

Energia interna

$U \rightarrow$ variabili di stato : T, P, V, N, \dots

\nearrow empiriche, fenomenologiche : g.p. legge di Joule

\searrow microscopico \rightarrow fisica statistica

$$U = U(T)$$

I pr: $dE_c + dU = 0$ isolato

$d(E_c + U) = 0$ -//-

def.: $dE_c + dU = \delta W + \delta Q$


$dU = \delta W + \delta Q$

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Teor. di equipartizione dell'energia : equilibrio

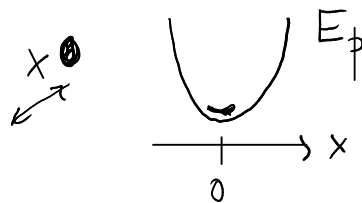
Ogni termine di energia elementare e quadratico dà un contributo $\frac{1}{2} k_B T$ all'energia interna

1) g.p. 2d una particella $E = E_c + E_p = \frac{1}{2} m |\vec{v}|^2 = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 \rightarrow U = N \cdot 2 \cdot \frac{1}{2} k_B T$

 3d -//- $E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \rightarrow U = N \cdot 3 \cdot \frac{1}{2} k_B T$

$\rightarrow U = \frac{3}{2} N k_B T = \frac{3}{2} n R T \rightarrow U = U(T)$ monoatomic \rightarrow He, Ar, Xe

2) solido armonico: una particella $E = E_c + E_p$ \hookrightarrow  g.p. dia: $U = \frac{5}{2} N k_B T$

 3d: $E = \underbrace{\frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2}_{E_c} + \underbrace{\frac{1}{2} k x^2 + \frac{1}{2} k y^2 + \frac{1}{2} k z^2}_{E_p} \rightarrow U = N \cdot 6 \cdot \frac{1}{2} k_B T$
 $U = 3 N k_B T$

U funzione di stato $\rightarrow dU$ diff. esatto

$$dU = \delta W + \delta Q$$

$$dU = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV \quad \text{diff. totale}$$

$$\delta Q = dU - \underbrace{\delta W}_{QS \rightarrow -PdV} = \left. \frac{\partial U}{\partial T} \right|_V dT + \left. \frac{\partial U}{\partial V} \right|_T dV + PdV = \left. \frac{\partial U}{\partial T} \right|_V dT + \left(\left. \frac{\partial U}{\partial V} \right|_T + P \right) dV$$

$V = \text{cost}$ ($dV=0$) : $C_V = \left. \frac{\partial U}{\partial T} \right|_V$

$$d(PV) = \left. \frac{\partial(PV)}{\partial P} \right|_V dP + \left. \frac{\partial(PV)}{\partial V} \right|_P dV = VdP + PdV \rightarrow PdV = d(PV) - VdP$$

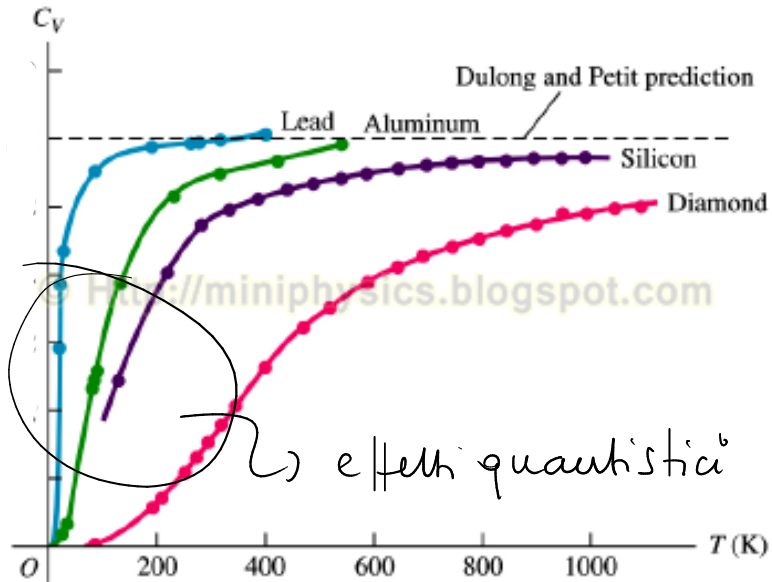
$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \quad f(x,y) = xy \quad C_P dT \quad (P = \text{cost})$$

$$\delta Q = dU + PdV = dU + d(PV) - VdP = d(U + PV) - VdP$$

$P = \text{cost}$ ($dP=0$) : definisco $H \equiv U + PV$ funzione stato ENTALPIA $\rightarrow C_P = \left. \frac{\partial H}{\partial T} \right|_P$

g.p. mono: $U = \frac{3}{2} Nk_B T \rightarrow C_V = \frac{3}{2} Nk_B \rightarrow C_V^{(m)} = \frac{3}{2} R$ g.p. dia: $C_V^{(m)} = \frac{5}{2} R$

solido armonico: $U = 3 Nk_B T \rightarrow C_V = 3 Nk_B \rightarrow C_V^{(m)} = 3 R$



Legge di DULONG e PETIT

$$C_V^{(cm)} \approx 25 \frac{J}{K mol}$$

Modello:

$$C_V^{(cm)} = 3R = 3 \times 8,314 \frac{J}{K mol} \approx 25 \frac{J}{K mol}$$

Solidi, liquidi: \approx incompressibili $C_V \approx C_P$

Gas: dipende molto $V = cost$ o $P = cost$

$$C_P = \left. \frac{dH}{dT} \right|_P = \dots = C_V + \underline{\underline{nR}}$$

↑
es. i g.p.

relazione di Meyer

$$\boxed{C_P - C_V = nR}$$

Parametro $\gamma \equiv \frac{C_P}{C_V}$

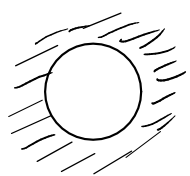
g.p. mono: $\gamma = \frac{5}{2} \cdot \frac{2}{3}$

$= \frac{5}{3} \approx 1,6$

g.p. dia: $\gamma = \frac{7}{5} = 1,4$

Trasformazioni adiabatiche

$\delta Q = 0$ nessun scambio di calore con l'ambiente



$dT \neq 0$

$$\delta Q = 0$$



$$dU = \delta W$$

$$P = \frac{nRT}{V}$$

$$C_v dT = -P dV \quad (QS)$$

$$C_v dT = -nRT \frac{dV}{V}$$

- 1) g.p.
- 2) adiabatica
- 3) QS

Separazione delle variabili

$$\frac{dT}{T} = - \frac{nR}{C_v} \frac{dV}{V}$$

$$\int_{T_i}^{T_f} \frac{dT}{T} = - \frac{nR}{C_v} \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\rightarrow \ln\left(\frac{T_f}{T_i}\right) = - \frac{nR}{C_v} \ln\left(\frac{V_f}{V_i}\right) = \ln\left[\left(\frac{V_f}{V_i}\right)^{1-\gamma}\right]$$

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$\rightarrow \underline{TV^{\gamma-1} = \text{cost}}$$

$$\rightarrow PV V^{\gamma-1} = \text{cost} \Rightarrow \underline{PV^\gamma = \text{cost}}$$

	W	ΔU	Q
T = cost	v		
P = cost	v		
V = cost	v		

$$U = C_v T$$

$$dU = C_v dT \quad \text{g.p.}$$

$$U = \underbrace{\frac{3}{2} N k_B T}_{C_v} \quad \text{monow}$$

$$\frac{C_p - C_v}{C_v} = \gamma - 1$$

$$T \sim PV$$

es. P, T

