3. The First Law of Thermodynamics

Thermodynamics deal with the movement and conversion of energy in various forms. The well-known forms of energy are the kinetic energy (half the mass of an object times its velocity squared), potential energy (due to potential ability of, for example, gravitational field or a spring to do work), internal energy (kinetic energy and chemical energy of all molecules that make up an object), electromagnetic energy (associated with electric and magnetic fields), etc. The important thing is that all forms of energy are equivalent, and can be converted into each other.

In atmospheric physics, we deal with thermodynamics of moist air, which is a mixture of dry air, water vapor, and, if in clouds, suspended liquid water droplets and ice crystals. The atmospheric air is a gas that is characterized by such *intensive* properties (not depending on mass or volume) as temperature T, pressure p, and density ρ, which are continuous three-dimensional fields. These fields are related through the equation of state (1.2), so that any one variable, such as pressure, can be computed from the other two.

The air does mechanical work when it expands. Let's consider a parcel of expanding air so tiny that we can ignore variation of pressure across it. The pressure is defined as the force per area, so the force the expanding parcel applies to a small area dA of its boundary is pdA. Let the parcel's boundary be expanded by infinitesimal distance ds is all directions. Then, the mechanical work performed by such an expanding parcel is given by

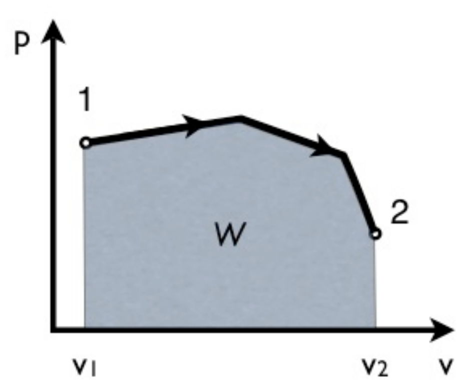
$$\delta w = \int_A p\,dA\,ds = p\,ds\int_A dA = pA\,ds = p\,dV \tag{3.1}$$

where we integrate over the whole area of the parcel, and dV is the displaced volume. Thus, the thermodynamic work done by pressure equals that pressure times change of the volume. Here and further in the text we will follow the convention that the work done by expanding gas (increasing volume) is positive.

Let's use the *specific* volume $v = 1/\rho$, or the volume of unit mass. Then, w is a *specific work*. For brevity, unless explicitly stated, we'll drop the word 'specific' implying that all variables are 'per unit mass'. The total amount of work performed by a unit mass of air expanding from volume v_1 to volume v_2 is given by

$$W = \int_{v_1}^{v_2} p\,dv \tag{3.2}$$

In thermodynamics, it is customary to use the so-called *pv-diagrams*, which are simple pressure-vs-volume plots. On a pv-diagram, area under the *path* connecting the initial and final states of the gas is equal to the integral (3.2), and thus



pv-diagram illustrating work done by expanding gas

gives work performed along that path (see figure). Obviously, there are many possible paths connecting the initial and final states. Therefore, the area under the path and, hence, the total work, depend on the chosen path on pv-diagram. However, it is known from the calculus that the integral of a true differential of a function depends only on the initial and final states, but not on the path that connects them. That means that δw is not really a differential, which we stressed by using δ in (3.1) instead of d. Note that for contracting air parcel, the integral (3.2) becomes negative, meaning that the work done by the parcel is negative, or there is work done by the environment *on* the parcel rather than by the parcel.

The main property of energy is that *energy is conserved*. The energy conservation means that if we have a group of physical objects that 'work on each other', that is, exchange energy in various forms and convert energy from one form to another, the total amount of energy in that group of objects does not change with time. The conservation principle is the essence of the *1st Law of Thermodynamics*, which, in relation to air, states that the amount of internal energy u in the air can be increased only by adding *heat* (thermal energy) q from the environment and by the work w done on the volume of air by the environment. Conversely, u can be decreased by giving away the heat q back to the environment and by work w done by the parcel on its environment. Mathematically, this fundamental conservation law can be written as

$$\delta q = du + pdv \tag{3.3}$$

Note that the change of internal energy du is the true differential, as the internal energy is characterized only by the parcel's temperature. Temperature is fully defined by the *p-v* pair (by the ideal gas law), and therefore, the change of internal energy is determined only by the difference between the final and initial temperature regardless of the trajectory on the pv-diagram.

Let's define u by assuming that the heat is added to a specific volume of air while keeping that volume constant (dv=0). Then, according to (3.3), all that heat will be converted into the internal energy, which would raise the air temperature. It is assumed that the increase of temperature is directly proportional to the amount of heat applied, that is, $dq\big|_{v=const} = c_v dT$, where the coefficient of proportionality c_v is called a *specific heat at constant volume*. Now the 1st Law of Thermodynamics will read

$$\delta q = c_v dT + pdv \tag{3.4}$$

The equation (3.4) can be rewritten in a different form using the equation of state:

$$\delta q = c_v dT + d(pv) - vdp = c_v dT + d(RT) - vdp = (c_v + R)dT - vdp \tag{3.5}$$

Now, if we assume that the heat is applied to air while keeping the pressure constant (dp=0), then $dq\big|_{p=const} = c_p dT$, where c_p is a *specific heat at constant pressure*. From (3.5), it follows that

$$c_p = c_v + R \tag{3.6}$$

Thus, for the same temperature change, the air kept at constant pressure (that is, allowed to expand) can absorb more heat than the same air parcel kept at constant volume (any idea why it is the case?). Thus, the 1st Law of thermodynamics can also be written as

$$\delta q = c_p dT - vdp \tag{3.7}$$

In atmosphere, a unit volume of air or air parcel can undergo various processes. Here is the list of several of them by name:

Adiabatic: $\delta q = 0$, that is no external heat is added/subtracted to/from a parcel. For example, ascending air parcel can be closely described by adiabatic process.

Isothermal: $dT = 0$. For example, condensation/evaporation of water is the isothermal process. From (3.4) it follows that in isothermal process all the added heat goes into the work done by the parcel.

Isobaric: $dp = 0$. Condensation/evaporation also isobaric processes. Also, heating by the radiation occurs at constant pressure.

Isochoric: $dv = 0$. It doesn't usually happen in atmosphere as there are no limiting boundaries. That's one of the reason why the form (3.7) is preferably used in atmospheric thermodynamics.