

# Θερμοδυναμική μέθοδος – Σχέσεις Maxwell

$$TdS = dU + p dV \rightarrow dU = TdS - pdV \rightarrow \left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial p}{\partial S} \right|_V$$

$$H = U + pV \rightarrow dH = dU + Vdp + p dV$$

$$dU = TdS - pdV \rightarrow dH = TdS + Vdp \rightarrow \left. \frac{\partial T}{\partial p} \right|_S = \left. \frac{\partial V}{\partial S} \right|_p$$

$$F = U - TS \rightarrow dF = dU - TdS - SdT$$

$$dU = TdS - pdV \rightarrow dF = -pdV - SdT \rightarrow \left. \frac{\partial p}{\partial T} \right|_V = \left. \frac{\partial S}{\partial V} \right|_T$$

$$G = U - TS + pV \rightarrow dG = dU - TdS - SdT + pdV + Vdp$$

$$dU = TdS - pdV \rightarrow dG = Vdp - SdT \rightarrow \left. \frac{\partial V}{\partial T} \right|_p = - \left. \frac{\partial S}{\partial p} \right|_T$$

# Θερμοδυναμικές εξισώσεις καταστάσεως

$$dU = T dS - p dV \rightarrow \left. \frac{\partial U}{\partial V} \right|_T = T \left. \frac{\partial S}{\partial V} \right|_T - p$$

όμως  $\left. \frac{\partial p}{\partial T} \right|_V = \left. \frac{\partial S}{\partial V} \right|_T$  επομένως  $\left. \frac{\partial U}{\partial V} \right|_T = T \left. \frac{\partial p}{\partial T} \right|_V - p$

$$dH = T dS + V dp \rightarrow \left. \frac{\partial H}{\partial p} \right|_T = T \left. \frac{\partial S}{\partial p} \right|_T + V$$

όμως  $\left. \frac{\partial S}{\partial p} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_p$  επομένως  $\left. \frac{\partial H}{\partial p} \right|_T = V - T \left. \frac{\partial V}{\partial T} \right|_p$

# Ελαστική ράβδος

$$\sigma = \frac{df}{A}, \varepsilon = \frac{dl}{l}, \text{ μέτρο του Young } \Upsilon = \frac{\sigma}{\varepsilon},$$

$$\frac{df}{dl} = \frac{A \Upsilon}{l} \quad \left( \frac{\partial f}{\partial l} \Big|_T = \frac{A \Upsilon}{l} \right)$$

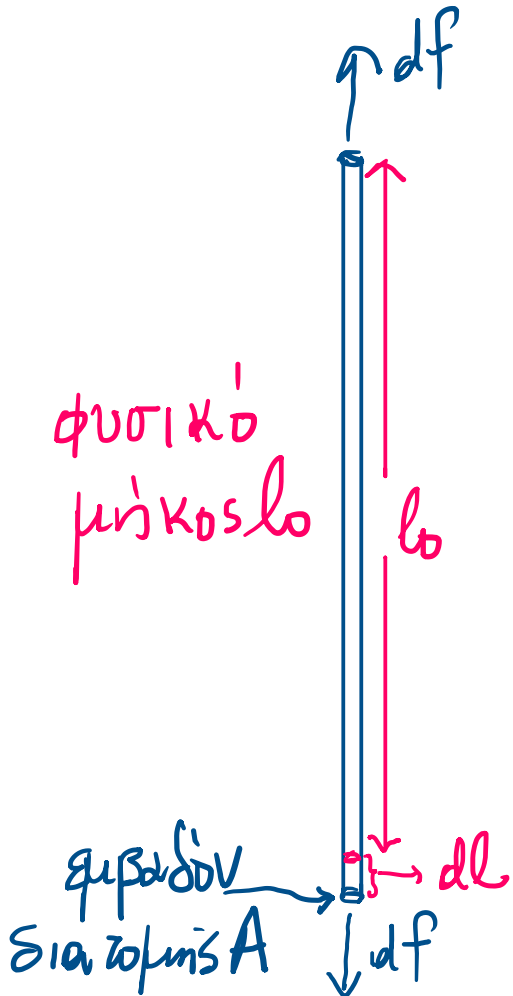
συντελεστής θερμικής διαστολής  $a_f = \frac{1}{l} \frac{\partial l}{\partial T} \Big|_f$

Είναι ένα σύστημα  $(T, f, l)$ , επομένως

$$dl = \frac{\partial l}{\partial T} \Big|_f dT + \frac{\partial l}{\partial f} \Big|_T df$$

Θεωρούμε σταθερό  $l$ , δηλ.  $dl = 0$ ,

$$0 = \frac{\partial l}{\partial T} \Big|_f + \frac{\partial l}{\partial f} \Big|_T \frac{\partial f}{\partial T} \Big|_l \quad \text{άρα} \quad \frac{\partial f}{\partial T} \Big|_l = - \frac{\partial l}{\partial T} \Big|_f \frac{\partial f}{\partial l} \Big|_T = -A \Upsilon a_f$$



# Ελαστική ράβδος ( $T, f, l$ )

Έχουμε  $dU = TdS + fdl$  και ορίζοντας  
 $F = U - TS$

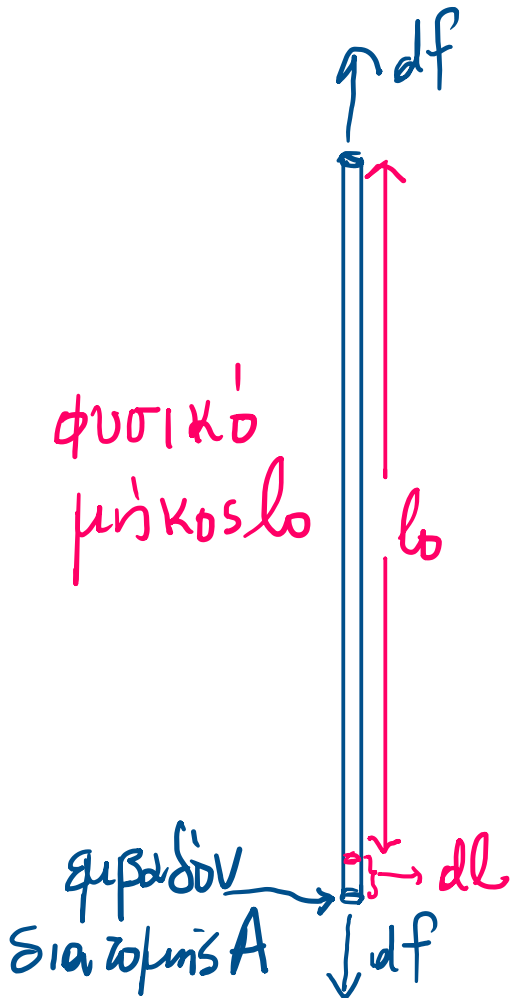
$$dF = -S dT + f dl$$

άρα έχουμε τη σχέση

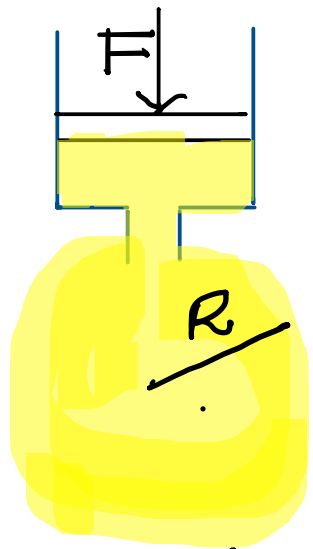
$$\left. \frac{\partial S}{\partial l} \right|_T = - \left. \frac{\partial f}{\partial T} \right|_l$$

και αφού

$$\left. \frac{\partial f}{\partial T} \right|_l = -A\gamma a_f \text{ έχουμε } \left. \frac{\partial S}{\partial l} \right|_T = A\gamma a_f$$

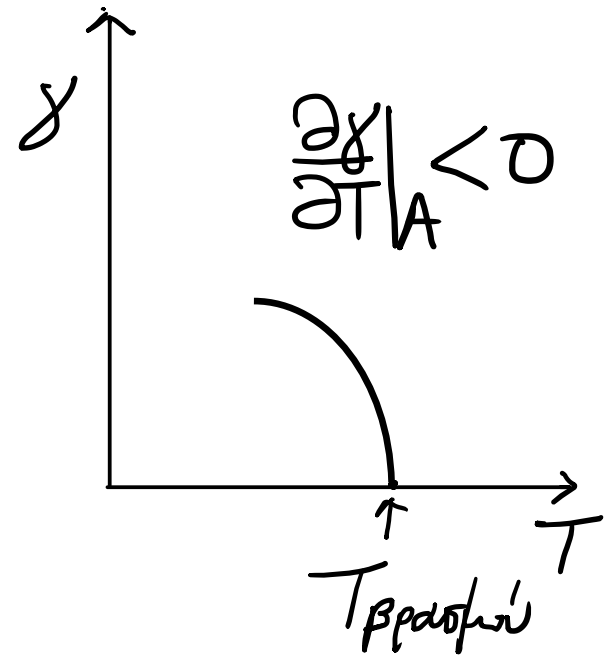


# Επιφανειακή τάση ( $T, \gamma, A$ )



$$dU = TdS + \gamma dA, F = U - TS, dF = -SdT + \gamma dA$$

$$\left. \frac{\partial S}{\partial A} \right|_T = - \left. \frac{\partial \gamma}{\partial T} \right|_A$$



$$\delta W = \gamma dA$$

$$\delta W = p dV$$

$$dA = d(4\pi R^2) \Rightarrow$$

$$dA = 8\pi R dR$$

$$\gamma dA = p dV$$

$$dV = d\left(\frac{4}{3}\pi R^3\right)$$

$$dV = 4\pi R^2 dR$$

$$p = \frac{2\gamma}{R}$$

$$\left. \frac{\partial U}{\partial A} \right|_T = T \left. \frac{\partial S}{\partial A} \right|_T + \gamma$$

$$\left. \frac{\partial U}{\partial A} \right|_T = \gamma - T \left. \frac{\partial \gamma}{\partial T} \right|_A$$

$$\chi = \lim_{H \rightarrow 0} \frac{M}{H}$$

$$m = M \cdot V$$

για παραμαγνητικές  $\chi \ll 1$

επομένως

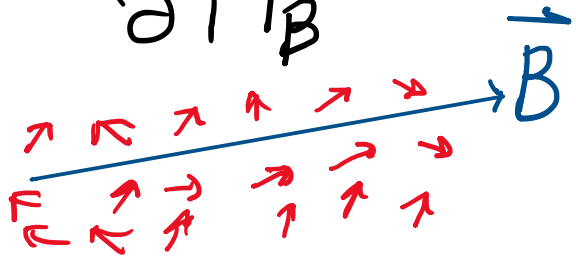
$$B = \mu_0 (H + M) \approx \mu_0 H$$

$$\chi \approx \frac{\mu_0 M}{B}$$

Νόμος Curie  $\chi \propto \frac{1}{T}$



$$\left. \frac{\partial \chi}{\partial T} \right|_B < 0$$



# Παραμαγνητισμός (T, m, B)

$$dU = T dS - m dB,$$

$$F = U - TS, dF = -S dT - m dB$$

$$\left. \frac{\partial S}{\partial B} \right|_T = \left. \frac{\partial m}{\partial T} \right|_B \approx \frac{VB}{\mu_0} \left. \frac{\partial \chi}{\partial T} \right|_B < 0$$

$$dS = \left. \frac{\partial S}{\partial T} \right|_B dT + \left. \frac{\partial S}{\partial B} \right|_T dB$$

Θεωρούμε σταθερό S, δηλ.  $dS = 0$ ,

$$0 = \left. \frac{\partial S}{\partial T} \right|_B + \left. \frac{\partial S}{\partial B} \right|_T \left. \frac{\partial B}{\partial T} \right|_S \text{ άρα } \left. \frac{\partial B}{\partial T} \right|_S = - \left. \frac{\partial S}{\partial T} \right|_B \left. \frac{\partial B}{\partial S} \right|_T$$

$$\text{Ορίζοντας } C_B = T \left. \frac{\partial S}{\partial T} \right|_B \text{ έχουμε } \left. \frac{\partial B}{\partial T} \right|_S = - \frac{C_B \mu_0}{TVB} \left. \frac{\partial T}{\partial \chi} \right|_B$$