How the planetary atmosphere maintains disorder under the net loss of entropy: A multi-level primer that seeks to minimize complexity while elaborating entropy

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1 Introduction

The complexity of the Earth’s atmosphere presents a formidable challenge to those who study its characteristics. Attempts to generalize about gross features are often met with the realization that there are as many anomalous cases as not, such that generalizations are rendered almost useless. Differentiating aspects include scale, geographic location, height, season, moisture content, and many more. Those inclined to study this chaotic system sometimes yearn to envelope this complexity into a single quantity, the behaviors of which they hope might inform predictions about the future state of the atmosphere, and from which other relevant quantities may be derived. One possible candidate to serve in this capacity is thermodynamic entropy.

A critical impediment to formulating analyses of the atmosphere based on its entropy content is the lack of an accurate measurement of the entropy budget during processes that govern its evolution through time. This is largely a challenge due to limitations in instrumentation and observational opportunity such that the lack of data in many situations leads to an accounting of the entropy based on analyses derived from scarce observations that are then constrained by assumptions founded in theory. Computer models can often extend such analyses by incorporating the limited empirical data into an environment that is governed by extant theoretical knowledge of that which motivates behaviors of the atmospheric fluid.

In this paper, entropy is presented as a fundamental physical quantity of great import towards satisfactory knowledge of atmospheric processes. It is shown how the macroscopic quantities that effect significant change within the atmosphere are related to this singular quantity, and also how the entropy may be monitored via the combination of theoretical assumptions and empirical observations that serve as tools to this end. In Section 2, aspects of entropy are presented and the quantity is related to other macroscopic characteristics of the environment. In section 3, atmospheric processes are discussed in terms of their attendant effects on the local entropy. Lastly, in the spirit of extracting simplicity from the above concerns, section 4 provides a non-technical perspective of entropy and aims to satisfy the intended audience of this paper – a graduate-level physics student.

2 Entropy

Entropy is a fundamental characteristic of all physical systems. It is a state variable, meaning that its value at any given time completely characterizes the state of the system, irrespective of how the system arrived in that state. In general, entropy is a function of the extensive quantities of a system, that is, quantities whose magnitudes change when the amount of the substance of interest changes.\footnote{If the number of moles changes, an extensive quantity will change, while an intensive quantity will not [Tien and Lienhard, 1971].} For example, the volume of water in a bucket, an extensive quantity, increases when more water is added while the density of the water, an intensive quantity, remains the same. Entropy
can be expressed as a function of the extensive quantities energy, $U$, volume, $V$, and the number of moles, $N_i$ of each component of a system with $n$ components:

$$S = S(U, V, N_1, N_2, \ldots, N_n).$$  \hspace{1cm} (1)

In differential form, this becomes

$$dS = \left( \frac{\partial S}{\partial U} \right)_{V,N_i} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N_i} dV + \left( \frac{\partial S}{\partial N_i} \right)_{V,N_j} dN_i (i \neq j).$$  \hspace{1cm} (2)

Defining the partial derivatives as

$$\left( \frac{\partial S}{\partial U} \right)_{V,N_i} = \frac{1}{T}, \quad \left( \frac{\partial S}{\partial V} \right)_{U,N_i} = \frac{p}{T}, \quad \left( \frac{\partial S}{\partial N_i} \right)_{V,N_j} = -\frac{\mu_i}{T},$$  \hspace{1cm} (3)

and solving for the change in energy we can write

$$dU = TdS - pDV + \sum_{i=1}^{n} \mu_i dN_i,$$  \hspace{1cm} (4)

which is an expression of the change in a system’s internal energy due to changes in the other extensive quantities [Tien and Lienhard, 1971]. Furthermore, the partial changes in entropy due to the quantities shown in (3) give the intensive quantities that are often of interest: temperature $T$, pressure $p$ and the chemical potential $\mu$.

We can also describe entropy in microscopic terms, though we will use an analogy to macroscopic behavior to do so. A system that changes in time can exist in many different states, due to the variability inherent in the composite nature of the system. For example, a seesaw holding four children might exist in six possible configurations: all children might be on the left or right side, one could be on the left side and the rest on the right, one could be on the right side and the rest on the left, or there could be equal numbers on both sides (see Table 1). But the latter configuration, the equal configuration, is special because there are five different ways that it can occur (see Table 2). Significantly, there are more possibilities in this case than in any other configuration.

If we assume that any of the states shown in Table 1 can happen with equal probability, then at any given time the

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Table 1: All possible states of the children’s positions. For each state, each child can be on the left (L) or right (R) side of the seesaw. The states with two children on each side are underlined.
children might be in any of the states. However, since they can be in the *equal* configuration six different ways, it is most likely that their state will be of this configuration. Furthermore, if we initially place all of the children on one side of the seesaw, soon after they will likely get up and run around at random. However, our analysis shows that it is again most likely that they will end up in the equal configuration, and those are the states they will most likely revisit in the future. Such an equal configuration is typically referred to as an equilibrium state.

I want to point out the subtlety and simplicity of what is going on here. The children are most likely to be in the equilibrium state, not because that is the most entertaining configuration for them, but simply because that is the configuration that can be expressed by the largest number of states. Every time we look at the seesaw any one of the states is likely to occur with equal probability. It is simply the way that we have defined these broad categories or configurations that gives rise to the fact that one configuration is more likely than another. Furthermore, ignoring which particular child is on the left or right has allowed us to define these configurations in the first place, otherwise every state listed in Table 1 is unique. So, the most probable configuration arises from two notions: (1) the elements of the configuration (the children) are indistinguishable, and (2) we have defined configurations in terms of the indistinguishable elements (all children on the left, for instance). In the case of the atmosphere, the indistinguishable elements are the molecules such as dry air and water vapor, while the configurations are macroscopic properties such as temperature and pressure. Thus, if a system is in equilibrium at temperature $T$ and pressure $p$, then there is an overwhelming majority of states or combinations of positions and momenta of the molecules such that we would measure $T$ and $p$ for each state we measured. As discussed above, the system is in equilibrium simply because of this majority condition. Less probable configurations occur less often and thus equilibrium persists until some external agent acts to perturb it.

The microscopic entropy of a system is then simply a function of the number of possible states by which a particular configuration can be expressed. A system is in equilibrium when its macroscopic properties remain roughly constant in time due to the high probability of existing in one of the many states that express the configuration. Since the most probable configuration can be manifested via the largest number of states, that is the configuration with the largest entropy.

A corollary to these properties is the second law of thermodynamics, which states that heat flows from a warmer region to a cooler one. This implies that energy cannot spontaneously collect in one side of an unpartitioned system, i.e. the entropy will not spontaneously decrease. In fact it always increases; though, in the analysis of certain processes, we sometimes say that a process is reversible – that the entropy remains approximately constant. This occurs when, for each little change in the entropy, the system is brought back to equilibrium so that the system is about as likely to be in the equilibrium state as to be in a slightly perturbed state, so that it is easy to move from one to the other [Bowley and Sanchez, 1999].
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Table 2: The number of possible states for each of the five configurations of the children on the seesaw.

### 2.1 Reversibility

Since atmospheric processes can be both approximately reversible and irreversible, it is worthwhile to investigate the subtle differences between the two. Two important equations come in handy here. The first law of thermodynamics states that the change in energy of a system is due to the work done on the system and heating of the system by external influences. Thus, the first law is stated

$$dU = Q + W.$$  \hspace{1cm} (5)

A similar expression is equation (4). Neglecting the change in particle number $N$, we can often assume that $W = -pdV$ and that $Q = TdS$. However, this is only true in the case of slow (quasistatic) changes in volume. If the change occurs very quickly, something special happens that we must account for. In particular, if the piston moves close to the speed of the molecules in the gas\(^2\), the molecules get bunched up behind the piston and don’t have time to move out of the way. Thus, the piston mostly acts to accelerate the particles in front of it, rather than merely decreasing the volume available to the air, so that

$$W_{total} = -pdV + Ma$$  \hspace{1cm} (6)

where the last term on the right side is the acceleration of the air molecules behind the piston. Equating (4) and (5), we find

$$Q + W = TdS - pdV.$$  \hspace{1cm} (7)

Since the actual work is larger than the change in volume times the pressure,

$$Q + -pdV + Ma = TdS - pdV,$$  \hspace{1cm} (8)

\(^2\)Assuming $U = KE = \frac{1}{2}mv^2 = \frac{1}{2}Nk_B T$, this is about 500 m/s for air molecules at room temperature!
so that the term in (4) usually associated with heat exchange is larger than the actual heat exchanged:

\[ T \, dS = Q + Ma > Q. \]  
(9)

Lastly, the change in entropy is

\[ dS = \frac{Q}{T} + dS_{\text{irreversible}}, \]  
(10)

where we have defined the force acting on the air molecules divided by the temperature as the irreversible change in entropy.

In this case, the change in entropy is larger than it would be if only heat were exchanged with the environment. The extra bit of entropy is due to the extra bit of work done, which added an extra bit of energy to the system. Therefore, the change in entropy in the universe, where \( dS_{\text{universe}} = dS_{\text{piston}} + dS_{\text{environment}} \), has a net nonzero value. The part of the entropy change due to heat exchange from the piston to the environment can be zero if we assume the cylinder was isolated, yet we cannot eliminate the irreversible change due to the fast compression by the piston. This is one example of many irreversible processes.

3 Entropy changes due to atmospheric processes

The Earth is in equilibrium with the rest of the universe in the sense that energy into our environment is approximately equal to the energy that leaves it. The incoming energy is overwhelmingly in the form of solar radiation incident upon the planetary surface, while the outgoing energy is mostly radiation emitted from the middle and top of the atmosphere, as illustrated in Fig. 1. In short, photons come in and photons go out; though, they enter and exit at different locations and at different wavelengths. Photons from the Sun are mostly in the visible region of the electromagnetic spectrum, a condition owing to the high temperatures of the Sun’s outer layers. In contrast, photons leaving our atmosphere are mostly in the infrared spectrum as they are products of the warmed planetary surface and various atmospheric components, which are far cooler than the sun.

Therefore, while photons leaving the atmosphere each carry far less energy than do those coming in, together they nevertheless equal the total incoming energy such that the net energy exchange with the universe is approximately zero. Even though the energy is balanced however, the entropy is not. Why is this?

The net entropy change in the atmosphere is given by the sum of that which comes in and that which goes out:

\[ \Delta S_{\text{net}} = \Delta S_{\text{in}} + \Delta S_{\text{out}}. \]  
(11)
Figure 1: The energy equilibrium between the Earth and the rest of the universe is due to the balance between incident solar radiation $Q_{in}$ (left), which heats one side of the planet at any given time, and outgoing longwave radiation $Q_{out}$ (right), which expels energy in all directions. (Figure generated using xfig.)

Since the change in entropy is due to photons coming and going, i.e., heat exchange,

$$\Delta S_{net} = \frac{Q_{in}}{T_{in}} + \frac{Q_{out}}{T_{out}}.$$ \hspace{1cm} (12)

Now, we’ve already stated that the magnitude of the incoming energy equals that of the outgoing, so that $Q_{in} = -Q_{out} = Q$, but the key difference is that the temperature where the incoming energy is absorbed (near the surface) is different than the temperature where energy is expelled (aloft). The entropy change is then

$$\Delta S_{net} = Q \left( \frac{1}{T_{surf}} - \frac{1}{T_{aloft}} \right).$$ \hspace{1cm} (13)

Since $T_{surf} > T_{aloft}$, $\Delta S_{net} < 0$. Thus, there is a continual net entropy sink in the atmosphere due to radiation. In the words of Li et al. (1994),

“The solar radiation brings in a small amount of entropy in comparison with what the longwave radiation takes out. It is this negative entropy stream that maintains the orderly appearance of the atmosphere.” [Li et al., 1994]

This entropy sink must be balanced by entropy sources within the atmosphere, else the second law of thermodynamics would be violated within the atmospheric system; that is, atmospheric entropy must increase or remain constant. Since we have already seen that the exchange of photons with the rest of the universe effects a net drain in entropy, and photons are the only thing the Earth exchanges with the rest of the universe (a few spacecraft and meteors notwithstanding), there must be entropy sources within the local environment that at least compensate for this deficit. Thus, if constant emission of solar radiation from the top of the atmosphere depletes entropy, irreversible processes within the
atmosphere generate it.

3.1 Irreversible atmospheric processes

Warner (2005) estimated the entropy deficit to be 55 mWm$^{-2}$K$^{-1}$. That is, in an atmospheric column 1 meter square extending from the surface to the top of the atmosphere, about 55 millijoules of energy are lost every second for each Kelvin of local temperature. In comparison, a cylinder whose volume is compressed isothermally by one liter per second loses entropy merely\(^3\) at the rate of $\Delta S \approx 0.0003$ mJs$^{-1}$K$^{-1}$. Warner conceded that the value quoted above represents small differences between large numbers and is therefore subject to significant error. Nevertheless, barring contradictory evidence, we must account for at least this much entropy loss in our examination of irreversible processes.

In his study of entropy production over tropical oceans, Warner found the largest offsets (with respective contributions in mWm$^{-2}$K$^{-1}$) to this deficit to be the evaporation of precipitation (20), viscous stress around falling precipitation (16), mixing of atmospheric constituents (8), and surface evaporation (5.9). Less significant contributors were found to be mechanical dissipation by turbulence (2.8), gravity wave\(^4\) generation (0.5), and surface sensible heat fluxes (0.2). A similar, though less comprehensive study by Pauluis and Held (2002a; 2002b) revealed similar values for the few processes they studied.

Let us attempt to understand how a few of the more significant processes leads to the generation of entropy. We begin with an analysis of evaporative processes.

3.1.1 Entropy production via evaporation of precipitation and surface fluxes of moisture

Atmospheric precipitation is a phenomenon whereby condensed water vapor accretes by some process into a droplet heavy enough to overcome local random motions that thereby succumbs to gravity. The droplet quickly attains a terminal velocity owing to the balance of drag and gravitational forces acting upon it and falls to a lower region of the atmosphere where, if the conditions are right, the droplet evaporates back into the vapor phase. Evaporation represents an increase in entropy by an irreversible process.

Bohren and Albrecht (1998) provide a simple explanation of the increase in entropy due to evaporation, presented here as an aspect of precipitation. Imagine a little pocket of the atmosphere containing only a raindrop that is falling to the ground. Let’s follow this pocket as the drop falls and only consider what happens inside the pocket. Within this box, we have only a mass of liquid water (plus some air molecules, but we’ll ignore them for now). During evaporation, nothing changes inside the box except that some of the liquid water becomes gaseous vapor. Since we are ignoring the dry air molecules in the box, we can write the total energy, entropy and volume of the water phases in the pocket as

\[ dU = 0 \implies pdV = TdS \implies dS = pdV/T. \]

Let $p = 100000$ Pa, $T = 300$ K. Then $dS = (1x10^9 \text{ Pa})(1x10^{-3} \text{ m}^3/(3x10^2 \text{ K})=10^{-6}/3 \text{ JK}^{-1} = 0.0003 \text{ mJK}^{-1}$ (the cylinder would need to remain in contact with a large heat bath to maintain constant $T$).

\(^3\)Gravity waves are waves that propagate through a fluid under the influence of gravitational and buoyancy forces.

\(^4\)Gravity waves are waves that propagate under the influence of the buoyancy and gravitational forces. The expanding waves around a stone dropped into a pond are an example.
Figure 2: The various sources of entropy due to atmospheric processes around a simplified precipitating convective tower and requisite cirrus shield over the ocean. Figure generated using xfig.

\[ U = (1 - \alpha)U_w + \alpha U_v, \]
\[ S = (1 - \alpha)S_w + \alpha S_v, \]
\[ V = (1 - \alpha)V_w + \alpha V_v, \]

(14)

where \( \alpha \) is the ratio of the mass of water vapor to that of the sum of vapor and liquid and \( v \) and \( w \) denote vapor and liquid properties, respectively. The first law (5) can be written

\[ T \frac{\partial S}{\partial V} = \frac{\partial U}{\partial V} + p, \]

(15)

and we can perform a change of variables to make use of (14)

\[ \frac{\partial S}{\partial V} = \frac{\partial S}{\partial \alpha} \frac{\partial \alpha}{\partial V}, \]
\[ \frac{\partial U}{\partial V} = \frac{\partial U}{\partial \alpha} \frac{\partial \alpha}{\partial V} \]

(16)

so that

\[ T \frac{S_v - S_w}{V_v - V_w} = \frac{U_v - U_w}{V_v - V_w} + p, \]

(17)

which yields

\[ T(S_v - S_w) = U_v - U_w + p(V_v - V_w) = H_v - H_w = L_v, \]

(18)
where $H_i$ is the enthalpy of each constituent and $L_v$ is the enthalpy (a. k. a. latent heat) of vaporization. Dividing by the mass of the entire drop, $M$, we find

$$T(s_v - s_w) = l_v \implies \Delta s = \frac{l_v}{T},$$

that is, the difference in specific entropies is positive (since $l_v > 0$) and thus evaporation increases atmospheric entropy.

Now, this is a naive explanation due to the simplified and idealized contents of the pocket. We can express the total specific entropy of the pocket (including dry air) by adding expressions of the entropy of each constituent and using the difference in enthalpies expressed in terms of entropies [Emanuel, 1994]:

$$s = (c_{pd} + \alpha c_l) \ln T - R_d \ln p_d + \frac{l_v}{T} \alpha - \alpha R_v \ln H,$$

where $R_d$ and $R_v$ are the dry air and water vapor gas constants, $\alpha_t = \alpha + \alpha_l$ is the total water mixing ratio, $p_d$ is the partial pressure of dry air, $H$ is the relative humidity, and $c_{pd}$ and $c_l$ are the specific heats at constant pressure of dry air and liquid water, respectively. By differentiating this expression, it can be further shown that the net change in entropy is

$$ds = -R_v \ln H \, d\alpha.$$

Evaporation can only occur when $H < 1$. Since the generation of water vapor makes $d\alpha > 0$, the change in entropy is necessarily positive. This represents a source of entropy under the condition of evaporation of liquid water into unsaturated air and includes the effect of dry air molecules surrounding the drop. Thus, falling raindrops can generate entropy.

We can put this expression into a more usable form by considering the measurable rate of precipitation. Pauluis and Held (2002) defined the change in water vapor as a function of the precipitation and condensation rates. Initially, we assume that precipitation in the atmospheric column is the rate of condensation of water vapor $C$ minus the rate of evaporation $E$ (the units of $C$ and $E$ are per unit area per unit time),

$$P = C - E.$$  

Since not all of the condensed vapor becomes rain, Pauluis and Held furthermore defined a precipitation efficiency $\varepsilon_p = P/C$ so that the evaporation is given by

$$E = C - P = P/\varepsilon_p - P = P\left(\frac{1}{\varepsilon} - 1\right).$$
Substituting $d\alpha$ for this expression in (21) gives a new statement of the irreversible entropy:

$$ds_{irr} = P(1 - \frac{1}{\varepsilon_P})R_v \ln H.$$  \hspace{1cm} (24)

Using typical empirical values for $P$, $\varepsilon_P$, and $H$ (near the level of evaporation), Warner found the value for the entropy source due to falling precipitation quoted above. Since surface evaporation is a similar process occurring at the boundary between the atmosphere and water-laden surface features such as bodies of water and vegetation, we have thus explained two of the largest sources of entropy in the atmosphere.

3.1.2 Entropy production due to the viscous stress upon falling precipitation

The next most significant entropy source is that due to viscous stress acting upon precipitation falling through the air. In their study of the entropy budget of the atmosphere, Pauluis and Held (2002) found that the total mechanical work done by convection upon the atmosphere is balanced by the dissipative mechanical processes occurring in radiative-convective equilibrium. The time rate of change of mechanical work done is simply that due to expansion

$$W = \int p \nabla \cdot v d\Omega,$$

where $p$ is the local pressure, $\nabla \cdot v$ is the divergence of the velocity and $d\Omega$ is a volume element. Thus, the rate at which work is done by convection upon the atmosphere is simply the rate that the convective plumes diverge, i.e., the rate that a plume’s volume increases is the rate of compression upon the greater atmosphere. Much of this work is spent on dissipative processes such as the formation of gravity waves and viscous stresses. While the requisite entropy sources accompanied by gravity waves and viscous dissipation due to turbulence are small (see introduction to section 3.1), dissipation due to falling precipitation is significant.

The dissipation rate can be expressed in terms of the power generated by the gravitational force $F_g$ acting on a raindrop falling at its terminal velocity $V_T$,

$$P = F_g V_T = F_g V_T.$$  \hspace{1cm} (26)

Newton’s second law states that a force is equal to the product of the mass and its acceleration, where the infinitesimal mass of the drop is the density of the drop $\rho_c$ times the volume element $d\Omega$

$$dP = (dmg) V_T = \rho_c g V_T d\Omega.$$  \hspace{1cm} (27)

The dissipation of energy in the atmosphere due to the drag of air upon falling precipitation is then [Pauluis and Held, 2002a]
We can put this in a more useful form that doesn’t require knowledge of the distribution of precipitation in the atmosphere, $\rho_c$. In statistical equilibrium, the amount of water substance going up is approximately that which comes down at every level. Since the total water content can be expressed as the sum of condensate and vapor, we require that

$$F_{tot} = F_c + F_v = 0 \implies F_c = -F_v,$$

(29)

where $F_i$ are the integrated vertical fluxes of condensate\(^6\) and vapor [Pauluis et al., 2000]. The condensate experiences vertical motion via advection\(^7\) due to the local vertical air velocity $w$ and also via the terminal velocity at which it falls through the air $V_T$. Thus, the integrated vertical flux of condensate is given by

$$F_c = \int (\rho_c w + \rho_c V_T) d\Omega.$$

(30)

Since water vapor is only advected at the local air velocity, the integrated flux of water vapor is

$$-F_v = \int \rho_v w d\Omega.$$

(31)

Then, gathering the advection terms and multiplying by the acceleration of gravity, we find that

$$\int \rho_c g V_T d\Omega = \int (\rho_c + \rho_v) g w d\Omega.$$

(32)

The left side is simply the dissipation expression from (28). Writing the density in terms of the mass mixing ratios of condensate and vapor, $\alpha_c$ and $\alpha_v$, the right side becomes

$$\int (\alpha_c + \alpha_v) \rho w d\Omega.$$

(33)

Finally, we find that

$$D_p = \int \alpha_c g \rho w d\Omega,$$

(34)

where $\alpha_t$ is the total water mixing ratio and $\rho$ is the moist air density [Pauluis and Held, 2002a]. Thus, we can estimate the rate of dissipation due to falling precipitation if we can measure the vertical velocity and the total water mixing ratio at some level of the atmosphere below the level of precipitation formation.

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\(^6\)Condensate here refers to condensed water vapor, either in the solid or liquid state.

\(^7\)Advection is motion caused by motions of the mass of fluid itself. A canoe pulled along by a river current undergoes advection.
If the dissipation rate can be measured, the corresponding entropy source is given by [Warner, 2005]

\[ ds_d = \frac{d_p}{T_p}, \]  

(35)

where \( d_p \) is (34) divided by the mass and \( T_p \) is the temperature at which the dissipation occurs. The temperature varies with height, but a mean value from the region of precipitation should give a fair estimate of the entropy generation without knowledge of the precipitation mixing ratio at every elevation.

### 4 An intuitive account

Entropy holds an esteemed place among the less intuitive concepts of physics. Like energy, it is a somewhat mysterious quantity manifested in many forms that can be exchanged and transformed. Unlike energy, however, entropy can be generated – even within isolated systems. In fact, the quantity must increase over time and perhaps this is why Rudolf Clausius [Bohren and Albrecht, 1998] named the quantity after the Greek word for evolution [Prigogine, 1967].

Although we have derived mathematical expressions for the most significant atmospheric sources of entropy, we may nevertheless feel nonplussed. “Because the math says so” can be an unsatisfying explanation in physics, as it suggests that the universe is merely a necessary manifestation of mathematics. While this may yet be true, a common-sense explanation is in order.

Bohren and Albrecht (1998) go to great lengths to dispel the long-held popularization that entropy is a measure of disorder. One confusing example they present is an isolated supersaturated solution, which is a solid dissolved into a liquid beyond the equilibrium value. It is possible for the solid to crystallize within the liquid, and it is further possible for the temperature to decrease during the process. Since we intuitively consider a crystal more ordered than the solution, it is surprising to consider that the entropy of an isolated system must increase! The authors go on to point out that

“Generations of desperate teachers, faced with the cries of anguished students for an immediate, concise, and readily digestible explanation of what this mysterious quantity entropy really is, have seized upon a pacifier: Don’t fret, entropy is just a measure of disorder; in fact, entropy is disorder” [Bohren and Albrecht, 1998].

Keeping these notions in mind, let’s consider the two forms of atmospheric entropy generation we have described. The source of entropy due to evaporation occurs when water molecules attain a greater tendency to detach from the mass of liquid water than they have to reattach to the liquid. But the molecules constantly leave and enter the water phase in equilibrium, so what is special about the state of evaporation that leads to entropy generation?

Since more molecules leave the liquid than enter it, more molecules find a larger space to explore with their
respective velocities. Since there is more space to move around in for a larger number of molecules, there are more states available to them, and as entropy is a measure of the number of possible states obtainable by the molecules, their entropy naturally increases. Why is this process irreversible? Because the molecules aren’t obligated to sit around waiting to recondense into the water phase – they are free to fly off into the greater atmosphere.

What about the dissipation of energy due to viscous drag? In this case, air molecules in the paths of raindrops continuously impede the downward motion of the drops as they fall. Thus, the macroscopic motions of the falling drops are immediately transferred to much smaller scale motions. This increases the energy of the surrounding air, which allows the air molecules to explore a greater number of energy states. Like the case of evaporation described above, the increased number of states leads to an increase in entropy.

Although both of these cases of entropy production accompany an increase in disorder, it remains useful to heed the words of Bohren and Albrecht. If we wish to seek out sources of entropy, it is useful to count the number of states. However, when this is prohibitively difficult, macroscopic expressions can help to fill in the gaps. Monitoring the entropy budget of the atmosphere can be useful because entropy is usually conserved, unless there is precipitation, evaporation or heating via radiation. Thus, it can serve as an indicator of these processes or, alternately, these processes can serve as indicators of changes in entropy of either air parcels or the atmospheric column itself.
References


