Spring 2001 #14.

$F = -kT \ln Z$ $\qquad Z = \left[\sum_r e^{-\beta E_r}\right]^N$ eq 9.4.4 Reif

$\approx z_1^N$

$F = -kTN \ln\left[\sum_r e^{-\beta E_r}\right]$

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$= -kTN \ln\left[\sum_r e^{-\frac{E_r}{kT}}\right]$

$$z_1 = \sum_r e^{-E_r\beta} = \frac{1}{h_0^3}\int_{-\infty}^{\infty} e^{-\beta\frac{p^2}{2m}}\, d^3p \int_0^L d^3r$$

$$= \frac{V}{h_0^3}\int_{-\infty}^{\infty} e^{-\beta\frac{p^2}{2m}}\, d^3p = \frac{V}{h_0^3}\int e^{-\frac{(\beta p_x^2)}{2m}}\, dp_x \int e^{-\frac{\beta p_y^2}{2m}}\, dp_y \ldots$$

$$= \left(\sqrt{\pi 2m \cancel{kT}}\right)^3 \frac{V}{h_0^3}$$

b)

$$= \frac{V}{h_0^3}(2\pi m kT)^{3/2} \qquad \text{Reif } 7.2.6$$

$$F = -kTN \ln\left[\frac{V}{h_0^3}(2\pi m kT)^{3/2}\right]$$

b) For the electronic motion (excited statese)

$$z_1 = \sum_r e^{-E_r\beta} + \sum_d \Omega_0 e^{\beta E_d} \qquad E_d \text{ is negative.}$$

Reif 9.12.7

degeneracy of ground state.

$\Rightarrow F = -kTN \ln\left[z_1\right] \ldots^{3/2} \sum_d \Omega_0 e^{\beta E_d}$ diverges since you have a positive exponent.

The cut off in a real gas is that the ground state is smaller than the next closest state by a wide energy gap so electrons have an overwhelming probability to be in the ground state