II _ Dry thermodynamics.

1_ First law of thermodynamics

a _ Thermodynamics : what is it ?

Thermodynamics is a field closely related to experiments. It treats phenomena at a macroscopic scale (T, p, ρ) which can be measured with instruments, unlike the microscopic scale (molecular agitation...)

Broadly $\begin{cases} \text{First law: energy is conserved} \\ \text{Second law: entropy increases} \end{cases}$

These laws become meaningful through examples.
We will see several relevant to atmospheric thermodynamics

b_ Energy conservation : case of a point mass

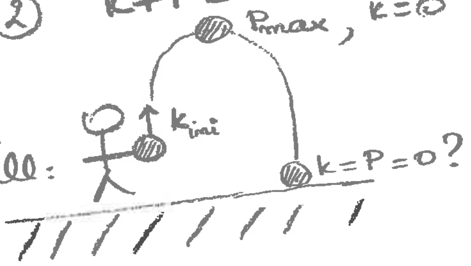
e.g. under the force of gravity:

$$① \; m \frac{d\vec{v}}{dt} = m\vec{g} \qquad \left(v = \frac{dz}{dt} \right) \Rightarrow \frac{d}{dt}\left(\frac{1}{2} m \|\vec{v}\|^2 \right) = mg \frac{dz}{dt}$$

$$\Rightarrow \frac{d}{dt}(K+P) = 0 \; , \quad K \text{ kinetic energy, } P \text{ potential energy } mgz$$

$$\Rightarrow ② \quad K + P = \text{constant} .$$

Example
Throw a ball:



c _ Energy conservation : System of point masses

Let's consider a system of point masses interacting (e.g. by collisions), with masses m_i $(i=1,2,\dots)$ and positions $\vec{x_i}$ $(i=1,2,\dots)$. The mass j yields a force $\vec{F}_{ji}$ on mass i. There is also an external force $\vec{F}^e_i$ on mass i. Note that $\vec{F}_{ji} = -\vec{F}_{ij}$ (3^{rd} law of Newton).

① $m_i \dfrac{d^2 \vec{x_i}}{dt^2} = \sum_{j \neq i} \vec{F_{ji}} + \vec{F_i^e}$

$$\Rightarrow \sum_i m_i \frac{d^2 \vec{x_i}}{dt^2} = \vec{F^e} := \sum_i \vec{F_i^e} .$$

If we introduce the location of the center of mass $\vec{x} = \dfrac{\sum_i m_i \vec{x_i}}{\sum_i m_i}$ and the total mass $M = \sum_i m_i$, we obtain

$$\boxed{M \frac{d^2 \vec{x}}{dt^2} = \vec{F^e}}$$

The movement of the center of mass is uniquely determined by external forces.

And energy?

We decompose the movement of each mass into a mean and a perturbation

$$\vec{x_i} = \vec{x} + \vec{x}'_i \quad , \quad \vec{v_i} = \vec{v} + \vec{v}'_i \quad , \text{ where } \vec{v} = \frac{\sum m_i \vec{v_i}}{\sum m_i}$$

Note that the mass-weighted mean of a perturbation is zero:

$$\frac{\sum_i m_i \vec{v}'_i}{M} = \frac{\sum_i m_i (\vec{v} - \vec{v_i})}{M} = \frac{\sum_i m_i}{M} \vec{v} - \frac{\sum_i m_i \vec{v_i}}{M} = \vec{v} - \vec{v} = \vec{0}.$$

The energy equation is obtained from ① $\cdot \vec{v_i}$:

$$\sum_i m_i \vec{v_i} \cdot \frac{d \vec{v_i}}{dt} = \sum_i \sum_{j \neq i} \vec{v_i} \cdot \vec{F_{ji}} + \sum_i \vec{v_i} \cdot \vec{F_i^e}$$

- Left hand side:

$$= \frac{d}{dt} \left(\sum_i \frac{1}{2} m_i \| \vec{v_i} \|^2 \right) = \frac{d}{dt} \left(\sum_i \frac{1}{2} m_i \left(\| \vec{v} \|^2 + \| \vec{v}'_i \|^2 + \underbrace{2 \vec{v} \cdot \vec{v}'_i}_{= 0 \text{ car } \sum m_i \vec{v}'_i = \vec{0}} \right) \right)$$

$$= \frac{1}{2} M \| \vec{v} \|^2 + \frac{1}{2} \sum_i m_i \| \vec{v}'_i \|^2$$

$$= \boxed{K_{\text{center of mass}} + K_{int}}$$

"internal" kinetic energy, related to temperature

- Right hand side 2nd term:

let's go back to the example $\vec{F_i^e} = m_i \vec{g} = -\nabla(P_i^e)$, $P_i^e = m_i g z$

More generally if P_i^e is a function of space only $P_i^e(x_i, y_i, z_i)$ then

$$\frac{dP_i^e}{dt}(x_i, y_i, z_i) = \frac{\partial P_i^e}{\partial x_i} \frac{dx_i}{dt} + \frac{\partial P_i^e}{\partial y_i} \frac{dy_i}{dt} + \frac{\partial P_i^e}{\partial z_i} \frac{dz_i}{dt} = \vec{v_i} \cdot \nabla P_i^e .$$

Thus $\sum_i \vec{v}_i . \vec{F}_i^e = -\frac{d}{dt}\left(\sum_i P_i^e\right) = \boxed{-\frac{dP^e}{dt}}$

. Right hand side 1^{st} term:
Can be supposed to take on the same form:

$\sum_i \sum_{j\neq i} \vec{v}_i . \vec{F}_{ji} = -\frac{d}{dt} \frac{1}{2} \sum_i \sum_{j \neq i} P_{ij}$, where P_{ij} is the potential of interaction between masses i & j (thus the factor $1/2$ not to count twice this interaction when summing over all couples (i,j)).

$= -\frac{d}{dt}(P_{int})$, internal potential energy due to interaction forces between masses.

$\Rightarrow$ Therefore the energy equation is

$$\frac{d}{dt}\left(k_{cm} + k_{int} + P^e + P_{int}\right) = 0$$

ie ② $\boxed{k_{cm} + k_{int} + P^e + P_{int} = \text{constant}}$

d - General case (when $\vec{F^e}$ is not just $m\vec{g}$): Work & heat.

For a point mass: $m\vec{v} . \frac{d\vec{v}}{dt} = \vec{v} . \vec{F} \Rightarrow \frac{dk}{dt} = \dot{W}$ work (per time), ie force acting through a distance.

For a system of point masses: $\frac{d(k_{cm} + k_{int} + P_{int})}{dt} = \sum_i \vec{v}_i . \vec{F}_i^e = \begin{cases} \dot{Q} \left(\Leftrightarrow \sum_{i \in I} \vec{F}_i^e = \vec{0}\right., \text{eg by contact and collision with other molecules having different kinetic energy).} \\ + \\ \dot{W} \left(\Leftrightarrow \sum_{i \notin I} \vec{F}_i^e \neq \vec{0} \text{ eg gravity}\right) \end{cases}$

If we write $U = k_{int} + P_{int}$ and suppose $k_{cm} = 0$, $\boxed{\frac{dU}{dt} = \dot{W} + \dot{Q}}$

U: internal energy due to intermolecular forces and motion around the center of mass. This law is also written $\boxed{dU = \delta W + \delta Q}$