

Atmospheric thermodynamics

Textbooks and web sites references for this lecture:

- A. Longhetto - Dispense di Fisica dell'atmosfera
- Adrian M. Tomkins - Atmospheric Physics - [ictp_atmospheric_physics.beamer.pdf](#)
- Physik der Atmosphäre - Institut für Umweltphysik - Universität Heidelberg

The first law of thermodynamics

- Two empirical facts:
 1. Heat is a form of energy
 2. Energy is conserved
- The internal energy of a closed system (U) can change only if heat (Q) is added or if work (W) is done on the system by its surroundings:

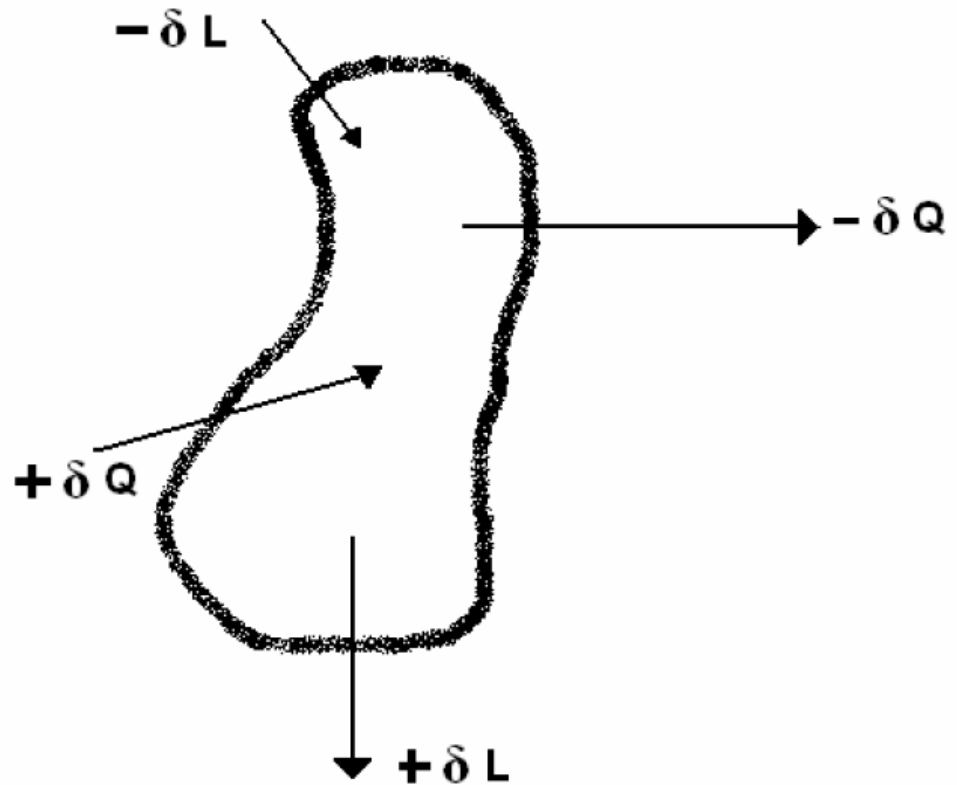
$$dU = \delta Q - \delta W \qquad du = \delta q - \delta w$$

(lowercase letters for unit of mass)

- The rate of work is given by:
$$\delta W = -pdV$$

Sign convention

- Physical convention:
 - a) $[-\delta Q]$ indicates heat given (lost) from the thermodynamic system to the environment;
 - b) $[-\delta L]$ indicates mechanical energy given (lost) from the environment to the system as external work (i.e. the system will shrink)
- Such form of work can be expressed as:
$$W = - p\Delta V = p(V_1 - V_2)$$
where V_1 and V_2 represent initial and final volume, respectively
- If $V_2 > V_1$ there is a system expansion, i.e. external work of the system



Law zero of the thermodynamics

- Thermal equilibrium among two bodies:
 - Two bodies are in thermal equilibrium when they possesses the same temperature
- Law zero of the thermodynamics
 - Two bodies in thermal equilibrium reach, after a certain time, the thermal equilibrium
- Equilibrium temperature T_{eq} among two bodies (same material) m_1 and m_2 =
$$T_{eq} = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2}$$
- Heat exchanges:
 - If several bodies in contact reach thermal equilibrium, the total amount of heat exchanged between each other is zero

System and environment

- Thermodynamic system:
 - Body, or body ensemble, characterized by a well defined physical composition
- External environment
 - “material” or empty space surrounding the system and with which the system exchanges heat and work
- In traditional thermodynamic
 - the system is bordered by rigid or flexible, diabatic or adiabatic, walls
 - → external environment may be represented by thermostats or electromagnetic energy sources
- In atmosphere
 - It is not possible to border with well identified walls the air volume considered as system
 - The system is identified by an ideal closed surface made of air molecule (*material surface*) which enclose the air particle considered as system
 - volume and surface of such system may change continuously depending on air motions, even without real exchange of particles

Thermodynamic transformations

- Atmospheric (thermo)dynamic properties:
 - defined considering a great number of molecules (statistical informations)
 - neglecting the knowledge relative to each molecule
 - Conditions of a system are defined by some variables (volume, temperature, pressure, ...) in each point of the body
 - Individual properties of each molecule are converted in ensemble properties of the system
- Thermodynamic transformations are related to changes of continuous variables defined at macroscopic scale, without considering the microscopic structure of the fluid

Equilibria in physics

1. Mechanical equilibrium

- Non equilibrated forces do not exist inside the system or do not act externally on the system;

2. Thermal equilibrium

- All system parts which may exchange heat between each other possesses the same temperature
 - Eventually this temperature may equal external temperature if the walls of the container allow heat exchanges between system and environment;

3. Chemical equilibrium

- When chemical reactions or matter movements (solution, diffusion, convective motions) did not occur within the system
- Such equilibria, if verified, have the consequence that the state variables have the same value in the whole system
- State variables for ideal gases are 3: p , T and V
 - They identify a 3-D space $[p, V, T]$
- As only 2 variables among p , T and V are independent, the equilibrium state of a system is represented only by 2 variables
 - They identify a 2-D space: $[p, T]$ o $[p, V]$ o $[V, T]$

Reversible transformations

- When variables vary in the system, the system is not in equilibrium
 - the state of the system is unknown
 - thermodynamic transformations cannot be defined macroscopically
- Introduction of the concept of thermodynamic system "*infinitely close to a state of equilibrium*":
 - a. **Causes** producing an eventual transformation must be **infinitely small**
 - b. The **transformation** must be **infinitely slow**
- A transformation which satisfies a) and b) is called **reversible**
 - c. For a reversible transformation it is **possible to revert the sense** by changing infinitely few its factors
- Real transformations can approximately (but not exactly) be considered reversible
 - Friction forces are one of the major reasons
 - They are always present, never null, altering the mechanical equilibrium
 - They do not reverse by reverting the transformation (violation of condition c)

Real transformations

- All real transformations are not reversible
- Those who develop sufficiently slowly and for which the sequence of states is characterized by well defined values of macroscopic variables changing regularly with the time can be considered *practically reversible*
- If the transformation is (not) reversible, all intermediate states between A and B (do not) are states of equilibrium and can(not) be characterized by definite values of macroscopic variables
 - (non) reversible transformation trajectories are indicated by a solid (dashed) line

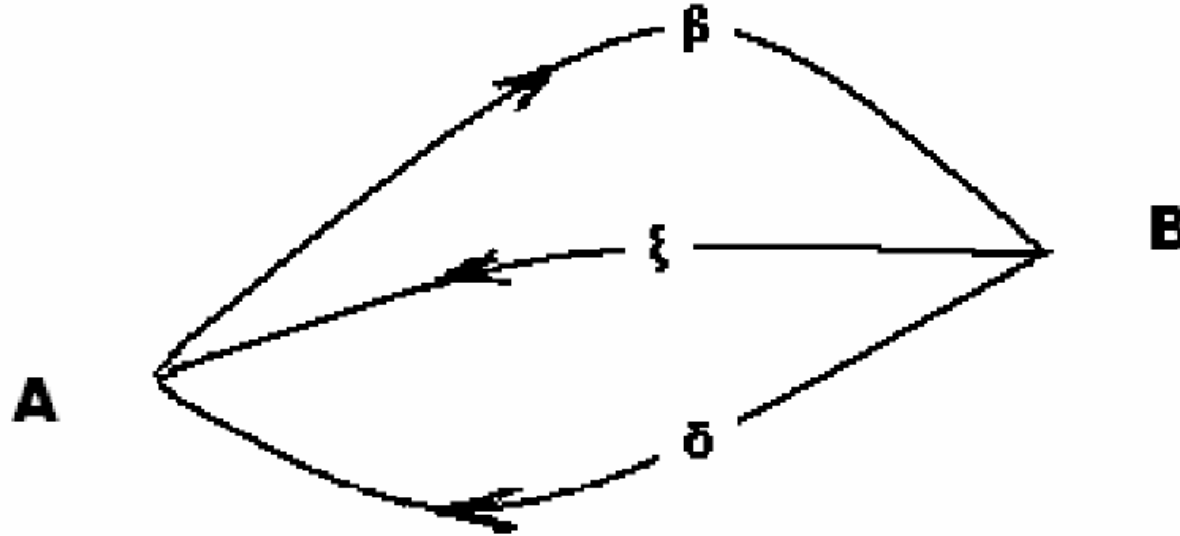
Conservation theorem: mechanics

- In mechanics, the conservation theorem states that, in a conservative forces field, the mechanic energy (i.e. the sum of potential and kinetic energy) of a moving body is constant in the time
 - The energy of a body is intended as the capacity to produce work
 - This occurs because the body moves (i.e. possesses kinetic energy) or because of the particular position of the body (i.e. its potential gravitational energy)
- This theorem is only partially valid in atmosphere, because there are non-conservative forces (i.e. friction)
- The mechanic energy is not conserved in atmosphere

Conservation theorem: thermodynamics

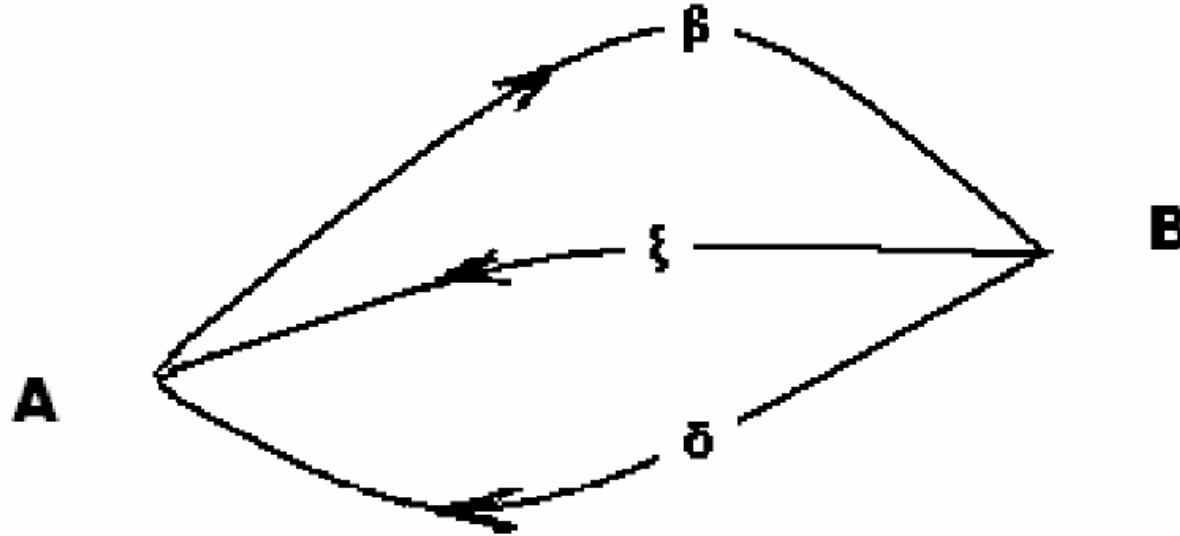
- When mechanic energy is not conserved, the production or loss of other forms of energy (thermal, luminous, electric, ...) is observed
- Summarizing:
 - In the purely mechanic phenomena, the mechanic energy is conserved
 - In the purely thermal phenomena, the global heat quantity is conserved (calorimetry)
 - In the phenomena characterised by the contemporary presence of mechanic and thermal (heat) energies, they do not conserve separately
- Mechanic energy and heat are two different aspects of energy (equivalence principle)
- Thus it is possible to obtain a general energy conservation law: the first principle of the thermodynamics
- For a cyclic transformation, expressing the heat in Joule, it is:
 $L = Q$

The 1st principle of thermodynamics for cyclic transformations (1)



- A, B are two general equilibrium states in the Clapeyron plane (V, p)
- To go from A to B there are infinite ways, both reversible or not reversible
- Let β (from A to B) and δ (from B to A) be two reversible ways, and ξ a third path
- " $\beta+\delta$ " together constitute a cyclic reversible transformation, while " $\xi+\beta$ " constitute a cyclic mixed transformation

The 1st principle of thermodynamics for cyclic transformations (2)



- In " $\beta+\delta$ ": $Q_{\beta} - L_{\beta} = + Q_{\delta} - L_{\delta}$
- In " $\xi+\beta$ ": $Q_{\xi} - L_{\xi} = + Q_{\delta} - L_{\delta}$
- Thus we obtain: $Q_{\beta} - L_{\beta} = Q_{\xi} - L_{\xi}$
- For a transformation from A to B, the total quantity $Q-L$ is independent from the way (both reversible or non-reversible)
- Limitation: it is valid only for cyclic transformations

Isobaric transformations and enthalpy

- Let us consider an isobaric transformation: the work is given by $L=p\Delta V$ or $dL=pdV$
- How the system can produce a work if the external pressure field is constant?
- The expression of the First Principle of the thermodynamics is:

$$\delta Q = \delta L + dU = d(pV) + dU = d(pV+U) = dH$$

where $H = pV + U$ is the enthalpy

- For an isobaric transformation, $dQ=dH$
 - i.e. dQ is an exact differential, it depends only on 1 and 2
 - H is a state function
- Similar to the case of isocoric transformations
 - being $\delta L=0$, $\delta Q=dU=C_vdT$ is an exact differential, and U , internal energy, is a state function

Isentropic transformations (1)

- State equation per unit of mass ($\alpha=1/V$):

$$p\alpha = R_d T$$

- First principle of thermodynamics per unit of mass:

$$c_v dT = du = \delta q - \delta w = \delta q - p d\alpha$$

- For an adiabatic ($\delta q=0$) i.e. isentropic ($ds=\delta q/T=0$): $du = c_v dT = -p d\alpha$

- Dividing for the state equation: $c_v \frac{dT}{T} + R_d \frac{d\alpha}{\alpha} = 0$

- And integrating:

$$c_v \ln T + R_d \ln \alpha = \text{const} \rightarrow T^{c_v} \alpha^{R_d} = \text{const}$$

- Being $c_p - c_v = R_d$ and $c_p / c_v = \gamma \rightarrow R_d / c_v = \gamma - 1$ thus: $T \alpha^{\gamma-1} = \text{const}$

- And, substituting T from state equation: $p \alpha^\gamma = \text{const}$

- Substituting α from state equation: $T^\gamma / p^{\gamma-1} = \text{const}$

- Thus, for a transformation from state 1 to state 2:

$$T_2 / T_1 = (\alpha_2 / \alpha_1)^{\gamma-1} = (p_2 / p_1)^{(\gamma-1)/\gamma} = (p_2 / p_1)^{R_d / c_p} \quad \text{Poisson equation}$$

$$\rho_1 / \rho_2 = (p_1 / p_2)^{1/\gamma}$$

Isentropic transformations (2)

- Taking logarithm and then differentiating with respect to z the above expression, and manipulating it:

$$T/T_0 = (p/p_0)^{R_d/c_p} \qquad \ln T - \ln T_0 = \frac{R_d}{c_p} (\ln p - \ln p_0)$$

$$\frac{1}{T} \left(\frac{dT}{dz} \right)_a = \frac{R_d}{c_p} \frac{1}{p} \frac{dp}{dz} = - \frac{R_d \rho g}{c_p \rho R_d T} = - \frac{g}{c_p T} \qquad \left(\frac{dT}{dz} \right)_a = - \frac{g}{c_p}$$

where the suffix "a" stands for adiabatic, or isentropic

- The value γ_a is the adiabatic lapse rate for non-saturated air ("dry adiabatic lapse-rate), equal to about -10^{-2} K/m (-10 K/km)
- It is the maximum (negative) temperature variation with the height which do not causes unstability $\rightarrow$ if in atmosphere $\gamma = \gamma_a$, the atmosphere is in indifferent equilibrium, because each particle perturbed from its equilibrium position will be again in equilibrium with the environment (same density)

The first principle of thermodynamics for the atmosphere, considered as a continuous and indefinite fluid (1)

- For a system in equilibrium, the principle of conservation of energy can be stated as: $\delta Q = \delta L + dU$ or $\delta q = \delta l + du$
 - The heat δQ supplied to a system in equilibrium is distributed in the sum of two forms of energy:
 - the change of internal energy of the system
 - the external work carried out by the system environment
- However, the irreversible or nearly irreversible thermodynamic processes in the real atmosphere do not allow to assume the same pressure for system and environment
- Moreover we could no longer speak of mechanical systems in equilibrium, since the velocity is not the same in the initial and final states of the transformation

The first principle of thermodynamics for the atmosphere, considered as a continuous and indefinite fluid (2)

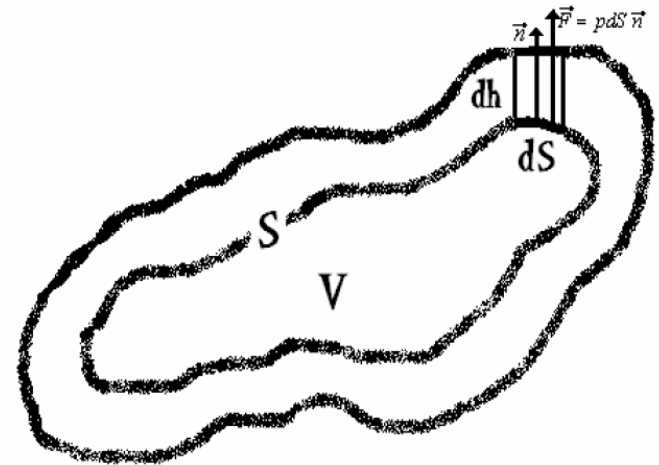
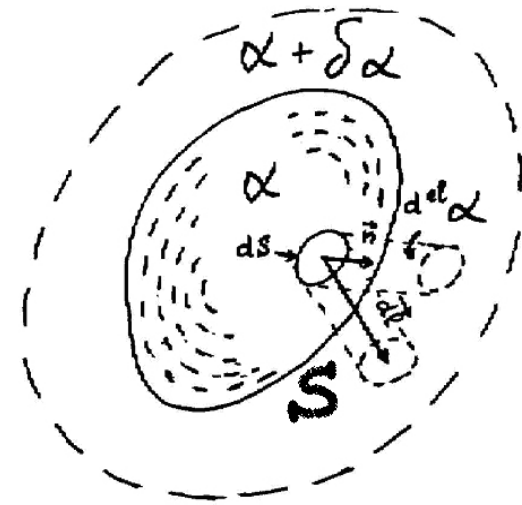
- If the volume delimited by the surface S increases, the work made by the system is equal and opposite to the work made by the environment ($df_e = -p_e dS \vec{n}$):

$$\delta L_s = - \int_S d \vec{f}_e \cdot \vec{dl} = \int_S p_e dS \vec{n} \cdot \vec{dl} = p_e d\alpha$$

- The gas exerts over each element dS of S the pressure p
- Being dh the shift of dS , the work done by gas over dS will be:

$$\delta L = \int_S p \vec{n} dS \cdot \vec{dh} = p \int_S \vec{n} dS \cdot \vec{dh} = p dV$$

- For a finite transformation, $L = p \Delta V$
- If the transformation is a succession of equilibrium states (ideally reversible or, in real cases, rather slow), in each moment the internal pressure can be considered in balance with the external one
- Thus: $\delta L = p d\alpha$ and $\delta q = p d\alpha + c_v dT$



Specific heats (1)

- Differentiating the state equation and substituting:

$$d(p\alpha) = p d\alpha + \alpha dp = R_d dT$$

$$\delta q = R_d dT - \alpha dp + c_v dT = c_p dT - \alpha dp$$

$$\delta q = c_p dT - R_d T dp/p$$

- Remembering that, for an unit mass of gas:

$$u = u_0 + \frac{nKfT}{2} = u_0 + \frac{R_d fT}{2}$$

being:

$n = N/\mu$ the number of molecularae per kg (N is the Avogadro number and μ the molecular mass of the gas),

$K = 1.38 \cdot 10^{-23} \text{ JK}^{-1}$ the universal Boltzmann constant,

f the number of degrees of freedom of the molecularae

Specific heats (2)

- Remembering now the definitions of specific heat at constant pressure and volume:

$$c_v = \frac{du}{dT} = \frac{nKf}{2} = \frac{R_d f}{2} \quad c_p = R_d + c_v = R_d \left(1 + \frac{f}{2}\right) \quad \gamma = \frac{c_p}{c_v} = \frac{2+f}{f}$$

- For a diatomic gas, $f=5$ (1 vibrational and 4 rotational degrees of freedom), thus:

$$c_v = \frac{5}{2} R_d = 716 \text{ J kg}^{-1} \text{ K}^{-1} \quad c_p = \frac{7}{2} R_d = 1003 \text{ J kg}^{-1} \text{ K}^{-1} \quad \gamma = \frac{7}{5} = 1.4$$

- For a triatomic gas, like water, $f=6$, and the gas constant is R_v , thus:

$$c_v = 4 R_v = 1385 \text{ J kg}^{-1} \text{ K}^{-1} \quad c_p = 3 R_v = 1846 \text{ J kg}^{-1} \text{ K}^{-1} \quad \gamma = \frac{4}{3} = 1.\bar{3}$$