Ideal Gas:

2D

$$Z_1 = \int \frac{d^2r\, d^2p}{h^2} e^{-p^2/2mT}$$

$$\boxed{Z_1 = \frac{A}{\lambda_{th}^2}} \qquad \frac{1}{\lambda_{th}^2} \equiv 2\pi \frac{m k_B T}{h^2}$$

1D

$$Z_1 = \int \frac{dr\, dp}{h} e^{-p^2/2mT}$$

$$\boxed{Z_1 = \frac{L}{\lambda_{th}}} \qquad \frac{1}{\lambda_{th}} \equiv \frac{\sqrt{2\pi m k_B T}}{h}$$

So $\quad Z_1 \equiv L^d / \lambda_{th}^d$

$$Z_{TOT} = \frac{1}{N!} Z_1^N \simeq \left(\frac{e Z_1}{N}\right)^N$$

So

$$F = -kT \ln Z_{TOT} = -kTN \left[\ln \frac{Z_1}{N} + 1 \right]$$

$$= -kTN \left[-\ln (N/Z_1) + 1 \right]$$

So

$$\boxed{F = -kTN\left[-\ln(n\lambda_{th}^{d}) + 1\right]}$$

where $d = 1, 2, 3$ for dimensions 1, 2, 3

$$S = -\frac{\partial F}{\partial T}$$

Now $\lambda_{th} = \dfrac{h}{\sqrt{2\pi m k T}} = c\,T^{-1/2}$. Then

$$S = Nk\left[-\ln(n\lambda_{th}^{d}) + 1\right] + NkT\frac{\partial}{\partial T}\left(-\ln n\lambda_{th}^{d}\right)$$

Now

$$\ln n\lambda_{th}^{d} = \ln(T^{-d/2}) + \text{const} \qquad \frac{\partial}{\partial T}\ln n\lambda_{th}^{d} = \frac{-d}{2T}$$

So

$$\boxed{S = Nk\left[-\ln(n\lambda_{th}^{d}) + 1\right] + \frac{NkT\,d}{2T}}$$

or

$$S = Nk\left[-\ln(n\lambda_{th}^{d}) + \frac{d+2}{2}\right] \quad \text{with } d = 1, 2, 3$$

The Energy

$$F = E - TS \qquad E = F + TS$$

So

$$E = -kTN\left[-\ln(n\lambda^d) + 1\right] + TNk\left[-\ln(n\lambda_{th}^d) + \frac{d+2}{2}\right]$$

$$\boxed{E = NkT\frac{d}{2}}$$

So finally we need the pressure

$$F = -kTN\left[-\ln\left(\frac{N}{V_d}\lambda_{th}^d\right) + 1\right]$$

Where $V_d = L, A, V = L^d$ in d-dimensions

$$p = -\left(\frac{\partial F}{\partial V_d}\right)_T = kTN\frac{\partial}{\partial V_d}\left(\ln V_d + \text{const}\right)$$

$$\boxed{p = \frac{kTN}{V_d}}$$

Degeneracy

$$Z_{TOT} = \frac{Z_1^N}{N!} \simeq \left(\frac{eZ_1}{N}\right)^N$$

where

$$Z_1 = Z_{trans} Z_{atom}$$

So

$$E = -\frac{\partial}{\partial\beta} \log Z_{TOT}$$

$$= N\left[-\frac{\partial}{\partial\beta}\left(\log\left(\frac{eZ_{trans}}{N}\right) + \log Z_{atom}\right]$$

Where

$$Z_{trans} = \int \frac{d^3r\, d^3p}{h^3} e^{-p^2/2mkT} = \frac{V}{\lambda_{th}^3} = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$Z_{atom} = \sum e^{-\varepsilon_{int}/kT} = g_1 + g_2 e^{-\beta\Delta}$$

So

internal energy

$$E = N(\varepsilon_{trans} + \varepsilon_{atom})$$

$$\varepsilon_{trans} = -\frac{\partial}{\partial\beta} \ln Z_{trans} = -\frac{\partial}{\partial\beta} \ln \beta^{-3/2} = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2}kT \checkmark$$

Similarly

$$\mathcal{E}_{atom} = -\frac{\partial}{\partial\beta} \ln Z_{atom} = \frac{g_2 \Delta e^{-\beta\Delta}}{g_1 + g_2 e^{-\beta\Delta}}$$

Finally we need to compute C_V.
We use

$$\left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial E}{\partial\beta}\frac{\partial\beta}{\partial T} = -k\beta^2\left(\frac{\partial E}{\partial\beta}\right)_V$$

So

$$C_V = \frac{\partial}{\partial T}\left(\frac{3}{2}NkT + \frac{N g_2 \Delta e^{-\beta\Delta}}{(g_1 + g_2 e^{-\beta\Delta})}\right)$$

$$= \frac{3}{2}Nk + -k\beta^2 \frac{\partial}{\partial\beta}\frac{\Delta N g_2 e^{-\beta\Delta}}{(g_1 + g_2 e^{-\beta\Delta})}$$

$$= \frac{3}{2}Nk - k\beta^2 \frac{\partial}{\partial\beta}\frac{\Delta N g_2}{g_1 e^{\beta\Delta} + g_2}$$

$$= \frac{3}{2}Nk + Nk\Delta \frac{g_2 \beta^2 g_1 e^{\beta\Delta}\Delta}{(g_1 e^{\beta\Delta} + g_2)^2}$$

$$\boxed{C_V = Nk\left[\frac{3}{2} + \frac{g_1 g_2 (\beta\Delta)^2 e^{\beta\Delta}}{(g_1 e^{\beta\Delta} + g_2)^2}\right]}$$

Problem 2.6

$$Z_1 = \sum_{\substack{int \\ states}} \int \frac{d^3r\, d^3p}{h^2} e^{-(p^2/2m + \varepsilon_{int})/k_B T}$$

- The internal energy levels of Hydrogen are labelled by the quantum numbers

$$n, l, m$$

- With only n determining the internal energy

$$\varepsilon_{int}^{nlm} = -\frac{R}{n^2} \qquad R = 13.6\ eV$$

and $n = 1, 2, \ldots \infty$

$$Z_1 = \underbrace{\int \frac{d^3r\, d^3p}{h^3} e^{-p^2/2mkT}}_{Z\ trans} \cdot \sum_{nlm} e^{-\varepsilon_{in}/k_B T}$$

- In the sum over nlm, lets just keep $n=1$ $l=0$, $m=0$, i.e. the ground state

$$Z_1 = Z_{trans} \cdot \left(e^{-(-R/1^2)kT} + \text{higher states} \right)$$

$$Z_1 \simeq Z_{trans}\, e^{R/kT}$$

Finally evaluating

$$Z_{trans} = \int \frac{V d^3p}{h^3} e^{-p^2/2mkT} = V \frac{1}{\lambda_{th}^3}$$

So

$$\boxed{Z_1 = \frac{V}{\lambda_{th}^3} e^{\beta R}}$$