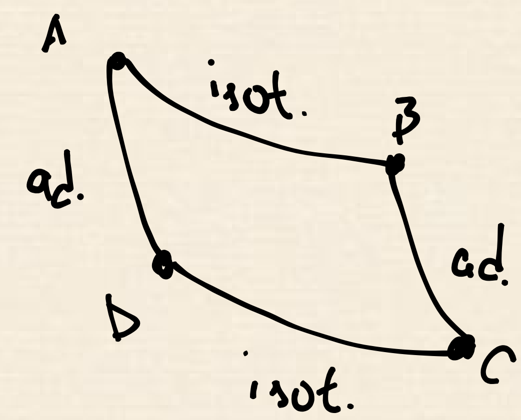
GABARITO DA PROVA
DE TERMODINÂMICA E MEC. ESTATÍSTICA
PROF. RONALDO BATISTA

① $PV = Nk_BT$, $U = \frac{3}{2}Nk_BT = \frac{3}{2}PV$

Ciclo de Carnot:



$(V_A, P_A) \to (V_B, P_B)$ $\quad P_AV_A = Nk_BT_A$

$P_BV_B = Nk_BT_A \Rightarrow P_AV_A = P_BV_B$

$(V_C, P_C) \to (V_D, P_D)$ $\quad P_CV_C = P_DV_D$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

$$dS = \frac{1}{T}\frac{3}{2}Nk_B \cancelto{0}{dT} + \frac{P}{T}dV \Rightarrow dS = \frac{P}{T}dV$$

$$\Delta S_{AB} = \int_A^B \frac{P}{T}dV = \int_{V_A}^{V_B} \frac{1}{T_A}\frac{Nk_BT_A}{V}dV$$

$$\Delta S_{AB} = Nk_B \ln(V_B/V_A)$$

$$\Delta S_{CD} = Nk_B \ln(V_C/V_D)$$

$A \to B$, Isot. $\quad P_A V_A = P_B V_B$

$B \to C$, Ad. $\quad P_B^3 V_B^5 = P_C^3 V_C^5$

$C \to D$, Isot. $\quad P_C V_C = P_D V_D$

$D \to A$, Ad. $\quad P_D^3 V_D^5 = P_A^3 V_A^5$

$\Delta S_{AB} = k_B \ln(V_B/V_A)$

$\Delta S_{CD} = k_B \ln(V_D/V_C)$

Vamos expressar $\dfrac{V_D}{V_C}$ em função de $\dfrac{V_B}{V_A}$.

$$\left(\frac{V_D}{V_C}\right)^3 = \left(\frac{P_C}{P_D}\right)^3 = \frac{P_B^3 V_B^5}{V_C^5} \cdot \frac{V_D^5}{P_A^3 V_A^5} = \frac{P_B^3}{P_A^3} \frac{V_D^5}{V_C^5} \frac{V_B^5}{V_A^5} = \left(\frac{V_D}{V_C}\right)^5 \frac{V_A^3}{V_B^3} \frac{V_B^5}{V_A^5}$$

$$\left(\frac{V_D}{V_C}\right)^{-2} = \left(\frac{V_B}{V_A}\right)^2 \Rightarrow \frac{V_D}{V_C} = \left(\frac{V_B}{V_A}\right)^{-1}$$

$$\Delta S_{CD} = k_B \ln(V_D/V_C) = -k_B \ln(V_B/V_A)$$

$$\Delta S_T = \Delta S_{AB} + \Delta S_{CD} = k_B \ln(V_B/V_A) - k_B \ln(V_B/V_A) = 0$$

$$\Delta S_T = 0$$

② Gás ideal monoatômico clássico

Função de partição: $Z = \dfrac{1}{N!}\left(\dfrac{2\pi m}{\beta h^2}\right)^{3N/2} V^N$

A energia livre de Helmholtz é dada por

$$f = -\frac{1}{\beta} \lim_{\substack{N\to\infty \\ V\to\infty \\ V/N = v}} \frac{\ln Z}{N}$$

$$\frac{\ln Z}{N} = \frac{1}{N}\left[-\ln N! + \frac{3N}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) + N\ln V\right]$$

$$= \frac{1}{N}\left[-N\ln N + N + \frac{3}{2}N\ln\left(\frac{2\pi m}{\beta h^2}\right) + N\ln V\right] = \ln\left(V/N\right) + 1 + \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right)$$

$$f = -\frac{1}{\beta}\left[\ln v + 1 + \frac{3}{2}\left(\frac{2\pi m}{\beta h^2}\right)\right].$$ Queremos $c_v = \left(\dfrac{\partial u}{\partial T}\right)_v = T\left(\dfrac{\partial s}{\partial T}\right)_v$

$$f = u - Ts, \quad df = du - Tds - s\,dT = \cancel{Tds} - p\,dv - \cancel{Tds} - s\,dT$$

$$df = -p\,dv - s\,dT, \quad s = -\left(\frac{\partial f}{\partial T}\right)_v, \quad p = \left(\frac{\partial f}{\partial v}\right)_T$$

$$s = \frac{\partial}{\partial T}\left\{k_B T\left[\ln v + 1 + \frac{3}{2}\ln\left(\frac{2\pi m\, k_B T}{h^2}\right)\right]\right\}$$

$$s = k_B\left[\ln v + 1 + \frac{3}{2}\ln\left(\frac{2\pi m\, k_B T}{h^2}\right)\right] + k_B \cancel{T}\left[\frac{\cancel{h^2}}{\cancel{2\pi m}\, \cancel{k_B T}}\;\frac{\cancel{2\pi m}\, k_B}{\cancel{h^2}}\right]$$

$$s = k_B\left[\ln v + 1 + \frac{3}{2}\ln\left(\frac{2\pi m\, k_B T}{h^2}\right)\right] + k_B$$

$$s = 2k_B + k_B \ln v + \frac{3k_B}{2} \ln\left(\frac{2\pi m k_B T}{h^2}\right)$$

$$c_v = T\frac{\partial s}{\partial T} = k_B T \cdot \frac{3}{2} \frac{\cancel{h^2}}{\cancel{2\pi m k_B T}} \frac{\cancel{2\pi m k_B}}{\cancel{h^2}}$$

$$\boxed{c_v = \frac{3}{2} k_B}$$

Para eq. de estado: $-p = \left(\frac{\partial f}{\partial v}\right)_T$

$$p = k_B T \frac{1}{v} \Rightarrow \boxed{pv = k_B T}$$

(3) Sistema com níveis $E \in \{0, \varepsilon, 2\varepsilon\}$.

$$\mathcal{H} = \sum_{i=1}^{N} t_i \varepsilon, \quad t_i \in \{0,1,2\} \quad Z = \sum_{\{t_i\}} \exp(-\beta \mathcal{H})$$

$$Z = \sum_{\{t_i\}} \exp[-\beta\varepsilon(t_1 + t_2 + \cdots t_N)] = [\exp(0) + \exp(-\beta\varepsilon) + \exp(-2\beta\varepsilon)]^N$$

$$Z = \left[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}\right]^N$$

$$f = -\frac{1}{\beta} \lim_{N\to\infty} \frac{1}{N} \ln Z = -\frac{1}{\beta} \ln\left(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}\right)$$

$$f(T) = -k_B T \ln\left[1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}\right]$$

(b) $$s = -\frac{\partial f}{\partial T} = k_B \ln\left[1 + e^{-\varepsilon/k_BT} + e^{-2\varepsilon/k_BT}\right] + k_BT \frac{\left[\frac{\varepsilon}{k_BT^2} e^{-\varepsilon/k_BT} + \frac{2\varepsilon}{k_BT^2} e^{-2\varepsilon/k_BT}\right]}{1 + e^{-\varepsilon/k_BT} + e^{-2\varepsilon/k_BT}}$$

$$s = k_B \ln\left[1 + \exp\left(-\frac{\varepsilon}{k_BT}\right) + \exp\left(-\frac{2\varepsilon}{k_BT}\right)\right] + \frac{\frac{\varepsilon}{T}\left(e^{-\varepsilon/k_BT} + 2e^{-2\varepsilon/k_BT}\right)}{1 + \exp\left(-\frac{\varepsilon}{k_BT}\right) + \exp\left(-\frac{2\varepsilon}{k_BT}\right)}$$

(c) limite $\varepsilon \to \infty$, $\lim_{\varepsilon \to \infty} \exp\left(-\frac{\varepsilon}{k_BT}\right) = 0$

$$s = k_B \ln(1) + \frac{1}{T} \lim_{x \to \infty} k_BT \underbrace{\frac{x\left(e^{-x} + e^{-2x}\right)}{1 + e^{-x} + e^{-2x}}}_{\propto\, x e^{-2x} \to 0}, \quad x = \frac{\varepsilon}{k_BT}$$

$$s = k_B \ln(1) = 0$$

Para $\varepsilon \to \infty$, $s \to 0$

Se $\varepsilon \to \infty$, o sistema só pode acessar o estado de energia zero, logo, com apenas um estado acessível, temos $s = k_B \ln(1) = 0$.

O estado com $\varepsilon \to \infty$ é, de fato, impossível pois sua probabilidade é

$$P = \lim_{\varepsilon \to \infty} \frac{\exp(-\beta\varepsilon)}{Z} = 0$$