical variables, entropy and volume. Indeed, the very mathematical properties of the fundamental relations provide all the other relations that we need. But we would need to go a little deeper into thermodynamics territory than I am ready to go at this point. Therefore, we will limit ourselves to the two most well-known *equations of state* for the ideal gas.

1.3.1 Mechanical equations of state

The first, which is probably what most people would remember if they were asked to remember something about thermodynamics at gunpoint, is

$$\boxed{p = \rho R T} \tag{1.51}$$

where R is specific constant of the gas, which is given by $R = R^\star/M$, where $R^\star$ is the famous molar gas constant and M is the molar mass of the gas considered. There would be plenty to say about this equation, but nothing new, so let's move on.

1.3.2 Scale height

The equation of state for the ideal gas (Eq. (1.51)) already allows us to derive some interesting results on the structure of a hydrostatic atmosphere. Substituting the density in the hydrostatic equilibrium equation, Eq. (1.33), yields

$$\frac{\mathrm{d}p}{p} = -\frac{g}{RT}\mathrm{d}z, \tag{1.52}$$

which leads us to define the so-called pressure scale height

$$H_p = \frac{RT}{g}, \tag{1.53}$$

which is the characteristic scale of the exponential decrease of the pressure in the atmosphere.

Its meaning becomes readily clear when we integrate Eq. (1.52) from the surface for an isothermal atmosphere in a constant gravity field, which yields

$$p = p_\mathrm{s}\, e^{-z/H_p}, \tag{1.54}$$

where p_s is the surface pressure. This means that the pressure in an isothermal atmosphere decreases by a decade every $-\ln(0.1) \approx 2,302585093$ scale heights. This equation can be inverted to define a *log-pressure* altitude once an arbitrary reference scale height is chosen.

1.3.3 Caloric equation of state

If the temperature is not provided *a priori*, or if one wants to compute a thermal evolution in time, we need a second relation to specify how the internal energy varies with the other state variables of the system. This second relation is called the *caloric* equation of state.

The definition of an ideal gas specifies that this internal energy depends only on temperature so that

$$\mathrm{d}u = c_v(T)\mathrm{d}T, \tag{1.55}$$

where c_v is the specific heat of the gas at constant volume. Its name comes from the fact that it is the heat needed to increase the temperature of a kilogram of gas by one Kelvin when the volume of the gas is kept constant. As pointed out earlier, another interesting state function is the specific enthalpy, which for a general ideal gas writes

$$h = u + p\upsilon = u + p/\rho = u(T) + RT, \tag{1.56}$$

so that the enthalpy of an ideal gas also depends only on the temperature. Just like the internal energy, the increase in enthalpy can be linked to the heat needed to increase the temperature of a kilogram of gas by one Kelvin when the pressure of the gas is kept constant, i.e. the specific heat at constant pressure, c_p, so that

$$\mathrm{d}h = c_p(T)\mathrm{d}T. \tag{1.57}$$

Combining Eqs. (1.55) and (1.56) allows us to demonstrate Mayer's relation for an ideal gas:

$$c_p(T) = c_v(T) + R. \tag{1.58}$$

This still leaves us with several possible equations of state depending on how c_v and c_p will vary with temperature. Yet, because we know that the internal energy and the enthalpy vary only with temperature, we can integrate to yield

$$u(T) = u^\circ + \int_{T^\circ}^{T} c_v(T)\,\mathrm{d}T, \tag{1.59}$$

$$h(T) = h^\circ + \int_{T^\circ}^{T} c_p(T)\,\mathrm{d}T, \tag{1.60}$$

where u° and h° are the reference internal energy and enthalpy at some conventional reference temperature T°.

If we stick to the very simple model of the calorically perfect ideal gas, which is a rather valid approximation for many gases of interest in the range of temperatures encountered in the atmosphere, c_v is constant so that this simplifies to

$$u = u^\circ + c_v(T - T^\circ), \tag{1.61}$$

$$h = h^\circ + c_p(T - T^\circ). \tag{1.62}$$

1.3.4 Potential temperature

The caloric equation of states allows us to compute how much heat is needed to increase the temperature of a gas. But it can also be used to compute the increase in temperature when only

mechanical work and no heat is exchanged with the environment. This is the well-known *adiabatic* expansion problem.

Let just introduce our caloric equation of state in our statement of the first law for a reversible transformation where only pressure acts on the fluid (Eq. (1.34)). Using the enthalpy formulation this yields

$$\delta\tilde{Q} = c_p \mathrm{d}T - \upsilon \mathrm{d}p. \tag{1.63}$$

Using the ideal gas equation of state and assuming no heat transfer yields

$$\frac{\mathrm{d}T}{T} = \frac{R}{c_p}\frac{\mathrm{d}p}{p}. \tag{1.64}$$

For a calorically prefect gas[2], this can be integrated into

$$\mathrm{d}\ln\left(\frac{T}{p^{R/c_p}}\right) = 0, \tag{1.65}$$

which leads us to define the *potential temperature*

$$\boxed{\theta \equiv T\left(\frac{p}{p_0}\right)^{-R/c_p} \equiv T\Pi^{-1},} \tag{1.66}$$

where p_0 is an arbitrarily chosen reference pressure and Π is called the Exner function. The potential temperature thus remains constant during an adiabatic expansion of the gas. This is very useful because θ is a passive tracer for any adiabatic motion.

It is worth mentioning for those who tolerate thermodynamics only as long as the name of You-Know-Who remains unspoken that we did not need to introduce He-Who-Must-Not-Be-Named or the second law to define potential temperature. This is because we assume that we are only dealing with adiabatic and reversible dynamics at the scale we are looking at. But for those who like that, it is also worth mentioning that $s = c_p \ln\theta$ is in fact the specific *entropy* (oopsy daisy) of our calorically perfect ideal gas.

If the dynamics is not adiabatic anymore but still reversible, then the application of the second law for a chemically homogeneous fluid states that

$$D_t s = \frac{\dot{\tilde{Q}}}{T}. \tag{1.67}$$

Combining this with the concept of potential temperature allows us to isolate the adiabatic and diabatic terms in the energy equation and write the conservation of energy as follows

$$\boxed{c_p D_t\theta = \frac{\theta}{T}\dot{\tilde{Q}}.} \tag{1.68}$$

This equation is particularly useful because there is no compression term to deal with. As we already said, θ is a passive tracer for adiabatic motion. So it is passively transported and mixed by the circulation. Only external diabatic heating terms can alter it.

In particular, when we consider motion that happens much faster than radiative cooling, we can consider that the potential temperature remains constant during that motion. This is why dry convective zones, like the troposphere of planets without abundant condensible species like Mars of Venus can be relatively well approximated by zones with a constant potential temperature (i.e. a constant entropy). This will be discussed in depth in Chapter 4.

[2]For a gas whose heat capacity varies with temperature, one can still define a potential temperature with $\ln(\theta/T) = \int \frac{R}{c_p}\mathrm{d}\ln p$.

Chapter 2

Chemical potentials, open systems, and the energy equation for heterogeneous atmospheres

Thermodynamics is a funny subject.
The first time you go through it, you don't understand it at all.
The second time you go through it, you think you understand it, except for one or two small points.
The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more.

Arnold Sommerfeld

Contents

Homogeneous atmospheres are fun to play with and provide a great tool to have a first-order understanding of many atmospheric processes. But as we experience daily when looking out the window, our atmosphere is far from homogeneous. Surface water evaporates to fill the atmosphere with vapor that can later condense to form clouds of liquid droplets and ice crystals that sediment or precipitate and the cycle goes on. Along the way, both the vapor and the condensed particles (or aerosols) interact with solar and thermal radiation, creating a non-trivial radiative forcing pattern on top of the heating due to latent heat release. Finally, vapor can also be photodissociated and react chemically with other species to produce a host of other species. In short, Earth's atmosphere is far from homogeneous, and so are most others: Mars has its water and carbon dioxide clouds, Venus its sulfuric acid ones, ammonia can condense in Jupiter's atmosphere and Titan, Uranus and Neptune exhibit methane storms. Even when no major species condense, thermo- or photo-chemistry can create huge variations in the chemical composition of the atmosphere from one region to another.

So it is now time to turn to heterogenous atmospheres. But the question is the following: how can we alter the equations derived in Chapter 1 to *rigorously* account for the energetics of chemical heterogeneities, phase transitions and chemical reactions ? I insist on the *rigorously* because it might seem to the reader that there is no deep mystery here and that this is laid out in many textbooks. But although I agree that it is often *done* in a satisfactory way, I found that this is often *derived* or *explained* in a very misleading, if not completely wrong fashion.

For example, Holton (2004), which is one of the best references in dynamical meteorology, simply affirms in a peremptory manner that the equation for the specific internal energy of the atmosphere derives from the first law and writes exactly like what we have found in Chapter 1 for a dry atmosphere (Eq. (1.39))[1]:

$$\rho D_t u = -p\nabla\cdot\mathbf{v} + \rho\dot{\tilde{Q}}, \tag{2.1}$$

except for the fact that

> *Here [$\dot{\tilde{Q}}$] is the rate of heating per unit mass due to radiation, conduction, and latent heat release.* (1)

Although I confess that I have been kind-of-okay with this explanation for the past decade and used it many times, I always found it a little odd and not very satisfactory because latent heat release happens because of an internal change to the air parcel's composition while the first law talks only about external heat supplied to the system. I can now safely say that this equation, with the inclusion of latent heat in the heating term, is totally wrong, as will be demonstrated hereafter (See § 2.5). And

[1] Compare, for example, to Eq. (2.39) of Holton (2004) where the internal energy is noted e, the velocity U, and the specific heating rate J. The quote can be found a few lines before Eq. (2.39) in section 2.6.

if it leads to a *working* equation on the temperature later on, it is only because Holton (2004) does an equally incorrect assumption on the definition of the internal energy so that the two mistakes cancel out. This does lead *rapidly*[2] to a working set of equations, but I suspect that this may have confused many students has it confused me, and I think that it does not really help us understand the energetics of the problem.

But if this approach is incorrect, which one is ?

When thinking of the energetics of a system whose composition can vary, the thermodynamicist's mind can't help but be drawn to the *fundamental relation* of thermodynamics :

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \gamma_i \mathrm{d}m_i, \tag{2.2}$$

where γ_i and m_i are the specific chemical potential and the mass of species i in the system considered and the sum on repeated indices is always implicitly assumed. This equation entails that a change in mass and/or composition of a system impacts its internal energy just as a change in volume does. And such processes happen all the time in atmospheric science. Phase change during condensation of cloud droplets or mixing of air parcels with different vapor contents are perfect examples of compositional change at fixed mass, but one can also think of evaporation over a body of water — in which case both the composition and total mass of the atmosphere vary — or of the precipitation of droplets — involving no phase change but leaving only moist air behind. In a more exotic context, one can think of the atmosphere of brown dwarfs where a convective region can span a large enough temperature range to have the equilibrium chemical composition of the air change during a convective overturn.

This looks promising, but the fact remains that I managed to perform research in atmospheric sciences for over a decade without having to compute a single chemical potential. Yet, all those years I kept wondering why it was never really developed in any textbook on atmospheric dynamics[3]. Of course, it does not help that among the various concepts encountered in thermodynamics, the chemical potential probably deserves the prize for least intuitive. I feel that even the concept of entropy, as far as I have understood it anyway[4], is more intuitive. Maybe the reason is that during the thermodynamics course I have followed, chemical potentials were either completely disregarded as useless or quickly introduced to demonstrate some overarching results of thermochemistry to be as quickly forgotten once those results could be used on their own.

Notwithstanding, why are this equation and chemical potentials *not* the backbone of any climate model ? Even Vallis (2006), who writes down Eq. (2.2), discusses the chemical potential term for about only a paragraph before discarding it as negligible without much justification and never mentioning it again through the whole book. Is it because *i)* this term is negligible or because, for some reason, *ii)* it always vanishes in the cases we consider or because, somehow, *iii)* we just take it into account implicitly through other terms ?

The goal of this chapter is to answer this question. Of course, as you might imagine, the following pages will not suddenly reveal that the whole atmospheric-science community has been wrong neglecting this term for years. But this question has been haunting me for some time now. Probably more so than others because I have been interested in atmospheres for which condensable species can become the dominant constituent of the atmosphere, which has forced me to question many other common assumptions. So I hope that these considerations will help put the mind of other readers with the same demons at ease.

[2] Which is, I think, the reason the author used this shortcut knowingly.

[3] I am of course leaving out the field of atmospheric chemistry where this concept is central in defining equilibrium compositions. Yet, Eq. (2.2) is general and should apply even in cases where there is no chemical reactions.

[4] i.e. much better than before sitting down to write this manuscript, but probably much less than next time I'll have the opportunity to read another thermodynamics textbook.

Yet, doing so, we will still come to correct some false statements or ambiguities related to the implementation of energy and entropy equations found along the way. For example, why do we take into account the heat released internally by phase transitions inside a parcel into the entropy, temperature, or potential temperature equation even though entropy variation is usually due to external heat sources ? As will become clear, these errors almost *always happen when a given interpretation, valid for a closed system, is incorrectly applied to an open one*. Therefore, resolving those ambiguities will also allow us to delineate a robust framework for the derivation of the energy equation in a heterogeneous atmosphere and the treatment of open systems that will help us treat more rigorously, or at least more transparently, the exchanges of the atmosphere with surface reservoirs in subsequent chapters.

2.1 Statement of the problem

2.1.1 Definitions and textbook interpretations

Let us start by defining a little more precisely the notion of chemical potential and see where it comes from. Again, this manuscript is not expected to be a general textbook on thermodynamics, so we refer the interested reader to the excellent reference books by Bruhat (1968) or Callen (1985) for more details. Yet it is interesting to recall that Eq. (2.2) comes from the realization that in a system composed of n species, the fundamental relation for the internal energy depends only on the extensive variables of the system, i.e. the entropy (S), the volume (V), and the n masses for each species ($\{m_i\}$) so that a variation of the internal energy can be written

$$\mathrm{d}U = \left.\frac{\partial U}{\partial S}\right|_{V,\{m_i\}} \mathrm{d}S + \left.\frac{\partial U}{\partial V}\right|_{S,\{m_i\}} \mathrm{d}V + \left.\frac{\partial U}{\partial m_i}\right|_{S,V,\{m_j\}} \mathrm{d}m_i. \tag{2.3}$$

The notation $\{m_j\}$ stands for all the masses except the i-est one. Turning this into Eq. (2.2) is actually only a matter of defining

$$\begin{aligned}
\left.\frac{\partial U}{\partial S}\right|_{V,\{m_i\}} &\equiv T, \\
\left.\frac{\partial U}{\partial V}\right|_{S,\{m_i\}} &\equiv -p, \\
\left.\frac{\partial U}{\partial N_i}\right|_{S,V,\{m_j\}} &\equiv \gamma_i.
\end{aligned} \tag{2.4}$$

Of course, these notations could remain purely academic if not for the fact that the above T and p can be shown to agree with our intuitive definitions of temperature and pressure (Callen 1985). The first and second terms in Eq. (2.2) can therefore be rapidly intuitively understood. For a closed system that undergoes a quasi-static, reversible transformation :

- $T\mathrm{d}S$ is the change in internal energy due to an exchange of heat with the environment,
- $-p\mathrm{d}V$ is the change in internal energy due to the mechanical work of the environment on the system through pressure forces.

But, as put rather bluntly by Callen (1985, Sect 2.1)):

> *The remaining terms in [Eq. (2.2)] represent an increase of internal energy associated with the addition of matter to a system. This type of energy flux, although intuitively meaningful, is not frequently discussed outside thermodynamics and does not have a familiar distinctive name. We shall call $\gamma_i \mathrm{d}N_i$ the quasi-static chemical work [$C = \gamma_i \mathrm{d}m_i$ in our notations where we have decided to use masses instead of mole numbers]* (2)

Despite reinforcing the fact that chemical potentials and chemical work are not easily linked to our everyday life experience, I think that this quote, which can be found in a similar way in several textbooks including Vallis (2006), embodies most of the ambiguity hampering a proper understanding of these concepts. Indeed, because the other terms have an explanation when no exchange of matter is present, it implicitly entails that this term is *the* term accounting for the change of energy when mater is added to the system. We will see that this interpretation is wrong. But to demonstrate that, we first need to recall some well-known properties of chemical potentials.

2.1.2 Properties of chemical potentials

Again, as the demonstrations of the various properties discussed here can be found in many textbooks, I will not reproduce the demonstrations. However, I felt that these properties, along with their physical meaning, needed to be written for the reader to be able to follow the various arguments put forward in the remainder of this chapter.

Invariance of the chemical work in different thermodynamical representations

Although the two first right-hand-side terms in Eq. (2.2) have a different form when we look at the expression of the fundamental relation for other thermodynamical energy state functions like the enthalpy ($H \equiv U + pV$), the Helmholtz free energy ($F \equiv U - TS$), or the Gibbs free enthalpy ($G \equiv U + pV - TS$), the chemical work always keeps the same form

$$\begin{aligned} \mathrm{d}U &= \quad T\mathrm{d}S - p\mathrm{d}V + \gamma_i \mathrm{d}m_i, \\ \mathrm{d}H &= \quad T\mathrm{d}S + V\mathrm{d}p + \gamma_i \mathrm{d}m_i, \\ \mathrm{d}F &= -S\mathrm{d}T - p\mathrm{d}V + \gamma_i \mathrm{d}m_i, \\ \mathrm{d}G &= -S\mathrm{d}T + V\mathrm{d}p + \gamma_i \mathrm{d}m_i. \end{aligned} \tag{2.5}$$

This means that the chemical potential can be defined as the partial differential of any of these energy functions by just choosing carefully the variables kept constant during differentiation

$$\gamma_i \equiv \left.\frac{\partial U}{\partial m_i}\right|_{S,V,\{m_j\}} \equiv \left.\frac{\partial H}{\partial m_i}\right|_{S,p,\{m_j\}} \equiv \left.\frac{\partial F}{\partial m_i}\right|_{T,V,\{m_j\}} \equiv \left.\frac{\partial G}{\partial m_i}\right|_{T,p,\{m_j\}}. \tag{2.6}$$

Integral relations

One of the postulates of thermodynamics is that our thermodynamical energy state functions are additive. In other words, if I bring together two subsystems with the same energy, entropy, volume and composition, I get a system with twice the energy, entropy, volume and mass. Mathematically, this leads to the fact that for any number λ,

$$U(\lambda S, \lambda V, \{\lambda m_i\}) = \lambda U(S, V, \{m_i\}). \tag{2.7}$$

This is the definition of an homogeneous function of degree one, and we can thus use Euler's theorem that states that for such a function $f(\{X_i\},\{Y_i\})$[5] where

$$f(\{\lambda X_i\},\{Y_i\}) = \lambda f(\{X_i\},\{Y_i\}), \tag{2.8}$$

we can write

$$f(\{X_i\},\{Y_i\}) = \left.\frac{\partial f}{\partial X_i}\right|_{X_j,Y_i} X_i. \tag{2.9}$$

Applying this to our four energy functions and remembering what are their canonical variables and which of them are extensive yields

$$\begin{aligned} U &= TS - pV + \gamma_i m_i, \\ H &= TS + \gamma_i m_i, \\ F &= -pV + \gamma_i m_i, \\ G &= \gamma_i m_i, \end{aligned} \tag{2.10}$$

which agrees with the definition of the energy functions based on the internal energy

$$\begin{aligned} H &= U + pV, \\ F &= U - TS, \\ G &= U + pV - TS. \end{aligned} \tag{2.11}$$

These integral relations (Eq. (2.10)) clearly show that the Gibbs free enthalpy is just the sum of the chemical potentials weighted by the mass of each species, so that the chemical potentials can be identified with the specific Gibbs enthalpy of each species in the mixture. This goes along well with the picture described in Quote 2: when we add some matter, m_i, to the system, we "add some energy equal to $\gamma_i m_i$" to it. But I think that this leads to more misunderstanding, as will become clearer in a moment.

Equality of chemical potentials in different phases

This one is fundamental to our argument, but its demonstration would be rather cumbersome and would need us to go through the whole shebang of demonstrating that for a transformation at constant temperature and pressure, the equilibrium state is characterized by a minimum of the Gibbs free enthalpy. For the interested reader, there is a nice demonstration in Sect. 137 of Bruhat (1968).

But the result goes like this: *When a system made of several physical phases and several species is in thermodynamical equilibrium, the chemical potential of each species has the same value in all the phases.*

This important result, established in 1875 by Willard Gibbs, is actually the reason that the variance of a system is reduced when a new phase is present.

2.2 A confusing Gedanken experiment

Now that we have all the necessary background, let us consider a simple thought experiment that perplexed me for a while and is the reason I initially decided to write down this chapter.

[5] In physical terms, the X_i are the extensive variables and the Y_i are intensive variables that, by definition, remain the same in the bigger system

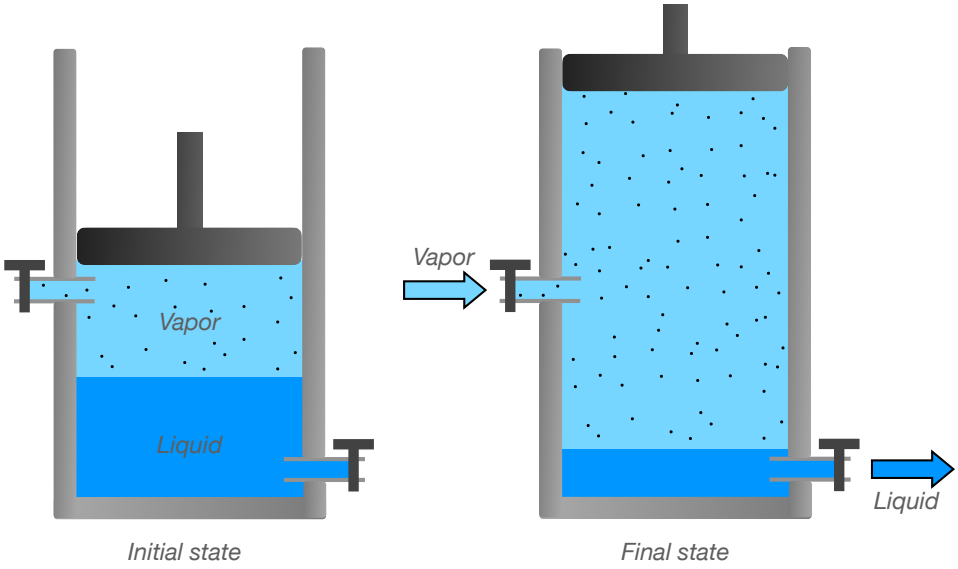

Figure 2.1: Schematic of the adiabatic enclosure. In the final state, almost all the liquid is replaced by vapor.

2.2.1 Setup

In an adiabatic enclosure depicted in Fig. 2.1 we have some liquid — let it be water to make things concrete — that is initially in equilibrium with its vapor at a given temperature and pressure. Pressure is kept constant by a moving piston on top of the enclosure. Thanks to two valves, we can add or remove water and water vapor independently. When matter is added, it is introduced at the exact same temperature and pressure as in the enclosure so that we remain at the liquid-vapor equilibrium.

Now, we start slowly removing water from the enclosure while introducing water vapor with the same mass flux so that the total mass in the container remains constant. At some point, there is almost no liquid water left in the enclosure which is filled with water vapor, even though, for the sake of argument, we will leave a tiny amount of liquid water in the tank to formally remain in liquid-vapor equilibrium. The important point is that in this experiment, the intensive parameters in the tank — temperature, pressure, and thus chemical potential — have not changed and we remained in liquid-vapor equilibrium the whole time.

2.2.2 An "intuitive" interpretation

Now, if we stick to the "intuitive" interpretation of Callen (1985) in Quote 2, the change in the internal energy associated with the addition/removal of matter is $\gamma_i \mathrm{d}m_i$. But in our case, we made sure that the added vapor, $\mathrm{d}m_\mathrm{v}$, strictly cancels out with the removed condensed phase, $\mathrm{d}m_\mathrm{c}$, so that $\mathrm{d}m_\mathrm{v} = -\mathrm{d}m_\mathrm{c}$. Here we can finally make use of the important fact that when at liquid-vapor equilibrium, the chemical potential of water must be the same in the two phases (See § 2.1.2), $\gamma_\mathrm{v} = \gamma_\mathrm{c}$. So the chemical work is

$$\delta C = \gamma_\mathrm{v} \mathrm{d}m_\mathrm{v} + \gamma_\mathrm{c} \mathrm{d}m_\mathrm{c} = \gamma_\mathrm{v}(\mathrm{d}m_\mathrm{v} + \mathrm{d}m_\mathrm{c}) = 0. \tag{2.12}$$

Because the walls of the enclosure are adiabatic, there has not been any heat loss and δQ also vanishes. Finally, because vapor takes more space than water (actually, the schematic is probably

not to scale), the system has had to push on the piston to increase its volume so that the mechanical work it received, δW, is negative.

So, overall, the internal energy should have changed by

$$\mathrm{d}U = \delta Q + \delta W + \delta C = 0 + \delta W + 0 < 0. \tag{2.13}$$

It has decreased during the process ! This is rather surprising because any thermodynamic table will tell you that water vapor has a larger internal energy than liquid water. Much larger, in fact. And we are very familiar with that because we know quite well that we need to provide quite a lot of heat to vaporize water, the so-called latent heat that we have already encountered. In our experiment, the internal energy of our system must therefore have increased, and not the opposite.

So what is wrong with this interpretation — that I could quite frankly see an average undergrad fall for ?

2.2.3 Reinterpretation using the additivity property

The careful reader should have noticed by now that our thought experiment involves an open system while our reasoning used some results derived from the first law as interpreted for a closed system. And as advertised in the introduction, we will now show that the apparent paradox comes from this mistake.

Basically, we implicitly assumed that we could express the chemical work with a perfect differential form in Eq. (2.12), but keep the heat and mechanical work term in their imperfect "δ" form and keeping their physical interpretation as in § 2.1.1. In particular, δQ should have been replaced by $T\mathrm{d}S$. Because if it is true that there has not been any heat exchange with the environment thanks to the adiabatic walls, it is not true that the entropy of our system has remained constant. This is because we must account for the entropy (and volume) of the fluids that we have added to or removed from our system.

With that in mind, we can just use the derivative of the fundamental relation, Eq. (2.2), where we now interpret the various infinitesimal variations as having two terms: one originating from internal changes to the system and one due to the contribution of matter entering or leaving the system. We will develop this approach more concretely in § 2.4.

In the case of our thought experiment, it is even easier to interpret it using the integral relations given in Eq. (2.10). Because we consider a system where the vapor and liquid are well separated and that, in keeping with the thermodynamic limit, surface effects can be considered negligible, we can use the additivity rule to compute the global internal energy in the initial and final states (with subscripts "ini" and "fin") as the sum of the internal energies of both liquid and vapor:

$$\begin{aligned}
U_{\mathrm{ini}} &= U_{\mathrm{c,ini}} && + U_{\mathrm{v,ini}} \\
&= TS_{\mathrm{c,ini}} - pV_{\mathrm{c,ini}} + \gamma_{\mathrm{c}} m_{\mathrm{c,ini}} && + TS_{\mathrm{v,ini}} - pV_{\mathrm{v,ini}} + \gamma_{\mathrm{v}} m_{\mathrm{v,ini}} \\
U_{\mathrm{fin}} &= U_{\mathrm{c,fin}} && + U_{\mathrm{v,fin}} \\
&= TS_{\mathrm{c,fin}} - pV_{\mathrm{c,fin}} + \gamma_{\mathrm{c}} m_{\mathrm{c,fin}} && + TS_{\mathrm{v,fin}} - pV_{\mathrm{v,fin}} + \gamma_{\mathrm{v}} m_{\mathrm{v,fin}}.
\end{aligned} \tag{2.14}$$

The internal energy variation thus writes

$$\begin{aligned}
\Delta U = \quad & T\left[\left(S_{\mathrm{v,fin}} - S_{\mathrm{v,ini}}\right) + \left(S_{\mathrm{c,fin}} - S_{\mathrm{c,ini}}\right)\right] \\
& - p\left[\left(V_{\mathrm{v,fin}} - V_{\mathrm{v,ini}}\right) + \left(V_{\mathrm{c,fin}} - V_{\mathrm{c,ini}}\right)\right] \\
& + \gamma_{\mathrm{v}}\left(m_{\mathrm{v,fin}} - m_{\mathrm{v,ini}}\right) + \gamma_{\mathrm{c}}\left(m_{\mathrm{c,fin}} - m_{\mathrm{c,ini}}\right).
\end{aligned} \tag{2.15}$$

Finally, because no intensive variable has changed, the specific entropies, $s_i = S_i/m_i$, and volumes, $\upsilon_i = V_i/m_i$, have also remained constant so that, denoting $\Delta m_\mathrm{v} = m_{\mathrm{v,fin}} - m_{\mathrm{v,ini}} = m_{\mathrm{c,ini}} - m_{\mathrm{c,fin}}$, we get

$$\begin{aligned}\Delta U = \quad & T\left[s_\mathrm{v}\left(m_{\mathrm{v,fin}} - m_{\mathrm{v,ini}}\right) + s_\mathrm{c}\left(m_{\mathrm{c,fin}} - m_{\mathrm{c,ini}}\right)\right] \\ & - p\left[\upsilon_\mathrm{v}\left(m_{\mathrm{v,fin}} - m_{\mathrm{v,ini}}\right) + \upsilon_\mathrm{c}\left(m_{\mathrm{c,fin}} - m_{\mathrm{c,ini}}\right)\right] \\ & + \gamma_\mathrm{v}\left(m_{\mathrm{v,fin}} - m_{\mathrm{v,ini}}\right) + \gamma_\mathrm{c}\left(m_{\mathrm{c,fin}} - m_{\mathrm{c,ini}}\right) \\ = \quad & \left[T\left(s_\mathrm{v} - s_\mathrm{c}\right) - p\left(\upsilon_\mathrm{v} - \upsilon_\mathrm{c}\right) + \left(\gamma_\mathrm{v} - \gamma_\mathrm{c}\right)\right]\Delta m_\mathrm{v} \\ = \quad & \left(u_\mathrm{v} - u_\mathrm{c}\right)\Delta m_\mathrm{v}, \end{aligned} \tag{2.16}$$

where $u_i = Ts_i - p\upsilon_i + \gamma_i$ is the specific internal energy of each component.

Now remembering that $\gamma_\mathrm{v} = \gamma_\mathrm{c}$, this formula makes it immediately obvious that the change in internal energy has no contribution from the chemical potentials. The change is only due to the difference in specific internal energies of the two phases, which is just due to different specific entropies and volumes[6].

2.3 Real-life misinterpretations

So we now see that it is not only misleading, but also *plain wrong* to say that the chemical work term represents an increase of internal energy associated with the addition of matter to a system. This should be rephrased as

> *The increase of internal energy associated with the addition of matter to a system is just the difference between the internal energy of the added matter and the one of the removed matter,*

however tautologic this statement may be.

Of course, one could complete Callen's statement to say that the chemical work is an increase of internal energy associated with the addition of matter to a system *at constant entropy and volume.* This is most certainly what the author had in mind. But then, at the very least, I guess it is a little far fetched to call this term *intuitively meaningful* (Quote 2). Indeed, in a general setup, introducing matter at constant entropy and volume would require to otherwise control the heat and work applied to the system in such a peculiar way that this would severely restrict the level of intuition that can be gained. We can even show that this would be impossible in our example because the only way to keep both the entropy and volume of the system constant while staying in liquid-vapor equilibrium is to do nothing at all[7] !

One could argue that the problem outlined above is purely a matter of interpretation and has no real-life implications. Indeed, our thought experiment looks rather academic. But is it ? No. In fact, it is what happens in a cloud when condensates start precipitating. If one looks at the specific enthalpy or entropy of the fluid — which is equivalent to looking at a parcel with a constant total mass, as we usually do in the models — the change in composition must be accompanied by a change in those quantities, even though the chemical work in the sense of Callen (1985) is nil. This is because the mass of condensed water that falls down is replaced by vapor (or more generally moist air).

[6] And we recover that this is positive because both the specific entropy is much larger for the vapor compared to the liquid, outweighing the volume term.

[7] This is because in liquid-vapor equilibrium, the variance of the system is reduced.

This is not fully appreciated nor transparent in many implementations. Let us consider, for example, the derivation of the entropy equation in Sect 1.6 of Vallis (2006). It starts from the internal energy equation written as[8]

$$D_t u + p D_t \upsilon = \dot{\tilde{Q}}_T \equiv \dot{\tilde{Q}} + \dot{C}, \tag{2.17}$$

where it is explicitly said that

> *$\dot{Q}_T$ is the rate of total energy input, per unit mass, with possible contributions from thermal fluxes (including radiative heating, thermal diffusion and heat generated by viscous damping) and from diffusive fluxes of composition.* (3)

To eliminate the contribution from the composition, the demonstration then introduces equations for the various constituents specific concentrations

$$D_t q_i = \dot{q}_i, \tag{2.18}$$

where $\dot{q}_i$ would be any sink or source of constituent i not linked to the global fluid motion, typically diffusion or sedimentation and precipitation of droplets. Then, Vallis (2006) states that one can use the material derivative of the fundamental equation,

$$D_t u = T D_t s - p D_t \upsilon + \gamma_i D_t q_i, \tag{2.19}$$

and combine it with Eq. (2.17) and Eq. (2.18) to get

$$\begin{aligned} T D_t s &= \dot{\tilde{Q}} + \dot{\tilde{C}} - \gamma_i D_t q_i \\ &= \dot{\tilde{Q}} + \dot{\tilde{C}} - \gamma_i \dot{q}_i. \end{aligned} \tag{2.20}$$

Until that point, there is (almost) nothing wrong with this demonstration. But it goes one step too far when making the final leap and saying that $\dot{\tilde{C}} = \gamma_i \dot{q}_i$ to simplify this into his Eq. (1.95):

$$D_t s = \frac{\dot{\tilde{Q}}}{T}, \tag{2.21}$$

where $\dot{\tilde{Q}}$ is explicitly said to account only for heating terms. This entropy equation — which is used in many models, not the least of which is the Weather Research and Forecast model (WRF ; Skamarock et al. 2019) which is the dynamical core we have used to study convection in condensible-rich atmospheres in Leconte et al. (2024) and Clément et al. (2024) — however correct when the composition is fixed, is wrong in general. It is well known, for example, that even though moist convection can be seen as adiabatic in many ways, the fact that condensates are not fully retained during ascent makes the thermal gradient in the plume follow a *pseudo-isentrope*, even though no irreversible process has been involved. One way to salvage Eq. (2.21) would be to say that because we are looking at material derivative, we follow a closed particle of fluid whose composition cannot change. However this is not

[8] I apologize in advance to any reader that will be trying to look it up in the original book as most notations are different. Vallis (2006) denotes the internal energy I, the specific volume α, the entropy η, $\dot{\tilde{Q}}_T$ is the sum of the heat and chemical work, and most troubling of all, its compositional variable is called S ! I have also chosen to use masses and specific concentrations as compositional variables. I will therefore adapt his demonstration here with the local notations while keeping the argumentation untouched.

accounting for diffusion processes that arise at the smallest scales and, anyway, cannot be consistent with using Eq. (2.18).

I must say at that point that I am a huge fan of Goeff Vallis' book in general and found it to be a go-to reference in many occasions. This is in part why I think that this misinterpretation of the chemical work is a subtle issue and deserves to be fully looked into so that we can stand on more solid ground. For example, in the aforementioned demonstration, it is not necessarily easy to spot the problem right away as all the steps sound logical. But just as in our thought experiment, the problem is that Vallis (2006) implicitly assumed that he could express the chemical work with a perfect differential form ($\gamma_i \dot{q}_i$), but keep the heat term in an imperfect "$\dot{\bar{Q}}$" form and keep its physical interpretation as for a closed system (i.e. neglecting the entropy of the incoming material).

2.4 A more transparent way of dealing with open systems

Of course, again, I am not saying that all models are wrong[9]. Although I maintain that the entropy equation as formulated in Eq. (2.21) is incorrect in general, even the models that do claim using this equation, like WRF, do not actually solve this equation ! Their dynamical core does. But afterward comes a physical step where they actually take into account the non dynamically-resolved exchange of matter between the various grid cells and, hopefully, the whole process ends up conserving energy. Or, in other words, their $\dot{\bar{Q}}$ term includes more than just the external heating terms.

But to understand how this process works and why it never involves chemical potentials, we have to come back to the first and second principles of thermodynamics and see how they can be expressed for an open system. This will lead us to a decomposition of the fundamental relation (Eq. (2.2)) into the usual energy and entropy equation, but terms arising from changes that are internal to the system and those coming from exchange of matter with the environment will become obvious. As a result, we will be able to reformulate the energy equation for fluid dynamics and hopefully see why chemical potentials are actually never used.

2.4.1 The first law for an open system

It should come as no surprise if I tell you that the first law of thermodynamics, i.e. the conservation of energy, writes

$$\mathrm{d}U = \delta Q + \delta W, \tag{2.22}$$

where $\mathrm{d}U$ is the variation of the internal energy of the system and δQ and δW are infinitesimal amounts of heat and work applied to the system. If it does, then it is probably best to read or re-read any textbook on basic thermodynamics, as I will not discuss here in detail the fondations for this principle, nor the difference between total differentials (d) and infinitesimal increments (δ).

What is important for the matter at hand is that this Eq. (2.22) is valid only for closed systems, i.e. a system that does not exchange matter with its environment. Our goal here is to extend this to open systems. There exists various demonstrations in the literature but the ones I found either worked only for open systems with a fixed volume (Powers 2020) or used too hand-wavy arguments through some of the crucial steps to feel satisfactory to me, although they were crucial helps in understanding the problem (Dutton 1976). So I present here a revisited version of the demonstration of Powers (2020) extended to moving volumes.

[9] Although you should know by now that all models are wrong...

Another difficulty with Eq. (2.22) is that it is valid only for a system that is macroscopically at rest. In the situations we are dealing with, mechanical work, even by pressure forces, can be used to change the kinetic and the potential energy as well as the internal energy. It is in fact the force coupling these various forms of energy. We thus have to use the first law for the total energy

$$\mathrm{d}E_{tot} = \delta Q + \delta W. \tag{2.23}$$

The other approach, if we only wanted to derive an energy equation for a system close to thermodynamic equilibrium and at rest, would be to assume that we are close to such an equilibrium. This would however considerably limit the scope of our demonstration because the atmosphere is far from being at rest. Pressure is certainly not uniform because of both motion and gravity. This is the reason that our demonstration will use the total energy. But we will later try to see how our equation writes in the thermodynamic equilibrium limit.

First, we have to express Eq. (2.23) into an integral over a material volume, V_m, i.e. a volume which moves with the fluid so that no matter may enter nor leave it. This volume is enclosed in the surface A_m which is characterized at every point by its outward-facing normal vector, $\mathbf{n}$. The velocity of the fluid at every location is $\mathbf{v}$. Because the volume is a material volume, its surface moves with the fluid at $\mathbf{v}$. The pressure work on an infinitesimal surface area is thus $-p\,\mathbf{v}\cdot\mathbf{n}\,\mathrm{d}A$. The work of external forces (except for pressure and gravity, that are already accounted for through other terms) is $\rho\mathbf{v}\cdot\mathbf{F}_{\text{ext}} \equiv \rho\dot{\tilde{W}}_{\text{ext}}$. Turning the differentials into time derivatives and restricting ourselves to pressure work yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_m}\rho e\,\mathrm{d}V = \int_{V_m}\rho\left(\dot{\tilde{Q}}+\dot{\tilde{W}}_{\text{ext}}\right)\mathrm{d}V - \oint_{A_m} p\mathbf{v}\cdot\mathbf{n}\,\mathrm{d}A, \tag{2.24}$$

where $\dot{\tilde{Q}}$ is the specific heat input per unit time.

Now we can use some mathematical tricks such as the Leibniz's rule, Eq. (1.1), and the divergence theorem, Eq. (1.2), encountered in § 1.1.1 to turn this into

$$\begin{aligned}
0 &= \int_{V_m}\partial_t\rho e\;\mathrm{d}V + \oint_{A_m}\rho e\mathbf{v}\cdot\mathbf{n}\,\mathrm{d}A - \int_{V_m}\rho\left(\dot{\tilde{Q}}+\dot{\tilde{W}}_{\text{ext}}\right)\mathrm{d}V + \oint_{A_m} p\mathbf{v}\cdot\mathbf{n}\,\mathrm{d}A\\
&= \int_{V_m}\left[\partial_t\rho e\;-\rho\left(\dot{\tilde{Q}}+\dot{\tilde{W}}_{\text{ext}}\right)\right]\mathrm{d}V + \oint_{A_m}\rho\left\{e+p\upsilon\right\}\mathbf{v}\cdot\mathbf{n}\,\mathrm{d}A\\
&= \int_{V_m}\left[\partial_t\rho e\;+\nabla\cdot\left(\rho\left\{e+p\upsilon\right\}\mathbf{v}\right)-\rho\left(\dot{\tilde{Q}}+\dot{\tilde{W}}_{\text{ext}}\right)\right]\mathrm{d}V,
\end{aligned} \tag{2.25}$$

where we recognize the enthalpy in curly brackets. Because this equation is valid whatever the size of the volume, the integrand must vanish as well so that

$$\partial_t\rho e\;+\nabla\cdot\left(\rho\left\{e+p\upsilon\right\}\mathbf{v}\right) = \rho\left(\dot{\tilde{Q}}+\dot{\tilde{W}}_{\text{ext}}\right). \tag{2.26}$$

We recognize here the total energy conservation equation in flux form, Eq. (1.49), that can be used to complement other dynamical equation presented in Chapter 1.

If we want to present it in an extensive form closer to Eq. (2.2), we need to reintegrate over an arbitrary volume $V(t)$ whose surface now moves with the arbitrary velocity field $\mathbf{w}$. This will be our open system because matter can enter and leave the system in areas of the surface where $\mathbf{v}\neq\mathbf{w}$. Yet, we are not restricted to a fixed volume as in Powers (2020) so that we will be able to account for a volume change of the system. To do so, we first perform some algebraic manipulations noticing

that

$$\begin{aligned}\nabla\cdot(\rho\{e+p\upsilon\}\mathbf{v}) &= \nabla\cdot(\rho\{e+p\upsilon\}\mathbf{v})+\nabla\cdot(\rho e\mathbf{w})-\nabla\cdot(\rho e\mathbf{w})\\ &= \nabla\cdot(\rho\{e+p\upsilon\}\mathbf{v})+\nabla\cdot(\rho e\mathbf{w})-\nabla\cdot(\rho\{e+p\upsilon\}\mathbf{w})+\nabla\cdot(p\mathbf{w})\\ &= \nabla\cdot(\rho\{e+p\upsilon\}(\mathbf{v}-\mathbf{w}))+\nabla\cdot(\rho e\mathbf{w})+\nabla\cdot(p\mathbf{w})\,. \end{aligned} \tag{2.27}$$

Integrating Eq. (2.26) over $V(t)$, and with the use of our usual mathematical tricks and some reordering, we can finally show that

$$\boxed{\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}\int_{V(t)}\rho e\,\mathrm{d}V}_{\mathrm{d}E_{tot}/\mathrm{d}t}=\underbrace{\int_{V(t)}\rho\dot{\tilde{Q}}\,\mathrm{d}V}_{\dot{Q}}-\underbrace{\oint_{A(t)}p\mathbf{w}\cdot\mathbf{n}\,\mathrm{d}A}_{\dot{W}}+\underbrace{\int_{V(t)}\rho\dot{\tilde{W}}_{\mathrm{ext}}\,\mathrm{d}V}_{\dot{W}_{\mathrm{ext}}}+\underbrace{\oint_{A(t)}\rho\{e+p\upsilon\}(\mathbf{w}-\mathbf{v})\cdot\mathbf{n}\,\mathrm{d}A}_{\dot{C}}\,.} \tag{2.28}$$

We can now easily recognize the terms as, by order of appearance, the rate of change in total energy of the system, $\mathrm{d}E_{tot}/\mathrm{d}t$, the total heat input rate, $\dot{Q}$, the pressure work on the surface of the volume (including the minus sign), $\dot{W}$, the work of other external forces, $\dot{W}_{\mathrm{ext}}$, and finally the chemical power, $\dot{C}$, which is just the net flux of total enthalpy — i.e. the sum of kinetic energy, potential energy, and enthalpy — through the surface of our system.

As discussed earlier, in order to compare with a more common expression for the first law like Eq. (2.22), we must make the usual assumptions to reduce to the thermodynamic simplified framework: that the system has negligible macroscopic kinetic energy and that only pressure forces are at play. As a result, the total enthalpy reduces to the normal enthalpy. A slightly less intuitive side effect is that we can actually identify the work of pressure forces as $-\int_{A(t)}p\mathbf{w}\cdot\mathbf{n}\,\mathrm{d}A=-p\mathrm{d}V/\mathrm{d}t$.

Indeed, this might seem completely obvious, but this equation is not true in an atmosphere subjected to gravity where the pressure is not homogeneous (Blackadar 1997). Consider for example a column of air close to hydrostatic equilibrium being pushed upward uniformly for some reason, by evaporating water for example. Because of gravity, the pressure at the top and bottom are not the same so that $\int_{A(t)}p\mathbf{w}\cdot\mathbf{n}\,\mathrm{d}A\neq 0$ even if the velocity is the same everywhere. However, because the volume does not change, $p\mathrm{d}V/\mathrm{d}t$ is in fact nil. In this case, the work of pressure forces acts to increase the potential energy of the column. Similar examples can be found where the work of pressure forces changes the kinetic energy. These pressure terms are important in general because they are the ones coupling the microscopic and macroscopic forms of energy in the equations. But, in order to compare the first law for a closed and open system, it is easier to put ourselves in the simplified thermodynamic framework.

With these simplifications, the chemical work term writes $\dot{C}=h_i(\mathrm{d}_{\mathrm{ext}}m_i/\mathrm{d}t)$, which is simply the flux of enthalpy through the boundary of the system. Note the subscript ext in $\mathrm{d}_{\mathrm{ext}}m_i$ to remind us that these are only changes to the composition due to *external* fluxes. The case of chemical reactions will be discussed a little further below. Also note that here the subscript i is there to track which species is entering and leaving the system, but we could also apply the same analysis to a large control volume, like a compressor or a chemical reactor, and that the subscript i could be used to track which inlet/outlet we are talking about and that the matter entering or leaving the system could be the same species but at different temperatures and pressures.

Finally multiplying by $\mathrm{d}t$, we get a more familiar expression of the first law for an open system

$$\boxed{\mathrm{d}U=\delta Q-p\mathrm{d}V+h_i\mathrm{d}_{\mathrm{ext}}m_i,} \tag{2.29}$$

or

$$\boxed{\mathrm{d}H = \delta Q + V\mathrm{d}p + h_i \mathrm{d}_{\mathrm{ext}} m_i.} \tag{2.30}$$

The most important points worth noting are that

- The $p\mathrm{d}V$ term is not only a work-term anymore since the volume of the system can increase due to the flux of matter
- The chemical term uses neither the internal energy nor the chemical potential of the matter entering/leaving the system, but its enthalpy. The reason is that any matter entering the volume needs to exert a pressure work which must be added to the system along with the incoming internal energy.

This last point, which is often taken for granted or not well argued in many demonstrations, is the reason why I used this rather technical approach where it appears seamlessly.

What appears troubling is that even though our energy equation for open systems has a new term in its extensive form, Eq. (2.29), compared to the usual equation for a closed system, the intensive flux-form equation for the total energy, Eq. (2.26), is exactly the same as the one we found for a homogeneous atmosphere, Eq. (1.49). The reason is that the enthalpy flux due to matter flow is completely embedded into the equations of fluid dynamics. So it would seem as if we could simply describe our heterogeneous atmosphere using the internal energy equation derived for a homogeneous atmosphere, Eq. (1.38), but with a more complete model for the expression of the internal energy itself. And that would be true if the atmosphere acted as a mono-fluid. But, unfortunately, because the various components do not always move together — the most striking example being convective plumes where you can have the air and vapor moving upward while the condensate and precipitations fall downward — a more complete multi-fluid approach is required.

Such a complete approach is provided in Bannon (2002) and discussed in Lauritzen et al. (2022). This framework accounts for many sources of energy exchange, including gravitational energy changes due to precipitations and dissipation of kinetic energy due to friction between the gas and condensates. It is however very complex and may not be practical to implement for some planetary implementations where such an accuracy is not needed. So, for the matter at hand, we will just mention here that a specific chemical term, $\dot{\tilde{C}}$, should be added to the energy equation

$$\boxed{D_t u = -pD_t \upsilon + \dot{\tilde{Q}} + \dot{\tilde{C}}.} \tag{2.31}$$

or

$$\boxed{D_t h = \frac{1}{\rho} D_t p + \dot{\tilde{Q}} + \dot{\tilde{C}}.} \tag{2.32}$$

The exact form of the chemical term may be model dependent but there are three points that are made much clearer by our analysis: i) the chemical term should just include composition changes that are not due to the flow described by the velocity field (in most cases, the gas flow), ii) it should not include composition changes due to internal processes (like condensation or evaporation) and ii) the chemical term should use the specific enthalpies of the various species and not the chemical potentials as was implied in Vallis (2006). Typically, if $\dot{q}_{\mathrm{c}}$ is the rate of change of the specific concentration of condensates due to transport by sedimentation or precipitations, and $\dot{q}_{\mathrm{v}}$ and $\dot{q}_{\mathrm{a}}$ the corresponding

changes to the vapor and air (because the sum of specific concentrations needs to be unity), the chemical term should write

$$\dot{\tilde{C}} = h_i \dot{q}_i. \tag{2.33}$$

In practice, however, we will see that this term is rather transparent in many cases because the energy equation is often written as a temperature equation. In this case, matter leaving or entering a resolution element does it with its own enthalpy content leaving the temperature unchanged.

2.4.2 The second law for an open system

Now if we want to make the connection with entropy to get the fundamental relation, we need to apply the same process to the definition of entropy for a reversible transformation of a closed system:

$$\mathrm{d}S = \frac{\delta Q}{T}. \tag{2.34}$$

In integral form, this gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V_m} \rho s \,\mathrm{d}V = \int_{V_m} \rho \frac{\dot{\tilde{Q}}}{T}\,\mathrm{d}V. \tag{2.35}$$

Applying again the transport theorem, we get the local specific entropy equation

$$\frac{\partial \rho s}{\partial t} + \nabla \cdot (\rho s \mathbf{v}) = \rho \frac{\dot{\tilde{Q}}}{T}. \tag{2.36}$$

Finally, integrating over an arbitrary open volume and using the same approach as above yields the expression of the second law for an open system

$$\boxed{\mathrm{d}S = \frac{\delta Q}{T} + s_i \mathrm{d}_{\mathrm{ext}} m_i,} \tag{2.37}$$

where s_i is the specific entropy of each component of the fluid. Again, we see that we now have a term that is due the the specific entropy brought about by the matter entering/leaving the system in addition to the heat transmitted to the system.

2.4.3 Accounting for chemical reactions and phase changes

One can see that Eqs. (2.29) and (2.37) can be combined to eliminate the heat input and get

$$\begin{aligned} \mathrm{d}U &= T\mathrm{d}S - p\mathrm{d}V + (h_i - Ts_i)\,\mathrm{d}_{\mathrm{ext}} m_i \\ &= T\mathrm{d}S - p\mathrm{d}V + \gamma_i \mathrm{d}_{\mathrm{ext}} m_i. \end{aligned} \tag{2.38}$$

And although this is very close to the fundamental relation, we can see that we do not take into account chemical reactions[10] that can change the composition internally. Let's call the mass variations linked to such reactions $\mathrm{d}_{\mathrm{int}} m_i$ with the constraint that $\sum_i \mathrm{d}_{\mathrm{int}} m_i = 0$.

[10] In this section, we understand the term chemical reaction to include phase changes as well.

To take these into account, we first have to realize that the definition of the variation of entropy given in Eq. (2.34) is not valid any longer since a spontaneous chemical reaction is not reversible so that

$$\mathrm{d}S > \frac{\delta Q}{T}. \tag{2.39}$$

To transform this inequality into an equality, one needs to make use of the fundamental relation and use the energy equation, Eq. (2.29), to eliminate the internal energy. This yields

$$\delta Q - p\mathrm{d}V + h_i \mathrm{d}_{\mathrm{ext}} m_i = T\mathrm{d}S - p\mathrm{d}V + \gamma_i \mathrm{d}m_i, \tag{2.40}$$

so that

$$\mathrm{d}S = \frac{\delta Q}{T} + \frac{h_i}{T}\mathrm{d}_{\mathrm{ext}} m_i - \frac{\gamma_i}{T}\mathrm{d}m_i. \tag{2.41}$$

Remembering that, by definition, $\mathrm{d}m_i = \mathrm{d}_{\mathrm{ext}} m_i + \mathrm{d}_{\mathrm{int}} m_i$, and that $\gamma_i = h_i - T s_i$[11] finally yields

$$\boxed{\mathrm{d}S = \frac{\delta Q}{T} + s_i \mathrm{d}_{\mathrm{ext}} m_i - \frac{\gamma_i}{T}\mathrm{d}_{\mathrm{int}} m_i.} \tag{2.42}$$

This equation looks just like Eq. (2.37) but with an additional term of entropy production due to the internal chemical reactions (or phase transitions) only. This term can be shown to be positive definite by applying this equation to an isolated system. Because its entropy can only increase, it means that chemical reactions will always occur in the direction for which $-\gamma_i \mathrm{d}_{\mathrm{int}} m_i > 0$.

Like for the energy equation, Eq. (2.42), now makes it very clear that the $T\mathrm{d}S$ term in the fundamental relation does not have its usual interpretation as for closed systems. It is not purely the heat input to the system anymore. It also integrates the contribution of the flow of matter in and out of the system and the production of entropy due to chemical reactions, which is definitely **not** encompassed in the chemical term alone.

2.4.4 The energy equation: or why we never use chemical potentials in climate models

We now finally have everything at hand to answer one of the central question of this chapter: why do we never use chemical potentials in climate models even when we have heterogeneities and compositional changes ?

Well, there are severals ways to look at this question, depending on the variable that one uses in their model: energy or entropy.

For those who are using an energy equation, the answer is rather simple: they actually mostly do **not** use the fundamental relation to derive their energy equation, even when mass transfers occur. While it would seem that the fundamental relation (Eq. (2.2)) is well suited to deal with this problem, it bears two major issues. First it introduces the entropy as a new variable, which can be avoided if an energy equation is used. Second, as we already mentioned, the $\mathrm{d}S$ term is not just a heat input term anymore.

It is actually much more straightforward to use the expression of the first law for an open system, i.e. Eq. (2.31) for the energy or Eq. (2.32) for the enthalpy where the chemical term is present. The terms in these equations have a straightforward *intuitive interpretation,* and one just needs to specify

[11] This can be inferred from the integral relations in Eq. (2.10) applied to a system of unit mass of substance i.

a caloric equation of state for either the internal energy or enthalpy of the fluid and its components (this is what will be done in Chapter 3) and a model for the heat inputs.

It is to be noted that when doing this, we recover an equation that is very similar to Eq. (1.93) of Vallis (2006) except for the chemical term which is left unspecified in Eq. (1.93) but which appears in the form $\gamma_i D_t q_i$ in Eq. (1.95). As discussed previously, this confusion in Vallis (2006) probably comes from the fact that he pushes a little too far the analogy with the terms in the fundamental relation. But it now appears clearly from our demonstration that the chemical term should be written in terms of differences of specific enthalpies, not chemical potentials (we will come back to that in Chapter 5).

This is why, since we do not need to add any other equation, nor variables to treat the problem, we do not need to introduce or use the chemical potentials at any time in the formulation. But of course, we implicitly take them into account when specifying, for example, the saturation pressure for a given condensable vapor, or when we assume that all the gases in a given grid-cell instantaneously mix because that is their equilibrium state. These amount to homogenizing the chemical potential over the system, just as we tend to homogenize the pressure and temperature at equilibrium.

For the models using an entropy equation, one first has to use $\mathrm{d}m_i = \mathrm{d}_{\mathrm{ext}}m_i + \mathrm{d}_{\mathrm{int}}m_i$ and $\gamma_i = h_i - Ts_i$ to rewrite Eq. (2.42) into

$$\mathrm{d}S = \frac{\delta Q}{T} + s_i \mathrm{d}m_i - \frac{h_i}{T}\mathrm{d}_{\mathrm{int}}m_i. \tag{2.43}$$

This equation makes it clear that, in addition to the heat input, one needs to add the incoming entropy due to the flow of matter as well as the excess enthalpy released by chemical reactions and phase changes. But again, chemical potentials never need to appear explicitly.

Finally, another way to see it, is that, as discussed above, since we treat separately the computation of the properties of equilibrium state, we want our energy equation to deal only with the energetic aspect of things, and so express the energy in a representation where entropy is left out. To do that we can comme back to the expression of the enthalpy

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \gamma_i \mathrm{d}m_i, \tag{2.44}$$

and express the the differential of the enthalpy as

$$\mathrm{d}S = \left.\frac{\partial S}{\partial T}\right|_{p,m_i} \mathrm{d}T + \left.\frac{\partial S}{\partial p}\right|_{T,m_i} \mathrm{d}p + \left.\frac{\partial S}{\partial m_i}\right|_{T,p,m_j} \mathrm{d}m_i. \tag{2.45}$$

Combining the two we get

$$\mathrm{d}H = \left[T\left.\frac{\partial S}{\partial T}\right|_{p,m_i}\right]\mathrm{d}T + \left[V + T\left.\frac{\partial S}{\partial p}\right|_{T,m_i}\right]\mathrm{d}p + \underbrace{\left[\gamma_i + T\left.\frac{\partial S}{\partial m_i}\right|_{T,p,m_j}\right]}_{\left.\frac{\partial H}{\partial m_i}\right|_{T,p,m_j} \equiv h_i}\mathrm{d}m_i. \tag{2.46}$$

The last term is obviously the contribution of the specific enthalpies. Hence, this shows that

$$h_i = \gamma_i + T\left.\frac{\partial S}{\partial m_i}\right|_{T,p,m_j}, \tag{2.47}$$

i.e. that the specific enthalpies are just the chemical potential that are corrected for the entropy part. So, as discussed above, because we often already take into account the entropy part when assuming the equilibrium state, we do not need to take it into account again when dealing with the energetics of the transformation of our system. This is why chemical potentials reduce to specific enthalpies almost all the time.

2.5 Relation with the latent heat and enthalpy of reaction

For now, we have been happy with just getting rid of the chemical potentials in our prognostic equations. But we have replaced it with specific enthalpies which, at first sight, look no more intuitive. It is now time to turn to the physical meaning of those $h_i \mathrm{d}m_i$ terms in very explicit situations to see if we can connect them to well-known concepts.

2.5.1 Latent heat

To start with, let us come back the our thought experiment described in § 2.2. Remember that we have shown using the additivity principle that the change in internal energy is just given by the net difference in the internal energy of the matter coming in and out which writes

$$\Delta U = (u_\mathrm{v} - u_\mathrm{c})\,\Delta m_\mathrm{v}. \tag{2.48}$$

It is worth noting that with our expression of the first law for an open system, it is now trivial to re-demonstrate this result. Because the enclosure is adiabatic, there is no exchange of heat with the environment so that Eq. (2.29) immediately gives

$$\begin{aligned}\Delta U &= -p\mathrm{d}V + (h_\mathrm{v} - h_\mathrm{c})\,\Delta m_\mathrm{v} \\ &= -p\,(\upsilon_\mathrm{v} - \upsilon_\mathrm{c})\,\Delta m_\mathrm{v} + (u_\mathrm{v} + p\upsilon_\mathrm{v} - u_\mathrm{c} - p\upsilon_\mathrm{c})\,\Delta m_\mathrm{v} \\ &= (u_\mathrm{v} - u_\mathrm{c})\,\Delta m_\mathrm{v}.\end{aligned} \tag{2.49}$$

The reasoning is now much more straightforward and the result does not look like a coincidence. It is now clear that since there is no heat input to the system, the volume and internal energy of the system just change due to the flux of matter.

Because the experiment was designed to keep the enclosure at constant pressure, it will be no surprise that it is a little easier to consider the enthalpy variation from which the pressure term disappears. Again, using our expression of the first law for an open system, but in terms of enthalpy (Eq. (2.30)), directly yields

$$\Delta H = (h_\mathrm{v} - h_\mathrm{c})\,\Delta m_\mathrm{v}. \tag{2.50}$$

But remember that the enthalpy is a function of state. So the enthalpy change will be the same however we make the transformation from our initial to our final state. And there is another simple path to get there: instead of using the valves, we can just heat the water until we have vaporized a mass Δm_v of the condensed phase at constant pressure. In this case, because the pressure does not change and there is no exchange of matter through the valves, we see that the enthalpy difference is equal to the heat input needed to vaporize the liquid and that, by definition, this heat input is equal to the specific latent heat times the mass vaporized

$$\Delta H = Q = L\Delta m_\mathrm{v}. \tag{2.51}$$

Comparing Eqs. (2.50) and (2.51) shows us that the difference of specific enthalpies between the vapor and liquid is just the specific latent heat of vaporization

$$L \equiv h_\mathrm{v} - h_\mathrm{c}. \tag{2.52}$$

Interestingly this now makes it clear that there is no need for either condensation or vaporization to occur for the latent heat to appear in the variation of enthalpy of the system. Whenever some vapor

replaces some liquid, the enthalpy of the system increases because the vapor *contains* more enthalpy than the liquid — enthalpy that can be released later on as heat if condensation occurs.

This is why expressions for the specific enthalpy of moist air (the so-called moist enthalpy) such as (Emanuel 1994)[12]

$$h = \frac{1}{m_\mathrm{a} + m_\mathrm{v} + m_\mathrm{c}} \left[(m_\mathrm{a} c_{p,\mathrm{a}} + (m_\mathrm{v} + m_\mathrm{c}) c_{p,\mathrm{c}}) T + L(T) m_\mathrm{v} \right], \tag{2.53}$$

are valid even when there is no phase change involved, even though they are often derived by considering a transformation that involves some phase transition. To make it clearer that L is not some internal property of vapor but actually a *difference* between the properties of the vapor and the condensed phase, it is interesting to note that there is *almost* no change to the physics of the system if we decide to write the moist enthalpy as

$$h = \frac{1}{m_\mathrm{a} + m_\mathrm{v} + m_\mathrm{c}} \left[(m_\mathrm{a} c_{p,\mathrm{a}} + (m_\mathrm{v} + m_\mathrm{c}) c_{p,\mathrm{v}}) T - L(T) m_\mathrm{c} \right]. \tag{2.54}$$

Indeed, taking the difference of these two expressions gives $(m_\mathrm{v} + m_\mathrm{c}) \left[L(T) - (c_{p,\mathrm{v}} - c_{p,\mathrm{c}}) T \right]$ which is not equal to zero in general. But this term remains constant when the temperature varies (since $\mathrm{d}L/\mathrm{d}T = c_{p,\mathrm{v}} - c_{p,\mathrm{c}}$ as we will demonstrate in § 3.3.3) or when a phase change occurs (since $m_\mathrm{v} + m_\mathrm{c}$ remains constant). The difference between both formulae therefore just expresses the fact that enthalpy is always defined with respect to some reference value that does affect its physical interpretations only in a "sea level" kind of fashion[13]. So it is only the difference between the enthalpies of vapor and condensed phase that matter and that we can choose either the condensate (Eq. (2.53)), the vapor (Eq. (2.54)), or anything else, to be our reference (Lauritzen et al. 2022).

Lastly, let us note that the latent heat due to phase changes does not appear explicitly in the energy equation because the "chemical term" in Eq. (2.30) only includes mass variations due to matter flow ($\mathrm{d}_\mathrm{ext} m_i$). This is because a phase change in an isolated system does not actually change its enthalpy. Consider for example some water that has been carefully placed into a clean glass and heated above a hundred degree Celsius in a microwave oven from which we have removed the rotating tray. By simply flicking our finger against the glass we can initiate the vaporization almost instantaneously. The system does not have time to exchange heat with the environment so that its enthalpy does not change: the energy needed to vaporize is drawn from the thermal energy and the temperature of the water decreases. To make the latent heat appear explicitly, one needs to use an expression for the enthalpy of the system like Eq. (2.54) and turn Eq. (2.30) into a diagnostic equation for the temperature, as will be discussed in Chapter 3.

By the way, this might be the right moment to explain the problem about the way Holton (2004) incorporates the latent heat release by condensation in his energy equation (see Quote 1). Indeed he writes the variation of internal energy as

$$\rho D_t u = -p \nabla \cdot \mathbf{v} + \rho \dot{\tilde{Q}}_\mathrm{tot} = -p \nabla \cdot \mathbf{v} + \rho \left(\dot{\tilde{Q}}_\mathrm{heat} + \dot{\tilde{Q}}_\mathrm{lat} \right), \tag{2.55}$$

where $\dot{\tilde{Q}}_\mathrm{heat}$ and $\dot{\tilde{Q}}_\mathrm{lat}$ are the specific heating rates due to external diabatic processes (e.g. radiation) and latent heat respectively. We have seen that this is wrong. Indeed, if some condensation happens,

[12] This expression is valid only when the heat capacities do not vary with temperature. For those who are confused by the $(m_\mathrm{v} + m_\mathrm{c}) c_{p,\mathrm{c}} T$ term and would have expected a $(m_\mathrm{v} c_{p,\mathrm{v}} + m_\mathrm{c} c_{p,\mathrm{c}}) T$ term just like with a regular mix of two gases, remember that the latent heat varies with temperature which accounts for the difference (Emanuel 1994). See Chapter 3 for the notations and a full discussion.

[13] Although it is true that enthalpy is defined up to a constant that does no affect the physics, this statement is not completely equivalent to saying that Eqs. (2.53) and (2.54) can be used indifferently. We will come back extensively on this issue in § 3.4.

it is not the internal energy that changes. Latent heat is just transformed into specific heat. The latent heat release due to a phase change should not appear in the equation above as it is an internal change and not an external addition of energy. The reason why this still leads to the correct equation later in Holton (2004) is that in his definition of the internal energy, he does not account for the internal energy of the vapor and just considers the dry gas. So when a phase change occurs, the vapor gives/takes specific energy as heat to the dry gas whose internal energy does change. In other words, he kinds of considers the vapor as an external component that can heat or cool the dry gas when it vaporizes or condenses. This indeed leads to the right equation for the temperature, but I think that it does not really help understand the real meaning of the latent heat or of the energetics of the atmosphere.

Interestingly, however, the latent heat *does* appear explicitly in the entropy equation (Eq. (2.43)). This cleanly demonstrates why (and how) we need to account for the latent heat term in the potential temperature equation that is used in some implementations (for example in WRF), even though it is not an external heating term (unlike what is presented in Eq. (1.95) of Vallis (2006)).

2.5.2 Enthalpy of reaction

Now that we have talked about the case of phase change in depth, the case of chemical reactions is rather straightforward. In fact, a phase change can be seen as a chemical reaction where a molecule in one of the phases reacts to transform into a molecule into another phase. This reaction releases some heat equal to the difference between the enthalpy of the reactants and the one of the products, which in this case is equal to the latent heat.

To generalize this to any reaction r, one needs to rewrite the reaction. Starting from the usual form

$$\sum_{i\in\,\text{reactants}} \nu'_{r,i}\mathcal{C}_i \rightleftarrows \sum_{j\in\,\text{products}} \nu'_{r,j}\mathcal{C}_j, \tag{2.56}$$

where the reactants $\mathcal{C}_i$ combine with the stoichiometric numbers $\nu'_{r,i}$ to give the products $\mathcal{C}_j$ combine with the stoichiometric numbers $\nu'_{r,j}$, we can rewrite this as

$$\sum_i \nu_{r,i}\mathcal{C}_i \rightleftarrows \varnothing, \tag{2.57}$$

where the sum is now on all the constituents and the only difference is that the $\nu_{r,i} \equiv \pm\nu'_{r,i}$ can now be negative for reactants. We can now parametrize the advancement of the reaction from any initial state be defining a reaction advancement (ξ ; in mole numbers) so that the change in the mass of each species is given by $\mathrm{d}m_i = M_i\nu_{r,i}\mathrm{d}\xi_r$, where the M_i's are the molar masses.

Assuming that only this reaction is taking place in the system, the chemical term in the entropy equation now writes

$$\sum_i h_i \mathrm{d}_{\text{int}} m_i = \left(\sum_i h_i M_i \nu_{r,i}\right) \mathrm{d}\xi_r = \Delta_r H_r^* \mathrm{d}\xi_r, \tag{2.58}$$

where $\Delta_r H_r^* = \sum_i h_i M_i \nu_{r,i}$ is the well-known molar enthalpy of reaction, i.e. the heat released when a mole of a reactant that would have $\nu_{r,i} = -1$ is consumed by the reaction. Appart from the fact that it can involve more than two species, the enthalpy of reaction can be used pretty much like the latent heat when dealing with the energetics of the reaction.

Chapter 3

Equations of state for a moist atmosphere

Toute tentative de faire rentrer les questions chimiques dans le domaine de la doctrine mathématique, doit être réputée jusqu'ici, et sans doute à jamais, profondément irrationnelle, comme étant antipathique à la nature des phénomène.

[...]

J'ai fais ressortir, dans le volume précédent, le tort général fait jusqu'ici à la physique par l'abus de l'analyse mathématique.

[...]

Ici, au contraire, on ne doit pas craindre de garantir que si, par une aberration heureusement presque impossible, l'emploi de l'analyse mathématique acquérait jamais, en chimie, une semblable prépondérance, il déterminerait inévitablement, et sans aucune compensation, dans l'économie entière de cette science, un immense et rapide rétrogradation, en substituant l'empire des conceptions vagues à celui des notions positives, et un facile verbiage algébrique à une laborieuse exploration des faits.

Auguste Compte, Cours sur la philosophie positive, 1830, Tome 3, p41

Contents

Now that we have derived proper energy equations for an inhomogeneous fluid in a completely generic fashion, it is time to describe how the energy of our fluid depends on its temperature, pressure and composition to close the system. For this we need to derive the so-called equations of state, one of which will concern the mechanical properties of the fluid and the other its energetics.

This is at this stage that things usually get messy. Indeed, this is where we need a microphysical model of our system and that many approximations are commonly made to make the equations tractable. In the first part of this Chapter, we will first review the various variables used to describe the composition of a heterogeneous atmosphere and underline the pros and cons of each formulation. In the second part, we will derive the equations of state.

The most geocentric readers out there might be shocked that we will very seldom make the difference between the solid and liquid phases of our condensible species and lump them together into a unique "condensed" phase. However, for most planetary bodies, the conditions are far enough from the triple point so that only the liquid or solid phase can exist or the observational constraints on the energetics are just not good enough for the precision to matter. Therefore, we have made this choice to simplify the equations and focus on the big questions without carrying many additional terms.

3.1 Composition variables

When dealing with a heterogeneous atmosphere where some of the species can condense, additional *compositional* variables are necessary. However, there is no unique choice for the variables to use and all have their pros en cons. We quickly review the most common ones.

3.1.1 Specific variables

Let us consider a parcel of gas of mass m_g containing a mass m_a of a gas a and m_v of a gas v (for the moment, these could be any two gases[1], although we use these notations because soon one will be a background non-condensible gas called "air" and the other our condensible "vapor"), then we can define the specific concentration[2] as the mass of each gas over the total mass

$$q_a \equiv \frac{m_a}{m_g} = \frac{m_a}{m_a + m_v}, \; q_v \equiv \frac{m_v}{m_g} = \frac{m_v}{m_a + m_v}. \tag{3.1}$$

One can also use the mass mixing ratios, i.e. the ratios of the mass of the gas in question over

[1] We limit ourselves to a mixture of two gases, but note that one can recursively do this for any number of species

[2] Also called specific humidity for a vapor, especially if it is water.

the mass of a reference gas (e.g. "dry air")

$$r_v \equiv \frac{m_v}{m_a}. \tag{3.2}$$

CAUTION: in many articles and codes (most importantly for me in the LMDZ Global Climate Model), q is actually called the "mass mixing ratio" because it was often used for trace species for which $r \approx q$!

It can be shown that

$$q_v = \frac{r_v}{1 + r_v}, \tag{3.3}$$

and conversely

$$r_v = \frac{q_v}{1 - q_v}. \tag{3.4}$$

3.1.2 Pros and cons

The mass mixing ratio is an interesting variable to work with. Indeed, because condensation processes will not change the mass of non-condensible gas in a parcel, the variation of the mass mixing ratios of the various gases are uncorrelated. However, using mass mixing ratios requires that we single out a given non-condensible gas in the atmosphere. This obviously will cause problems if we want the model to be able to treat an atmosphere dominated by a condensible component (like Mars for example). Another problem is that mass mixing ratios are not "normalized": they can be greater than one and do not add up to one. This makes the expressions for some global quantities of the mixture less esthetically pleasing.

On the contrary, no lead role is given when using specific concentration. However, here, the problem is that if one gas condenses, the total mass of gas changes so that all the other specific concentrations are changed as well. In a numerical implementation of the equations, this entails some renormalisation of all the specific concentrations whenever there is some condensation to conserve the mass of all the species, as detailed in Forget et al. (2006) and Leconte et al. (2013).

3.1.3 Volumic variables

The parcel can also be described by the number of particles it contains in total (N), and for each species (N_a and N_v) and the number concentrations

$$x_a \equiv \frac{N_a}{N} = \frac{N_a}{N_a + N_v}, \; x_v \equiv \frac{N_v}{N} = \frac{N_v}{N_a + N_v}, \tag{3.5}$$

or volume mixing ratios

$$\eta_v \equiv \frac{N_v}{N_a}. \tag{3.6}$$

Note again that in many texts, x is actually called the volume mixing ratio.

3.1.4 Mean molecular weight

Denoting M_a and M_v the molar mass M of each species (in kg/mol), the mean molar mass of the gas M_g is

$$M_g \equiv \frac{\sum_i M_i N_i}{\sum_i N_i} = M_a x_a + M_v x_v. \tag{3.7}$$

By definition, we also have $m_a \equiv N_a M_a$ and $m_v \equiv N_v M_v$, so that

$$\frac{1}{M_g} \equiv \frac{\sum_i \frac{m_i}{M_i}}{\sum_i m_i} = \frac{q_a}{M_a} + \frac{q_v}{M_v}. \tag{3.8}$$

In the specific case of a mixture of two gases where $q_a + q_v = x_a + x_v \equiv 1$, it is useful to define the molar mass ratio

$$\varepsilon \equiv \frac{M_v}{M_a}, \tag{3.9}$$

so that

$$M_g = M_a \left(1 + (\varepsilon - 1)x_v\right), \text{ or } \frac{1}{M_g} = \frac{1}{M_a}\left(1 + (\frac{1}{\varepsilon} - 1)q_v\right). \tag{3.10}$$

To be consistent with the literature on convection in Chapter 4, we will often call the mean molar mass the mean molecular weight, μ, although this name often refers to the mean molecular mass in AMU/molecules, which is close to the molar mass in g/mol. Hereafter, except if explicitly stated, μ will be equal to M_g and will be expressed in kg/mol.

3.2 Adding condensates

But the atmosphere can also contain condensates and aerosols, i.e. solid or liquid particles that are in suspension in the gas, like cloud particles, pollens, salts or chemical hazes. In the remainder of this manuscript, we will deal mostly with cloud particles, i.e. particles of condensed vapor in solid or liquid form, that we will refer to with the subscript c for "condensed" phase.

The mass mixing ratio of the condensed phase can be defined just like for the vapor

$$r_c \equiv \frac{m_c}{m_a}. \tag{3.11}$$

However, for the specific concentration, there can also be a subtlety in the convention taken as the normalisation mass can either be the total mass (m) or the mass of gas only (m_g). And if ones wants to be consistent, this conventional choice also affects the specific concentrations of the gases. As for the choice between mass mixing ratios and concentrations, both conventions have their own pros and cons. Normalizing by the total mass ensures the decoupling of the various concentrations when vaporization or condensation occurs because the total mass is conserved. This will not be true if the gas mass is used for the normalization. On the other hand, sedimentation and precipitation will affect all the concentrations is normalized with the total mass and only the one of the precipitating species if normalized to the gas.

In addition, normalizing to the total mass has the inconvenient that the sum of the specific concentrations of the gaseous species do not add up to one. Therefore, expressions like Eq. (3.8) can no longer be used to compute average quantities for the gas without renormalizing. This is why normalization to the gas is often used, leading to

$$q_c \equiv \frac{m_c}{m_g} = \frac{m_c}{m_a + m_v}. \tag{3.12}$$

However, we will keep the two possibilities and define a slightly different specific concentration with a different symbol

$$\bar{q}_i \equiv \frac{m_i}{\sum_i m_i}, \tag{3.13}$$

where the summation is over all species.

3.3 Caloric equation of state for a condensible mixture

We now want to see how adding a condensible vapor affects the energetics of the atmosphere. We thus try to derive a caloric equation of state for our mixture. Because all *intensive* moisture variables have their drawbacks, we do not want to choose any particular set of variable for the moment. We will therefore deal with *extensive* variable such as the enthalpy of a parcel, $H \equiv mh$, as function of the masses of the various constituents, m_i.

By definition, the enthalpy of the mixture is thus the sum of the specific enthalpies of each constituent times the mass of this constituent in the parcel. This gives

$$H(p, T, \{m_i\}) = \sum_i m_i h_i(p, T, \{m_i\}). \tag{3.14}$$

At this stage, this equation is general because the specific enthalpy of each constituent depends on the global composition of the mix so that interactions can be taken into account.

However, to be able to move forward with analytical expressions, we will assume that the gases in our mixture are ideal and do not interact with each other or the condensed phases so that there will be no mixing enthalpy involved (which does not mean that there is no mixing entropy). This is equivalent to the assumption that the specific enthalpy of each constituent is equal to the enthalpy of the pure substance at the same temperature and pressure (noting that for the gases, the enthalpy does not depend on pressure at all), or $h_i(p, T, \{m_i\}) = h_i(p, T)$.

For a system with some dry air, vapor and a single condensed phase, this gives

$$H = m_\mathrm{a} h_\mathrm{a} + m_\mathrm{v} h_\mathrm{v} + m_\mathrm{c} h_\mathrm{c}. \tag{3.15}$$

Seen like that, this expression does not seem to tell us much. But I wanted to start from here because this allows me to demonstrate rigorously some expressions that we usually take for granted (and actually see what assumptions they rely on) and maybe show physically where some quantities come from. I also hope that this formulation will be shed light on some confusing statements as it did for me.

To derive the various calorimetric coefficients, we need to express the differential of the enthalpy as a function of the variables we are interested in, e.g. the ones we can easily measure: temperature, pressure, the masses of the constituents. This yields

$$\mathrm{d}H = \left.\frac{\partial H}{\partial T}\right|_{p,\{m_i\}} \mathrm{d}T + \left.\frac{\partial H}{\partial p}\right|_{T,\{m_i\}} \mathrm{d}p + \left.\frac{\partial H}{\partial m_i}\right|_{T,p,\{m_j\}} \mathrm{d}m_i, \tag{3.16}$$

where a sum on repeated indices is always implicitly assumed and the $\{m_j\}$ notation is a shorthand for all the species except the i-est one.

Note that for the moment, our system is open and its mass can vary, so the $\mathrm{d}m_i$ are independent of each other and of T and p. Because the h_i are also independent of the m_i (due to the ideal mixing) we can directly see that $\left.\frac{\partial H}{\partial m_i}\right|_{T,p,\{m_j\}}$ is the specific enthalpy of each species (h_i) so that

$$\mathrm{d}H = \left.\frac{\partial H}{\partial T}\right|_{p,m_i} \mathrm{d}T + \left.\frac{\partial H}{\partial p}\right|_{T,m_i} \mathrm{d}p + h_i \,\mathrm{d}m_i. \tag{3.17}$$

3.3.1 Specific heat at constant pressure

If we now focus on the rate of change of the enthalpy of the system when the temperature is increased at constant pressure and composition, that we usually call the specific heat at constant

pressure, c_p, we directly see that

$$c_p \equiv \frac{1}{m}\left.\frac{\partial H}{\partial T}\right|_{p,m_i} = \left.\frac{m_i}{m}\frac{\partial h_i}{\partial T}\right|_p \equiv \frac{m_i}{m} c_{p,i}. \tag{3.18}$$

So we recover the well-known fact that the heat capacity of the mixture is the weighted average of the heat capacities of the various components. However, I find it interesting to see that this property does not derive from first principle, and is in fact the result of the approximation of the ideal mixture. Indeed, if there had been a term for the enthalpy of mixing, and if this term had a dependency on temperature, this would affect the total heat capacity as well.

3.3.2 Pressure term

For the same reasons as above, we can see that the pressure term can be decomposed into

$$\left.\frac{1}{m}\frac{\partial H}{\partial p}\right|_{T,m_i} = \left.\frac{m_i}{m}\frac{\partial h_i}{\partial p}\right|_T. \tag{3.19}$$

Introducing a new caloric coefficient and using some mathematical relations, we can demonstrate (see Bruhat (1968) for example) that

$$\left.\frac{\partial h_i}{\partial p}\right|_T = \upsilon_i - T\left.\frac{\partial \upsilon_i}{\partial T}\right|_p, \tag{3.20}$$

where $T\left.\frac{\partial \upsilon}{\partial T}\right|_p$ is linked to the coefficient of dilatation at fixed pressure.

It appears directly that for an ideal gas,

$$T\left.\frac{\partial \upsilon}{\partial T}\right|_p = \upsilon, \tag{3.21}$$

so that the enthalpy is independent of pressure, which is the 2nd Joule's law. So we expect this term to be negligible, even for real gases. Within our framework where gases are considered ideal, we will drop this term for the gases.

For condensed phases, the small specific volume and compressibility usually make this term pretty small as well. Let us quantify this with liquid water: At room temperature, the volume is around $10^{-3}\,\mathrm{m^3/kg}$ and $T\left.\frac{\partial \upsilon}{\partial T}\right|_p \approx 10^{-4}\,\mathrm{m^3/kg}$. So, a pressure variation of 1 bar contributes around 100 J/kg, i.e. the amount of energy caused by a 0.1 K temperature increase. This term is thus rather negligible, even though we will keep it for the moment for generality.

3.3.3 Latent heat

An important quantity that appears quickly when we deal with the phase change of a condensible species is the specific latent heat (L): the amount of heat needed by a closed system to change a unit mass of the species from one phase (for example the condensed phase[3]) to another (for example the vapor phase) at constant temperature and pressure.

From this definition, and because enthalpy is a state variable, we can see that the latent heat is also equal to the increase in enthalpy of the system when a unit mass of the system undergoes the

[3] If the condensed phase in question is liquid, we will talk about the vaporization latent heat. If it is the solid, we will call it the sublimation latent heat. But we will keep it general here.

phase change at constant temperature and pressure. Considering a closed system, the vaporization of a mass $\mathrm{d}m_\mathrm{v}$ of condensed phase into vapor implies $\mathrm{d}m_\mathrm{c} = -\mathrm{d}m_\mathrm{v}$ so that the enthalpy change at constant p and T writes

$$\begin{aligned}\mathrm{d}H &= h_\mathrm{v}\mathrm{d}m_\mathrm{v} - h_\mathrm{c}\mathrm{d}m_\mathrm{c}\\ &= (h_\mathrm{v} - h_\mathrm{c})\,\mathrm{d}m_\mathrm{v}\\ &\equiv L\,\mathrm{d}m_\mathrm{v},\end{aligned} \tag{3.22}$$

so that

$$L = h_\mathrm{v} - h_\mathrm{c}. \tag{3.23}$$

The interest of this way of introducing the latent heat is that we clearly see that the heat released during phase change is due to an intrinsic difference in the enthalpy content of a mass of fluid in the various phases. Empirically, anyone having spent a little time in a kitchen knows that one needs to input energy to vaporize a liquid. Therefore, with our convention, L is positive so that $h_\mathrm{v} > h_\mathrm{c}$. Therefore, it becomes obvious that a moist atmosphere has more *potential* energy stored into it than a dry one, even though no phase change may be occurring. Of course, a phase change will be necessary to release this extra enthalpy.

Another interest of introducing the latent heat this way is that it becomes easy to see how it evolves with the state of the fluid, e.g. with p and T. Just differentiating Eq. (3.23) yields

$$\begin{aligned}\left.\frac{\partial L}{\partial T}\right|_p &= \left.\frac{\partial h_\mathrm{v}}{\partial T}\right|_p - \left.\frac{\partial h_\mathrm{c}}{\partial T}\right|_p\\ &= c_{p,\mathrm{v}} - c_{p,\mathrm{c}},\end{aligned} \tag{3.24}$$

and

$$\begin{aligned}\left.\frac{\partial L}{\partial p}\right|_T &= \left.\frac{\partial h_\mathrm{v}}{\partial p}\right|_T - \left.\frac{\partial h_\mathrm{c}}{\partial p}\right|_T\\ &= \left(\upsilon_\mathrm{v} - T\left.\frac{\partial \upsilon_\mathrm{v}}{\partial T}\right|_p\right) - \left(\upsilon_\mathrm{c} - T\left.\frac{\partial \upsilon_\mathrm{c}}{\partial T}\right|_p\right)\\ &= 0 - \left(\upsilon_\mathrm{c} - T\left.\frac{\partial \upsilon_\mathrm{c}}{\partial T}\right|_p\right).\end{aligned} \tag{3.25}$$

It might be confusing to see the latent heat depend on both temperature and pressure since the properties of a pure substance at liquid/vapor[4] equilibrium depend only on a single variable, which is either pressure or temperature. This comes from the fact that our definition of the latent heat as a difference of enthalpies remains valid even when there is no liquid/vapor equilibrium, i.e. when the pressure is different from the saturation vapor pressure, p_s.

Therefore, to get the full variation of the latent heat with temperature along the equilibrium curve, one must use

$$\begin{aligned}\frac{\mathrm{d}L}{\mathrm{d}T} &= \left.\frac{\partial L}{\partial T}\right|_p + \frac{\mathrm{d}p_\mathrm{s}}{\mathrm{d}T}\left.\frac{\partial L}{\partial p}\right|_T\\ &= \left(c_{p,\mathrm{v}} - c_{p,\mathrm{c}}\right) + \frac{\mathrm{d}p_\mathrm{s}}{\mathrm{d}T}\left(T\left.\frac{\partial \upsilon_\mathrm{c}}{\partial T}\right|_p - \upsilon_\mathrm{c}\right),\\ &\approx \left(c_{p,\mathrm{v}} - c_{p,\mathrm{c}}\right)\end{aligned} \tag{3.26}$$

[4] Or solid/vapor but for sake of conciseness, we will usually refer only to the liquid/vapor equilibrium although our conclusions hold for both.

For the reasons detailed above, except near the critical point, the second term on the first two lines is usually negligible.

3.3.4 Differential form

Combining all these coefficients, and dropping the pressure terms, we get the following form for the differential of the enthalpy of the system

$$\mathrm{d}H = m_i c_{p,i} \mathrm{d}T + h_i \,\mathrm{d}m_i. \tag{3.27}$$

This equation works for any gas and solid mix as long as gases are ideal and the volume of the condensed phases can be neglected and is valid even for an open system that can exchange components with the environment.

For the specific case of an atmosphere with a condensible species, the latent heat appears only when differentiating between changes of the mass of the various species due to exchange with the environment (external processes) or due to condensation/evaporation (internal processes). Because

$$\mathrm{d}m_i = \mathrm{d}_{\text{ext}} m_i + \mathrm{d}_{\text{int}} m_i \qquad \text{and} \qquad \mathrm{d}_{\text{int}} m_\text{v} = -\mathrm{d}_{\text{int}} m_\text{c}, \tag{3.28}$$

and using the definition of the latent heat, we get

$$\mathrm{d}H = m_i c_{p,i} \mathrm{d}T + L \,\mathrm{d}_{\text{int}} m_\text{v} + h_i \,\mathrm{d}_{\text{ext}} m_i, \tag{3.29}$$

where it should be clear that $\mathrm{d}_{\text{int}} m_\text{v}$ is the mass vaporized during the process.

3.3.5 Integral form

To get an integral form that makes the latent heat appear explicitly, it is easier to go back to Eq. (3.14) and to remember that $h_\text{v} = h_\text{c} + L$, entailing

$$H = m_\text{a} h_\text{a} + (m_\text{c} + m_\text{v}) h_\text{c} + m_\text{v} L = m_\text{a} h_\text{a} + m_\text{t} h_\text{c} + m_\text{v} L, \tag{3.30}$$

where $m_\text{t} = m_\text{v} + m_\text{c}$ is the total mass of condensable species in both vapor and condensed phase. Then, using the expression for the enthalpy of the individual components[5] from §1.3.3 we get

$$\begin{aligned} H = {} & m_\text{a} \left(h_\text{a}^\circ + \int_{T^\circ}^{T} c_{p,\text{a}}(T) \,\mathrm{d}T \right) \\ & + (m_\text{c} + m_\text{v}) \left(h_\text{c}^\circ + \int_{T^\circ}^{T} c_{p,\text{c}}(T) \,\mathrm{d}T \right) \\ & + m_\text{v} \left(L^\circ + \int_{T^\circ}^{T} c_{p,\text{v}} - c_{p,\text{c}} \,\mathrm{d}T \right). \end{aligned} \tag{3.31}$$

A common simplification is to assume that heat capacities are independent of temperature near a given reference temperature, T°, so that this simplifies to

$$\begin{aligned} H = {} & m_\text{a} \left[h_\text{a}^\circ + c_{p,\text{a}} (T - T^\circ) \right] \\ & + (m_\text{c} + m_\text{v}) \left[h_\text{c}^\circ + c_{p,\text{c}} (T - T^\circ) \right] \\ & + m_\text{v} \left[L^\circ + (c_{p,\text{v}} - c_{p,\text{c}}) (T - T^\circ) \right]. \end{aligned} \tag{3.32}$$

Interestingly, both of these expressions yield the same differential form given by Eq. (3.29).

[5] This expression implicitly assumes that the volume of the condensate is negligible so that only temperature terms appear.

3.4 Does the reference term in the enthalpy matter ?

Rearranging the terms in Eq. (3.32) we can rewrite the enthalpy as

$$\begin{aligned} H = \; & m_\mathrm{a} c_{p,\mathrm{a}} T + (m_\mathrm{c} + m_\mathrm{v}) c_{p,\mathrm{c}} T + m_\mathrm{v} L \\ & + m_\mathrm{a} \left[h_\mathrm{a}^\circ - c_{p,\mathrm{a}} T^\circ \right] + (m_\mathrm{c} + m_\mathrm{v}) \left[h_\mathrm{c}^\circ - c_{p,\mathrm{c}} T^\circ \right]. \end{aligned} \tag{3.33}$$

This can be compared to the formula for the moist enthalpy given by Emanuel (1994) who finds

$$k = m_\mathrm{a} c_{p,\mathrm{a}} T + (m_\mathrm{c} + m_\mathrm{v}) c_{p,\mathrm{c}} T + m_\mathrm{v} L, \tag{3.34}$$

so that

$$\begin{aligned} H &= k(T, \{m_i\}) + m_\mathrm{a} \left[h_\mathrm{a}^\circ - c_{p,\mathrm{a}} T^\circ \right] + (m_\mathrm{c} + m_\mathrm{v}) \left[h_\mathrm{c}^\circ - c_{p,\mathrm{c}} T^\circ \right] \\ &\equiv k(T, \{m_i\}) + \tilde{H}(\{m_i\}). \end{aligned} \tag{3.35}$$

Is this difference important ? Indeed, most of the time, energy is defined up to a constant. But here, interestingly, the difference is not a constant and depends on the composition. And we cannot choose a convention that makes $\tilde{H}$ disappear. Indeed, once T° is arbitrarily chosen, both h_a° and h_c° can vary by a constant, but it must be the same constant (Lauritzen et al. 2022). Otherwise, this would change the enthalpy difference between the two species and thus affect the physics of the system. Hence, with these constraints, we cannot choose a single reference value that would cancel both $h_\mathrm{a}^\circ - c_{p,\mathrm{a}} T^\circ$ and $h_\mathrm{c}^\circ - c_{p,\mathrm{c}} T^\circ$.

So, whether or not we include $\tilde{H}$ in the expression of the enthalpy not only changes the *absolute* enthalpy content of the system, it also affects the *relative* enthalpy content of different columns with different compositions and it will therefore affect enthalpy fluxes between such columns when they exchange matter.

This begs the following questions: which expression is correct and which one should we use ?[6]

Well, the tricky part is that if one of them definitely seems more correct than the other, the difference probably does not matter as long as one is not concerned with the value of the enthalpy itself but with measurable quantities. To show that, we first need to note that $\tilde{H}$ is constant for a closed system that undergoes only an *internal* transformation[7]. Indeed, it does not depend on either T or p, and both the mass of air and the total mass of the condensible species, m_t, are constant for such a transformation. Then, remember that we always can decompose, at least in principle, the transformation of an open system into a step with only exchanges of matter with the environment and a step with only internal transformations. Because of its properties, the inclusion of $\tilde{H}$ will affect the value of the flux of enthalpy during the first step, but this will in no way affect how the system will cool or interact with the environment in the second step.

For example, let us consider two columns of air with the same temperature and total mass, one of which is dry and the other initially enriched in vapor, as depicted in Fig. 3.1. Let us further

[6] Another way to phrase this question is the following: On one side, we have seen in Chapter 1 that the total energy equation involves enthalpy fluxes, and we will see in the next Chapter that the total enthalpy of the atmosphere can be conserved under some conditions. Yet, we have not detailed the definition of this enthalpy. On the other side, it is often easy to consider a system and to define a quantity that is conserved under an adiabatic and isobaric transformation, and it is tempting to call this quantity an "enthalpy". And yet, what tells us whether or not this newly defined "enthalpy" is the same as the one we defined in the total enthalpy equation ?

[7] To keep up with the nomenclature used in the preceding chapter, an *internal* transformation describes any transformation that does not include any exchange of matter with the environment, even though the system may receive external heat or work.

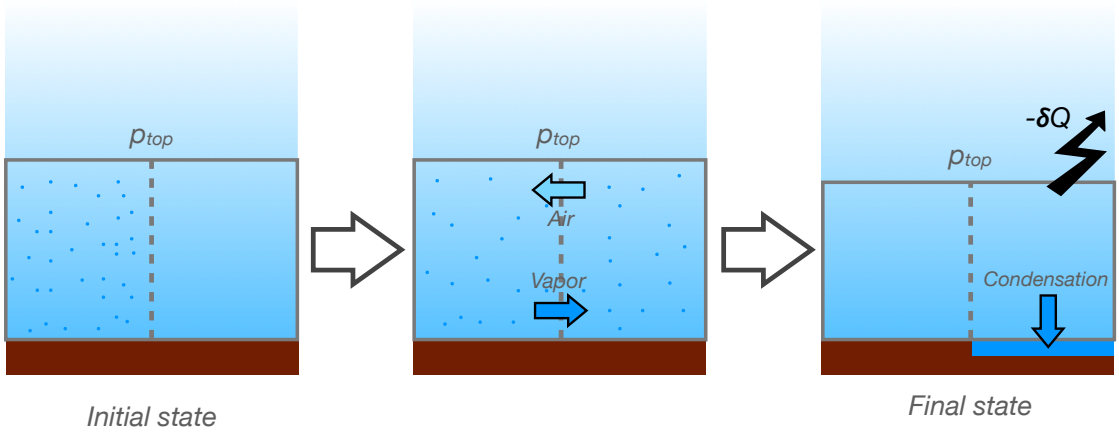

Figure 3.1: Schematic of the evolution of the two columns. Left: initial state where all the vapor is in column 1. Middle: intermediate state where the vapor is transported towards column 2 and air flows back to conserve the same mass in both columns. Right: final state where all the vapor as condensed in the cold trap at the surface of column 2 and released an amount of heat -δQ to the environment. The minus sign comes from the convention that δQ is counted positive when heat flows from the environment to the system. Both layers are a little less massive because they lost mass through condensation but the top pressure stays the same.

assume that the conditions are such that the vapor will be slowly homogenized before condensing and being cold trapped at the surface of the second column, leaving the entire atmosphere dry and slightly lighter than before. Let us now evaluate the enthalpy fluxes in both representations by evaluating the fluxes of $\tilde{H}$. For each mass, m_v, of vapor initially present, the first column has lost $m_v \left(\left[h_c^\circ - c_{p,c} T^\circ\right] - \frac{1}{2}\left[h_a^\circ - c_{p,a} T^\circ\right]\right)$ Joules more of enthalpy when using our expression over the one of Emanuel (1994), while the second column has lost $\frac{m_v}{2}\left[h_a^\circ - c_{p,a} T^\circ\right]$ Joules more and the surface gained $m_v \left[h_c^\circ - c_{p,c} T^\circ\right]$ Joules more.

Yet, if we combine our expression for the differential of the enthalpy, given by Eq. (3.29), and our expression of the first principle for an open system, Eq. (2.30), we get

$$m_i c_{p,i} \mathrm{d}T + L\, \mathrm{d}_{\mathrm{int}} m_v + h_i\, \mathrm{d}_{\mathrm{ext}} m_i = \delta Q + V \mathrm{d}p + h_i \mathrm{d}_{\mathrm{ext}} m_i, \tag{3.36}$$

which simplifies to

$$m_i c_{p,i} \mathrm{d}T + L\, \mathrm{d}_{\mathrm{int}} m_v = \delta Q + V \mathrm{d}p. \tag{3.37}$$

This is exactly the equation that we would get to by combining the expression of Emanuel (1994) with the first principle for a closed system. And Emanuel (1994) indeed states that his equation is valid only for a closed system. So we see that the contribution of matter fluxes between columns ($\mathrm{d}_{\mathrm{ext}} m_i$) are transparent when one wants to evaluate the amount of heat and work exchanged with the environment. In our example, if we assume that all the temperatures remain constant, and because the pressure has not changed, the condensation has released $-\delta Q = L\, m_v$ Joules of heat to the environment, whatever the enthalpy formulation used.

But does this mean that both formulations are correct ? Well, no. It is in our simple case where we consider only condensation and evaporation. But let us imagine a case where, for some reason, the vapor can react to give a non-condensible species that makes up the dry component of our atmosphere. In this case, our integral formula for the enthalpy, Eq. (3.30), is still valid. If vapor is

turned into air through the reaction, the enthalpy change per unit of reacting vapor is $(h_a - h_v)$, which is the specific enthalpy of reaction, as expected.

If we use the the formulation from Emanuel (1994), we see that in this case, the reaction entails a change in enthalpy per unit mass of reacting vapor of $(c_{p,a}T - c_{p,c}T - L)$, which is not equal to the specific enthalpy of reaction in general. This formulation of the enthalpy is therefore incorrect, although it can be used correctly in many cases of interest, in particular when only condensation is involved for a closed system.

Finally, let us come back to the fact that, as discussed earlier and detailed in Lauritzen et al. (2022), our formulation for the enthalpy is not unique, however. We still have a conventional choice to make on the reference enthalpies, h_i°, that are defined up to a single common constant that defines our energetic "sea level". This will change the absolute value of the enthalpy in the system, but not the relative values between species anymore. Therefore, this will not affect the physics of the system, even though keeping track of the convention used is crucial when comparing the energetics of different models or coupling different physical components which should use the same convention (Lauritzen et al. 2022).

3.5 Generalization to a chemically reactive mixture

Because condensation can be seen as a kind of chemical reaction, it is actually trivial to use these expressions for an arbitrary mixture of gases and condensates as long as they mix ideally and that the volume of the condensed phases can be ignored. This just writes

$$\mathrm{d}H = m_i h_i, \tag{3.38}$$

and

$$\mathrm{d}H = m_i c_{p,i} \mathrm{d}T + h_i \, \mathrm{d}m_i, \tag{3.39}$$

where the expressions in §1.3.3 can be used for the enthalpy of any single species. Now, if we want to separate the mass changes into internal and external changes as for condensation/vaporization, we can list all the possible reactions (with index r) and define an advancement, ξ_r, for each of these reaction as in §2.5.2 so that the enthalpy change writes

$$\mathrm{d}H = m_i c_{p,i} \mathrm{d}T + \Delta_r H_r^* \mathrm{d}\xi_r + h_i \, \mathrm{d}_{\mathrm{ext}} m_i, \tag{3.40}$$

where the summation over the reactions, r, and the species, i, is implicit.

3.6 Mechanical equation of state for a mixture

We have already seen that we consider a pure gas that is dilute enough to be considered ideal, we know that its pressure (p), temperature (T), number of particles (N) are linked through the perfect gas equation of state

$$p = \frac{N}{V} k_\mathrm{B} T = n k_\mathrm{B} T = \rho \frac{R^\star}{M} T, \tag{3.41}$$

where $n \equiv N/V$ and $\rho \equiv m/V$ are the number and mass densities, k_B is the Boltzmann constant, $R^\star$ is the universal molar gas constant ($R^\star \equiv k_\mathrm{B} N_A$, where N_A is Avogadro's number). Number and mass densities are linked through

$$\rho = M \frac{n}{N_A}. \tag{3.42}$$

For an ideal mixture of two ideal gases,

$$p = p_a + p_v \tag{3.43}$$
$$n = n_a + n_v, \tag{3.44}$$

and

$$p_a = n_a R^\star T \tag{3.45}$$
$$p_v = n_v R^\star T. \tag{3.46}$$

If we are interested in density, then one can see that $\rho = \rho_a + \rho_v$ and we can recover the usual equation of state

$$p = n k_B T \equiv \rho R T, \tag{3.47}$$

if we define the gas constant as

$$R = \frac{R^\star}{N_A}\frac{n_a + n_v}{\rho_a + \rho_v} = R^\star \frac{n_a + n_v}{M_a n_a + M_v n_v} = \frac{R^\star}{M_g} = q_a R_a + q_v R_v. \tag{3.48}$$

This type of relation is relatively general: any *specific* quantity defining the mixture (such as the specific gas constant or heat capacity) will be the combination of the specific quantity for each gas weighted by the specific concentration of the gases. Any *molar* quantity defining the mixture (such as the cross section or the molar heat capacity) will be the combination of the molar quantity for each gas weighted by the molar concentration of the gases.

Chapter 4

Adiabatic vs. Isentropic convection in heterogeneous fluids

Chauffe Marcel

"c'est pas sorcier", Jamy

Contents

Convection has always fascinated me. It occurs almost everywhere — from Earth's mantle, to storms, to Miso soup — so that it affects many parts of our daily lives. It is a simple process. If some lighter fluid lies below some heavier one, then gravity will tend to lift the lighter fluid, often producing mixing along the way[1]. Yet, even if the problem is rather well posed, it is so rich that it keeps motivating new research.

In fact, it would be fair to say that convection is probably the single theme that I have continuously been working on since I started in astrophysics: Semi-convection in the interior of giant planets during my PhD (Leconte and Chabrier 2012, 2013), *deep* convection in the atmosphere of the Earth (Leconte et al. 2013 ; Charnay et al. 2013), compositional convection in brown dwarfs (Leconte 2018), the inhibition of convection in hydrogen rich atmospheres (Leconte et al. 2017, 2024 ; Clément et al. 2024), etc.

Figure 4.1: Convective cells in miso soup. Darker regions are cooler downdrafts that are depleted in scattering particles because they settle down in these regions.

And during that time, if there is one property of convection that has come back repeatedly more than any other, it is that it should be *adiabatic*. So much that saying that a region is *adiabatic* or *follows an adiabat* has almost become a shorthand for a region where convection is present. And, roughly speaking, this is well deserved. As we will see, convection almost always leads to (quasi-)adiabatic conditions.

Intuitively, the reason is simple. When a parcel of fluid moves up, it does so quickly and does not have much time to exchange heat with its surroundings. It's motion is thus *adiabatic*. The interesting part is that because we assume the motion to be reversible, it means that the parcel is undergoing an *isentropic* transformation so that its entropy becomes a passive tracer that is mixed throughout the convective region. As a result, if the mixing is efficient, the whole convective region ends up exhibiting a uniform entropy so that it can be said to be *isentropic* or to *follow an isentrope*, which is really what we almost always have in mind when speaking of adiabats.

The problem however, is that I have often heard, and sometimes read that:

> *The stability of a fluid to convection can be determined by looking at the entropy gradient of the initial column alone,* (4) or

[1] In many contexts, convection more generally denotes any transfer of energy linked to a flow of mass in a fluid, but in this section, we will restrict ourselves to vertical motion due to buoyancy.

a similar statement that led to an erroneous conclusion. The problem is, of course, that this intuitive statement that is based on the simple reasoning above is right in many simple situations. Yet, it remains wrong in general, as will be rigorously demonstrated hereafter (the impatient reader might want to skip directly to § 4.3.1). But I feel that the conciseness and brevity of this demonstration does not really appeal to our intuition. The goal of this chapter is therefore to look at a couple examples to try to understand where this statement might have come from and explain where is the problem with these preconceptions. But before getting into that, let us present the most simple framework used to describe convection (§ 4.1.1).

4.1 The isentropic paradigm

4.1.1 The parcel framework

The common, simple method used to assert whether a column of fluid is (un)stable to convective instability is to make a thought experiment where we isolate a parcel of fluid that will be displaced vertically. Then, one only has to see whether the parcel is buoyant compared to the environment, i.e. if its density, ρ_p, is smaller than the one of the environment, ρ_e.

Several assumptions are made:

- When the parcel is moved from a pressure level p to $p + \mathrm{d}p$ [2], the mechanical equilibration is assumed to occur fast enough for the parcel pressure to be equal to the one of the environment.
- As you might have guessed, we assume that the parcel does not have time to exchange heat with the environment, so that it evolves in an adiabatic fashion.
- Yet we assume that the motion is gentle enough so as to be reversible. The parcel will thus follow an isentropic expansion.
- We also assume that the parcel does not have time to exchange matter (e.g. chemical species) with the environment.

Of course, although these assumptions are often used because they are rather valid in most Solar System planetary atmospheres, they are not necessarily valid in all cases. In cases where radiative and diffusive timescales might be comparable to convective timescales, a proper linear analysis becomes necessary (Rayleigh 1916 ; Spiegel and Veronis 1960 ; Leconte et al. 2017). But we will not delve into such complications here.

4.1.2 Application to a homogeneous fluid: the Schwarzschild criterion

In the case of a homogeneous fluid, an important simplification occurs because the macroscopic state of the fluid is a function of *only* two variables that we can take to be pressure and entropy.

With our assumptions, our convection instability criterion for an ascending parcel becomes

$$\rho_\mathrm{p}(p + \mathrm{d}p, s) < \rho_\mathrm{e}(p + \mathrm{d}p, s + \mathrm{d}s), \tag{4.1}$$

where s is the specific entropy at the starting level, hence the one in the parcel and $s + \mathrm{d}s$ is the entropy at the $p + \mathrm{d}p$ pressure level. Because ρ is a function of state, we can expand both sides to

[2] Note that $\mathrm{d}p$ will be negative for an upward motion

first order, which yields

$$\rho(p,s) + \left.\frac{\partial\rho}{\partial p}\right|_s \mathrm{d}p < \rho(p,s) + \left.\frac{\partial\rho}{\partial p}\right|_s \mathrm{d}p + \left.\frac{\partial\rho}{\partial s}\right|_p \mathrm{d}s. \tag{4.2}$$

Recognizing that $\mathrm{d}p < 0$ for an ascending parcel yields

$$\left.\frac{\partial\rho}{\partial s}\right|_p \frac{\mathrm{d}s}{\mathrm{d}p} < 0, \tag{4.3}$$

where full derivatives denote the variation in the environment. Thanks to following thermodynamic relation

$$\left.\frac{\partial\rho}{\partial s}\right|_p = \left.\frac{\partial\rho}{\partial T}\right|_p \left.\frac{\partial T}{\partial s}\right|_p = \left.\frac{\partial\rho}{\partial T}\right|_p \frac{T}{c_p}, \tag{4.4}$$

one can write this as

$$\frac{T}{c_p}\left.\frac{\partial\rho}{\partial T}\right|_p \frac{\mathrm{d}s}{\mathrm{d}p} < 0. \tag{4.5}$$

Because most fluids become less dense as they are heated, this finally yields the well-known Schwarzschild criterion (Schwarzschild 1958):

$$\frac{\mathrm{d}s}{\mathrm{d}p} > 0. \qquad \text{(Schwarzschild unstable)} \tag{4.6}$$

So if the entropy increases with depth in the fluid, the column in unstable to convection. In the case of an equality, the medium is said to be marginally stable, or neutral. When convection arises, parcels deeper down rise, bring their excess entropy aloft and mix there, homogenizing the entropy of the medium until we reach a neutral, *adiabatic*, stratification when $\frac{\mathrm{d}s}{\mathrm{d}p} = 0$.

This is the main reason that convective instability is often perceived as only being determined by the entropy gradient.

However, in practice, the entropy is rarely the variable that is being looked at because it is hard to measure directly. So this criterion is often written in terms of temperatures.

Criterion in terms of potential temperature

In atmospheric sciences, even people that are not very comfortable with the concept of entropy are very familiar with the concept of potential temperature, θ, defined in §1.3.4. For an ideal gas, because $s = c_p \ln\theta$, we recover the usual instability criterion

$$\frac{\mathrm{d}\theta}{\mathrm{d}p} > 0, \qquad \text{(Schwarzschild unstable)} \tag{4.7}$$

and a dry adiabat is just given by

$$T = T_0 \left(\frac{p}{p_0}\right)^{R/c_p}, \tag{4.8}$$

where T_0 is the reference temperature at a reference pressure level, p_0.

Criterion in terms of thermal gradients

In the interior of planets and stars, where the ideal gas approximation is far from valid, the Schwarzschild instability criterion is more often expressed with temperature gradients. Starting from Eq. (4.6) one just needs to express the variation of the entropy as a function two independent variables that we can advantageously choose to be T and p to give

$$\mathrm{d}s = \left.\frac{\partial s}{\partial T}\right|_p \mathrm{d}T + \left.\frac{\partial s}{\partial p}\right|_T \mathrm{d}p. \tag{4.9}$$

Now, since pressure and temperature are linked along the thermal profile of the environment, we have

$$\mathrm{d}s = \left(\frac{T}{p} \left.\frac{\partial s}{\partial T}\right|_p \frac{\mathrm{d}\ln T}{\mathrm{d}\ln p} + \left.\frac{\partial s}{\partial p}\right|_T \right) \mathrm{d}p. \tag{4.10}$$

Using the thermodynamic identity that states that

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1, \tag{4.11}$$

we can transform this in

$$\begin{aligned} \frac{\mathrm{d}s}{\mathrm{d}p} &= \frac{T}{p} \left.\frac{\partial s}{\partial T}\right|_p \left(\frac{\mathrm{d}\ln T}{\mathrm{d}\ln p} - \frac{p}{T} \left.\frac{\partial T}{\partial p}\right|_s \right) \\ &= \frac{T}{p} \left.\frac{\partial s}{\partial T}\right|_p \left(\frac{\mathrm{d}\ln T}{\mathrm{d}\ln p} - \left.\frac{\partial \ln T}{\partial \ln p}\right|_s \right). \end{aligned} \tag{4.12}$$

Finally, because $\left.\frac{\partial s}{\partial T}\right|_p > 0$, we get

$$\frac{\mathrm{d}\ln T}{\mathrm{d}\ln p} > \left.\frac{\partial \ln T}{\partial \ln p}\right|_s \equiv \left.\frac{\partial \ln T}{\partial \ln p}\right|_{\mathrm{ad}}, \qquad \text{(Schwarzschild unstable)} \tag{4.13}$$

where the last derivative is called the *adiabatic gradient* and can be derived from the equation of state. It is equal to R/c_p in the ideal gas limit.

4.2 The problem with heterogeneous fluids

4.2.1 The Ledoux criterion

Now that we have seen why the convective state of a column can be determined by looking at the entropy gradient alone in the homogeneous case, it is time to look at what happens in the case where the fluid is not fully mixed.

In this case, it has long been recognized that the contribution of the changing composition of the environment should be accounted for in Eq. (4.1). This leads to defining the so-called *Ledoux* criterion (Ledoux 1947) that can be expressed in a form similar to Eq. (4.13):

$$\frac{\mathrm{d}\ln T}{\mathrm{d}\ln p} + \frac{\left.\frac{\partial \ln \rho}{\partial \ln T}\right|_{p,\mu}}{\left.\frac{\partial \ln \rho}{\partial \ln \mu}\right|_{p,T}} \times \frac{\mathrm{d}\ln \mu}{\mathrm{d}\ln p} > \left.\frac{\partial \ln T}{\partial \ln p}\right|_{\mathrm{ad}}. \qquad \text{(Ledoux unstable)} \tag{4.14}$$

The gradient of mean molecular mass in the fluid[3] can now counteract a super-adiabatic thermal gradient or destabilize an otherwise thermally stable configuration as experienced in Earth's oceans with thermohaline processes (Stern 1960 ; Baines and Gill 1969).

This can be translated to a potential temperature formulation by slightly changing Eq. (4.7) to account for the mean molecular weight effect with

$$\frac{\mathrm{d}\theta_\mathrm{v}}{\mathrm{d}p} > 0, \qquad \text{(Ledoux unstable)}, \tag{4.15}$$

where θ_v is the virtual temperature

$$\theta_\mathrm{v} \equiv \frac{M_\mathrm{a}}{\mu}\theta, \tag{4.16}$$

with M_a a reference molar mass[4].

4.2.2 Examples where the Ledoux criterion is assumed to reduce to an entropy gradient

The question is now whether the Ledoux criterion can be expressed in terms of an entropy gradient ? In other words, is having $\mathrm{d}s/\mathrm{d}p > 0$ in a medium a *sufficient* condition for this medium to be Ledoux unstable ?

Why this question, you might ask ? Well, this first occurred to me when Tremblin et al. (2015) noticed that they could reproduce some features of brown dwarfs spectra at the L-T transition by simply reducing the temperature gradient near their photosphere from an adiabatic gradient (since the photosphere is located in a convective region) to a more isothermal profile. The reason they initially put forward for this thermal gradient reduction was a small scale instability called the *fingering instability* that usually occurs in a thermally-stable but top-heavy column of fluid. In Tremblin et al. (2015) this was triggered by the condensation of very thin dust at the top of the troposphere. In Tremblin et al. (2016), they argued that the triggering mechanism could rather be a sort of thermo-chemical instability linked to the CO/CH_4 chemical transition near the L/T transition. In this scenario, because the temperature decreases in the atmosphere as we move upward in the hydrogen dominated atmosphere, heavier CH_4+H_2O enriched gas overlies lighter CO enriched gas[5]. This creates a positive mean molecular weight gradient upward.

Without even discussing whether the mean molecular weight gradient can actually destabilize the medium[6], this caught my attention precisely because I was convinced that convection — and turbulent mixing in general — always leads to more isentropic regions. As explained in Leconte (2018),

[3] Note that in most cases, $\left.\frac{\partial \ln \rho}{\partial \ln T}\right|_{p,\mu}$ is négative.

[4] This formulation is commonly used to describe an atmosphere where one of the species, usually present in trace amounts, can condense — like water vapor in Earth's atmosphere. The reference molar mass is thus often the mass of the background, non-condensible gas.

[5] Which is lighter only because one needs to account for the 3 hydrogen molecules created when transforming CH_4+H_2O into CO.

[6] In a brown dwarf with solar metallicity, the change in molecular weight between the CO and CH_4 dominated region is on the order of 2×10^{-6} kg/mol so that $\delta\mu/\mu \approx 10^{-3}$. So according to the Ledoux criterion, the temperature difference needed to compensate for the change in molecular weight is on the order of $\delta T \approx 10^{-3} T \approx 1$ K for a 1000 K atmosphere. This does not seem like a big deal. This is why the simulation in Tremblin et al. (2019) increase the molar weight effect by a factor of 10 and concentrate the gradient in a tenth of a scale height to be able to see an effect of about 5 K. They however do not discuss the fact that in a real atmosphere, these 0.5 K (5/10) would be spread out over the whole chemical transition region...

the reason is the following: if turbulent transport (be it small- or large-scale) occurs following the ideal *parcel framework* described in § 4.1.1, the moving fluid parcels transport their composition and entropy as passive tracers. When the parcels finally mix, they thus homogenize both the composition and entropy of the column. This tends to produce a column where both the composition *and* the entropy are uniform. Of course, if the mixing is not efficient enough compared to the destabilizing source terms — because of a high viscosity or any other dynamical braking mechanism — the medium will not be fully isentropic, but it is hard imagining the convection process leaving the fluid *more* heterogeneous than before. This was contrary to the the mechanism presented in Tremblin et al. (2016) where the atmosphere was moved *away* from the isentrope by turbulent mixing.

This led Tremblin et al. (2019) to provide a related, yet slightly different, explanation for the reduction of the thermal gradient. While their argument still relied on the presence of a chemically induced composition/molecular weight gradient, they tried to explain how the convection created in a case where the atmosphere would be Ledoux unstable would indeed cool down the lower atmosphere. Their argument is summarized on page 8 of Tremblin et al. (2019) where they state that:

> *A blob description helps explain why the temperature gradient can be decreased. Figure 8 illustrates the behavior of a perturbed hot parcel with a high concentration of heavy elements. Because the [descending] blob is Ledoux unstable, its entropy is lower than the surroundings. On a compositional timescale for the source term, this excess of composition will be dissipated in the nonlinear regime. If we ignore the first energy source terms (no source term on the entropy equation), the compositional change will happen at constant entropy ; hence, it will lead to a temperature of the blob that is smaller than the temperature of the surroundings because of the expansion induced by the change in concentration (similar to haline expansion in the oceanic case) and the work of the pressure forces. If we reintroduce the thermal source terms in the analysis, the blob will pump energy from the environment, since it has a lower temperature ; hence, it will cool the deep cold atmosphere.* (5)

The underlined sentence clearly shows that the authors assume that the Ledoux criterion can be expressed as an entropy gradient just as we showed for the Schwarzschild one in § 4.1.2. In other words, if their column is Ledoux unstable, they assume the entropy gradient to be positive downward and that a descending parcel travelling adiabatically would necessarily have a lower entropy than its surroundings.

As a result, when the parcel chemically equilibrates adiabatically (i.e. at constant entropy), the parcel has the same pressure and mean molecular weight as the environment (see their Figure 8), but a lower temperature because of the lower entropy it started with. *In fine*, the parcel exchanges energy with the environment, cooling it down.

This is made even clearer in a follow up study by Daley-Yates et al. (2021) where it is stated in their section 2.2:

> *The situation is simpler in the context of Ledoux convection: the conserved quantity in the linear regime is simply proportional to the entropy. At saturation, the Ledoux criterion is equivalent to homogeneous entropy, hence the saturation is a nearly isentropic state.* (6)

4.2.3 Tentative explanations of the Ledoux criterion in terms of entropy: the virtual potential temperature approach

At the time, these articles really made me think and try to see if the Ledoux criterion could really be expressed in terms of entropy alone. So I tried to understand where this idea could come from.

I started from the schematic in Figure 8 of Tremblin et al. (2019) where we can see the following equation

$$s \propto \log\left(p^{1-\gamma}\,(T/\mu)^{\gamma}\right), \tag{4.17}$$

where $\gamma = c_p/c_v$ is the heat capacity ratio or adiabatic index. For an ideal gas, this leads to

$$\frac{R}{c_p} = \frac{\gamma - 1}{\gamma}, \tag{4.18}$$

so that if γ is considered constant, which is one of the approximations made in Tremblin et al. (2019), one can rewrite Eq. (4.17) within an additional constant into

$$s \propto \log\left(\frac{T}{\mu p^{R/c_p}}\right) \propto \log\left(\frac{\theta}{\mu}\right). \tag{4.19}$$

This is very reminiscent of how potential temperature and entropy are linked together for a homogeneous fluid as discussed in §1.3.4, for the exception of the molecular weight at the denominator. Of course, this factor is not a problem if the molecular weight is constant because it only changes the reference value of the entropy without changing any physical property of the gas. But this is not necessarily true — and in fact it is not — if the molecular weight can change. Yet, it seemed that Tremblin et al. (2019) assumed this expression for the entropy to be correct for an ideal gas of changing composition. This was further confirmed in Daley-Yates et al. (2021) where we can read:

> *This modification moves the system towards a constant entropy profile. This can be seen in the right hand-side of Fig. 10, where we plot the profile of the ratio of potential temperature to mean molecular weight.* (7)

and where Fig. 10 does show a constant profile of θ/μ.

This is interesting, because θ/μ — better known as the virtual potential temperature in the atmospheric science community — is indeed the right variable to express the Ledoux criterion. A Ledoux neutral profile does exhibit a constant θ/μ. But I have never seen any demonstration that this could also be related to the entropy of a mixture of gases with a variable molecular weight.

And there is none for the simple reason that one can show that this formulation of the entropy is not thermodynamically consistent.

To do that, let us start by reiterating the equations of state described in Daley-Yates et al. (2021)[7]:

$$\begin{aligned} u &= c_v T \\ c_v &= \frac{R^\star}{\mu(\gamma - 1)} \\ p &= \rho R^\star T/\mu \\ &= \rho u(\gamma - 1) \end{aligned} \tag{4.20}$$

[7] Note that we use our notations and that we take the convention to express the mean molecular weight as a molar mass.

with a constant γ. Now, introducing this into their entropy equation (Eq. (4.17)) and expressing it only as a function of its canonical variables ($\upsilon = 1/\rho$, u, and using μ as our compositional variable) yields

$$\begin{aligned} s &= A \ln \left[\left(\upsilon^{-1} u(\gamma - 1) \right)^{1-\gamma} \left(\frac{u}{c_v \mu} \right)^{\gamma} \right] + B \\ &= A \ln \left[\left(\upsilon^{-1} u(\gamma - 1) \right)^{1-\gamma} \left(\frac{u(\gamma - 1)}{R^\star} \right)^{\gamma} \right] + B \qquad (4.21) \\ &= A \ln \left[\frac{u}{\upsilon^{1-\gamma} R^{\star\,\gamma}} \right] + B \qquad (4.22) \end{aligned}$$

where A and B need to be constants if one wants to be consistent with Eq. (4.17).

It is already suspicious that the entropy of the fluid does not even depend on its composition. But we can go further and use the usual thermodynamic definitions of pressure and temperature (see for example Vallis 2006):

$$p \equiv T \left. \frac{\partial s}{\partial \upsilon} \right|_{u,\mu} = -TA(1-\gamma)/\upsilon \qquad (4.23)$$

and

$$T^{-1} \equiv \left. \frac{\partial s}{\partial u} \right|_{\upsilon,\mu} = A/u. \qquad (4.24)$$

To retrieve the equations of states described by Eq. (4.20), it is easy to see that we need to take $A = c_v$. But as we mentioned earlier, A needs to be independent of the other canonical variables if one is to retrieve that θ/μ is constant on an isentrope. Yet, Daley-Yates et al. (2021) uses a heat capacity that depends on the composition as $1/\mu$. In other words, their equations are not thermodynamically consistent.

As a result, the entropy of a mixture of gases cannot depend on the virtual potential temperature alone in such a simple setting.

4.2.4 Tentative explanations of the Ledoux criterion in terms of entropy: the thermal gradient approach

Yet, the problem with the demonstration above is that it relies on a specific equation of state, which is of course far from valid, as we demonstrated. It is thus difficult to see whether the result is general or due to a bad choice of equation of state.

So I dug a little deeper and unearthed a tentative demonstration by a researcher in stellar physics that is reproduced in Fig. 4.2 and where he claims to show that

$$\frac{\mathrm{d}s}{\mathrm{d}p} = -\frac{c_p}{p} \left(\frac{\mathrm{d}\ln T}{\mathrm{d}\ln p} - \left. \frac{\partial \ln T}{\partial \ln p} \right|_{\mathrm{ad}} + \frac{\left. \frac{\partial \ln \rho}{\partial \ln T} \right|_{p,\mu}}{\left. \frac{\partial \ln \rho}{\partial \ln \mu} \right|_{p,T}} \times \frac{\mathrm{d}\ln \mu}{\mathrm{d}\ln p} \right). \qquad (4.25)$$

Because the term in parentheses is exactly the expression in the Ledoux criterion in Eq. (4.14), stability would simply write $\mathrm{d}s/\mathrm{d}p < 0$.

As you might expect, this demonstration is incorrect. Showing why is actually a nice exercise for the thermodynamics student who needs reminding that partial derivatives should always explicitly

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Let s be the entropy per unit mass of a spherical configuration of matter in hydrostatic equilibrium. Then consider its variation as a function of other thermodynamic variables:

$$\frac{\mathrm{d}s}{\mathrm{d}r} = \left.\frac{\partial s}{\partial T}\right|_{P,\mu}\frac{\mathrm{d}T}{\mathrm{d}r} + \left.\frac{\partial s}{\partial P}\right|_{T,\mu}\frac{\mathrm{d}P}{\mathrm{d}r} + \left.\frac{\partial s}{\partial \mu}\right|_{P,T}\frac{\mathrm{d}\mu}{\mathrm{d}r},$$

where T, P, μ are respectively the temperature, pressure, and mean molecular weight (apologies to the statistical physicists). Defining the pressure scale height as $-P/H_p = \frac{\mathrm{d}P}{\mathrm{d}R}$ and the constants δ, ϕ through a differential equation of state

$$\frac{\mathrm{d}\rho}{\rho} \sim \alpha\frac{\mathrm{d}P}{P} - \delta\frac{\mathrm{d}T}{T} + \phi\frac{\mathrm{d}\mu}{\mu},$$

we proceed to rewrite the above as

$$\begin{aligned}\frac{\mathrm{d}s}{\mathrm{d}r} &= -\frac{P}{H_p}\left(\left.\frac{\partial s}{\partial T}\right|_{P,\mu}\frac{\mathrm{d}T}{dP} + \left.\frac{\partial s}{\partial \mu}\right|_{P,T}\frac{\mathrm{d}\mu}{dP} + \left.\frac{\partial s}{\partial P}\right|_{T,\mu}\right)\\ &= -\frac{P}{H_p}\left.\frac{\partial s}{\partial T}\right|_{P,\mu}\left(\frac{\mathrm{d}T}{dP} + \left.\frac{\partial T}{\partial s}\right|_{P,\mu}\left.\frac{\partial s}{\partial \mu}\right|_{P,T}\frac{\mathrm{d}\mu}{dP} + \left.\frac{\partial T}{\partial s}\right|_{P,\mu}\left.\frac{\partial s}{\partial P}\right|_{T,\mu}\right),\end{aligned}$$

but by the identity $\left.\frac{\partial x}{\partial y}\right|_z\left.\frac{\partial y}{\partial z}\right|_x\left.\frac{\partial z}{\partial x}\right|_y = -1$, we have that $\left.\frac{\partial T}{\partial s}\right|_P\left.\frac{\partial s}{\partial P}\right|_T = -\left.\frac{\partial T}{\partial P}\right|_s$, and $\left.\frac{\partial \log T}{\partial \log \rho}\right|_{\log\mu}\left.\frac{\partial \log \rho}{\partial \log \mu}\right|_{\log T} = -\left.\frac{\partial \log T}{\partial \log \mu}\right|_{\log\rho} = -\frac{\phi}{\delta}$. This gives us (with $c_p = T\left.\frac{\partial s}{\partial T}\right|_P$ as the specific heat capacity at constant pressure)

$$\begin{aligned}\frac{\mathrm{d}s}{\mathrm{d}r} &= -\frac{P}{H_p}\left.\frac{\partial s}{\partial T}\right|\left(\frac{\mathrm{d}T}{dP} - \left.\frac{\partial T}{\partial P}\right|_s - \left.\frac{\partial T}{\partial \mu}\right|_s\frac{\mathrm{d}\mu}{\mathrm{d}P}\right)\\ &= -\frac{T}{H_p}\left.\frac{\partial s}{\partial T}\right|\left(\frac{P}{T}\frac{\mathrm{d}T}{dP} - \frac{P}{T}\left.\frac{\partial T}{\partial P}\right|_s - \frac{P}{T}\frac{T}{\mu}\left.\frac{\partial \log T}{\partial \log \mu}\right|_s\frac{\mathrm{d}\mu}{\mathrm{d}P}\right)\\ &= -\frac{c_p}{H_p}\left(\frac{P}{T}\frac{\mathrm{d}T}{dP} - \frac{P}{T}\left.\frac{\partial T}{\partial P}\right|_s - \frac{\phi}{\delta}\frac{P}{\mu}\frac{\mathrm{d}\mu}{\mathrm{d}P}\right).\end{aligned}$$

Defining (per classical stellar astrophysics convention) the "nabla" quantities $\nabla = \frac{\mathrm{d}\log T}{\mathrm{d}\log P}, \nabla_{\mathrm{ad}} = \left.\frac{\partial \log T}{\partial \log P}\right|_s, \nabla_\mu = \frac{\mathrm{d}\log\mu}{\mathrm{d}\log P}$ allows us to rewrite this last expression as

$$\frac{\mathrm{d}s}{\mathrm{d}r} = -\frac{c_p}{H_p}\left(\nabla - \nabla_{\mathrm{ad}} - \frac{\phi}{\delta}\nabla_\mu\right).$$

Remarkably, when we compare this with the usual statement of Ledoux's criterion for stability against convection, which can be written as

$$\nabla < \nabla_{\mathrm{ad}} + \frac{\phi}{\delta}\nabla_\mu,$$

we find that this is equivalent to a statement that, for stability against convection, we require a constraint on the specific entropy gradient:

$$\boxed{\frac{\mathrm{d}s}{\mathrm{d}r} > 0.}$$

I find this a great deal more illuminating than (often quite contrived) arguments about displaced fluid packets. Rather than their usual interpretation as temperature gradients when reasoning about the various ∇-quantities, it appears that a more physically natural intuition about their significance should be as contributions to the entropy gradient, instead.

Figure 4.2: Tentative demonstration that a Ledoux neutral medium is isentropic. (from `https://hyad.es/ledoux`)

state the variables kept constant[8]. But the important point is that we intuitively want to believe this result so much that some people are trying to prove it ! Let us see why.

4.2.5 Tentative explanations of the Ledoux criterion in terms of entropy: the intuitive approach

Why do we implicitly want to believe that a Ledoux neutral atmosphere is isentropic ?

The main explanation to me is that, intuitively, we do **not** make the difference between an initially Ledoux neutral fluid and a fluid that has been brought to neutrality (or marginal stability) by the process of convection itself. Indeed, the role of convection is to bring an unstable medium back to the neutral state by mixing. Once the neutral state is reached, and if the destabilizing source term is no longer present, convection stops. So convection does bring back a Ledoux unstable medium to a Ledoux neutral configuration, and yes, this configuration is isentropic.

This is exactly what is implied in Quote 6 from Daley-Yates et al. (2021) that we already mentioned: "At saturation, the Ledoux criterion is equivalent to homogeneous entropy, hence the saturation is a nearly isentropic state."

But it is true only because convection tends to homogenize *both* the composition *and* the entropy at the same time. In the well-mixed limit — the saturation limit in the terms of Daley-Yates et al. (2021) — we recover the well-known case of a homogeneous atmosphere and being Schwarschild or Ledoux neutral is equivalent.

The mistake is to assume that this implies that *any* Ledoux neutral medium is isentropic. In the general case of a Ledoux neutral state, both entropy and composition are heterogeneous and one can compensate for the other in terms of stability. In fact, we will now demonstrate that a Ledoux neutral state where composition is heterogeneous **cannot** be isentropic.

[8] For those would would like to spot the error, try to figure out the variables kept constant when they are not explicitly stated.

Here the various mistakes revolve around the use of the relation given by Eq. (4.11) when you have a system with only two independent parameters and forgetting that in an heterogeneous system, you have a third independent variable. To use the relation, one needs to keep one variable fixed all along (let us call it λ) to reduce to a system of two independent variables so that Eq. (4.11) becomes

$$\left.\frac{\partial x}{\partial y}\right|_{z,\lambda} \left.\frac{\partial y}{\partial z}\right|_{x,\lambda} \left.\frac{\partial z}{\partial x}\right|_{y,\lambda} = -1. \tag{4.26}$$

It can be seen by comparing the various equations that, at some point, the demonstration can proceed only by performing the following transformation

$$\left.\frac{\partial T}{\partial s}\right|_{p,\mu} \left.\frac{\partial s}{\partial \mu}\right|_{p,T} \Rightarrow -\left.\frac{\partial T}{\partial \mu}\right|_{s}. \tag{4.27}$$

This can be deduced from Eq. (4.26) but only if the right hand side is implicitly understood to be taken at constant p and s, i.e. $\left(\left.\frac{\partial T}{\partial \mu}\right|_{s,p}\right)$.

Later on, we can see that the demonstration needs to transform again this derivative of the temperature at fixed entropy into

$$\frac{\mu}{T}\left.\frac{\partial T}{\partial \mu}\right|_{s} \Rightarrow \frac{\phi}{\delta} \equiv -\left.\frac{\partial \ln \rho}{\partial \ln T}\right|_{p,\mu} / \left.\frac{\partial \ln \rho}{\partial \ln \mu}\right|_{p,T}. \tag{4.28}$$

Again, this can be deduced from Eq. (4.26), but this time only if the derivative is implicitly understood to be taken at constant p and ρ, and not ρ and s as is implicitly assumed in the demonstration. But even if it were really a derivative at fixed ρ and s, it would still not be consistent with a derivative at fixed p and s as above. The demonstration therefore does not work.

4.3 A new interpretation of the Ledoux criterion

4.3.1 Derivation

Now let us come back to an atmosphere whose composition is not uniformly mixed. In this particular case, we will assume that no condensation takes place either in the parcel nor the environment. This would for example be the case of the ocean near a source of fresh water.

At first sight, it might not be obvious where the demonstration in § 4.1.2 becomes invalid since we just used the fact that the entropy in the rising parcel does not change. And this is true, the convection remains adiabatic and even isentropic in this case. And again, this is, I think, the main origin of the idea that the convective state can be determined by entropy alone.

But the problem here comes with the assumption behind our very first equation (Eq. (4.1)): Because now the fluid can be heterogeneous, its macroscopic properties do *not* depend on two variables alone. We must add at least one for composition. Let us use the mean molecular weight for that, μ, but we could use any other variable of our choice[9].

Now the instability can be inferred by comparing the density in the parcel lifted from a level p to a level $p+\mathrm{d}p$ and the environment at the new level $p+\mathrm{d}p$. Of course, because the parcel is assumed to be isolated, its entropy and composition remain the one of the starting level (s and μ) while the environment is characterized by $s+\mathrm{d}s$ and $\mu+\mathrm{d}\mu$. The instability criterion for an ascending parcel reads

$$\rho_\mathrm{p}(p+\mathrm{d}p, s, \mu) < \rho_\mathrm{e}(p+\mathrm{d}p, s+\mathrm{d}s, \mu+\mathrm{d}\mu). \tag{4.29}$$

As with the first demonstration, expanding to first order yields

$$\rho(p,s,\mu) + \left.\frac{\partial\rho}{\partial p}\right|_{s,\mu}\mathrm{d}p < \rho(p,s,\mu) + \left.\frac{\partial\rho}{\partial p}\right|_{s,\mu}\mathrm{d}p + \left.\frac{\partial\rho}{\partial s}\right|_{p,\mu}\mathrm{d}s + \left.\frac{\partial\rho}{\partial \mu}\right|_{p,s}\mathrm{d}\mu, \tag{4.30}$$

and simplifying and dividing by the pressure variation to get gradients finally gives the very simple form of the Ledoux criterion:

$$\left.\frac{\partial\rho}{\partial s}\right|_{p,\mu}\frac{\mathrm{d}s}{\mathrm{d}p} + \left.\frac{\partial\rho}{\partial \mu}\right|_{p,s}\frac{\mathrm{d}\mu}{\mathrm{d}p} < 0. \qquad \text{(Ledoux unstable)} \tag{4.31}$$

With a final transformation using Eq. (4.4) we get

$$\boxed{\frac{\mathrm{d}s}{\mathrm{d}p} + \left(\frac{c_p}{T}\frac{\left.\frac{\partial\rho}{\partial\mu}\right|_{p,s}}{\left.\frac{\partial\rho}{\partial T}\right|_{p,\mu}}\right)\frac{\mathrm{d}\mu}{\mathrm{d}p} > 0.} \qquad \text{(Ledoux unstable)} \tag{4.32}$$

Noticing that $\left.\frac{\partial\rho}{\partial T}\right|_{p,\mu} < 0$ is most cases, we see that the entropy and mean molecular weight gradients have competing effect.

[9] This of course assumes that the composition of the medium can be reduced to a single variable, but we could extend the argument to more complex situations. The only case where the choice of the mean molecular weight would not work would be for a mix of two gases with the same molar mass. In this case, we would need to use another variable.

4.3.2 Physical implications

It now appears very clearly from Eq. (4.32) that, not only being isentropic is not a sufficient condition for a fluid to be Ledoux neutral (i.e. marginally stable), but in fact, a *Ledoux neutral fluid* ***cannot*** *be isentropic if it is heterogeneous !*

In retrospect, this could have been intuited all along. Let us imagine that we have a column of fluid which is isentropic and Ledoux neutral. In this case, if we move a parcel to any other level and allow it to equilibrate mechanically, it will thus have the same pressure, entropy and density as the environment. Because the fluid's state depends only on three independent variables, the composition must be the same as well. This shows that an isentropic, Ledoux neutral fluid must be homogeneous.

Interestingly, this demonstration shows that this is true even in the case of a fluid where the composition does not have a direct impact on the density, like a ortho-para hydrogen mixture. This would not be obvious in Eq. (4.32)[10] because it would seem that the second term would vanish as $\left.\frac{\partial \rho}{\partial \mu}\right|_{p,s}$ is nil. The reason is that composition still directly affects the entropy of the fluid through the entropy difference of the various fluids mixed and through the entropy of mixing. This is made even more transparent in a formulation by Tejada Arevalo et al. (2024) who rewrite Eq. (4.32) as

$$\frac{\mathrm{d}s}{\mathrm{d}p} - \left.\frac{\partial s}{\partial Y}\right|_{p,T} \frac{\mathrm{d}Y}{\mathrm{d}p} > 0, \tag{4.33}$$

where Y is their chosen compositional parameter because their focus is on the Helium composition of giant planets. This formula shows that there is no need for a mean molecular weight effect to force a Ledoux neutral state to have an entropy gradient.

[10] We remind the reader that in this case, the mean molecular weight cannot be used as a composition variable, but the equations hold if μ is replaced by any other compositional variable.

Chapter 5

Energy conservation

Le travail c'est la santé,
Rien faire c'est la conserver...

Henri Salvador

Contents

nergy conservation. What a beautiful principle ! In times of trouble and uncertainty, energy conservation has often been a guiding light for me, my lighthouse in the tempest. Indeed, when developing complex models, it is very easy to make mistakes. And although it is not a sufficient condition, putting energy conservation as a prerequisite to the validation of any result has often saved me a lot of trouble.

Because a planetary atmosphere can, most of the time, be considered as a closed system overlain by mostly... nothing[1], the external sources and sinks of energy are often readily identified and global energy conservation once thermal equilibrium is reached reduces to

$$F_{\mathrm{TOA}}^{\uparrow\downarrow} = F_{\mathrm{int}}, \tag{5.1}$$

where $\uparrow\downarrow$ denotes net fluxes counted positive upward (up minus down), $F_{\mathrm{TOA}}^{\uparrow\downarrow}$ is the horizontally averaged net radiative flux at the top of atmosphere (TOA), and F_{int} is the flux provided by the subsurface[2].

This equation is a great tool to diagnose whether an atmospheric model has reached thermal equilibrium which is often paramount to be able to use the results. But because atmospheres are dynamically unstable in general, this equation is often valid only in a time-averaged sense. In addition, massive atmospheres have a large thermal inertia and opacity so that the equilibration timescale becomes huge. In such cases, top-of-atmosphere fluxes can be "almost" equilibrated while the thermal structure remains far from its equilibrium state (see Selsis et al. (2023) for example).

It is therefore crucial to make sure that energy conservation is preserved as closely as possible, ideally down to numerical precision, when modeling atmospheric processes. If this is not done properly, and some spurious energy sources/sinks remain, it becomes very tricky for the modeler to diagnose whether a given simulation has truly reached equilibrium.

Yet, it is not always so easy to know whether adding a particular term is actually improving the energy conservation by taking into account something that was missing or breaking it because the newly added term is not consistent with our set of approximations anymore. And there are some examples of the latter in the literature that we will discuss in due time.

In this Chapter, we thus make an attempt at providing modelers with a map of the various levels of approximation that can be made when modeling the energetics of a moist atmosphere and, most importantly, what are the various energy terms that must be included in each of them to ensure global energy conservation. To do that, we will start by deriving the equation for energy conservation for a heterogeneous moist atmosphere. Then we will discuss whether energy conservation can really be reduced to enthalpy conservation as is very often done in many models. Finally, we will list the various levels of approximation and demonstrate what needs to be done to make them energy conserving.

[1]The thermodynamicist would probably describe the upper boundary limit as a pressiostat with zero pressure.

[2]For a terrestrial planet, this can be geothermal flux or flux coming from the ocean. For a gaseous planet, the surface may be more of an arbitrary pressure level and the internal flux is therefore the net energy crossing this level.

5.1 Back to global energy conservation

We have seen in Chapter 2 that when considering open systems, the energy equation derived from the first principle now has a new term due to exchange of enthalpy with the environment due to matter fluxes through the boundary of the system.

But do we need to re derive a new equation for the conservation of total energy, Eq. (1.49) ? Well... yes and no.

On one side, if we look at the micro scale, we already discussed in § 2.4.1 that the local version of the energy equation already includes the transport of enthalpy through matter fluxes through the $\nabla \rho h \mathbf{v}$ term.

But on the other side, we also already mentioned that this framework has difficulties accounting for flux of matter that do not follow the average gas velocity field, like sedimentation of condensates and precipitations. To remedy this shortcoming, it is tempting to add a chemical term to the global energy equation just like we did to the internal energy equation, Eq. (2.29), which would yield something like

$$\partial_t \left[\rho \left(\frac{1}{2}\mathbf{v}^2 + u + \phi \right) \right] + \nabla \left[\rho \mathbf{v} \left(\frac{1}{2}\mathbf{v}^2 + u + \phi + \frac{p}{\rho} \right) \right] = \rho \left(\dot{\tilde{W}}_{\text{ext}} + \dot{\tilde{Q}} + \dot{\tilde{C}} \right). \tag{5.2}$$

But this approach is highly incomplete. Indeed, the matter that is transferred (almost "teleported") does not only bring its enthalpy with it, it also carries its kinetic and gravitational energy, its momentum, and even its mass. So the chemical term should at least account for these other forms of energy, but one should also bear in mind that for the conservation to be complete, the other dynamical equations, down to the conservation of mass, should be modified accordingly. In their appendix B, Lauritzen et al. (2022) make a similar attempt by adding a mass term in the continuity equation. Their solution amounts to replacing $\dot{\tilde{C}}$ by $\dot{q}(e + p\upsilon)$ in Eq. (5.2), where $\dot{q}$ is the total added mass per unit mass of fluid. This has the merit of accounting for these other sources of energy, but cannot account for the fact that the matter that is either added or removed can be in different states and thus have different enthalpies compared to the average fluid. This difficulty is already discussed in Lauritzen et al. (2022) at the end of section B2. To derive a proper local conservation equation, one needs to turn to a multi-fluid approach such as the one of Bannon (2002), but this is far beyond the scope of the present essay.

However, in the following, we will mostly be concerned with the conservation for layers or even entire columns. In this case, the integral equation for the total energy of an open system derived in Chapter 2, Eq. (2.28), is valid as long as the flux terms at the boundaries are properly represented:

$$\underbrace{\frac{\mathrm{d}}{\mathrm{d}t}\int_{V(t)} \rho e \,\mathrm{d}V}_{\mathrm{d}E_{tot}/\mathrm{d}t} = \underbrace{\int_{V(t)} \rho \dot{\tilde{Q}} \,\mathrm{d}V}_{\dot{Q}} - \underbrace{\oint_{A(t)} p\mathbf{w}\cdot\mathbf{n}\,\mathrm{d}A}_{\dot{W}} + \underbrace{\int_{V(t)} \rho \dot{\tilde{W}}_{\text{ext}} \,\mathrm{d}V}_{\dot{W}_{\text{ext}}} + \underbrace{\oint_{A(t)} \rho\varepsilon(\mathbf{w}-\mathbf{v})\cdot\mathbf{n}\,\mathrm{d}A}_{\dot{C}}, \tag{5.3}$$

where

$$\boxed{\varepsilon = e + p\upsilon = \mathbf{v}^2/2 + \phi + h,} \tag{5.4}$$

is the *total* enthalpy, and $\mathbf{v}$ and $\mathbf{w}$ are the fluid and volume boundary velocities, respectively. The advantages of this equation over the aforementioned approaches are that

- We can see that the chemical term, $\dot{C}$, is formulated with the *total* enthalpy, so that all the forms of energy of the incoming material are taken into account.

- Interestingly, the integration volume considered here is free so that we can either choose a fixed control volume or a material one. We can even choose a composite one ! In our case, detailed in § 5.3, we will follow an isobaric surface at the top boundary to allow us to use pressure coordinates simply. At the bottom, we will treat two cases: i) a stationary solid surface appropriate for rocky planets and ii) an isobaric surface that can be used for a gaseous planet or if one wants to deal only with a layer of the atmosphere. The originality of our approach will be to *explicitly* allow for condensible species to cross the boundaries to account for chemical sources.
- Finally, when integrating the $\dot{C}$ term, it is easy to follow what species are crossing the boundary so that we can account for the exact total enthalpy that it carries with it.

5.2 Do we really conserve enthalpy ?

Since I started to work on planetary atmospheres, just after my PhD thesis, I have been perplexed by the fact that it was the enthalpy that was enforced as a conserved quantity in many macroscopic descriptions of microscopic processes. For example, in a 1D radiative-convective model of the atmosphere or in a global climate model, when some heat ΔQ is absorbed by unit of mass of a layer of the atmosphere, this is the heat capacity at constant pressure, c_p, that is used to derive the resulting increase in temperature following

$$\Delta Q = c_p \Delta T = \Delta H. \tag{5.5}$$

This of course implies that the heating directly increases the enthalpy of the gas — for an ideal gas, $c_p \mathrm{d}T$ is the variation of enthalpy (Eq. (1.57)) — and not the variation of internal energy.

Although this might appear as completely intuitive or self-evident to many readers, this perplexed me precisely because the left-hand-side of the equation that we derived for the conservation of total energy, Eq. (5.3), exhibits the *internal energy* through u and not the *enthalpy*. It did not help that I had just finished writing my thesis on the internal structure of giant gaseous planets and that the word enthalpy had never appeared in it or in the books on stellar structure that I had read, even though the equations for the equilibrium of a gaseous planetary envelope and an atmosphere look rather similar at first sight. So why was it that stellar structure people did not use this concept ?

One intuitive explanation for using the enthalpy that François Forget gave me on day-one of me reading `physiq.F90`[3], the spine of the LMDZ global climate model, is that the heating is done at constant pressure so that part of the incoming heat is used to increase the volume of the atmospheric layer, pushing the overlying atmosphere upward, increasing its potential energy. This convinced me at the time. But I had several reserves

- First it was not easy to see how this argument could be used to generalize to the conservation of the total enthalpy of the column when there was some exchange of material and energy between several layers,
- Second, still, why was it not used in modeling planetary and stellar structures (and in astrophysics in general),
- Third, if such a conservation of the total enthalpy was indeed correct, there should be a clean demonstration, and I had never seen such a clean demonstration in the general case.

[3] A file that later became `physiq_mod.F90` when a brave soul finally decided to make the code fully enter the `FORTRAN` 90 era by putting routines into modules. Ehouarn, we will never thank you enough for that.

This is why I thought that the writing of this HDR manuscript was a perfect occasion to finally take the time to find such a demonstration in the literature or to come up with one.

The closest I could find was in Kasahara (1974) who derives energy equations for generalized vertical coordinate systems. As discussed at length in appendix B of Lauritzen et al. (2022), which extends the work of Kasahara (1974) to a moist atmosphere, one can show that when using pressure coordinates, the conservation of total energy expressed in Eq. (1.49) naturally converts into an enthalpy conservation as long as the top boundary is kept at constant pressure. This seemed rather general, but on closer inspection, I realized that both demonstrations actually used the shallow atmosphere approximation with a constant gravity, and as we will see in § 5.2.3, there is indeed a (much) simpler demonstration of enthalpy conservation in this case. So I kept digging.

And much to my surprise, I ended up demonstrating that, in general, the total enthalpy of the atmosphere is NOT a conserved quantity. As we will see, it turns out that enthalpy conservation is a good approximation in many cases of interest, but it should by no means be considered as deriving from first principle as the conservation of total energy does.

So in the remainder of this section I will start by showing a simple case where enforcing enthalpy conservation breaks down the total energy conservation. Then I will discuss under which conditions enthalpy is conserved and perform a clean demonstration in this case.

5.2.1 Why we do not

We will start by considering a very simple atmosphere made of a non-condensible ideal gas in hydrostatic equilibrium in a general gravitational potential, $\phi(z)$. Now let us input some heat ΔQ into an infinitesimal layer[4] of fluid at temperature T comprised between the pressure p and $p + \mathrm{d}p$. If we follow the common prescription, the temperature of this layer after the heating and the equilibration of the whole atmosphere should be $T + \Delta T$ where

$$\Delta T = \frac{\Delta Q}{c_p} \frac{g}{\mathrm{d}p}. \qquad \text{(Common prescription of conserved enthalpy)} \tag{5.6}$$

Because of the thermal expansion of the gas, the thickness of the layer should have increased by an amount

$$\mathrm{d}z = \frac{\mathrm{d}p}{p} \frac{R}{g(z)} \Delta T, \tag{5.7}$$

so that the whole overlying atmosphere has been shifted upward by that amount.

Now, let us compute the change in the total energy of the whole atmosphere induced by this change. Because the temperature has changed only in the heated layer, the total increase in internal energy is only

$$\mathrm{d}U = c_v \Delta T \frac{\mathrm{d}p}{g} = \frac{c_v}{c_p} \Delta Q. \tag{5.8}$$

Because only the altitude of the overlying atmosphere has changed, we will only compute that contribution for the potential energy. After the equilibration the potential energy is

$$\Phi^f = \int_{z+\mathrm{d}z}^{\infty} \rho^f(z') \phi(z') \mathrm{d}z', \tag{5.9}$$

[4] In this chapter, we will often consider a column of atmosphere and many quantities are implicitly assumed to be per unit area.

where ρ^f is the density after equilibration, which is linked to the density before equilibration, ρ^i, by the simple relation $\rho^f(z) = \rho^i(z - \mathrm{d}z)$ since the atmosphere has just been translated upward. The very obvious variable change $u = z - \mathrm{d}z$ yields

$$\begin{aligned}\Phi^f &= \int_u^\infty \rho^f(u' + \mathrm{d}z)\phi(u' + \mathrm{d}z)\mathrm{d}u' \\ &= \int_u^\infty \rho^i(u')\phi(u' + \mathrm{d}z)\mathrm{d}u'. \end{aligned} \tag{5.10}$$

Now, we can expand the geopotential in a series

$$\begin{aligned}\Phi^f &= \int_u^\infty \rho^i(u')\left[\phi(u') + \partial_z\phi\mathrm{d}z + \frac{1}{2}\partial_z^2\phi\mathrm{d}z^2\right]\mathrm{d}u' \\ &= \int_u^\infty \rho^i(u')\left[\phi(u') + g(z)\mathrm{d}z + \frac{1}{2}\partial_z g\,\mathrm{d}z^2\right]\mathrm{d}u' \\ &= \Phi^i + \mathrm{d}z\int_u^\infty \rho^i(u')g(u')\mathrm{d}u' + \frac{1}{2}\mathrm{d}z^2\int_u^\infty \rho^i(u')\partial_z g\mathrm{d}u'. \end{aligned} \tag{5.11}$$

One can recognize that the second term is the weight (and not the mass) per unit surface area of the column and is thus equal to the total pressure at the base of the overlying column, i.e. p. This yields

$$\begin{aligned}\mathrm{d}\Phi = \Phi^f - \Phi^i &= p\mathrm{d}z + \frac{1}{2}\mathrm{d}z^2\int_u^\infty \rho^i(u')\partial_z g\mathrm{d}u' \\ &= \frac{R}{c_p}\Delta Q + \frac{1}{2}\mathrm{d}z^2\int_u^\infty \rho^i(u')\partial_z g\mathrm{d}u'. \end{aligned} \tag{5.12}$$

Hence, the variation of the total energy, $\mathrm{d}E_{tot} = \mathrm{d}U + \mathrm{d}\Phi$ is

$$\begin{aligned}\mathrm{d}E_{tot} &= \frac{c_v + R}{c_p}\Delta Q + \frac{1}{2}\mathrm{d}z^2\int_u^\infty \rho^i(u')\partial_z g\mathrm{d}u' \\ &= \Delta Q + \frac{1}{2}\mathrm{d}z^2\int_u^\infty \rho^i(u')\partial_z g\mathrm{d}u', \end{aligned} \tag{5.13}$$

where the last equality stems from the Mayer's relation for ideal gases.

So one can see that the increase of the total energy is equal to the amount of heat put into the system **only** to first order in the expansion of the geopotential (i.e. in a constant gravity). Indeed, there is another term which is due to the variation of gravity with height. On a planet, for example, where gravity decreases with height as $1/(1 + z/R_\mathrm{p})^2$, this implies a loss of total energy when the conservation of enthalpy is enforced.

This explains why enthalpy is not used when computing the thermal evolution deep fluid enveloppes inside stars and giant planets: In such envelopes, the variation of gravity with height is an important factor to take into account (and do not even get me started on the self gravity of the fluid itself). The conservation of enthalpy is thus far from being justified.

5.2.2 What is wrong with the isobaric transformation argument

The reader that made it that far might be confused. Indeed, we mentioned earlier that the conservation of enthalpy in such a basic thermal expansion scenario can be justified by the fact that the heating of our layer of gas happens at constant pressure. So the heating should increase the

enthalpy of the layer and the pressure work due to the thermal expansion should be exactly equal to the increase of potential energy of the overlying atmosphere.

To see what is wrong with this picture, let us simplify further our thought experiment and get back to a good ol' textbook exercise: *A mass of ideal gas is kept in an adiabatic enclosure under a piston of mass M. Some heat ΔQ is transferred to the gas, by how much does its temperature increase.*

The textbook answer is that the transformation is isobaric so that one can easily compute the temperature change using enthalpy conservation, which yields Eq. (5.6). Yet, just as in many atmospheric codes, there is here a hidden assumption: *that gravity be constant with height*. Indeed, if it is not, the weight of the piston changes when it is lifted by the heated gas. Therefore, **the pressure in the gas is changing**, even if ever so slightly. The variation may not be significant in a school room, but it certainly can be in a tall planetary atmosphere.

We also see where the demonstration in Kasahara (1974) and Lauritzen et al. (2022) would fail in the general case. In their demonstrations, enthalpy is conserved as long as the pressure at the top of the domain is constant. This poses no problem in a constant gravity field where the weight of the remaining atmosphere above the model top would be constant irrespective of its altitude. This would not work in a general gravity field.

Of course, this will not change the face of the Earth (but for Titan it might). Indeed, this example also shows why the conservation of enthalpy is a good approximation in many cases: The variation of gravity with height is small in the densest regions of the atmosphere on a planet like the Earth. But I can now sleep better knowing what are the limits of this assumption !

5.2.3 Why we (approximately) do

Now that we have seen that the conservation of enthalpy can break down in some cases, let us demonstrate rigorously when it is valid. Although we could directly demonstrate the general conservation equation starting from Eq. (5.3), I prefer here to start with a lighter demonstration including only the potential and internal energies to avoid getting lost in the details.

Let us start from the integration of the internal and potential energy over an isolated column of atmosphere. Of course, now that we have seen that conservation of enthalpy requires a shallow atmosphere where gravity is constant, we will approximate $\phi = gz$. We further assume that the atmosphere is close enough from hydrostatic equilibrium that one can use the hypsometric equation ($\rho \mathrm{d}z = -\mathrm{d}p/g$). With these assumptions, the total internal and potential energy of a layer contained between z_1 and z_2 writes

$$\begin{aligned}
U_{z_1\to z_2} + \Phi_{z_1\to z_2} &= \int_{z_1}^{z_2} (u+\phi)\,\rho \mathrm{d}z \\
&= \int_{p_2}^{p_1} (u+gz)\,\frac{\mathrm{d}p}{g} \\
&= \int_{p_2}^{p_1} u\frac{\mathrm{d}p}{g} + \int_{p_2}^{p_1} z\mathrm{d}p \\
&= \int_{p_2}^{p_1} u\frac{\mathrm{d}p}{g} - \int_{p_2}^{p_1} p\mathrm{d}z + [zp]_{p_2}^{p_1} \\
&= \int_{p_2}^{p_1} \left(u+\frac{p}{\rho}\right)\frac{\mathrm{d}p}{g} + [zp]_{p_2}^{p_1} \\
&= H_{z_1\to z_2} + [zp]_{p_2}^{p_1}\,, \qquad (5.14)
\end{aligned}$$

where we have used a partial integration. We easily recognize the enthalpy $h = u + p/\rho$ in the integrand, and the last term is the pressure work term that can exchange energy with the air above or below the column. We can see that this term trivially goes to zero if we integrate from the ground ($z_1 = 0$) to the top of atmosphere ($p_2 = 0$).

We now see this magical result: when gravity is constant and the atmosphere in hydrostatic equilibrium, the total enthalpy of the atmosphere exactly equals the sum of the total internal and potential energies. This is truly remarkable because h is not equal to $u + \phi$ locally. It works only globally because of the relationship between altitude, gravity and pressure enforced by the hydrostatic equilibrium (see also the discussion in Lauritzen et al. (2022)).

The careful reader could object that we seldom consider the full atmosphere so that we have to consider the variation of the $[zp]_{p_2}^{p_1}$ term when heating a given layer. So the variation of the enthalpy of the layer, H is not equal to the variation of its internal and potential energy. The subtlety here is that even when we apply a thermodynamic transformation to a given layer that modifies $[zp]_{p_2}^{p_1}$, we may have left the surrounding layers unchanged from a thermal point of view, but we may have changed their potential energy nonetheless. Taking the example of our experiment, although the pressures have not changed since no mass has been transferred and z_1 has not changed either, the heating as changed z_2 into $z_2 + \mathrm{d}z$. So, in the framework of the hydrostatic equilibrium, we can *never* decouple the potential energy of the whole atmosphere. As discussed above, enthalpy is not locally equal to the sum of internal and potential energy. But if we consider the whole atmosphere we have

$$U_{0\to z_1} + \Phi_{0\to z_2} + U_{z_1\to z_2} + \Phi_{z_1\to z_2} + U_{z_2\to\infty} + \Phi_{z_2\to\infty} = H_{0\to z_1} + H_{z_1\to z_2} + H_{z_2\to\infty}. \tag{5.15}$$

If we now look at the variations of those quantities during the heating of the intermediate layer while keeping the others untouched (meaning that $\Delta U_{0\to z_1} = \Delta U_{z_2\to\infty} = \Delta H_{0\to z_1} = \Delta H_{z_2\to\infty} = 0$), we get

$$\begin{aligned}\Delta H_{z_1\to z_2} &= \Delta U_{z_1\to z_2} + \Delta\Phi_{0\to z_2} + \Delta\Phi_{z_1\to z_2} + \Delta\Phi_{z_2\to\infty}\\ &= \Delta U_{z_1\to z_2} + \Delta\Phi_{0\to\infty}\\ &= \Delta U + \Delta\Phi,\end{aligned} \tag{5.16}$$

as expected. So in the limit where gravity is constant and hydrostatic equilibrium holds, the conservation of enthalpy is equivalent to the conservation of total energy. CQFD.

5.3 Equation of conservation of the total enthalpy for an open atmosphere

It is now time to derive an integral form for the enthalpy conservation equation in the case of an *open* atmosphere, i.e. an atmosphere which can loose or gain mass. To do this, we will integrate Eq. (5.3) to yield an equivalent of the first law that is valid for any part of the atmosphere

$$\frac{\mathrm{d}}{\mathrm{d}t}E_{tot} = \dot{Q} + \dot{W} + \dot{W}_{\text{ext}} + \dot{C}, \tag{5.17}$$

where each term is an integral over either the volume of this part of the atmosphere or the surface enclosing it.

The originality of our approach is that we will use a volume that has some static boundaries and some isobaric surfaces that more or less follow the fluid motion. Our top boundary will follow an isobaric surface. Lateral boundaries will be static ($\mathbf{w} = 0$) or non existant if we integrate over the whole planet. For the bottom boundary, we will treat two cases of interest.

- First we will use a static surface, relevant for terrestrial planets. The choice of a static bottom boundary is not original in and of itself, but here, the interesting part is that we *explicitly* allow matter to flow through this boundary, when condensates precipitate or are vaporized or lifted from the surface for example.

- Second, we will treat the case of an isobaric bottom surface, which can be used for a gaseous planet or when one only wants to look at the budget of a given layer of the atmosphere.

We note that matter can flow through any isobaric surface, so our volume is not a material volume and we will have to account for these flows in the chemical term.

Let us now review each term in order:

- On the l.h.s., we have the time variation of the total energy

$$E_{tot} = K + U + \Phi = \int_{V(t)} \rho e \, \mathrm{d}V = \int_{M(t)} e \, \mathrm{d}M, \tag{5.18}$$

  where K is the kinetic energy. In this section, Φ is the potential energy of the atmosphere considered only. The important feature is that because the region considered can gain or loose mass, this integral may change because either the integrand or the total mass, $M(t)$, may change.

- The first term on the r.h.s. is also simply the total diabatic heat input into the system considered

$$\dot{Q} = \int_{V(t)} \rho \dot{\tilde{Q}} \, \mathrm{d}V = \int_{M(t)} \dot{\tilde{Q}} \, \mathrm{d}M. \tag{5.19}$$

  This heat input primarily includes radiative heating and cooling, but can also include more exotic processes like ion drag. Contrarily to what is said in Appendix B of Lauritzen et al. (2022), we do not believe that dissipation of gravity waves enters into this category as it is an internal transfer from kinetic to thermal energy[5].

  However, because we have decided to encompass all the energy fluxes linked to a transfer of matter in the chemical term, $\dot{C}$, any flux of energy that is not due to a transfer of mass, like conduction (including the diffusion of sensible heat near the surface), must be accounted in $\dot{Q}$ even though it is probably more appropriate to write such terms as integral of fluxes over the appropriate surface. Note that, by similarity with the chemical term, these fluxes are often called and written as *enthalpy* fluxes such as $-c_p\overline{\omega' T'}$ or $-L\overline{\omega' q'}$, which correspond to the turbulent flux of specific and latent heat (see below Eq. (B18) of Lauritzen et al. (2022) for example). The problem here is that, at the surface, a flux of latent heat is linked to a mass flux of vapor to the atmosphere which will already be counted in the chemical term (so that it is counted twice in Eq. (B18) of Lauritzen et al. (2022) because of the last $\dot{q}\varepsilon$ term). As for the sensible heat term, it is *in fine* only an energy flux at the surface, however one wants to parametrize it. The notation $-c_p\overline{\omega' T'}$ is thus formally appropriate only inside the atmosphere where the turbulence indeed creates an internal enthalpy flux.

[5] Although, in a global climate model where gravity waves are not explicitly captured by the dynamical core, there parametrization would certainly appear as a source term where they dissipate. The careful modeler should however make sure that the same amount of energy is removed from the kinetic energy of the large scale wind at the location where these gravity waves form.

If one wants to connect this to net energy fluxes at the top (counted positive upward), $F^{\uparrow\downarrow}_{\text{top}}$, and bottom, $F^{\uparrow\downarrow}_{\text{bot}}$, we can write

$$\dot{Q} = \int_S \left(F^{\uparrow\downarrow}_{\text{bot}} - F^{\uparrow\downarrow}_{\text{top}} \right) \mathrm{d}S. \tag{5.20}$$

Note that, if we integrate over the whome atmospehre, $F^{\uparrow\downarrow}_{\text{top}}$ is equal to $F^{\uparrow\downarrow}_{\text{TOA}}$ and usually only includes radiative fluxes, while $F^{\uparrow\downarrow}_{\text{bot}} = F^{\uparrow\downarrow}_{\text{s}}$, which encompasses the "sensible flux" (e.g. conduction between the surface and the air) as well as the radiative one. For the aforementioned reasons, the latent fluxes, that are linked to a mass transfer are counted separately.

- The second term on the r.h.s. is a little more tricky. It is obviously the work of the pressure force, but it needs to be written differently to be easily usable. We start by noticing that, thanks to our choice of boundary, the boundary velocity, hence the work, is nil on all our static boundaries. So this leaves only the work on the top boundary and on the bottom boundary in the *isobaric bottom* case to compute. Let's start with the top:

$$\dot{W}_{\text{top}} = -\int_S p\mathbf{w}\cdot\mathbf{n}\,\mathrm{d}S, \tag{5.21}$$

where we use the symbole S to denote the surface of the region considered. Then, one needs to realize that because we follow an isobaric surface, the surface normal follows the direction of the pressure gradient with a negative sign because the pressure increases downward so that $\mathbf{n} = -\nabla p/|\nabla p|$, which is equal to $-\nabla p/\rho g$ to leading order. The other important point is that $\mathbf{w}$ is the velocity at which the isobar moves, so it is also normal to the pressure gradient. This yields

$$\begin{aligned}\mathbf{w}\cdot\mathbf{n} &= -\frac{1}{\rho g}\left(w_i\frac{\partial p}{\partial x_i}\right)\\ &= -\frac{1}{\rho g}\left(-\rho w_i\left.\frac{\partial\phi}{\partial x_i}\right|_p\right)\\ &= \left.\frac{1}{g}\frac{\partial\phi}{\partial t}\right|_p,\end{aligned} \tag{5.22}$$

where the second equality stems from hydrostatic balance and the last one from the fact that the geopotential does not explicitly depend on time in the cartesian coordinate system. The last partial derivative is to be understood as the variation of the geopotential at the top of the volume, whose pressure is constant. Remembering that we assume constant gravity (i.e. $\phi = gz$), we have

$$\dot{W}_{\text{top}} = -\int_S p_{\text{top}}\left.\frac{\partial z_{\text{top}}}{\partial t}\right|_p \mathrm{d}S. \tag{5.23}$$

A maybe more intuitive demonstration is to simply consider that, to leading order in an hydrostatic system, the pressure gradient is vertical so that $\mathbf{w}\cdot\mathbf{n}$ is simply the change in altitude of the isobar, $\left.\frac{\partial z_{\text{top}}}{\partial t}\right|_p$, which directly yields the expected result.

We now need to do the equivalent of the partial integration in Eq. (5.14). Because the top pressure

is constant we can write

$$\begin{aligned} p_{\text{top}}\partial_t z_{\text{top}} &= \partial_t \left(p_{\text{top}} z_{\text{top}}\right) \\ &= \partial_t \left(p_{\text{bot}} z_{\text{bot}} + \int_{\text{bot}}^{\text{top}} \mathrm{d}\left(zp\right) \right) \\ &= \partial_t \left(z_{\text{bot}} p_{\text{bot}}\right) + \partial_t \left(\int_{\text{bot}}^{\text{top}} z\mathrm{d}p + \int_{\text{bot}}^{\text{top}} p\mathrm{d}z \right) \\ &= \partial_t \left(z_{\text{bot}} p_{\text{bot}}\right) + \partial_t \left(\int_{\text{bot}}^{\text{top}} gz\frac{\mathrm{d}p}{g} + \int_{\text{bot}}^{\text{top}} p\upsilon\rho\mathrm{d}z \right) \\ &= \partial_t \left(z_{\text{bot}} p_{\text{bot}}\right) + \partial_t \left(-\int_{\text{top}}^{\text{bot}} \phi\frac{\mathrm{d}p}{g} + \int_{\text{top}}^{\text{bot}} p\upsilon\frac{\mathrm{d}p}{g} \right). \end{aligned} \tag{5.24}$$

This yields

$$\dot{W}_{\text{top}} = -\int_S \partial_t \left(z_{\text{bot}} p_{\text{bot}}\right)\, \mathrm{d}S + \frac{\mathrm{d}}{\mathrm{d}t}\left(\Phi + U - H\right). \tag{5.25}$$

Now, let's have a look at the bottom boundary. In the *isobaric bottom* case, we can do the exact same treatment as the upper surface while remembering to change the sign because of the direction of $\mathbf{n}$ is now reversed. This yields

$$\dot{W}_{\text{bot}} = \int_S p_{\text{s}} \left.\frac{\partial z_{\text{bot}}}{\partial t}\right|_p \mathrm{d}S. \tag{5.26}$$

Fortunately, we see that we recover the *static bottom* case by simply saying that the surface does not move with time, yielding $\dot{W}_{\text{bot}} = \dot{W}_{\text{s}} = 0$.

Now we can combine both equations to get the total pressure work term

$$\boxed{\dot{W} = -\int_S z_{\text{bot}}\partial_t p_{\text{bot}}\, \mathrm{d}S + \frac{\mathrm{d}}{\mathrm{d}t}\left(\Phi + U - H\right),} \tag{5.27}$$

which works for our two cases, but where we see that the first term simply drops in the isobaric bottom case.

But even in the static surface case we could be tempted to remove the first term on the r.h.s. by setting $z_{\text{bot}} = z_{\text{s}} = 0$ by convention, but then we would miss the effect of topography, as we will discuss later on when we will deal with hydropower.

- We will leave the third term, $\dot{W}_{\text{ext}}$, rather generic for the moment, because many forces can cause work to be done. A typical example are the frictional forces. But note that viscous forces inside the atmosphere will contribute some viscous heating so that their net effect is nil. They just transfer kinetic into thermal energy. On the contrary, friction at the surface can be a net sink of energy, and this is why we will leave this term hereafter.

- Finally comes the chemical term:

$$\dot{C} = \oint_{A(t)} \rho\varepsilon(\mathbf{w} - \mathbf{v}) \cdot \mathbf{n}\, \mathrm{d}A. \tag{5.28}$$

Whatever the boundary we are looking at, because $\mathbf{w}$ is the outward normal velocity of this boundary (nil if static), we can recognize $J \equiv \rho(\mathbf{w}-\mathbf{v})\cdot\mathbf{n}$ as the mass flux per unit area *entering* the volume. Thus, the regular lateral transport by the circulation in and out of the column writes

$$\dot{C}_{\text{lat}} = \oint_{\delta S}\int_{\text{bot}}^{\text{top}} \varepsilon\, J\, \mathrm{d}z\mathrm{d}s, \tag{5.29}$$

where δS is the perimeter of the atmospheric column and $\mathrm{d}s$ an infinitesimal linear element over this perimeter. In this case where $\mathbf{w}=0$, J simply writes $\rho v_\perp$, where $v_\perp$ is the velocity of the fluid normal to the boundary and directed inward. This term simply vanishes if we integrate over the whole planet.

At the top and bottom, this term writes

$$\dot{C}_{\text{top/bot}} = \int_{S_{\text{top/bot}}} \varepsilon\, J\, \mathrm{d}S, \tag{5.30}$$

where J is always counted positive inward. Although it is often found under various forms in the literature, here it has not been added in an *ad hoc* fashion. It has been rigorously linked to the flux of matter entering or leaving the volume, and we see that this matter brings its kinetic and potential energy with it along its enthalpy (i.e. its total enthalpy).

Because different species have different enthalpies, it is enlightening to separate the fluxes of all the different species, $i = \{\mathrm{a}, \mathrm{v}, \mathrm{c}\}$, and write $\varepsilon J = \varepsilon_i J_i$, where the sum is again implicit. Finally, because we are in an hydrostatic system the mass fluxes through isobaric surfaces are not completely independent. Indeed, if we look at a laterally isolated column, or integrate over the whole planet, the mass above an isobaric surface cannot change. This means that

$$\int_{S_{\text{isobar}}} (J_\mathrm{v} + J_\mathrm{c} + J_\mathrm{a})\ \mathrm{d}S = 0. \tag{5.31}$$

Finally combining all that, we get

$$\boxed{\dot{C} = -\oint_{\delta S}\int_{\text{bot}}^{\text{top}} \varepsilon_i\, J_i\, \mathrm{d}z\mathrm{d}s + \int_S \left(\varepsilon_i^{\text{top}}\, J_i^{\text{top}} + \varepsilon_i^{\text{bot}}\, J_i^{\text{bot}}\right) \mathrm{d}S.} \tag{5.32}$$

This formulation is completely general, and we will leave like that for the moment, but we will soon see two applications where we can connect these mass fluxes to measurable quantities.

Combining all these terms we finally get an equation on the conservation of the kinetic energy and enthalpy

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}[K+H] = \int_S \left[F_{\text{bot}}^{\uparrow\downarrow} - F_{\text{top}}^{\uparrow\downarrow} + \varepsilon_i^{\text{top}}\, J_i^{\text{top}} + \varepsilon_i^{\text{bot}}\, J_i^{\text{bot}} - z_{\text{bot}}\partial_t p_{\text{bot}}\right] \mathrm{d}S - \oint_{\delta S}\int_{\text{bot}}^{\text{top}} \varepsilon_i\, J_i\, \mathrm{d}z\mathrm{d}s + \dot{W}_{\text{ext}},} \tag{5.33}$$

where we remind the reader that the total specific enthalpy is

$$\boxed{\varepsilon_i = h_i + \phi_i + k_i.} \tag{5.34}$$

5.3.1 Case of an isolated layer between two isobars

When deriving an unidimensional model of the atmosphere, it is very practical to consider an isolated column, or to integrate over the whole planet laterally, which comes down to the same thing. Because we will want to separate our atmosphere in well defined layers parametrized by their top and bottom pressures, we can use our equation in this case to derive the energy equation for each layer, that will be coupled to the other layers by the surface fluxes.

In this cases, all the lateral boundary terms vanish. In addition, we can enforce the conservation of the mass of the layer through Eq. (5.31) at the top and bottom and $\partial_t p_{\text{bot}} = 0$ by construction. One complication however — as always with energy fluxes due to matter flows — is that we must somehow account for the heterogeneity of the advected matter, as will be discussed at length in Chapter 6. This entails that even if the net mass flux of a given species through a given boundary is nil, energy can still be transported so that

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\left[K+H\right] = F^{\uparrow\downarrow}_{\text{bot}} - F^{\uparrow\downarrow}_{\text{top}} + \dot{W}_{\text{ext}} + \sum_{k\in\{\text{top,bot}\}}\sum_{i\in\{\text{a,v,c}\}} \overline{\varepsilon_i^k J_i^k},} \tag{5.35}$$

where $\overline{\varepsilon_i^k J_i^k}$ is the average total enthalpy flux due to species i through interface k (remember that we have used a convention so that positive J always mean inward fluxes). This is almost the standard equation equation used in unidimensional models, although it often appears without the specific kinetic and potential energy of the added components (i.e. the enthalpy replaces the total enthalpy) nor the work of external forces like surface friction.

A slightly more counter-intuitive aspect of this equation is that we see that if the fluxes of the condensible components are not equilibrated at each surface – i.e. $\overline{J_\text{v}^k} + \overline{J_\text{c}^k} \neq 0$ – there must be a compensating flux of air to keep the pressures at the boundaries constant. As a result, every time some mass of condensible is added to the layer, one must not only add its total enthalpy, but also remove the total enthalpy of the air that is pushed outside. To see that, let us consider a case where the enthalpy of each component is homogeneous through the domain ($\varepsilon_i = \overline{\varepsilon_i}$) but different from one species to the other. In this case, and dropping the overbars on single averaged quantities, $\overline{\varepsilon_i^k J_i^k} = \varepsilon_i^k J_i^k$ and mass conservation yields $J_\text{v}^k + J_\text{c}^k + J_\text{a}^k = 0$ so that

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[K+H\right] = F^{\uparrow\downarrow}_{\text{bot}} - F^{\uparrow\downarrow}_{\text{top}} + \dot{W}_{\text{ext}} + \sum_{k\in\{\text{top,bot}\}} \left[\left(\varepsilon_\text{v}^k - \varepsilon_\text{a}^k\right) J_\text{v}^k + \left(\varepsilon_\text{c}^k - \varepsilon_\text{a}^k\right) J_\text{c}^k\right]. \tag{5.36}$$

The total enthalpy correction due to the compensating flow of air is often forgotten.

5.3.2 Case of an atmosphere above a solid surface

The other interesting case is when there is a solid surface at the bottom, like on our good'ol Earth. To simplify things further, we will encompass almost all the atmosphere so that the mass transfer at the upper boundary of our volume can be neglected along with the lateral ones.

In this case, we cannot assume the bottom pressure to be constant anymore. However, things simplify a bit because non-condensing air cannot cross our bottom boundary ($J_\text{a} = 0$). Now, to get things a little more concrete, we can realize that the vapor mass flux entering the atmosphere in kg per unit time and surface is equal to the evaporation, $J_\text{v} = \dot{E}$ while the flux of condensates is equal to minus the precipitations, $J_\text{c} = -\dot{P}$. This yields

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\left[K+H\right] = \int_S \left[F_\text{s}^{\uparrow\downarrow} - F_{\text{TOA}}^{\uparrow\downarrow} + \varepsilon_\text{v}^\text{s}\dot{E} - \varepsilon_\text{c}^\text{s}\dot{P} - z_\text{s}\partial_t p_\text{s}\right]\mathrm{d}S + \dot{W}_{\text{ext}}.} \tag{5.37}$$

One could be confused that the right hand side depends on an arbitrary choice of the reference level for the geopotential while the left hand side does not. However, hydrostasy enforces that the atmospheric mass be given by

$$gM_{\text{atm}} = \int_S p_s \mathrm{d}S, \tag{5.38}$$

while its variation is

$$\dot{M}_{\text{atm}} = \int_S \left(\dot{E} - \dot{P}\right) \mathrm{d}S. \tag{5.39}$$

If we define an arbitrary reference altitude and geopotential, $\phi_{\text{ref}} = g z_{\text{ref}}$, then

$$\int_S \phi_{\text{ref}} \left(\dot{E} - \dot{P}\right) \mathrm{d}S = \int_S z_{\text{ref}} \partial_t p_s \mathrm{d}S, \tag{5.40}$$

and

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}[K+H] &= \dot{W}_{\text{ext}} \\ &+ \int_S \left[F_s^{\uparrow\downarrow} - F_{\text{TOA}}^{\uparrow\downarrow} + (h_v + k_v + \phi_v - \phi_{\text{ref}})\dot{E} - (h_c + k_c + \phi_c - \phi_{\text{ref}})\dot{P} - (z_s - z_{\text{ref}})\,\partial_t p_s\right] \mathrm{d}S. \end{aligned} \tag{5.41}$$

One can see that if evaporation and precipitations are not equilibrated, their contribution to the *arbitrary* part of the potential energy is compensated by an equally arbitrary contribution through the variation of the surface pressure with an opposite sign.

To make things even clearer, we can consider an isolated column and take the reference altitude to be the surface altitude so that the equation reduces to

$$z_s \partial_t p_s = z_s g(\dot{E} - \dot{P}) = \phi_s(\dot{E} - \dot{P}), \tag{5.42}$$

and

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}[K+H] = F_s^{\uparrow\downarrow} - F_{\text{TOA}}^{\uparrow\downarrow} + (h_v + k_v + \phi_v - \phi_s)\dot{E} - (h_c + k_c + \phi_c - \phi_s)\dot{P} + \dot{W}_{\text{ext}}.} \tag{5.43}$$

Again, we recover an almost standard equation although it is now explicit that the added components bring their own total enthalpy with them. While seemingly intuitive, our derivation highlights that it is not completely trivial to see how to deal with the potential energy of the added material, as we have just seen that in this case, there is a compensation between the gravitational energy added and the work of the pressure forces on the top boundary.

Although it may be tempting to always use Eq. (5.42) and to further remove the ϕ_s term by choosing the surface as the reference level in the definition of the geopotential, always canceling out the derivative of the surface pressure and the potential energy of the added material in Eq. (5.37), we will see hereafter that this is incorrect because the variation of the surface pressure can also result from atmospheric motion. This term is especially important when the surface of our planet has some topography, as we will now discover.

5.4 Potential energy of precipitations: or why sometimes, less is more

Now that we are armed with a rigorous energy (or enthalpy) conservation equation, we can finally have a proper look at the energetics of some physical processes linked to moist atmospheres.

To start with, I wanted to have a look at how to properly account for the potential energy of precipitations. It is an interesting example, because it shows very well how one might want to add a term to model some energy flux which *looks like* an improvement, but finally ends up breaking energy conservations. While investigating this issue, I realized that it was profoundly linked to the following question: where does hydroelectricity come from ? From the Sun, you might answer. And you would not be wrong. There is not really any other sizable energy source in the atmosphere after all. But the question is rather: through which channel is energy transformed from thermal energy to potential energy of water ? And I hope you'll find that the answer is a little subtler that you might have guessed.

5.4.1 Conservation issues

For me, this story started, again, when I first worked on the LMDZ GCM. To get acquainted with the model, François Forget asked me to run a little sensitivity study of how supersaturation could affect the effect of CO_2 ice clouds on the climate of early Mars for a paper he was working on (Forget et al. 2013). To that purpose, I had to understand the approach used to compute the condensation of CO_2 ice clouds, which was explained in Forget et al. (1998). In this study of the martian polar cap, they realized that because a sizable fraction of the atmosphere could collapse at the surface and re-sublimate, taking into account the potential and sensible energy carried by sedimenting CO_2 ice crystals could have some significant effect. In their Eq. (9), they thus added a term $g\Delta z\delta m_c$ to the energy balance of their layers, where δm_c was the mass of condensates sedimenting from the layer above and Δz the height difference between the two layers.[6] It seems rather straightforward to understand that this term is supposed to take into account the dissipation of potential energy into heat along the descent due to the friction of the air on the falling crystals — provided they instantaneously fall at their terminal speed, which is a rather good approximation.

This seemed perfectly correct to me until I read Ding and Pierrehumbert (2016), a study on convection in vapor rich atmospheres. In this study, the authors take a slightly different approach because they assume that all the precipitations directly reach the surface after condensation. But they do mention adding the potential energy of the precipitations[7] to the surface budget to model the fact that potential energy is converted into kinetic energy that is then converted to thermal energy when the droplets strike the surface.

However, interestingly, they mention that to close the energy budget, they have to take into account the fact that, when falling, the condensates stop weighing on the atmosphere, which expands, exerting pressure work on the atmosphere above the condensation level. And like when you lift a brick off a piston, the adiabatic expansion leads to a decrease in the temperature of the gas. It is not completely intuitive to understand why the potential energy of the brick is exactly equal to the enthalpy lost by the whole remaining atmosphere. To show that it is, we can use Eq. (5.33) for an isolated column that we integrate over a given time so that the precipitated mass per unit surface is equal to $\delta m_c = \dot{P}\delta t$. If we assume that there is no other energy fluxes with the exterior and that the

[6] They also added a term linked to the temperature variation of the condensates during their fall, but we will have a look at this term in the next sections.

[7] In addition to the enthalpy of the condensates themselves.

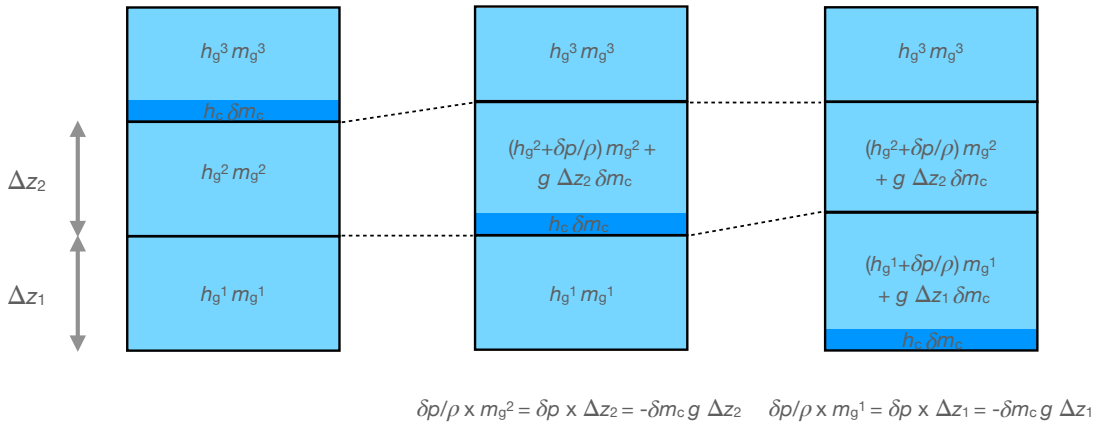

Figure 5.1: Energetics of condensates sedimenting through multiple layers while dissipating their potential energy into heat. Left: initial condition after the condensation. Middle: The condensates have gone through layer 2. Right: The condensates have reached the bottom.

atmosphere starts and finishes at rest, the decrease in the enthalpy of the atmosphere is

$$\delta H = -\varepsilon_c \dot{P} \delta t = -(h_c + k_c + \phi_c - \phi_s)\delta m_c. \tag{5.44}$$

Now, whether you want to compute the energy of the precipitations when they form, i.e. when $k_c = 0$ and $\phi_c - \phi_s = g(z_c - z_s)$ where z_c is the condensation altitude, or when they leave the atmosphere, i.e. when $\phi_c = \phi_s$ and $k_c = g(z_c - z_s)$ because they considered no friction, you see that the atmosphere loses an enthalpy equal to the potential energy of the precipitating condensates along with their own specific enthalpy. The temperature of the atmosphere must thus be decreased to enforce energy conservation. Another way to see this is to compute the change in enthalpy of the gas per unit surface using $V\mathrm{d}p/A$ where A is the column surface, $\mathrm{d}p = -g\delta m_c$ and the initial volume of the column that is decompressed is $V = A(z_c - z_s)$. This yields $V\mathrm{d}p/A = -\delta m_c g(z_c - z_s)$, as expected.

So we now see the problem in the approach of Forget et al. (1998). Because they do not take into account the adiabatic decompression, their gravitational heating term leads to breaking conservation—contrary to what is said in Ding and Pierrehumbert (2016). But one might argue that things are a little different because Forget et al. (1998) dissipates the gravitational energy in each layer as the condensates sediment. And they are probably right to do so because the condensates reach equilibrium velocity in a very small time compared to their whole descent. To understand what happens, let us consider the setup in Fig. 5.1. We have three layers and condensates in the third and top layer.[8] Initially, each layer i has a given enthalpy due to the gas, $h_g^i m_g^i$. In addition, the top layer has some condensates which contribute $h_c \delta m_c$. When the condensates sediment trough layer 2, they loose a potential energy equal to $g\Delta z_2 \delta m_c$, which is assumed to be converted to heat that is added to the enthalpy of layer 2, as proposed by Forget et al. (1998). However, at the same time, layer 2 extends upward due to the removal of the weight and the decrease of the top pressure by $\delta p = -\delta m_c g$. The resulting decrease in the enthalpy of the gaseous part is $(\delta p/\rho)m_g^2 = \delta p \Delta z_2 = -g\Delta z_2 \delta m_c$.

So we see that when we assume that friction completely dissipates locally the potential energy of the condensates, the heat source cancels *exactly* the loss in enthalpy due to the decompression and the

[8] We will assume that the condensates are concentrated at the bottom of the layer, but it does not change the argument because the problem is linear and we can always somehow decompose a complex distribution of condensates into an infinite sum of infinitely thin layers that we can treat separately.

pressure work on the overlying atmosphere. In essence, in the framework of this assumption, energy conservation is enforced by doing... nothing ! ! ! As advertised, although it is tempting to add the gravitational energy of the condensates to the layers they traverse, not removing the corresponding energy taken to the gas leads to an imbalance. To understand this in the context of Eq. (5.33), one can simply see that in the framework where condensates reach their terminal velocity instantaneously, dissipating their gravitational energy during the fall, they reach the surface with both zero potential energy and a negligible kinetic energy. The loss term in Eq. (5.33) is thus limited to $h_c \dot{P} \delta t$, i.e. the specific enthalpy of the condensates, as advertised. The enthalpy of the atmosphere remains otherwise unchanged.

In a large scale model in hydrostatic equilibrium, not doing anything thus does take into account the falling precipitations, although only in the limit where friction is efficient. Note, however, that in a cloud resolving model where the decompression will be dealt within the dynamical step — as long as the dynamical core accounts for the mass loading effect of vapor and condensates, like WRF — one does need to add the heating term in the physical step to impose conservation. This is what is done in Leconte et al. (2024) for example.

5.4.2 But where does hydropower come from ?

The result from the previous section raises an issue. Indeed, Ding and Pierrehumbert (2016) states that

> *One knows intuitively that part of the energy carried by the precipitation should be in the form of potential energy— that is after all where hydroelectric power comes from, namely, the potential energy of water vapor stored in the atmosphere when solar energy is used to drive convection, which lifts the water vapor to higher altitudes.* (8)

But if the potential energy of precipitations is entirely dissipated by friction directly back into the atmosphere, the process is energy neutral and no potential energy is left into the condensates when they reach the surface. So where does hydroelectricity come from ?

Of course, the careful reader will argue that hydro electricity requires some topography. Indeed water is mostly evaporated at sea level and it is only the part that precipitates over high lands that still has potential energy when reaching the surface, potential energy that can be harvested as hydro electricity. Yet, this does not explain by which channel the atmosphere manages to transform thermal energy into gravitational energy of water.

Quote 8 seems to imply that solar energy is transferred to water vapor during convection. The problem with this picture is that the atmosphere does not gain potential energy when a dry convective event sets in. In fact it loses some. This is this very fact that renders dry convection possible at all. Some excess of Convective Available Potential Energy (CAPE) needs to be present for convection to spontaneously occur. And part of this CAPE is released as kinetic energy to power the convective motion. This kinetic energy is eventually dissipated as heat by viscosity so that the net enthalpy change is nil for the whole atmosphere. One could even argue that, on Earth, since water vapor is lighter than nitrogen, a sufficient excess of water vapor near the surface is sufficient to drive convection. For moist convection, the enthalpy change, before precipitations are removed, is also nil because phase transitions just transfer enthalpy from latent to sensible while leaving the sum constant (Ding and Pierrehumbert 2016). This is also why this energy does not come from the evaporation because phases changes are transparent from the point of view of the enthalpy budget.

To understand what is happening, let us use our enthalpy equation on two connected atmospheric columns with the same area, one of which is over the ocean, the other being over a mountain with

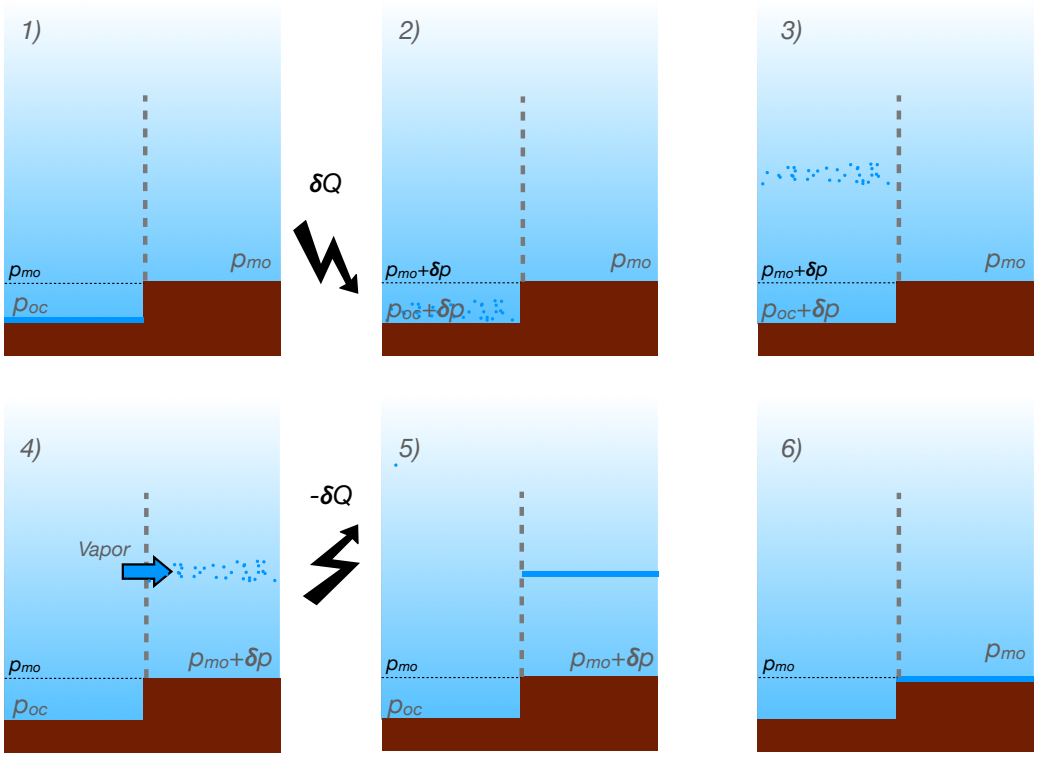

Figure 5.2: Energetics of the conversion of thermal energy into hydropower. Panel numbers refer to the text.

an altitude Δz. We will decompose what happens to our mass of water into idealized steps depicted in Fig. 5.2. As we will see, our simplifications do not render our exemple completely dynamically consistent. For exemple, convection would not spontaneously develop in an isothermal atmosphere, except if the mean molecular weight gradient due to vapor is sufficient. It is also true that in a realistic settings, all those steps would happen continuously. But using less idealized conditions would just make the equations a little less transparent while changing nothing on the energetics side.

1. To make things as tractable and transparent as possible, we will assume the whole atmosphere is isothermal and initially dry, at rest, and in complete equilibrium. Because our equation is not limited to the gaseous part of the atmosphere, our initial state will just encompass an additional mass δm_c[9] of liquid water as a thin layer at the surface of our ocean.

2. Solar energy received by the surface (δQ) is used to vaporize the water at constant temperature, temporarily increasing the enthalpy of the atmosphere by $\delta Q = \delta m_c L$.

3. Convection sets in and transports the water vapor aloft. As discussed above, this step does not change the global enthalpy of the atmosphere as CAPE is transformed into kinetic energy which is then dissipated back to heat.

4. Because some mass has been added to the column above the ocean, the resulting pressure gradient initiates some horizontal circulation transferring the vapor over mountains.

5. The vapor can now condense. As we assume that the atmosphere still remains at the same temperature, it gives back the latent heat, $\delta m_c L = \delta Q$, to space as infrared radiative cooling.

6. Finally, the condensed water falls back to the ground, dissipating its potential energy through friction as it falls. As we discussed in the previous section, this does not change the enthalpy of the atmosphere either, as frictional heating exactly compensates adiabatic decompression.

If we follow the steps, we seem to see that the final enthalpy of the atmosphere is the same as the initial one. Latent heat used to vaporize water has been given back. The convective part of the process has not left any excedent enthalpy to the atmosphere as implied by Quote 8. So where does the additional gravitational energy of the water that is now on top of the mountain come from ?

Well, we missed something in one of the steps, and again, Eq. (5.33) will allow us to follow what is happening. During the horizontal transport of vapor toward high lands, our isothermal atmosphere approximation is no longer energetically consistent anymore. In fact, we can see using Eq. (5.33) that the enthalpy of the atmosphere varies during this step because of the surface pressure variation term

$$\delta H = \int_A z_s \partial_t p_s \, \mathrm{d}A = A \delta p_s \Delta z = \delta m_c g \Delta z, \tag{5.45}$$

which is *exactly* the additional energy that we get back in hydro power in the end. So this is horizontal transport and not convection that actually taps into the energy of the atmosphere. Indeed, the troubling part is that, once we do extract the water from the system with its enthalpy, this is now the atmosphere that is missing $\delta m_c g \Delta z$ of enthalpy — the specific enthalpy of the extracted water being otherwise equal to the specific enthalpy of the initial water that we added in at the ocean's surface. Where is this enthalpy gone ?

[9] In this specific instance, because we deal with two separate columns with different properties, we have to account for their respective surface areas, even though we will take the area of the two columns equal for simplicity. Therefore, δm_c is actually a mass and not a mass per unit area. The area of each column, A, will thus appear in the relation between the mass of water and the pressure increment it imposes, $\delta p_s = g \delta m_c / A$

Well, in step 4, we forgot that the whole atmosphere below the water vapor layer in the oceanic column has undergone an adiabatic decompression because we lifted a brick off of it. The temperature of this part of the atmosphere has therefore decreased. On the mountain side, the atmosphere has been compressed, increasing the temperature. These two changes do not compensate each other because there is more air on the oceanic side : the air that is between the sea surface and the altitude of the mountain top. When everything is said and done, the enthalpy lost by this portion of the atmosphere is exactly equal to $\delta m_c g \Delta z$. So this is actually the dry atmosphere that is providing the gravitational energy of the water. And the sun does not provide this energy by heating the water... but the dry atmosphere !

Another way to look at this is that the water vapor does gain potential energy during the convection phase. But this is not the sun that provides directly this energy. This is the dry portion of the atmosphere that decreases its potential energy at that moment, but it is yet invisible. It is only when the vapor is transferred over the mountains that the dry atmosphere is decompressed and that the loss of enthalpy manifests itself by a decrease in temperature that will later be compensated by solar heating. But of course, in a real atmosphere, this is rather hidden by the fact that all these processes occur continuously and simultaneously.

5.5 Treating the thermodynamics and energetics of condensible species consistently

We have seen in Chapter 3 that a mixture of moist air can be described by the following caloric equation of state (Eq. (3.30)) :

$$\begin{aligned} H &= m_a h_a(T) + (m_c + m_v) h_c(T) + m_v L(T) \\ &= m_a \left(h_a^\circ + \int_{T^\circ}^{T} c_{p,a}(T)\, \mathrm{d}T \right) \\ &+ (m_c + m_v) \left(h_c^\circ + \int_{T^\circ}^{T} c_{p,c}(T)\, \mathrm{d}T \right) \\ &+ m_v \left(L^\circ + \int_{T^\circ}^{T} c_{p,v} - c_{p,c}\, \mathrm{d}T \right). \end{aligned} \tag{5.46}$$

In principle, one just needs to substitute this expression for the enthalpy in the energy equation of the model and bob is your uncle. In practice, this is often more easily said than done, and many approximations are made to make the equations as easily tractable as possible. To list only a few:

- The most common approximation by far is certainly to assume that all the heat capacities are independent of temperature, which makes the equation linear in T. This can be justified in atmospheres with a small temperature range. As it is used in many models, we will make it all along this section for the reader to be able to compare with known formulas.
- A step further is to assume that the latent heat is independent of temperature.
- A second very common assumption is to neglect the mass of condensates in the atmosphere, along with their heat content. Although it is a problem to verify absolute conservation, this is often a good approximation in practice because is difficult to imagine a setup where a significant fraction of condensates would remain aloft and be transported with the gas. Note that an

atmosphere can have a very vigorous condensation cycle, i.e. a large condensate flux, without having a large condensate to gas ratio.

- A stronger version of the above is to neglect the mass and/or heat capacity of the vapor along with the condensates while keeping the latent heat term. Although this is a practical approximation is many cases, it can become very wrong in vapor rich atmospheres.

- Finally, the simplest approximation is to treat everything as a dry gas. This is obviously very far from realistic, but it can sometimes be of interest to get a first order approach.

Although all these approximations have their utility and validity range, the point of this section is to explicit the fact that choosing one or the other also impacts the energetics of your model and that some additional terms must be accounted for to preserve energy conservation. We will therefore go through them

5.5.1 Baseline representation

In order to provide a base case against which to compare all the other cases, let us briefly discuss one of the simplest representation possible, which is to completely neglect the heat capacity of the condensible species, except for the latent heat, which is considered independent of temperature. The heat capacity of the dry gas is also considered independent of temperature. This yields

$$H = m_{\mathrm{a}} h_{\mathrm{a}}(T) + m_{\mathrm{v}} L(T) = m_{\mathrm{a}} \left[h_{\mathrm{a}}^{\circ} - c_{p,\mathrm{a}} T^{\circ} \right] + m_{\mathrm{a}} c_{p,\mathrm{a}} T + m_{\mathrm{v}} L^{\circ}, \tag{5.47}$$

which is often simplified by getting rid of the reference state term into

$$H = m_{\mathrm{a}} c_{p,\mathrm{a}} T + m_{\mathrm{v}} L^{\circ}. \tag{5.48}$$

Note that the modeler is free to either account for the mass of the vaporized water when it enters or leave the atmosphere as discussed in Leconte et al. (2013). The system remains self consistent. However, the physical approximation made is subtly different. In the case where the mass is not taken into account, this amount to neglecting the heat capacity of vapor, as advertised. When the mass is taken into account, the heat capacity of vapor is taken into account but is approximated to be equal to that of dry air.

5.5.2 Sensible heat of precipitations

We have discussed the fact that precipitations transport their potential energy. But what about their specific enthalpy ? Indeed, the level where precipitations are formed is usually much colder than the surface (or the level where it will eventually reevaporate in a gaseous planet). Assuming that this temperature difference is ΔT, a precipitation flux, $\dot{P}$, entails that precipitations transport $c_{p,\mathrm{c}} \Delta T \dot{P}$ between the two levels.

The question is whether this should entail another flux with the vapor on the way up. The difficulty is that, compared to potential energy, which acted as a source of thermal energy, here, we are dealing only with a flux of thermal energy here. This is therefore sneaky as this will not bias the whole energy budget of the atmosphere and will not show up as an imbalance between the absorbed and emitted flux of the whole atmosphere. We thus cannot highlight an inconsistency by just looking at the precipitation process. We must look at where and when this thermal energy got created.

Indeed, it is rather intuitive that the aforementioned flux comes from adding the contribution of the condensates to the simple form of the enthalpy in Eq. (5.47) as follows

$$\begin{aligned} H &= m_{\mathrm{a}} h_{\mathrm{a}}(T) + m_{\mathrm{c}} h_{\mathrm{c}}(T) + m_{\mathrm{v}} L^{\circ} \\ &= m_{\mathrm{a}} \left[h_{\mathrm{a}}^{\circ} - c_{p,\mathrm{a}} T^{\circ} \right] + m_{\mathrm{c}} \left[h_{\mathrm{c}}^{\circ} - c_{p,\mathrm{c}} T^{\circ} \right] + m_{\mathrm{a}} c_{p,\mathrm{a}} T + m_{\mathrm{c}} c_{p,\mathrm{c}} T + m_{\mathrm{v}} L^{\circ}. \end{aligned} \tag{5.49}$$

This is the $m_{\mathrm{c}} c_{p,\mathrm{c}} T$ term that entails that condensates need to be heated by the neighboring gas to increase their temperature on the way down. To see the inconsistency, we can just look at the condensation process in the cloud. With this expression, we see that when a mass δm_{c} of vapor is transformed into condensates at constant temperature, the variation of enthalpy of the parcel is

$$\delta H = \delta m_{\mathrm{c}} [h_{\mathrm{c}}(T) - L^{\circ}] \neq -\delta m_{\mathrm{c}} L^{\circ}. \tag{5.50}$$

We immediately see that this is not equal to the latent heat released by condensation as it should be. In addition to this latent heat, we have *created* some enthalpy.

The problem obviously comes from the fact that we account for the specific enthalpy of the newly created condensates, but forgot to deduce the specific enthalpy of the vapor that disappeared in addition to the latent heat. We must thus come back to the full expression of the moist enthalpy in one of its various forms

$$\begin{aligned} H &= m_{\mathrm{a}} h_{\mathrm{a}}(T) + m_{\mathrm{c}} h_{\mathrm{c}}(T) + m_{\mathrm{v}} h_{\mathrm{v}}(T) \\ &= m_{\mathrm{a}} h_{\mathrm{a}}(T) + (m_{\mathrm{c}} + m_{\mathrm{v}}) h_{\mathrm{c}}(T) + m_{\mathrm{v}} L(T). \end{aligned} \tag{5.51}$$

With this, we directly see that forming a mass δm_{c} of condensates entails an enthalpy change equal to

$$\delta H = \delta m_{\mathrm{c}} [h_{\mathrm{c}}(T) - h_{\mathrm{v}}(T)] = -\delta m_{\mathrm{c}} L(T), \tag{5.52}$$

as it should be (See also Chapter 3).

The practical conclusion to bear in mind is that when a model wants to take into account either the transport of sensible energy by the vapor or the condensates, it must always take both into account to be at the same level of approximation and to be thermodynamically consistent.

5.5.3 Variation of latent heat with temperature and heat capacity of vapor and condensates

It is well-known that latent heat changes with temperature. This is particularly important if one wants to compute precisely the saturation temperature/pressure curve for any given species as the evolution of the saturation pressure is linked to the latent heat by the Clausius-Clapeyron relation

$$\frac{\mathrm{d}p_{\mathrm{s}}}{\mathrm{d}T} = \frac{L(T)}{T \Delta \upsilon} = \frac{L(T)}{T^2 R_{\mathrm{v}}} p_{\mathrm{s}}, \tag{5.53}$$

where $\Delta \upsilon$ is the difference in the specific volume of vapor and condensates and the second equality comes from neglecting the volume of condensates and using the ideal gas law.

However, we see that if we use our simple enthalpy equation, Eq. (5.47), and just make the latent heat vary with temperature, we create a spurious energy source. For example, if we consider a parcel of moist air that cycles on an isobar[10] between a warm region at a temperature T_{v} where δm_{c}

[10] The analysis could be done along a cycle involving some adiabatic (de)compression to model a convective cycle. However, the conclusions would be the same, and this would just make the analysis a little more complex.

kilograms of condensible evaporate and a cloud where they recondenses at a temperature T_c, we see that for each cycle, the parcel receives $\delta m_c L(T_v)$ Joules of heat to vaporize and releases $\delta m_c L(T_c)$ Joules upon condensation. The use of Eq. (5.47) implies that we only consider the heat capacity of the dry gas. So, during the heating phase from T_c to T_v, the heat needed to warm the fluid is equal to $m_a c_{p,a}(T_v - T_c)$, which is exactly equal to heat released during the the cooling phase after the evaporation.

As a result, the whole enthalpy change during the cycle is

$$\begin{aligned}\delta H &= \underbrace{m_a c_{p,a}(T_v - T_c)}_{\text{Heating}} + \underbrace{\delta m_c L(T_v)}_{\text{Vaporization}} - \underbrace{m_a c_{p,a}(T_v - T_c)}_{\text{Cooling}} - \underbrace{\delta m_c L(T_c)}_{\text{Condensation}} \\ &= \delta m_c \left(L(T_v) - L(T_c)\right) \neq 0, \end{aligned} \tag{5.54}$$

which is not equal to zero — as it should be for a cycle — if the latent heat varies with temperature. So this will bias any model toward a non-zero radiative balance.

To understand where this comes from, remember that we have seen in Chapter 3, that

$$\frac{\mathrm{d}L}{\mathrm{d}T} \approx \left(c_{p,v} - c_{p,c}\right). \tag{5.55}$$

This means that the variation of latent heat with temperature is actually compensating for the fact that vapor and condensates do not carry the same amount of enthalpy per temperature increment. Since the Latent heat is the difference between the enthalpy of the vapor and the one of the condensate, it has to change if the heat capacities are different. But this means that we have to take into account this difference in heat capacities in the other parts of the model as well to compensate for this.

Indeed, if we now include the heat capacity of both the vapor and condensates, the enthalpy budget of our cycle now writes

$$\begin{aligned}\delta H &= \underbrace{\left(m_a c_{p,a} + m_v c_{p,v} + m_c c_{p,c}\right)(T_v - T_c)}_{\text{Heating}} + \underbrace{\delta m_c L(T_v)}_{\text{Vaporization}} \\ &\quad - \underbrace{\left(m_a c_{p,a} + (m_v + \delta m_c) c_{p,v} + (m_c - \delta m_c) c_{p,c}\right)(T_v - T_c)}_{\text{Cooling}} - \underbrace{\delta m_c L(T_c)}_{\text{Condensation}} \\ &= -\delta m_c (c_{p,v} - c_{p,c})(T_v - T_c) + \delta m_c \left(L(T_v) - L(T_c)\right) \\ &= -\delta m_c (c_{p,v} - c_{p,c})(T_v - T_c) + \delta m_c (c_{p,v} - c_{p,c})(T_v - T_c) \\ &= 0, \end{aligned} \tag{5.56}$$

where the penultimate equality stems from integrating Eq. (5.55)[11]. The cycle is now balanced.

As a corollary, although we discussed in the previous section that accounting for the heat capacities of both the vapor and the condensates was necessary to be consistent, we now see that there is another constraint : if we want to keep the latent heat independent of temperature, both condensates and vapor *must* use the same heat capacity. If we want to use different heat capacities for them, the latent heat *must* vary with temperature accordingly.

5.5.4 Latent Heat of melting

Until now we have not differentiated between solid and liquid condensates. This is usually because i) the latent heat of melting is rather small compared to either the vaporization or sublimation latent

[11] This demonstration can trivially be extended to the case of varying heat capacities. All the integrals cancel each other just the same.

heats so that the impact in the atmosphere is limited and ii) it forces the modeler to follow an extra species. However, if one wants to model the thermal inertia created by ice melting at the surface after winter, for example, this effect can be important.

But as we have discussed in the previous sections, latent heats and heat capacities are intimately linked. So one cannot take one into account without consistently treating the other. In addition, latent heats are intimately linked as well. Since the vaporization latent heat is the enthalpy difference between vapor and liquid and the melting latent heat is the enthalpy difference between liquid and solid, the sublimation latent heat — between vapor and solid — must be equal to the sum of the other two. So if one wants to account for the melting of solid condensates, they need to use a different latent heat when condensing liquids and solids and keep track of the amount of both species. And as previously seen as well, if they want to make the latent heat vary with temperature, they must use consistent heat capacities as well...

5.5.5 Practical summary

For those who do not care about the demonstration, you can find here a summary of the assumptions and terms that must be included together:

- If the gravitational energy of precipitations is taken into account, the decompression of the gas column during precipitations must also be accounted for,
- If the heat capacity of the condensible substance is not taken into account, the latent heat of vaporization cannot vary with temperature,
- If one wants to use a different value of the heat capacity for the vapor and condensates, the latent heat fo vaporization *must* change with temperature in a consistent fashion,
- If a different latent heat is used for vaporization and sublimation, the latent heat of melting must be accounted for in precipitations or at the ground.

Chapter 6

Turbulent transport

Quand je rencontrerai Dieu, je lui poserai deux questions :
pourquoi la relativité ?
Et pourquoi la turbulence ?
Je crois vraiment qu'il aura une réponse à la première.

Werner Heisenberg

Contents

Atmospheric turbulent motion usually occurs much faster than heat losses so that the motion of an air parcel can often be considered adiabatic in this context. Hence, turbulent transport redistributes the specific entropy in the fluid (See Chapter 4). However, we often forget, or do not know, that redistributing the entropy of an atmospheric column does not conserve its enthalpy. Not properly taken into account in simulations, this can create a spurious source or sink of energy.

For example, let us consider a convectively unstable fluid column which is initially at rest. Then the buoyancy force will cause colder eddies (in term of potential temperature) to sink and hotter ones to rise, converting gravitational into kinetic energy. Because gravitational and internal energy are in equipartition in an atmosphere in quasi hydrostatic equilibrium (see § 5.2.3), the mixing has caused a decrease in the total enthalpy or static energy of the column. This can also be seen using our enthalpy conservation equation, Eq. (5.33). In the present case, all the terms on the right are nil. So there is conservation of the sum of the total kinetic energy and enthalpy. If the former increases, the latter must decrease.

To close the energy cycle, one needs to account for the viscous friction that turns turbulent kinetic energy back into heat. The same problem arises with turbulence created by strong wind-shears (or mesoscale meteorological events such as storms ; Zhang and Altshuler 1999 ; Businger and Businger 2001) that transfer energy from macro/meso- to microscopic turbulent kinetic energy. Viscosity is then needed at the microscopic level to dissipate the turbulent kinetic energy back into heat.

The contribution of the viscous diffusion to the global energy budget of the atmosphere is often neglected in numerical models, including the LMDZ GCM up until 2013, because this viscous heating has a limited impact on global Earth climate. For example, we may read in Businger (1982):

> *The viscous dissipation is always negligible as a heat source in the boundary layer, so this term is only significant where the heating occurs primarily through thermal conduction. [...] Otherwise we consider this term negligible.* (9)

This is mainly i) because present Earth atmosphere is rather transparent and that the energy absorbed at the surface is carried away mostly by thermal radiation and latent heat, and ii) because at lower wind speeds typical of conditions for which direct observations of the friction velocity are available, the dissipative heating is negligibly small (Zhang and Altshuler 1999). This helps to explain the lack of attention paid historically to this dissipative heating and its absence in many numerical models, whether global (Holloway and Manabe 1971 ; Haberle et al. 1997 ; Swinbank et al. 1998 ; Forget et al. 1999 ; Hourdin et al. 2006) or mesoscale (Savijärvi 1999 ; Spiga et al. 2010). However, as will be shown hereafter, if the atmospheric greenhouse effect is strong (as for Venus, early Mars or a runaway greenhouse Earth), or if turbulence is enhanced by wind shears, this heat source can significantly affect and warm the lower troposphere.

When I started working on the Generic GCM in 2013, I wanted to model runaway atmospheres

with strong greenhouse effects where we could not afford to have too many numerical energy sources/sinks. I quickly discovered, as will be quantified at the end of this chapter, that the scheme handling the planetary boundary layer and turbulent diffusion in general was causing such an energy imbalance. I thus decided to find a simple, yet physical, way to close the energy budget, but I never found time to publish the parametrization used. The primary role of this chapter is thus to document the equations that are in the so-called `turbdiff` routine for the model users, but also to explain their physical basis.

Thus, in this section, we will first review the energy conservation properties of the canonical set of turbulent diffusion equations in the an elastic approximation (§ 6.1). Then, in § 6.2, we will show that the complete potential temperature equation can be rewritten as a purely conservative equation on the temperature were the viscous heat source terms are simply incorporated to the enthalpy flux. This result has important practical implications, as it allows us to easily implement an energy conservative numerical scheme to solve turbulent transport equations. This is this formulation that I implemented in the LMDZ GCM to deal with an energy imbalance for Leconte et al. (2013) and that has been in use since. Finally, in § 6.3, we will quantify the magnitude of the heating due to viscous dissipation in several practical cases.

6.1 Energy conservation properties of turbulent diffusion equations

6.1.1 Turbulent transport of potential temperature

As seen in Chapter 1, for a dry perfect gas, the Navier-Stockes equation describing the transport of potential temperature (or entropy) writes (see Eq. (1.68))

$$c_p \, D_t\theta = c_p \, (\partial_t\theta + v_i\partial_i\theta) = \Pi^{-1}\dot{\tilde{Q}}, \tag{6.1}$$

where $\Pi \equiv (p/p_0)^{R/c_p} = T/\theta$ is the Exner function, p_0 is a reference pressure, and θ is the specific gas constant of the gas considered. The redistribution of the power deposited per unit mass in the fluid, $\dot{\tilde{Q}}$ is ensured by advection and turbulent mixing which are encompassed by the advection term of the Lagrangian derivative, $D_t = \partial_t + v_i\partial_i$, where an implicit sum over $i = \{x, y, z\}$ is assumed.

In climate modeling, however, we can only resolve the large scale component of the velocity field and turbulent mixing must be parametrized. To do this, an approach is to rely on Reynolds decomposition of the various fields into a mean component and a turbulent one which averages to zero:

$$\theta = \bar{\theta} + \theta' \quad \text{and} \quad v_i = \bar{v}_i + v_i', \tag{6.2}$$

where the over line stands for averaging operator, and $\overline{\theta'} = \overline{v_i'} = 0$. The interested reader is referred to Garratt (1992) and Blackadar (1997) for a comprehensive discussion. In our case where motions are mostly subsonic, pressure inhomogeneities can be neglected ($p' = 0$). An additional simplification comes from the fact that density fluctuations are small and can be disregarded except when they are coupled to gravity to affect buoyancy, the so-called Boussinesq approximation. However, in those textbooks, they are interested mostly with the near surface boundary layer on Earth and they therefore use an even more stringent incompressibility assumption where the vertical variation of ρ is ignored. Although this is justified in their case, it is not in ours where we will also want to use the Reynolds decomposition to treat unstable convective regions covering several scale heights (See appendix in Businger 1982). Therefore, the Reynolds averaged equations in the anelastic approximation are rederived in Appendix A.

For the potential temperature, the anelastic averaged equation reads

$$c_p\,\bar{D}_t\bar{\theta} + \; c_p\,\rho^{-1}\partial_z\left(\rho\,\overline{w'\theta'}\right) = \Pi^{-1}\dot{\bar{Q}}, \tag{6.3}$$

where $\bar{D}_t$ is now the *large-scale* lagrangian operator $\partial_t + \bar{v}_i\partial_i$. We will not put an overbar over the heat term as only the average value will appear. The first term on the left hand side now represents only the transport by the large scale motion, and the second term represents the transport of entropy by the small scale turbulent eddies.

6.1.2 Non conservation of total enthalpy

The energy conservation problem stated earlier comes from the fact that this equation does not conserve the total enthalpy of an atmospheric column if viscous heating is not accounted for along the other sources of heating generally considered in $\dot{\bar{Q}}$ (radiative heating, etc.).

While this has already been demonstrated globally in the general case, let us consider what is happening at the turbulent scale to understand which terms are involved. For this, we will limit ourselves to the case of a dry atmosphere for which the potential temperature takes a simple form. The variation of enthalpy per unit surface in an isolated column in quasi hydrostatic equilibrium is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}H \equiv \int \bar{D}_t h\,\mathrm{d}m = \int c_p\,\bar{D}_t\bar{T}\,\mathrm{d}m, \tag{6.4}$$

where h is the specific enthalpy, and $\mathrm{d}m \equiv \rho\,\mathrm{d}z$. Because of the hydrostatic equilibrium, an horizontal layer of constant mass is always bounded by the same two pressure levels. Thus, the *large scale*, Lagrangian vertical derivative which follows the vertical fluid motion, also follows pressure levels. This means that

$$\bar{D}_t\Pi = 0 \;\Rightarrow\; \bar{D}_t\bar{T} = \Pi\,\bar{D}_t(\Pi^{-1}\bar{T}) = \Pi\,\bar{D}_t\bar{\theta}. \tag{6.5}$$

Combining Eqs. (6.3), (6.4) and (6.5) yields

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}H &= \int \dot{\bar{Q}}\,\mathrm{d}m - \int c_p\,\Pi\,\partial_z\left(\rho\,\overline{w'\theta'}\right)\mathrm{d}z \\ &= \dot{Q} - \int c_p\,\partial_z\left(\rho\,\Pi\,\overline{w'\theta'}\right)\mathrm{d}z + \int \rho\,c_p\,\overline{w'\,\theta'}\partial_z\Pi\,\mathrm{d}z.\end{aligned} \tag{6.6}$$

The second term is readily integrated and is equal to the sensible heat flux provided by the surface to the atmosphere, $F^0_{\mathrm{sen}} \equiv \rho\,c_p\,\Pi\,\overline{w'\theta'}|_{z=0}$. Thanks to the hydrostatic equilibrium yielding

$$-\partial_z\Pi = \rho\,g\,\partial_p\Pi = \frac{g}{c_p}\frac{\rho R}{p}\Pi = \frac{g}{c_p}\frac{\Pi}{T} = \frac{g}{c_p\,\theta}, \tag{6.7}$$

and to the anelastic approximation of the equation of state, $\theta'/\theta = -\rho'/\rho$, the last term can be rewritten to yield

$$\frac{\mathrm{d}}{\mathrm{d}t}H = \dot{Q} + F^0_{\mathrm{sen}} + \int \frac{g}{\rho}\,\overline{w'\rho'}\,\mathrm{d}m. \tag{6.8}$$

This shows that, in addition to the heating incorporated into $\dot{\bar{Q}}$ and to the heating by the surface through the sensible heat flux, enthalpy has been lost (created) due to the work exerted by the buoyancy forces on the turbulent density fluctuations.

6.1.3 Taking turbulent kinetic energy into account

This apparently creates a sink (source) of enthalpy in convectively (un)stable regions of the atmosphere. But, as mentioned earlier, this paradox is solved when turbulent kinetic energy is taken into account into the energy budget (Ball 1956).

Indeed, following Garratt (1992), we can derive the anelastic equation for the evolution of turbulent kinetic energy, $k_* \equiv \overline{v_i' v_i'}/2$, in the horizontally homogeneous case. This reads

$$\begin{aligned} \bar{D}_t k_* = &-\frac{g}{\rho}\,\overline{w'\rho'} - \left(\overline{u'w'}\,\partial_z \bar{u} - \overline{v'w'}\,\partial_z \bar{v}\right) \\ &- \rho^{-1}\,\partial_z\left(\rho\,\overline{w' k_*'}\right) - \dot{\bar{Q}}_{\text{vis}}, \end{aligned} \tag{6.9}$$

where $k_*' = v_i' v_i'/2$, and the velocity field has been rewritten $\{v_i\} \equiv \{u, v, w\}$, and $\dot{\bar{Q}}_{\text{vis}}$ is the viscous dissipation rate per unit mass.

The first term on the right hand side is obviously the counterpart to the additional enthalpy sink from Eq. (6.8). The energy that has been taken from the potential energy part of the enthalpy has been transformed into kinetic energy. To solve our energy leak, we thus simply need to account for thermal heating induced by small scale viscous dissipation by incorporating $\dot{\bar{Q}}_{\text{vis}}$ in $\dot{\bar{Q}}$ in Eqs. (6.3) and (6.8).

The third term does not involve any sink or source into a column because it is the divergence of a flux. Specifically, it is the vertical flux of turbulent energy that is transported by the turbulent velocity itself. It can thus only transport energy inside the column because no turbulent kinetic energy can be extracted from the ground.

6.1.4 Mean flow kinetic energy

However, the second term on the right hand side of Eq. (6.9) does not appear to conserve energy. In fact, it describes the conversion of a part of the kinetic energy of the mean flow toward the smaller turbulent scales by the wind shear. When including this term, we also need to incorporate the mean flow kinetic energy, $k \equiv \bar{v}_i \bar{v}_i/2$, to the energy budget. It can be shown that the turbulent part of the equation for the mean flow kinetic energy writes (still in the horizontally homogeneous case ; Garratt 1992)

$$\begin{aligned} \bar{D}_t k\Big|_{\text{turb}} &= -\rho^{-1}\bar{v}_i \partial_z \rho\,\overline{v_i' w'} \\ &= -\rho^{-1}\partial_z \rho\,\bar{v}_i\,\overline{v_i' w'} + \overline{v_i' w'}\,\partial_z\,\bar{v}_i. \end{aligned} \tag{6.10}$$

Recognizing that the second term on the right hand side of Eq. (6.10) is the same as in Eq. (6.9), and adding all the contributions together finally yields

$$\bar{D}_t(h + k + k_*) = \dot{\bar{Q}} - \rho^{-1}\partial_z\left(F_{\text{sen}} + F_{k^*} + F_k\right), \tag{6.11}$$

where $F_{\text{sen}} \equiv \rho\, c_p\, \Pi\, \overline{w'\theta'}$ is the sensible heat flux at all levels, $F_{k^*} \equiv \rho\,\overline{w' k_*'}$ the turbulent flux of turbulent kinetic energy, and $F_k \equiv \rho\left(\bar{u}\,\overline{u'w'} + \bar{v}\,\overline{v'w'}\right)$ a flux of kinetic energy that arises from the flux of momentum due to the vertical wind shear.

Thus, including all the necessary contributions to the energy budget, we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\int (h + k + k_*)\,\mathrm{d}m = \dot{Q} + F_{\text{sen}}^0 + F_k^0, \tag{6.12}$$

and the total energy is conserved, as expected. Note that we recover the result in Eq. (5.35) for a dry case where we now see explicitly that $\dot{W}_{\text{ext}}$ is equal to the flux of kinetic energy due to friction at the surface, F_k^0.

6.2 A simple energy conservative model for turbulent transport

Theoretically, this energy conservation problem is just solved by adding Eq. (6.9) to the set of equations usually solved in a numerical global climate model. However, in practice, the numerical price of adding an equation for turbulent kinetic energy can be high, in particular if the latter must be advected in the dynamical part of the GCM. In addition, to include Eq. (6.9), one must add several parametrization, such as the one for the viscous dissipation term.

Considering the lack of data we are facing when modeling exotic planetary climates, this approach seems too sophisticated and not robust enough for our purpose. We thus developed another approach based on simple physical approximations. As describe hereafter, this allows us to directly describe both turbulent kinetic energy and entropy transport by a single equation on enthalpy.

6.2.1 An enthalpy transport equation

Our main assumption is that the total turbulent kinetic energy of the column is always in a quasi steady state, meaning that the production of turbulence by buoyancy and shear are always almost compensated by viscous dissipation. The local variation of the turbulent kinetic energy can thus be neglected on average, which yields $\bar{D}_t k_* = 0$. This approximation is particularly justified in the troposphere of thick atmospheres, where the diurnal cycle is very weak.

We further assume that there is no large-scale or turbulent transport of turbulent kinetic energy. Thanks to this approximation, energy conservation is readily enforced by re-injecting all the kinetic and gravitational energy taken from the mean flow directly into thermal energy. In this case, the heating rate due to viscous dissipation is given by

$$\dot{\tilde{Q}}_{\text{vis}} = -\frac{g}{\rho}\,\overline{w'\rho'} - \left(\overline{u'w'}\,\partial_z \bar{u} - \overline{v'w'}\,\partial_z \bar{v}\right), \tag{6.13}$$

which can directly be incorporated in Eq. (6.3) for potential temperature.

In addition to the fact that accounting for viscous friction allows us to conserve energy in the system, our model has another profound physical significance. Indeed, either by substituting $\dot{\tilde{Q}}_{\text{vis}}$ by its value in Eq. (6.3) and manipulating this equation, or directly setting $\bar{D}_t k_* = 0$ in Eq. (6.11), one can see that the energy transport equation can be expressed in term of an enthalpy transport equation based on the thermodynamic temperature[1] instead of the potential temperature:

$$\bar{D}_t(h + k) = \dot{\tilde{Q}} - \rho^{-1}\partial_z \left(F_{\text{sen}} + F_k\right), \tag{6.14}$$

or

$$c_p \bar{D}_t \bar{T} = \dot{\tilde{Q}} - \rho^{-1}\partial_z \left(F_{\text{sen}} + F_k\right) - \bar{D}_t k. \tag{6.15}$$

As that last equation is written in a conservative form, it is directly usable in a GCM numerical code as we will now see.

[1] Note that if $c_p \Pi\,\overline{w'\theta'} = c_p \overline{w'T'} = \overline{w'h'}$, the two last expressions (and consequently Eq. (6.14)) are not easy to use in practice. This is due to the fact that both T and h are not constant during an adiabatic motion, meaning that $\overline{w'T'}$ and $\overline{w'h'}$ cannot be modeled by a term of the form $-K_X \partial_z X$ where K_X is an effective eddy diffusivity for the appropriate variable (Garratt 1992).

6.2.2 Implementation in the code

The initial turbulent diffusion scheme in the Generic GCM, inherited from the Earth LMDZ GCM, was based on the diffusion of potential temperature as written in Eq. (6.3). The turbulent fluxes were parametrized using

$$\overline{w'\theta'} = -K_\theta \partial_z \theta, \tag{6.16}$$

where the so-called eddy diffusion coefficient, K_θ, is computed following Mellor and Yamada (1982). The turbulent part of the equation can be rewritten

$$D_t\theta|_{\text{turb}} = g^2 \partial_p \left(\rho^2 K_\theta \, \partial_p \theta \right). \tag{6.17}$$

Discretizing using a finite-volume type of approach with an implicit time stepping, the new potential temperature at time $t+\Delta t$ in layer i, $\theta_i^{t+\Delta t}$, was computed following

$$\frac{\Delta m_i}{\Delta t}\left(\theta_i^{t+\Delta t} - \theta_i^t\right) = \left[\frac{g\rho^2 K_\theta}{\Delta p}\right]_{i+1/2}\left(\theta_{i+1}^{t+\Delta t} - \theta_i^{t+\Delta t}\right) - \left[\frac{g\rho^2 K_\theta}{\Delta p}\right]_{i-1/2}\left(\theta_i^{t+\Delta t} - \theta_{i-1}^{t+\Delta t}\right), \tag{6.18}$$

where the index $i+1/2$ indicates a value computed at the interface between the i-th and the $(i+1)$-th layers, and Δp is the pressure difference between the center of these two layers, $\Delta p|_{i+1/2} = p_{i+1} - p_i$. This convention ensures that the convention on the numbering of the layers (top to bottom or vice versa) does not change the sign of the terms. This can be rearranged into

$$\Xi_{i-1/2}\theta_{i-1}^{t+\Delta t} + \left[\Delta m_i - \Xi_{i+1/2} - \Xi_{i-1/2}\right]\theta_i^{t+\Delta t} + \Xi_{i+1/2}\theta_{i+1}^{t+\Delta t} = \Delta m_i \theta_i^t, \tag{6.19}$$

where

$$\Xi_{i+1/2} \equiv -\left[g\rho^2 K_\theta \frac{\Delta t}{\Delta p}\right]_{i+1/2}. \tag{6.20}$$

This is a well known set of equations that can be solved using a tridiagonal solver[2].

To make this set of equations conservative, we can start from Eq. (6.15) and neglect the variations of kinetic energy. Focusing on the diffusive terms, this leaves us with

$$D_t T|_{\text{turb}} = D_t \Pi\theta|_{\text{turb}} = g^2 \partial_p \left(\rho^2 \Pi K_\theta \, \partial_p \theta \right). \tag{6.21}$$

Thanks to the similarity with the equation above, we can easily convince ourselves that the corresponding discretized equation is

$$\boxed{\Pi_{i-1/2}\Xi_{i-1/2}\theta_{i-1}^{t+\Delta t} + \left[\Pi_i \Delta m_i - \Pi_{i+1/2}\Xi_{i+1/2} - \Pi_{i-1/2}\Xi_{i-1/2}\right]\theta_i^{t+\Delta t} + \Pi_{i+1/2}\Xi_{i+1/2}\theta_{i+1}^{t+\Delta t} = \Pi_i \Delta m_i \theta_i^t.} \tag{6.22}$$

This is this formulation that I implemented in the LMDZ GCM to deal with an energy imbalance for Leconte et al. (2013), and that has been in use since.

[2]The equation for the transport of any conservative tracer, q, follows exactly the same equation by simply replacing θ by q.

6.2.3 The convective adjustment limit

The temperature increase implied by the conservative model can be easily seen by considering the limiting case where turbulent transport dominates in a given region, for example in a strongly convective layer. In this case, because mixing is caused by a gradient of potential temperature, mixing stops when the potential temperature reaches a constant value, say $\bar{\theta}_1$ in the layer.

When the contribution of turbulent kinetic energy is disregarded (Eq. (6.3)), this is the entropy which is advected and conserved by the turbulence. The final potential temperature is thus given by

$$\int \bar{\theta}_0(z)\mathrm{d}m = \int \bar{\theta}_1 \mathrm{d}m \;\Rightarrow\; \bar{\theta}_1 = \frac{\int \bar{\theta}_0(z)\mathrm{d}m}{\int \mathrm{d}m}, \tag{6.23}$$

where $\bar{\theta}_0(z)$ is the initial potential temperature profile and the integration is performed over the convective layer.

However, when the dissipation of turbulent energy is taken into account (Eqs. (6.15) and (6.14)), this is the enthalpy, or the actual temperature, $\bar{T} = \Pi\,\bar{\theta}$, that is homogenized. the final potential temperature thus reads

$$\int \Pi\,\bar{\theta}_0(z)\mathrm{d}m = \int \Pi\,\bar{\theta}_1 \mathrm{d}m, \tag{6.24}$$

or

$$\theta_1^\star = \frac{\int \Pi\,\bar{\theta}_0(z)\mathrm{d}m}{\int \Pi\,\mathrm{d}m} > \theta_1. \tag{6.25}$$

This can also be shown by saying that the total enthalpy of the layer must be conserved by the mixing. Because the Exner function gives more weight to the lower altitude regions of the initially convectively unstable layer, where the potential temperature is higher, the final potential temperature computed with Eq. (6.25) is necessarily higher than the one given by Eq. (6.23).

6.3 Quantifying energy losses

While it has been known that viscous dissipation of turbulent kinetic energy must be taken into account to *strictly* conserve the enthalpy of an air column, this fact is often disregarded in global climate simulations because it represents a negligible fraction of the energy budget in standard earth global climate simulations. However, in this section, we will show that this source cannot always be neglected.

To have an idea of the magnitude of the effect, let us use Eq. (6.7) to compute the third term on the right hand side of Eq. (6.6). This yields

$$\begin{aligned} |\dot{Q}_{\text{vis}}| \equiv \int \rho\, c_p\, \overline{w'\,\theta'}\partial_z \Pi\,\mathrm{d}z &= \int \rho\, c_p\, \Pi\, \overline{w'\,\theta'}\frac{g}{c_p\, T}\,\mathrm{d}z \\ &= \frac{R}{c_p}\int F_{\text{turb}}\,\frac{\mathrm{d}z}{H_p} \\ &= \frac{R}{c_p}\int F_{\text{turb}}\,\mathrm{d}\ln p, \end{aligned} \tag{6.26}$$

where $F_{\text{turb}} \equiv \rho\, c_p\, \Pi\, \overline{w'\,\theta'}$ is the turbulent flux and H_p is the pressure scale height. We see that the turbulent kinetic energy contribution is proportional to the total flux transported by the turbulence

times the effective height (in units of the pressure scale height) over which this flux is transported (times a R/c_p factor that is related to the partition of energy between potential and internal energy).

This tells us that, on Earth where thermals carry around 20 W/m^2 over the height of the convective boundary layer ($\sim H_p$), the integrated effect, $\dot{Q}_{\text{vis}}$, is less than 5 W/m^2 or 1.5% of the incident stellar flux. Note that this estimation is an upper limit because the turbulent flux decreases with altitude. The effect is thus quite small because most of the outgoing flux is carried out by radiation as the atmosphere exhibits many transparent windows.

This is not the case on planets where a thick atmosphere causes a strong greenhouse effect. Indeed, in the lower part of such atmospheres, most of the flux must be carried out by convective motions, and the troposphere can extend quite deep below the infrared photosphere. The magnitude of the dissipation thus increases. In addition, because of the strong greenhouse effect, any small source of energy has an enhanced impact on the temperature.

To quantify this warming, we have computed thermal profiles for thick CO_2 atmospheres with a time marching radiative/convective equilibrium model: `Exo_k` (Leconte 2021 ; Selsis et al. 2023). In this simple experiment, the equations of the thermal evolution of the atmosphere are integrated in time until thermal equilibrium is reached. This is performed for various surface pressures and incoming fluxes with a spectral distribution of the incoming stellar light modeled as a blackbody with the Sun's effective temperature and a planetary surface gravity and albedo of 9.81 m/s^2 and 0 respectively. To have an estimate of the maximum effect of the turbulent dissipation, we compare a baseline case where the convective adjustment in the convective boundary layer is performed using Eq. (6.25) with a case where diffusive heating is neglected — which is equivalent to performing the dry convective adjustment with Eq. (6.23). We disregard the effect of turbulent diffusion outside of the convective boundary layer.

Examples of equilibrium thermal profiles are shown in Fig. 6.1. In this example, one can see that the troposphere is warmed by more than 10 K when turbulent energy dissipation is taken into account. The troposphere also extends a little higher because the convective flux does not suffer any losses other than the radiative cooling, and is thus stronger.

Fig. 6.2 shows the dissipative heating, and the absolute surface temperature increase as a function of the mean incoming stellar radiation and for various atmospheric total pressures. As expected, the dissipative heating increases with the insolation. Indeed, to zeroth order, the ratio of the dissipation to the convective flux remains relatively constant and increasing the isolation increases the energy to be transported by convection. This ratio however increases with the surface pressure because the convection needs to carry energy higher above the surface to reach the photosphere, as predicted by Eq. (6.26). This explains why, at low surface pressures, increasing the pressure also increases the dissipation because the atmosphere becomes more opaque and needs a more vigorous convection to equilibrate. Above 10 bar, this tendency reverses: the atmosphere becomes so opaque that less starlight is able to reach the surface, thus decreasing the energy to be carried away by convection. Yet, the increase in surface temperature due to the dissipation keeps increasing with pressure due to the stronger greenhouse effect.

6.4 Conclusion

In thick atmospheres where the greenhouse effect is strong, even small sink/source of energy can significantly affect the thermal profile. Here we have shown that dissipation of turbulent kinetic energy, which is negligible on Earth, can warm the troposphere of such thick atmosphere by tens of degrees depending on several parameters, especially atmosphere total pressure/optical depth. In

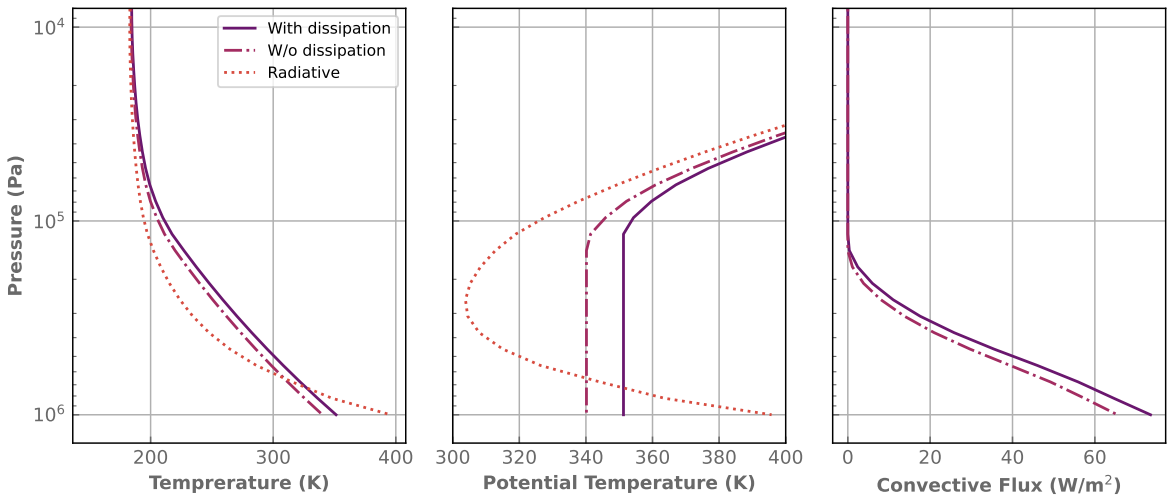

Figure 6.1: Temperature profiles for a 10 bar CO_2 atmosphere receiving 300 W/m^2 at the top of atmosphere (Left panel). The middle panel shows the potential temperature to highlight the unstable convective boundary layer. The right panel shows the vertical profile of the convective flux in the conservative model. The dash-dotted curves are obtained without taking into account the dissipation of turbulent kinetic energy whereas the solid curves have been obtained with the conservative scheme. The dotted lines are the radiative equilibrium profiles (no turbulent transport). There is a 12 K warming of the troposphere due to the dissipation of turbulent kinetic energy.

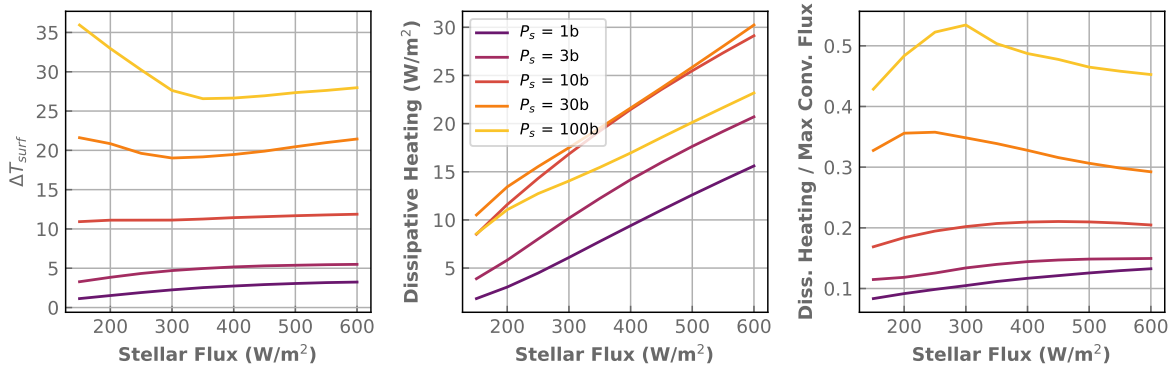

Figure 6.2: Left: Surface temperature difference between the model with and without dissipation of turbulent energy as a function of the average stellar incoming radiation for various pressures. Middle: Total energy dissipated by the viscous damping of turbulent kinetic energy. Right: Total viscous dissipation normalized by the maximum convective flux in the model.

general, this heating increases with the amount of flux to be carried away by convection and with greenhouse warming. As a result, such an effect can have a significant impact on the determination of the limits of the habitable zone in particular and on the global climate of planets in general.

Moreover, we have shown that energy conservation can be enforced by simply rewriting the entropy (potential temperature) transport equation in terms of an enthalpy (actual temperature) transport whose form is very similar. It is thus easy to implement energy conservation in a numerical turbulent-transport scheme.

In conclusion, with the wide diversity of radiative forcing encountered by recently discovered extrasolar planets, and with the even wider expected diversity of their atmospheric composition and mass, extreme care must be taken when applying assumptions used to model Earth atmospheric dynamics and climate to these other worlds.

Perspectives

The ability to quote is a serviceable substitute for wit.
William Somerset Maugham

Quelles perspectives futures ces pages ouvrent-elles ? Et bien tous les modèles atmosphériques auxquels j'ai eu affaire — et je ne pense pas me tromper beaucoup si j'étend cela à la plupart des modèles existants — utilisent une thermodynamique relativement simpliste, et pas toujours cohérente, des changements de phase. La raison en est souvent que la robustesse des prédictions desdits modèles est majoritairement déterminée par des aspects radiatifs ou microphysiques pour lesquels les incertitudes sont plus grandes et les contraintes observationnelles ou expérimentales bien moindres.

Néanmoins, mes travaux récents sur les planètes de type Neptune — qu'elles soit au sein ou en dehors du système solaire — ont montré que l'espèce condensable peut passer de trace à majoritaire entre différentes couches très proches de leur atmosphère et donc entrainer des variations massives des propriétés thermodynamiques de celle ci, variations qui ne sont pas prisent en compte à l'heure actuelle. Nous sommes donc en train d'effectuer une refonte majeure du coeur physique et dynamique du modèle de climat pour intégrer ces effets. Mais comme tout édifice ne peut être plus solide que ses fondations, il me paraissait impossible de faire une telle refonte sans reposer clairement toutes les bases théoriques sous tendant une telle entreprise.

C'est maintenant chose faite. Les équations et formalismes développés ici seront un atout précieux pour pouvoir tester et valider nos développements, notamment à travers une bonne vérification de la conservation de l'énergie de l'atmosphère — où plutôt, devrais-je dire, de la somme de son enthalpie et de son énergie cinétique. En cela, j'ai l'espoir que les conclusions du Chapter 5 nous permettrons, à nous et aux futurs étudiants, d'éviter de tomber dans certaines ornières.

Appendix A

Reynolds Averaged Navier-Stockes equation

Contents

Reynolds averaging has been a great tool to study the turbulent atmospheric boundary layer. However, most of the time, textbooks use an extreme version of the incompressibility approximation which is valid close to the surface but not when looking at the whole atmosphere because of the vertical gradient of density. This is why I rederive here the general Reynolds averaged Navier-Stockes equations using the Boussinesq approximation but retaining the vertical density gradient.

Most of the time in climate modeling, we can only resolve the large-scale components of the various fields we model and small-scale, turbulent motion must be parametrized. To do this, an approach is to rely on Reynolds decomposition of the various fields into a mean component and a turbulent one which averages to zero (see Garratt (1992) for a comprehensive discussion). In practice this reads

$$x = \bar{x} + x', \tag{A.1}$$

where the over line stands for an averaging operator, and $\overline{\bar{x}} = \bar{x}$ and $\overline{x'} = 0$. The important feature of the averaging operator is that we consider it linear so that it can get in and out of derivatives

$$\overline{\partial_i x} = \partial_i \bar{x}. \tag{A.2}$$

The averaging of a product of two fields proceeds as follows

$$\overline{xy} = \overline{(\bar{x} + x')(\bar{y} + y')} = \overline{\bar{x}\bar{y}} + \overline{\bar{x}y'} + \overline{x'\bar{y}} + \overline{x'y'} = \bar{x}\bar{y} + \overline{x'y'}. \tag{A.3}$$

A.1 Continuity equation and anelastic approximation

The conservation of mass can be written

$$D_t \rho + \rho \partial_i v_i = 0. \tag{A.4}$$

Using Reynolds decomposition and averaging we get

$$\begin{aligned} 0 &= \overline{\partial_t (\bar{\rho} + \rho') + (\bar{v}_i + v_i')\partial_i (\bar{\rho} + \rho') + (\bar{\rho} + \rho')\ \partial_i(\bar{v}_i + v_i')} \\ &= \partial_t\overline{(\bar{\rho} + \rho')} + \overline{(\bar{v}_i + v_i')\partial_i (\bar{\rho} + \rho')} + \overline{(\bar{\rho} + \rho')\ \partial_i(\bar{v}_i + v_i')} \\ &= \partial_t \bar{\rho} + \bar{v}_i\partial_i\bar{\rho} + \overline{v_i'\partial_i\rho'} + \bar{\rho}\,\partial_i\bar{v}_i + \overline{\rho'\,\partial_i v_i'}. \end{aligned} \tag{A.5}$$

This is where we usually introduce an approximation to make the computation tractable. In many textbooks such as Garratt (1992), they assume that, because velocities are mostly subsonic, one can consider the motion incompressible ($D_t\rho = 0$). This entails that , $\partial_i\bar{v}_i = \partial_i v_i' = 0$, which is valid in the surface layer.

However, if one wants to deal with a deep convective region with this formalism, as we will, the vertical density stratification and buoyancy effects are important. Therefore, $D_t\rho \neq 0$ for ascendent and subsident motions. We will thus use the anelastic approximation which states that pressure inhomogeneities can be neglected ($p' = 0$), but that density fluctuations are kept only when they are coupled to gravity (over lines will thus be dropped for pressure and density for simplicity). Our approximation departs from the traditional Boussinesq approximation by the fact that the mean density is not constant along the vertical axis and the full continuity equation must be used. It reads

$$\boxed{\bar{D}_t\rho + \rho\,\partial_i\bar{v}_i = 0 \quad \Leftrightarrow \quad \partial_t\rho + \partial_i\rho\,\bar{v}_i = 0,} \tag{A.6}$$

where $\bar{D}_t$ is now the *large-scale* lagrangian operator $\partial_t + \bar{v}_i\partial_i$. By subtracting the averaged equation to the full equation (with $\rho' \approx 0$), we get the equation for the fluctuations

$$\begin{aligned} 0 &= \partial_t\rho + (\bar{v}_i + v_i')\partial_i\rho + \rho\,\partial_i(\bar{v}_i + v_i') - \partial_t\rho - \bar{v}_i\partial_i\rho - \rho\,\partial_i\bar{v}_i \\ &= v_i'\partial_i\rho + \rho\,\partial_i + v_i' \\ &= \partial_i\left(\rho\,v_i'\right). \end{aligned} \tag{A.7}$$

A.2 Momentum equation

The general Navier Stockes equation writes

$$\rho D_t v_i = \partial_t\rho\,v_i + \partial_j\rho\,v_j\,v_i = -\partial_i p + \partial_j\sigma_{i,j} + F_i, \tag{A.8}$$

where F_i are the forces per unit volume acting on the fluid,

$$\sigma_{i,j} = 2\eta\left(S_{i,j} - \frac{1}{3}\,S_{k,k}\delta_{i,j}\right) \quad \text{and} \quad S_{i,j} = \frac{1}{2}\left(\partial_i v_i + \partial_i v_i\right). \tag{A.9}$$

Note that if η is constant, then the viscous terms takes the usual form of a laplacian, $\partial_j\sigma_{i,j} = \eta\,\partial_j\partial_j v_i$. The reynolds averaged equation for the momentum is thus

$$\boxed{\partial_t\rho\,\bar{v}_i + \partial_j\rho\,\bar{v}_i\,\bar{v}_j + \partial_j\rho\,\overline{v_i'\,v_j'} = -\partial_i p + \partial_j\sigma_{i,j} + F_i.} \tag{A.10}$$

Noting that

$$\begin{aligned} \frac{1}{2}\,\partial_t\rho\,v_i\,v_i &= v_i\,\partial_t\rho\,v_i + \frac{1}{2}\,\rho^2\,v_i\,v_i\,\partial_t\rho^{-1} \\ &= v_i\,\partial_t\rho\,v_i + \frac{1}{2}\,v_i\,v_i\,\partial_i\rho\,v_i, \end{aligned} \tag{A.11}$$

we can show that the mean kinetic energy, $k \equiv \frac{1}{2}\bar{v}_i\,\bar{v}_i$, verifies[1]

$$\boxed{\partial_t\rho\,k + \partial_i\rho\,\bar{v}_i\,\left(k + p/\rho\right) + \partial_i\rho\,\bar{v}_i\,\overline{v_i'\,v_j'} - \rho\,\overline{v_i'\,v_j'}\,\partial_j\bar{v}_i = -\frac{p}{\rho}\,\bar{D}_t\rho + \bar{v}_i\,\partial_j\sigma_{i,j} + \bar{v}_i\,F_i.} \tag{A.12}$$

For the turbulent velocity, the equation reads

$$\partial_t\rho\,v_i' + \partial_j\left(\rho\,v_i'\,\bar{v}_j + \rho\,\bar{v}_i\,v_j' + \rho\,v_i'\,v_j' - \rho\,\overline{v_i'\,v_j'}\right) = F_i'. \tag{A.13}$$

[1] Note that it is also possible to first compute the equation for the total kinetic energy, $(\bar{v}_i + v_i')^2/2$, and to average it. However, doing this, it is impossible to separate the contribution from the small and large scales.

Before computing the turbulent kinetic energy, $k_* = \frac{1}{2}\, v_i'\, v_i'$, we first need to compute the equation for the Reynolds stress, $\overline{v_i'\, v_j'}$. Multiplying the equation on v_i' by v_j' and summing this to the corresponding equation for v_j' multiplied by v_i', we get[2]

$$\partial_t \rho\, \overline{v_i'\, v_j'} + \partial_k \rho\, \bar{v}_k\, \overline{v_i'\, v_j'} + \partial_k \rho\, \overline{v_i'\, v_j'\, v_k'} + \rho\, \overline{v_i'\, v_k'}\, \partial_k \bar{v}_j + \rho\, \overline{v_j'\, v_k'}\, \partial_k \bar{v}_i = \\ - \left(\overline{v_j'\, \partial_i p'} + \overline{v_i'\, \partial_j p'}\right) + \left(\overline{v_j'\, \partial_k \sigma_{i,k}'} + \overline{v_i'\, \partial_k \sigma_{j,k}'}\right) + \left(\overline{v_j'\, F_i'} + \overline{v_i'\, F_j'}\right). \quad \text{(A.14)}$$

Taking half the trace of the Reynolds stress tensor, we get an equation for the turbulent kinetic energy:

$$\boxed{\partial_t \rho\, k_* + \partial_i \rho\, v_i'\, k_* + \frac{1}{2}\partial_i \rho\, \overline{v_j'\, v_j'\, v_i'} + \rho\, \overline{v_j'\, v_i'}\, \partial_i \bar{v}_j = -\overline{v_i' \partial_i p'} + \overline{v_i'\, \partial_j \sigma_{i,j}'} + \overline{v_i'\, F_i'}.} \quad \text{(A.15)}$$

A.3 Potential energy

While the aforementioned equations are general, we can consider the case of a conservative force. In this case, the force per unit volume derives from a potential as follows

$$F_i = -\rho \partial_i \phi. \quad \text{(A.16)}$$

Hence, thanks to the continuity equation

$$v_i\, F_i = \phi \partial_i \rho\, v_i - \partial_i \rho\, v_i\, \phi = -\phi\, \partial_t \rho - \partial_i \rho\, v_i\, \phi. \quad \text{(A.17)}$$

Then, if ϕ does not explicitly vary with time, we get

$$v_i\, F_i = -\partial_t \rho\, \phi - \partial_i \rho\, v_i\, \phi. \quad \text{(A.18)}$$

Here, we recognize the conservation and transport of the potential energy. However, the conservation gets tricky when fluctuations are taken into account. Indeed, the work exerted on the turbulent part of the flow reads

$$\overline{v_i'\, F_i'} = -\overline{v_i'\, \rho'} \partial_i \phi = -\partial_i \overline{v_i'\, \rho'}\, \phi + \phi\, \partial_i \overline{v_i'\, \rho'}, \quad \text{(A.19)}$$

where the last term is not conservative. This paradox can be understood by looking more carefully at the continuity equation. Indeed, in the Boussinesq approximation, we have taken into account the density fluctuations only when they were interacting with gravity (a special case of F_i), and thus disregarded them in deriving Eq. (A.17). If we now try to include it, we find that the averaged continuity equation rewrites

$$\partial_t \rho + \partial_i \rho\, \bar{v}_i = -\partial_i \overline{\rho'\, v_i'}. \quad \text{(A.20)}$$

This yields

$$\bar{v}_i\, F_i = -\partial_t \rho\, \phi - \partial_i \rho\, \bar{v}_i\, \phi - \phi\, \partial_i \overline{\rho'\, v_i'}. \quad \text{(A.21)}$$

and

$$\bar{v}_i\, F_i + \overline{v_i'\, F_i'} = -\partial_t \rho\, \phi - \partial_i \left(\rho\, \bar{v}_i\, \phi + \overline{v_i'\, \rho'}\, \phi\right). \quad \text{(A.22)}$$

[2] While the terms in p' are retained here for completeness, they are small compared to the others in the Boussinesq approximation and should be set to zero.

This shows that only the total kinetic energy is conserved when gravity is present. Indeed, the $\phi\,\partial_i\overline{\rho'\,v_i'}$ is a term that transfers gravitational work from the small to the large scale:

$$\partial_t\rho\,(k+\phi)+\partial_i\rho\,\bar{v}_i\,\left(k+\phi+{}^{p}\!/_{\rho}\right) + \partial_j\rho\,\bar{v}_i\,\overline{v_i'\,v_j'}-\rho\,\overline{v_i'\,v_j'}\,\partial_j\bar{v}_i+\phi\,\partial_i\overline{\rho'\,v_i'}=-\frac{p}{\rho}\,\bar{D}_t\rho+\bar{v}_i\,\partial_j\sigma_{i,j}. \tag{A.23}$$

A.4 Thermodynamic equation

Thanks to the second law of thermodynamics, we know that the entropy per unit mass of a medium, s, follows

$$\rho\,T\,D_t s=\rho\,\dot{\bar{Q}}+\sigma_{i,j}\,\partial_j v_i, \tag{A.24}$$

where $\dot{\bar{Q}}$ is an arbitrary heating source (in watt per unit mass), and $\sigma_{i,j}\,\partial_j\bar{v}_i$ is the term of viscous heating. Noting that

$$T\,D_t s=D_t u+p\,D_t\left({}^{1}\!/_{\rho}\right)=D_t u-\frac{p}{\rho^2}\,D_t\rho, \tag{A.25}$$

the energy equation can also be written

$$\partial_t\rho u+\partial_i\rho\,\bar{v}_i\,u=\rho\,\dot{\bar{Q}}+\sigma_{i,j}\,\partial_j\bar{v}_i+\frac{p}{\rho}\,D_t\rho. \tag{A.26}$$

When taking the Reynolds average of this equation, the turbulent terms arise

$$\partial_t\rho u+\partial_i\rho\,\bar{v}_i\,u+\partial_i\rho\,\overline{v_i'\,u'}=\rho\,\dot{\bar{Q}}+\sigma_{i,j}\,\partial_j\bar{v}_i+\overline{\sigma_{i,j}'\,\partial_j v_i'}+\frac{p}{\rho}\,\bar{D}_t\rho-\overline{p'\,\partial_i v_i'}. \tag{A.27}$$

A.5 Total energy

If we now try to write a conservative equation for the total energy (in the case where F_i is conservative)

$$e=u+k+k_*+\phi, \tag{A.28}$$

we have

$$\partial_t\rho\,e+\partial_i\rho\,\bar{v}_i\,\left(e+{}^{p}\!/_{\rho}\right)+\partial_j\rho\,\left(\frac{1}{2}\,\overline{v_i'\,v_i'\,v_j'}+\bar{v}_i\,\overline{v_i'\,v_j'}+\overline{v_j'\,u'}\right)= \rho\,\dot{\bar{Q}}+\partial_j\sigma_{i,j}\,\bar{v}_i+\partial_j\overline{\sigma_{i,j}'\,v_i'}+\partial_i\overline{p'\,v_i'}+\partial_i\overline{\rho'\,v_i'}\,\phi. \tag{A.29}$$

Note that except for $\rho\,\dot{\bar{Q}}$, all the right hand side terms are divergences of fluxes. Thus, they generally only transfer energy from one part of the system to another. They are able to inject or extract energy from the system as a whole only through the boundaries (e.g. the surface for an atmosphere).

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