PHY294, Winter 2019, Term Test 2

Possibly Useful Equations:

$$dU = Tds - PdV + \mu dN \qquad S = k\ln(\Omega) \qquad T = \left(\frac{\partial S}{\partial U}\right)_{V,N}^{-1} \qquad F = U - TS \qquad F = -kT\ln Z$$

$$\int_0^\infty (2x+1)e^{-x(x+1)C}dj = 1/C \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \qquad U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \qquad Z = \sum_s e^{-E(s)/kT} \qquad \int_0^\infty x^2 e^{-x^2}dx = \sqrt{\pi}/4$$

For a gas: $Z = \frac{1}{N!}\left(\frac{V}{v_Q}Z_{\text{int}}\right)^N$ where $v_Q = h^3(2\pi m k T)^{-3/2}$

$$P(s) = \frac{e^{-E(s)/kT}}{Z} \qquad \overline{X} = \sum_s X(s)P(s)$$

$\ln(N!) \approx N\ln N - N$ for very large N.

For all of these questions, you need to show your work, but you can assume any equations listed in *Possibly Useful Equations:*

1) [10 points] Imagine a particle that can be in only three states, with energy 0, ε, and 2ε.

a) What is the the partition function for this system.

$$Z=\sum_{s} e^{-E(s)/kT}$$

$$Z=1+e^{-\epsilon/kT}+e^{-2\epsilon/kT}$$

b) What is the probability that the particle will be in each of the three states?

$$P(s)=\frac{e^{-E(s)/kT}}{Z}$$

$$P(E=0)=\frac{1}{Z}$$

$$P(E=0)=\frac{1}{1+e^{-\epsilon/kT}+e^{-2\epsilon/kT}}$$

$$P(E=\epsilon)=\frac{e^{-\epsilon/kT}}{Z}$$

$$P(E=\epsilon)=\frac{e^{-\epsilon/kT}}{1+e^{-\epsilon/kT}+e^{-2\epsilon/kT}}$$

$$P(E=2\epsilon)=\frac{e^{-2\epsilon/kT}}{Z}$$

$$P(E=2\epsilon)=\frac{e^{-2\epsilon/kT}}{1+e^{-\epsilon/kT}+e^{-2\epsilon/kT}}$$

2) [15 points] Consider rotational modes for a gas with rotational energy levels $E(j) = j(j+1)\varepsilon$, and degeneracy $2j+1$.

a) Write down the partition function as a sum.

$$Z=\sum_s e^{-E(s)/kT}$$
$$Z=\sum_{j=0}^{\infty}(2j+1)e^{-j(j+1)\epsilon/kT}$$

b) In the very low temperature limit, when $kT \ll \epsilon$, the sum can be cut off after the second term. In this limit, calculate the energy, U, stored in the rotational modes

$$Z=1+3e^{-2\epsilon/kT}$$
$$Z=1+3e^{-2\epsilon\beta}$$
$$U=-\frac{1}{Z}\frac{\partial Z}{\partial\beta}$$
$$U=\frac{6\epsilon e^{-2\epsilon/kT}}{1+3e^{-2\epsilon/kT}}=\frac{6\epsilon}{e^{2\epsilon/kT}+3}$$

c) In the same limit, calculate the heat capacity, C_v of the rotational modes.

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V$$

$$C_v=\frac{12\epsilon^2 e^{2\epsilon/kT}}{kT^2(e^{2\epsilon/kT}+3)^2}$$

3) [25 points] Consider N molecules of a diatomic gas with these properties:

- Molecular mass m, Temperature T, Volume V
- Rotational energy levels: $E(j) = j(j+1)\varepsilon$, with degeneracy $2j+1$.
- The electronic ground state is not degenerate.

In terms of these variables, and the Boltzmann constant, k, find, using the partition function, the following:

a) Energy, U
b) Heat capacity at constant volume, C_v
c) Helmholtz free Energy, F
d) Pressure, P
e) Chemical Potential, μ

Evaluate any sums in the high temperature limit using integrals. Assume N is very large.

$$Z=\frac{1}{N!}\left(\frac{V}{v_Q}Z_{\text{int}}\right)^N$$

$$Z=\sum_s e^{-E(s)/kT}$$

$$Z_{\text{int}}=\sum_{j=0}^{\infty}(2j+1)e^{-j(j+1)\epsilon/kT}$$

$$Z_{\text{int}}\approx\int_{j=0}^{\infty}(2j+1)e^{-j(j+1)\epsilon/kT}dj \quad \text{when} \quad kT\gg\epsilon$$

From "Possibly Useful Equations", $\int_0^{\infty}(2x+1)e^{-x(x+1)C}dx=1/C$

so $Z_{\text{int}}\approx kT/\epsilon$

$$Z=\frac{1}{N!}\left(\frac{kTV}{\epsilon v_Q}\right)^N \quad \text{where} \quad v_Q=h^3(2\pi mkT)^{-3/2}$$

So $$Z=\frac{1}{N!}\left(\frac{kTV(2\pi mkT)^{3/2}}{\epsilon h^3}\right)^N=\frac{1}{N!}\left(T^{5/2}V\frac{(2\pi m)^{3/2}k^{5/2}}{\epsilon h^3}\right)^N$$

$$\ln Z=N\left(-\frac{5}{2}\ln\beta+\ln V+\ln\left(\frac{(2\pi m)^{3/2}}{\epsilon h^3}\right)-\ln N+1\right) \quad \text{where} \quad \beta=\frac{1}{kT}$$

a) Energy:

$$U=-\frac{\partial\ln Z}{\partial\beta}=\frac{5}{2}NkT$$

b) Heat Capacity

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=\frac{5}{2}Nk$$

c) Helmholtz free Energy, F

$$F=-kT\ln Z=-kTN\left(-\frac{5}{2}\ln\beta+\ln V+\ln\left(\frac{(2\pi m)^{3/2}}{\epsilon h^3}\right)-\ln N+1\right)$$

d) Pressure, P

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

e) Chemical Potential, μ

$$\mu=\left(\frac{\partial F}{\partial N}\right)_{T,V}=-kT\left(\frac{5}{2}\ln(kT)+\ln V+\ln\left(\frac{(2\pi m)^{3/2}}{\epsilon h^3}\right)\right)-\ln N$$

$$\mu=-kT\left(\ln\left(\frac{(kT)^{5/2}(2\pi m)^{3/2}V}{\epsilon N h^3}\right)\right)$$