F'98 # 6. Stat. Mech.

Here are the equations of states for an ideal gas:

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

where P is the pressure of the gas, N is the number of particles, T is the temperature, U is the internal energy, and k_B is Boltzmann's constant. Derive the Helmholtz free energy, $F(N,V,T)$, of the ideal gas. From this quantity, find the entropy as a function of temperature, number of particles, and volume.

See Reif pgs. 238-245 and p.50 for h_o definition

$$Z_1 = \frac{1}{h_o^3}\int_V\int_{-\infty}^{\infty} e^{-\beta E}\, d\tau\, d^3p \quad \text{now } E = \frac{\vec{p}^2}{2m} \text{ for an ideal gas}$$

$$= \frac{1}{h_o^3}\underbrace{\int d\tau}_{=V}\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}\vec{p}^2} d^3p = \frac{V}{h_o^3}\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}\vec{p}^2} d^3p$$

now $\vec{p}^2 = \vec{p}_x^2 + \vec{p}_y^2 + \vec{p}_z^2$, so $\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}\vec{p}^2} d^3p = \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}\vec{p}_x^2} dp_x \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}\vec{p}_y^2} dp_y \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}\vec{p}_z^2} dp_z$

we are dealing with an integral of the form $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$

so $\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}\vec{p}_x^2} dp_x = 2\int_0^{\infty} e^{-\frac{\beta}{2m}\vec{p}_x^2} dp_x = \cancel{2}\cancel{\frac{1}{2}}\sqrt{\frac{\pi}{\beta/2m}} = \sqrt{\frac{2\pi m}{\beta}} = \sqrt{2\pi mkT}$

hence $\int_{-\infty}^{\infty} e^{-\beta\frac{\vec{p}^2}{2m}} = (2\pi mkT)^{3/2}$

thermal de Broglie (similar to it actually as $h_o \to h$) classical quantum

and then $Z_1 = V\frac{(2\pi mkT)^{3/2}}{h_o^3} = \frac{V}{\lambda_{th}^3}$; $\lambda_{th} = \frac{h_o}{\sqrt{2\pi mkT}}$

so $Z = \frac{Z_1^N}{N!}$

Sterling's Approx.

$\ln N! = N \ln N - N$

$\Downarrow$

now $E = -kT \ln Z = -kT \ln \frac{Z_1^N}{N!} = -kT\left[N \ln \underbrace{Z_1}_{\frac{V}{\lambda_{th}^3}} - \ln N!\right]$

$= -NkT\left[\ln V/\lambda_{th}^3 - \ln N + 1\right] = -NkT\left[\ln V - \ln N - 3 \ln \lambda_{th} + 1\right]$

$$\boxed{= -NkT\left[\ln V/N - \frac{3}{2} \ln \frac{h_0^2}{2\pi m kT} + 1\right]}$$

as for S: $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk \frac{\partial}{\partial T} T\left[\ln V/N - \frac{3}{2} \ln \frac{h_0^2}{2\pi m kT} - 1\right]$

$$= Nk\left(\left[\ln V/N - \frac{3}{2} \ln \frac{h_0^2}{2\pi m kT} + 1\right] + T\left[\frac{-3}{2} \frac{1}{\left(\cancel{\frac{h_0^2}{2\pi m kT}}\right)} \frac{-\cancel{h_0^2}}{\cancel{2\pi m k}T^2}\right]\right)$$

$$= Nk\left(\left[\ln V/N - \frac{3}{2} \ln \frac{h_0^2}{2\pi m kT} - 1\right] + T\left[+\frac{3}{2} \frac{1}{T}\right]\right)$$

$$\boxed{= Nk\left[\ln V/N - \frac{3}{2} \ln \frac{h_0^2}{2\pi m kT} + 5/2\right]}$$