

The equations of state for an ideal gas are:

$$PV = NkT \quad ; \quad U = \frac{3}{2} NkT$$

where N is the number of particles. Derive the Helmholtz free energy, $F(N, V, T)$ of the ideal gas. From this quantity, find the entropy as a function of T, N, V .

→ (refer to Reif pgs 238-245)

Start with the partition function of the gas: $Z = \frac{(z_1)^N}{N!}$

where z_1 is the partition function of a single molecule.

$$z_1 = \int \int e^{-\beta E(r, p)} d^3r d^3p$$

for an ideal gas, the energy of a molecule is purely kinetic, so $E = \frac{1}{2m} p^2$, leaving:

$$z_1 = \int \int e^{-\beta \frac{p^2}{2m}} d^3r d^3p$$

Now the integral $\int d^3r$ gives the volume, while the integral $\int d^3p$ can be written as:

$$\int e^{-\beta \frac{p^2}{2m}} d^3p = \int_{-\infty}^{\infty} e^{-\beta \frac{p_x^2}{2m}} dp_x \int_{-\infty}^{\infty} e^{-\beta \frac{p_y^2}{2m}} dp_y \int_{-\infty}^{\infty} e^{-\beta \frac{p_z^2}{2m}} dp_z$$

$$= \sqrt{\frac{\pi 2m}{\beta}} \quad = \sqrt{\frac{\pi 2m}{\beta}} \quad = \sqrt{\frac{\pi 2m}{\beta}}$$

$$\text{So } z_1 = V (2\pi mkT)^{3/2}$$

Note: if one treats phase space as discrete, an extra factor $\frac{1}{h^3}$ appears in the expression for z_1 . In a quantum treatment this factor is $\frac{1}{h^3}$ where h equals Planck's constant.

$$Z = \frac{(z_1)^N}{N!} = \left(\frac{1}{N!} \right) V^N (2\pi mkT)^{3N/2}$$

$$F = -kT \ln Z = -kT \left[N \ln V + \frac{3N}{2} \ln (2\pi mkT) - \ln(N!) \right]$$

now use $\ln(N!) \approx N \ln N - N$ to write:

$$F = -kT \left[N \ln V + \frac{3N}{2} \ln (2\pi mkT) - N \ln N + N \right]$$

$$F = -NkT \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln (2\pi mkT) + 1 \right] \Rightarrow$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N}$$

$$S = Nk \ln \left(\frac{V}{N} \right) + \frac{3Nk}{2} \ln (2\pi m kT) + \frac{\frac{3}{2} NkT (2\pi m kT)^{3/2}}{(2\pi m kT)} + Nk$$

$$S(T, N, V) = Nk \ln \left(\frac{V}{N} \right) + \frac{3Nk}{2} \ln (2\pi m kT) + \frac{5}{2} Nk$$

As a side note, one can verify the equations of state using

$$\bar{p} = \frac{1}{A} \frac{\partial \ln Z}{\partial V} = kT \left(\frac{1}{V} \right) \underbrace{(N V^{N-1}) \left(\frac{1}{N!} (2\pi m kT)^{3/2} \right)}_{= \frac{Z}{V}}$$

$$\bar{p} = \frac{NkT}{V}$$

$$U = \bar{E} = - \frac{1}{\partial B} \ln Z = - \frac{1}{\partial B} \ln \left[\left(\frac{1}{N!} \right) V^N \left(\frac{2\pi m}{B} \right)^{3N/2} \right]$$

$$U = - \frac{1}{Z} \left(\frac{-3N}{2} \right) \underbrace{\left(\frac{3N-1}{2} \right) \left(\frac{1}{N!} \right) V (2\pi m)^{3/2}}_{= Z/B}$$

$$U = \frac{3}{2} \frac{N}{B}$$

$$U = \frac{3}{2} NkT$$