Last time, we spoke about $u(v,s)$ and $h(p,s)$

For many applications of the atmosphere/ocean, useful to use auxiliary functions
2 energy

Gibbs (free) energy: $g = u - Ts + pv = h - Ts$
Helmholtz energy: $a = u - Ts$

| so: | | |
|---|---|---|
| | $u$ | int. energy |
| | $u + pv$ | enthalpy |
| | $u - Ts$ | helmholtz |
| | $u + pv - Ts$ | G. free energy |

$$dg = d(u - Ts + pv) = du - Tds - s\,dT + \cancel{p\,dv} + v\,dp =$$

$$= -s\,dT + v\,dp \quad \text{so } \underbrace{g(T,p)}_{}$$

useful, b/c T, P are measurables.

$$da = d(u - Ts) = \underbrace{du \cancel{- Tds}}_{-p\,dv} - s\,dT = -p\,dv - s\,dT$$

$$\text{so } a(v,T)$$

useful, b/c v, T are measurable.

In atmospheres and oceans $v$ is often difficult to measure accurately (or changes alot), so it is more convenient to have $\underline{g}$

Equilibrium conditions : (out them to define)

- a state where things do not change with time.
- small variations ($dT$, $dp$) do not lead to large changes in the system properties.

$$du = +Tds \;\cancel{+}\; pdv$$

→ So for measurables not to change ($v, e, P$, etc) with time

$$\left.\begin{array}{l} du = 0 \\ ds = 0 \end{array}\right\} \text{ they have to both be zero}$$

→ In addition however, for the system to not change drastically with small changes in $dT, dp, dV$ it can be shown that

$$\left\{\begin{array}{ll} d^2u > 0 & \Rightarrow \text{internal energy has to be minimum} \\ d^2s < 0 & \Rightarrow \text{entropy has to be maximum} \end{array}\right.$$

→ These are the requirements for equilibrium.

However, since it is difficult to carry out real processes under constant $s$ or $u$, we can define criteria for conditions we can study, such as $p = \text{cst}$, $V = \text{cst}$.

This is where the other auxiliary energy functions become useful:

constant $s, v$ $\quad du = 0$ , $d^2u > 0$

constant $s, p$ $\quad dh = 0$ , $d^2h > 0$ (why?)

mostly used → constant $T, v$ $\quad da = 0$ , $d^2a > 0$

→ constant $T, p$ $\quad dg = 0$ , $d^2g > 0$

⟹ All the above are absolutely equivalent, only that they are described in terms of different variables

Thermodynamic relationships

Euler's relationship : $du = M\,dx + N\,dy$
and $du$ is an exact differential, then

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

Maxwell's relations

So: $du = -p\,dv + T\,ds \Rightarrow \frac{\partial(-p)}{\partial s} = \left(\frac{\partial T}{\partial v}\right)$

$dh = v\,dp + T\,ds \Rightarrow \left(\frac{\partial T}{\partial p}\right) = \left(\frac{\partial v}{\partial s}\right)$

$da = -p\,dv - S\,dT \Rightarrow \frac{\partial(-S)}{\partial v} = \frac{\partial(-p)}{\partial T}$

$dg = v\,dp - S\,dT \Rightarrow \frac{\partial(-S)}{\partial p} = \frac{\partial v}{\partial T}$

Also, from the definition of equilibrium:

$$du = 0 = T\,ds - p\,dv \Rightarrow \left(\frac{\partial s}{\partial v}\right)_{u=const} = \frac{p}{T}$$

$$dh = 0 = T\,ds + v\,dp \Rightarrow \left(\frac{\partial s}{\partial p}\right)_{h=const} = -\frac{v}{T}$$

$$da = 0 = -s\,dT - p\,dv \Rightarrow \left(\frac{\partial v}{\partial T}\right)_{a=const} = -\frac{s}{p}$$

$$dg = 0 = -s\,dT + v\,dp \Rightarrow \left(\frac{\partial p}{\partial T}\right)_{g=const} = -\frac{s}{v}$$

Finally, from the definition of an exact diff

$u(s,v)$: $$\left.\begin{aligned} du &= \frac{\partial u}{\partial s}\,ds + \frac{\partial u}{\partial v}\,dv \\ \text{but } du &= T \cdot ds - p\,dv \end{aligned}\right\} \Rightarrow \frac{\partial u}{\partial s} = T\,; \quad \frac{\partial u}{\partial v} = -p$$

$h(s,p)$: $$\left.\begin{aligned} dh &= \frac{\partial h}{\partial s}\,ds + \frac{\partial h}{\partial p}\,dp \\ \text{but } dh &= T\,ds + v\,dp \end{aligned}\right\} \Rightarrow \frac{\partial h}{\partial s} = T\,; \quad \frac{\partial h}{\partial p} = v$$

$a(T,v)$: $$\left.\begin{aligned} da &= \frac{\partial a}{\partial T}\,dT + \frac{\partial a}{\partial v}\,dv \\ \text{but } da &= -s\,dT - p\,dv \end{aligned}\right\} \Rightarrow \frac{\partial a}{\partial T} = -s\,; \quad \frac{\partial a}{\partial v} = -p$$

$g(T,p)$: $$\left.\begin{aligned} dg &= \frac{\partial g}{\partial T}\,dT + \frac{\partial g}{\partial p}\,dp \\ \text{but } dg &= -s\,dT + v\,dp \end{aligned}\right\} \Rightarrow \frac{\partial g}{\partial T} = -s\,; \quad \frac{\partial g}{\partial p} = v$$