21. Ineguaglianze termodinamiche e concavità di $S(E,V,N)$

- Parete mobile e permeabile al calore, stessa sostanza a destra e sinistra

$N\ V_1$	$N\ V_2$
E_1	E_2

- All'equilibrio ci aspettiamo $V_1 = V_2$, $E_1 = E_2$
- $E_1 + E_2 = 2E \qquad V_1 + V_2 = 2V$; fissati E, V, N!
- $S_t = S_1(E_1, V_1) + S_2(E_2, V_2) = S_1(E_1 V_1) + S_2(2E - E_1, 2V - V_1)$

  $= S_t(E_1 V_1)$
- S_t massima all'equilibrio
- Condizione di estremo

$$\left[\frac{\partial S_t}{\partial E_1}\right]_{E_1^* V_1^*} = 0 = \left[\frac{\partial S_t}{\partial V_1}\right]_{E_1^* V_1^*}$$

$$\frac{\partial S_t}{\partial E_1} = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = \frac{1}{\mathcal{T}_1} - \frac{1}{\mathcal{T}_2} = 0 \Rightarrow \mathcal{T}_1 = \mathcal{T}_2$$

$$\frac{\partial S_t}{\partial V_1} = \frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = -\frac{P_1}{\mathcal{T}_1} + \frac{P_2}{\mathcal{T}_2} = \frac{P_2 - P_1}{\mathcal{T}} \Rightarrow P_1 = P_2$$

$$\Rightarrow E_1^* = E_2^* = E \qquad V_1^* = V_2^* = V$$

②

– Condizione di massimo (necessaria)

$$\frac{\partial^2 S_t}{\partial E_1^2} \leq 0 \qquad \frac{\partial^2 S_t}{\partial E_1^2}\frac{\partial^2 S_t}{\partial V_1^2} - \frac{\partial^2 S_t}{\partial E_1 \partial V_1} \geq 0$$

(a) (b)

per $E_1 = E_2 = E$, $V_1 = V_2 = V$

(a)

$$\frac{\partial^2 S_t}{\partial E_1^2} = \frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2} = \frac{\partial}{\partial E_1}\left(\frac{1}{T_1}\right) + \frac{\partial}{\partial E_2}\left(\frac{1}{T_2}\right)$$

$$= -\frac{1}{T_1^2}\left.\frac{\partial T_1}{\partial E_1}\right|_V - \frac{1}{T_2^2}\left.\frac{\partial T_2}{\partial E_2}\right|_V$$

$$= -\frac{1}{T_1^2 C_{V_1}} - \frac{1}{T_2^2 C_{V_2}} = -\frac{2}{T^2 C_V} = 2\frac{\partial^2 S}{\partial E^2}$$

$$\Rightarrow \quad \frac{1}{C_V} \geq 0$$

(b) il calcolo è alquanto più complicato e viene delineato nelle pagine seguenti

(b1)

$$\frac{\partial^2 S_E}{\partial V_1^2} = \frac{\partial^2 S_1}{\partial V_1^2} + \frac{\partial^2 S_2}{\partial V_2^2} = \frac{\partial}{\partial V_1}\left(\frac{P_1}{T_1}\right)\Big|_E + \frac{\partial}{\partial V_2}\left(\frac{P_2}{T_2}\right)\Big|_E$$

$$= 2\left[\frac{\partial}{\partial V}\left(\frac{P}{T}\right)\right]_{E=\text{const}}$$

$$\frac{\partial(P/T)}{\partial V}\Big|_E = \frac{\partial(P/T, E)}{\partial(V, E)} = \frac{\partial(P/T, E)}{\partial(V, T)}\,\frac{\partial(V, T)}{\partial(V, E)}$$

$$= \frac{\dfrac{\partial(P/T, E)}{\partial(V, T)}}{\dfrac{\partial(V, E)}{\partial(V, T)}} =$$

$$= \det\begin{pmatrix} \frac{1}{T}\frac{\partial P}{\partial V}\Big|_T & \frac{\partial}{\partial T}\left(\frac{P}{T}\right)\Big|_V \\ \frac{\partial E}{\partial V}\Big|_T & \frac{\partial E}{\partial T}\Big|_V \end{pmatrix} \Bigg/ \det\begin{pmatrix} 1 & 0 \\ \frac{\partial E}{\partial V}\Big|_T & \frac{\partial E}{\partial T}\Big|_V \end{pmatrix}$$

$$\frac{\partial E}{\partial T}\Big|_V = C_V$$

$$\frac{\partial}{\partial T}\left(\frac{P}{T}\right) = -\frac{P}{T^2} + \frac{1}{T}\frac{\partial P}{\partial T}\Big|_V$$

④

$$\left.\frac{\partial E}{\partial V}\right|_{\mathcal{T}} = \frac{\partial}{\partial V}(A+\mathcal{T}S) = \frac{\partial}{\partial V}\left(A - \mathcal{T}\frac{\partial S}{\partial \mathcal{T}}\right)$$

$$= \frac{\partial}{\partial V}\left(A + \beta\frac{\partial A}{\partial \beta}\right) =$$

$$= \frac{\partial}{\partial V}\frac{\partial}{\partial \beta}(\beta A) = \frac{\partial}{\partial \beta}\left(\frac{\partial}{\partial V}(\beta A)\right)$$

$$= \frac{\partial}{\partial \beta}(-\beta P) = -P - \beta\frac{\partial P}{\partial \beta}$$

$$= -P + \mathcal{T}\left.\frac{\partial P}{\partial \mathcal{T}}\right|_{V}$$

Infine

(b1) $$\left.\frac{\partial (P/\mathcal{T})}{\partial V}\right|_{E} = \left[C_V \cdot \frac{1}{\mathcal{T}}\left.\frac{\partial P}{\partial V}\right|_{\mathcal{T}} - \frac{1}{\mathcal{T}^2}\left(P - \mathcal{T}\left.\frac{\partial P}{\partial \mathcal{T}}\right|_{V}\right)^2\right]\frac{1}{C_V}$$

$$= -\frac{1}{\mathcal{T}VK_{\mathcal{T}}} - \frac{1}{\mathcal{T}^2 C_V}\left(P - \mathcal{T}\left.\frac{\partial P}{\partial \mathcal{T}}\right|_{V}\right)^2 =$$

$$\boxed{= \frac{1}{2}\frac{\partial^2 S_E}{\partial V_1^2} = \frac{\partial^2 S}{\partial V^2}}$$

Calcoliamo ora

(b2) $$\frac{\partial^2 S}{\partial E\,\partial V} = \left.\frac{\partial}{\partial E}\left(\frac{P}{\mathcal{T}}\right)\right|_{V} = \frac{\partial(P/\mathcal{T}, V)}{\partial(E, V)}$$

$$= \frac{\partial(P/\mathcal{T}, V)}{\partial(\mathcal{T}, V)}\frac{\partial(\mathcal{T}, V)}{\partial(E, V)}$$

$$= \det\begin{pmatrix} \frac{\partial (P/T)}{\partial T}\Big|_V & \frac{\partial (P/T)}{\partial V}\Big|_T \\ 0 & 1 \end{pmatrix} \Big/ \det\begin{pmatrix} \frac{\partial E}{\partial T}\Big|_V & \frac{\partial E}{\partial V}\Big|_E \\ 0 & 1 \end{pmatrix}$$

$$= \left(-\frac{1}{T^2}P + \frac{1}{T}\frac{\partial P}{\partial T}\Big|_V\right)\Big/C_V \qquad = \frac{1}{2}\frac{\partial^2 S_t}{\partial E \partial V}$$

- Combinando (a), (b1) e (b2) otteniamo

$$\frac{\partial^2 S}{\partial E^2}\frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial E \partial V}\right)^2 =$$

$$= -\frac{1}{T^2 C_V}\left[-\left(\frac{1}{TV\kappa_T} + \frac{1}{T^2 C_V}\left(P - T\frac{\partial P}{\partial T}\Big|_V\right)^2\right)\right]$$

$$- \left[-\frac{1}{T^2}\left(P - T\frac{\partial P}{\partial T}\Big|_V\right)\frac{1}{C_V}\right]^2$$

$$= \frac{1}{T^3 V C_V}\frac{1}{\kappa_T} + \frac{1}{T^4 C_V^2}\left(P - T\frac{\partial P}{\partial T}\Big|_V\right)^2$$

$$- \frac{1}{T^4 C_V^2}\left(P - T\frac{\partial P}{\partial T}\Big|_V\right)^2$$

$$= \frac{1}{T^3 V C_V}\frac{1}{\kappa_T} \geq 0 \Rightarrow \frac{1}{\kappa_T} \geq 0$$

Q.E.D.