Problem 1

1) We have

\[ \langle E \rangle_{\text{EFP}} = \frac{1}{2} m \langle U^2 \rangle_{\text{EFP}} \]

\[ \langle E \rangle_{\text{Gas}} = \frac{1}{2} m \langle U^2 \rangle_{\text{Gas}} \]

\[ \langle U^2 \rangle_{\text{Gas}} = \frac{\int_{0}^{\infty} u^2 N(u) du}{\int_{0}^{\infty} N(u) du} = \frac{\int_{0}^{\infty} u^2 e^{-u^2/2kT} du}{\int_{0}^{\infty} u e^{-u^2/2kT} du} \]

\[ = \frac{\frac{2kT}{m} \frac{5}{2}}{\frac{2kT}{m} \frac{3}{2}} \left( \int_{0}^{\infty} x^2 e^{-x^2} dx \right) \]

\[ = \frac{3kT}{m} \]

\[ = \frac{2kT}{m} \frac{\Gamma(1.5)}{\Gamma(8/2)} \]
\[ \langle U^2 \rangle_{\text{eff}} = \frac{\int_0^\infty u^2 O(u) \, du}{\int_0^\infty v O(v) \, dv} = \frac{2kT}{m} \frac{\int_0^\infty x^5 e^{-x^2} \, dx}{\int_0^\infty x e^{-x^2} \, dx} = \frac{2kT}{m} \frac{\Gamma(3)}{\Gamma(2)} = \frac{4kT}{m} \]

\[ \Rightarrow \frac{\langle E^2 \rangle_{\text{eff}}}{\langle E^2 \rangle_{\text{ האמיתי}}} = \frac{\langle U^2 \rangle_{\text{eff}}}{\langle U^2 \rangle_{\text{リアル}}} = \frac{4}{3} \]

\[ \frac{\langle E^2 \rangle_{\text{実際に}}}{} \]

\[ \frac{\langle E^2 \rangle_{\text{リアル}}}{} \]
From geometry, $\theta_{\text{max}} = \cos^{-1}\left(\frac{R}{L}\right)$

$\Delta p (\text{per particle}) = 2mu \cos \theta$

\[ F = \frac{dp}{dt} = \frac{AP_0}{KT} \int_0^\infty du \int_0^{2\pi} d\phi \int_0^{\theta_{\text{max}}} d\theta \left( 2mu \cos \theta \frac{\sin \theta}{\sin \phi} \sqrt{\frac{\mu}{4\pi}} \right) \]

\[ = \frac{AP_0 \mu}{KT} \frac{1 - \cos^3(\theta_{\text{max}})}{3} \int_0^\infty du \ u^2 \cos \theta \ D(u) = \frac{\text{ALREADY DID IT IN PART 4}}{} \]
\[
\begin{align*}
&= \frac{4}{3} \frac{A P_0 m}{kT} \frac{6kT}{8m} \left( 1 - \cos^3(\theta_{mn}) \right) \\
&= P_0 A \left[ 1 - \cos^3 \left( \tan^{-1} \left( \frac{R}{L} \right) \right) \right] \\
&\text{Now, for } L \gg R \\
&\tan^{-1} \left( \frac{R}{L} \right) \approx \frac{R}{L} \\
&\cos^3 \left( \frac{R}{L} \right) = \left( 1 - \frac{L}{2R} \right)^3 \\
&\approx 1 - \frac{3}{2} \left( \frac{R}{L} \right)^2 \\
&\Rightarrow F = P_0 A \left[ 1 - 1 + \frac{3}{2} \left( \frac{R}{L} \right)^2 \right] \\
&= \frac{3}{2} P_0 A \left( \frac{R}{L} \right)^2
\end{align*}
\]
Problem 5.23. (Grand free energy.)
(a) Using the product rule for derivatives, an infinitesimal change in $\Phi$ can be written

$$d\Phi = dU - T \, dS - S \, dT - \mu \, dN - N \, d\mu.$$ 

Plugging in the ordinary thermodynamic identity for $dU$ and canceling terms, this becomes

$$d\Phi = -S \, dT - P \, dV - N \, d\mu.$$ 

Thus the natural variables for the function $\Phi$ are temperature, volume, and chemical potential. Holding any two of these fixed yields a partial-derivative formula:

$$\left( \frac{\partial \Phi}{\partial T} \right)_{V,N} = -S; \quad \left( \frac{\partial \Phi}{\partial V} \right)_{T,\mu} = -P; \quad \left( \frac{\partial \Phi}{\partial \mu} \right)_{T,V} = -N.$$ 

(b) As in the text (page 161), consider an infinitesimal change in the total entropy of the system plus its environment (the “reservoir”):

$$dS_{\text{total}} = dS + dS_R.$$ 

Applying the thermodynamic identity to $dS_R$ and assuming that $V$ is fixed, we can substitute

$$dS_R = \frac{1}{T} \, dU_R - \frac{\mu}{T} \, dN_R = -\frac{1}{T} \, dU + \frac{\mu}{T} \, dN,$$

where I’ve used the fact that the changes in the system’s $U$ and $N$ are minus the changes for the reservoir. Therefore,

$$dS_{\text{total}} = dS - \frac{1}{T} \, dU + \frac{\mu}{T} \, dN = -\frac{1}{T} (dU - T \, dS - \mu \, dN) = -\frac{1}{T} \, d\Phi,$$

provided that $T$ and $\mu$ are constant. Spontaneous changes are those for which $dS_{\text{total}}$ is positive, or equivalently, for which $d\Phi$ is negative.

(c) To prove that $\Phi = -PV$, you could make an argument analogous to that used to prove $G = N\mu$ on page 164. Given that result, however, we can simply write

$$\Phi = U - TS - \mu N = U - TS + PV - PV - \mu N = G - PV - \mu N = -PV.$$ 

Problem 6.42. (F and S for a harmonic oscillator.)
(a) The Helmholtz free energy of a single harmonic oscillator is

$$F_1 = -kT \ln Z_1 = -kT \ln (1 - e^{-\beta \varepsilon})^{-1} = kT \ln (1 - e^{-\beta \varepsilon}),$$

so since $F$ is an extensive quantity, the Helmholtz free energy for $N$ oscillators is

$$F = NkT \ln (1 - e^{-\beta \varepsilon}).$$

(b) To find the entropy just differentiate with respect to $T$:

$$S = -\left( \frac{\partial F}{\partial T} \right)_N = -Nk \ln (1 - e^{-\beta \varepsilon}) - NkT (1 - e^{-\beta \varepsilon})^{-1} e^{-\beta \varepsilon} \left( \frac{d\beta}{d\varepsilon} \right)$$

$$= -Nk \ln (1 - e^{-\beta \varepsilon}) + Nk \frac{\varepsilon / kT}{e^{\beta \varepsilon} - 1}.$$
Problem 6.45. The free energy is given by equation 6.90,

\[ F = -NkT\left[\ln V - \ln N - \ln v_Q + 1\right] + F_{\text{int}}. \]

Before differentiating with respect to \( T \) to get the entropy, note that \( v_Q = (\hbar^2/2\pi m kT)^{3/2} \), so \( -\ln v_Q = \frac{3}{2} \ln T \) plus a temperature-independent constant. Therefore the entropy is

\[
S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk\left[\ln(V/N) + 1\right] + NkT \cdot \frac{3}{2} \frac{1}{T} - \frac{\partial F_{\text{int}}}{dT}.
\]

The chemical potential is

\[
\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT\left[\ln(V/N) + 1\right] + NkT \cdot \frac{1}{N} + \frac{\partial F_{\text{int}}}{\partial N} = -kT \ln\left(V/N\right) - kT \ln Z_{\text{int}} = -kT \ln\left(VZ_{\text{int}} \right).
\]

where in the second line I've used the definition \( F_{\text{int}} = -NkT \ln Z_{\text{int}} \).

Problem 6.48. (\( S \) and \( \mu \) for a diatomic gas.)

(a) For a collection of \( N \) rotating diatomic molecules, the internal contribution to the free energy is

\[ F_{\text{int}} = -NkT \ln (Z_e Z_{\text{rot}}), \]

where (at ordinary temperatures) \( Z_{\text{rot}} \) is \( kT/\epsilon \) for a molecule composed of two different atoms, or \( kT/2\epsilon \) for a molecule composed of identical atoms. Either way, \( Z_{\text{rot}} \) is simply a constant times \( T \), so

\[
\frac{\partial F_{\text{int}}}{\partial T} = -Nk \ln (Z_e Z_{\text{rot}}) - NkT \frac{1}{T} = -Nk \left[\ln(Z_e Z_{\text{rot}}) + 1\right].
\]
Therefore, according to equation 6.92,

\[ S = N k \left[ \ln \left( \frac{V}{Nv_Q} \right) + \frac{5}{2} \right] + N k \ln (Z_e Z_{\text{rot}}) + 1 = N k \left[ \ln \left( \frac{VZ_e Z_{\text{rot}}}{Nv_Q} \right) + \frac{7}{2} \right]. \]

The rotational partition function for oxygen at room temperature is

\[ Z_{\text{rot}} = \frac{kT}{2\varepsilon} = \frac{(8.617^{-5} \text{ eV/K})(298 \text{ K})}{2(0.0018 \text{ eV})} = 71, \]

while the quantum volume is

\[ v_Q = \left( \frac{\hbar}{\sqrt{2\pi mkT}} \right)^3 = \left( \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2\pi(32)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}} \right)^3 = (1.79 \times 10^{-11} \text{ m}^3) = 5.73 \times 10^{-33} \text{ m}^3 \]

and the average volume per particle (at atmospheric pressure) is

\[ \frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{1.01 \times 10^5 \text{ N/m}^2} = 4.07 \times 10^{-26} \text{ m}^3. \]

From these numbers we can compute the logarithm

\[ \ln \left( \frac{VZ_e Z_{\text{rot}}}{Nv_Q} \right) = \ln \left( \frac{(4.07 \times 10^{-26} \text{ m}^3)(3)(71)}{5.73 \times 10^{-33} \text{ m}^3} \right) = 21.14. \]

Thus the entropy under these conditions is

\[ S = N k[21.14 + 3.50] = (24.6)nR = 205 \text{ J/K}, \]

precisely in agreement with the measured value (to the number of significant figures used in the calculation).

**Problem 6.49.** As shown in Section 6.2, the rotational energy of a diatomic molecule at room temperature is \( kT \), corresponding to two degrees of freedom. Therefore the total thermal energy of a mole of \( N_2 \) is

\[ U = \frac{3}{2}NkT + NkT = \frac{5}{2}NkT = \frac{5}{2}(1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(298 \text{ K}) = 6190 \text{ J}. \]

The enthalpy is just \( U + PV = U + nRT \), so it’s larger by

\[ nRT = (1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(298 \text{ K}) = 2480 \text{ J}, \]  

that is,  \( H = 8670 \text{ J} \).
To compute the remaining quantities we need the internal partition function, which in this case is purely rotational:

\[ Z_{\text{int}} = Z_{\text{rot}} = \frac{kT}{2c} = \frac{(8.617 \times 10^{-6} \text{ eV/K})(298 \text{ K})}{2(0.00025 \text{ eV})} = 51. \]

We also need the quantum volume,

\[ v_0 = \left( \frac{h}{\sqrt{2\pi mkT}} \right)^3 = \left( \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2\pi}(28)(1.66 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})} \right)^3 = (1.91 \times 10^{-11} \text{ m}^3) = 6.98 \times 10^{-33} \text{ m}^3, \]

and the average volume per particle,

\[ \frac{V}{N} = \frac{kT}{P} = \frac{(1.38 \times 10^{-23} \text{ J/K})(298 \text{ K})}{1.01 \times 10^5 \text{ N/m}^2} = 4.07 \times 10^{-26} \text{ m}^3. \]

From these numbers we can compute the logarithm

\[ \ln \left( \frac{VZ_{\text{int}}}{Nv_0} \right) = \ln \left( \frac{(4.07 \times 10^{-26} \text{ m}^3)(51)}{6.98 \times 10^{-33} \text{ m}^3} \right) = 19.5. \]

The Helmholtz free energy is therefore

\[ F = -nRT \left[ \ln \left( \frac{VZ_{\text{int}}}{Nv_0} \right) + 1 \right] = -(2480 \text{ J})(19.5 + 1) = -50.8 \text{ kJ}, \]

while the Gibbs free energy is

\[ G = F + PV = -50.8 \text{ kJ} + 2480 \text{ J} = -48.3 \text{ kJ}. \]

The easiest way to get the entropy is from the definition \( F = U - TS \):

\[ S = \frac{U - F}{T} = \frac{(6190 \text{ J}) - (-50,800 \text{ J})}{298 \text{ K}} = 191 \text{ J/K} \]

(in agreement with the measured value tabulated on page 405). And the easiest way to get the chemical potential is from \( G = N\mu \):

\[ \mu = \frac{G}{N} = \frac{-48.3 \text{ kJ}}{6.02 \times 10^{23}} = 8.03 \times 10^{-20} \text{ J} = -.501 \text{ eV}. \]

**Problem 6.52.** As in the nonrelativistic case, the allowed wavelengths (in one dimension) are \( \lambda_n = 2L/n \), and therefore the allowed momenta are \( p_n = h/\lambda_n = hn/2L \). Now, however, the relation between energy and momentum is \( E = pc \), so the allowed energies are \( E_n = hcn/2L \). Therefore the single-particle partition function is

\[ Z_{1d} = \sum_n e^{-E_n/kT} = \sum_n e^{-hcn/2LkT}. \]

When \( L \) is macroscopic the number of terms in the sum that are significant is very large, so we can convert the sum to an integral to obtain

\[ Z_{1d} = \int_0^\infty e^{-hcn/2LkT} dn = \frac{2LkT}{hc} \]

\[ \left. e^{-hcn/2LkT} \right|_0^\infty = \frac{2LkT}{hc}. \]

As expected, the partition function is directly proportional to \( L \) and increases with increasing temperature.