PHYSICS 281 SOLUTION SET 1

1a. 

\[ \Gamma(x+1) = \int_0^\infty dt \, e^{-t} \, t^x, \]

and integrating by parts, we find

\[ \Gamma(x+1) = -t^x e^{-t}|_0^\infty + x \int_0^\infty dt \, e^{-t} \, t^{x-1} = x \Gamma(x) \]

1b. 

\[ I_n(a) = \int_0^\infty dx \, x^n e^{-ax}, \]

and letting \( u = ax^2 \), we have

\[ I_n(a) = \frac{1}{2a} \int_0^\infty du \, u^{(n-1)/2} e^{-u} = \frac{\Gamma\left(\frac{n+1}{2}\right)}{2a^{(n+1)/2}}. \]

1c. 

\[ \int_0^\infty \frac{x^{k-1}}{e^x - 1} \, dx = \int_0^\infty e^{-x} \frac{x^{k-1}}{1 - e^{-x}} \, dx = \int_0^\infty e^{-x} \sum_{n=0}^\infty e^{-nx} x^{k-1} \, dx, \]

using the formula for the algebraic series. Setting \( t = (n+1)x \) and integrating, we find

\[ \int_0^\infty \frac{x^{k-1}}{e^x - 1} \, dx = \sum_{n=0}^\infty \frac{1}{(n+1)^k} \int_0^\infty dt \, e^{-t} \, t^{k-1} = \zeta(s) \Gamma(s). \]

\[ (1 - 2^{-s}) \zeta(s) = (1 - 2^{-s}) \sum_{k=1}^\infty k^{-s} = \sum_{k=1}^\infty k^{-s} - 2 \sum_{k=1}^\infty (2k)^{-s} = \sum_{k=1}^\infty k^{-s} - 2 \sum_{k=2,4,6,...}^\infty (k)^{-s} \]

and

\[ (1 - 2^{-s}) \zeta(s) = (1 - 2^{-s}) \sum_{k=1}^\infty k^{-s} = \sum_{k=1}^\infty k^{-s} - \sum_{k=2,4,6,...}^\infty (2k)^{-s} = \sum_{k=1}^\infty k^{-s} - \sum_{k=2,4,6,...}^\infty (k)^{-s} \]

2. The work is given by

\[ W = \int_{V_i}^{V_f} P(V) dV = \int_{V_i}^{V_f} \frac{P_i V_f^\gamma}{V^\gamma} dV = \frac{1}{1 - \gamma} P_i V_f^\gamma (V_f^{1-\gamma} - V_i^{1-\gamma}) = \frac{1}{1 - \gamma} (P_i V_f^\gamma V_f^{1-\gamma} - P_i V_i^\gamma V_i^{1-\gamma}) = \frac{P_i V_f - P_i V_i}{1 - \gamma} \]

3. We start from the point \((V_0, T_0)\) and integrate first at constant temperature to the point \((V, T)\), then at constant volume to the point \((V, T)\). Since

\[ dA = -SdT - PdV, \]

we find

\[ A(V, T) - A(V_0, T_0) = -\int_{V_0}^V PdV = -W = -RT_0 \ln \frac{V}{V_0} \]

from the first condition and
\[ A(V,T) - A(V,T_0) = -\int_{T_0}^{T} SdT = -\int_{T_0}^{T} R \frac{V}{V_0} \left( \frac{T}{T_0} \right)^a dT' = -R\frac{VT_0}{(a+1)V_0} \left[ \left( \frac{T}{T_0} \right)^{a+1} - 1 \right] \]

from the second. Adding these two equations, we obtain

\[ A(V,T) = -RT_0 \left\{ \ln \frac{V}{V_0} + \frac{V}{(a+1)V_0} \left[ \left( \frac{T}{T_0} \right)^{a+1} - 1 \right] \right\} + A(V_0,T_0). \]

Some editions have \( V_0/V \) in the entropy.

4a. Starting from

\[ dU = TdS - PdV, \]

we find

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P \left( \frac{\partial V}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P, \]

and using a Maxwell relation, we find

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P \left( \frac{\partial V}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P. \]

Also

\[ \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial Q}{\partial T} \right)_V = C_V \]

and these two relations yield

\[ dU = \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV + C_V dT. \]

4b. For the van der Waals gas we find

\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{Nk}{V-b}, \]

so that

\[ T \left( \frac{\partial P}{\partial T} \right)_V - P = T \frac{Nk}{V-b} - \left( \frac{NkT}{V-b} - \frac{a}{V^2} \right) = \frac{a}{V^2}. \]

Using 4a, we get

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P = \frac{a}{V^2}. \]

5. Let us assume we have one mole of water, since we are only looking at intensive properties of the system. Then the equation of state is \( PV = RT \), and denote \( a = \ell/R \), where \( \ell \) is the latent heat per mole. Then the Clausius-Clapeyron equation for the vapor-pressure curve is:

\[ \frac{dP}{dT} = \frac{\ell}{TV} = \frac{aP}{T^2}, \]

which gives

\[ \int_{P_a(T_0)}^{P_a(T)} \frac{dP}{P} = a \int_{T_0}^{T} \frac{dT}{T^2} \]

or

\[ \ln \left( \frac{P_a(T_0)}{P_a(T)} \right) = a \left( \frac{1}{T} - \frac{1}{T_0} \right). \]

5b. We now go off this curve into the gas side of the phase diagram by the adiabatic law:
\[ P_r(T) = P_\infty(T_0) \left( \frac{T}{T_0} \right)^{5/2}. \]

Finally we have the equation giving the equilibrium pressure at the surface of a drop (2.25):

\[ P_r(T) = P_\infty(T) \exp \left( \frac{2am}{\rho kT} \right) \]

which we rewrite as

\[
\begin{align*}
r &= \frac{2am}{\rho kT} \left[ \ln \left( \frac{P_r(T)}{P_\infty(T)} \right) \right]^{-1} = \frac{2am}{\rho kT} \left[ \ln \left( \frac{P_r(T)}{P_\infty(T_0)} \right) - \ln \left( \frac{P_\infty(T)}{P_\infty(T_0)} \right) \right]^{-1} \\
&= \frac{2am}{\rho kT} \left[ \ln \left( \frac{T}{T_0} \right)^{5/2} + \ln \left( \frac{P_\infty(T_0)}{P_\infty(T)} \right) \right]^{-1} = \frac{2am}{\rho kT} \left[ \frac{5}{2} \ln \left( \frac{T}{T_0} \right) + \alpha \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]^{-1}.
\end{align*}
\]

6a. Consider a set of \( n \) labeled balls distributed in \( m \) boxes with \( n_1 \) in box 1, \( n_2 \) in box 2, and so on. We can obtain exactly the same distribution with any permutation of the balls. There are \( n! \) such permutations. However, a permutation of the \( n_1 \) balls in box 1 is not a new choice. So we must divide by \( n_1! \). Likewise for \( n_2, n_3 \) and so on. The result is

\[
\frac{n!}{n_1! n_2! \cdots n_m!} = \frac{(n_1 + n_2 + \cdots + n_m)!}{n_1! n_2! \cdots n_m!}.
\]

6b. The number of configurations, corresponding to setting \( m = 2 \) above, is

\[
\Gamma(N, M) = \frac{(N + M)!}{N! M!} = \frac{(N + U/\Delta)!}{N! (U/\Delta)!},
\]

so

\[
S = k \ln \frac{(N + U/\Delta)!}{N! (U/\Delta)!} \approx k(N + U/\Delta) \ln(N + U/\Delta) - k(N + U/\Delta) - kN \ln N + kN - k(U/\Delta) \ln(U/\Delta) + k(U/\Delta).
\]

6c.

\[
\frac{1}{T} = \left( \frac{T}{U} \frac{\partial S}{\partial U} \right)_N = \frac{k}{\Delta} \ln(N + U/\Delta) - \frac{k}{\Delta} \ln(U/\Delta) = \frac{k}{\Delta} \ln(1 + N \Delta/U) = \frac{k}{\Delta} \ln(1 + N/M).
\]

This gives

\[
\frac{M}{N} = \frac{1}{e^{\Delta/kT} - 1}.
\]

7a. There are

\[
\Gamma = \frac{N!}{N_0! N_1!} = \frac{N!}{(N - N_1)! N_1!}
\]

states with the specified occupations. The energy is \( U = N_1 E \), so

\[
S(N, U) = k \ln \Gamma(N, U) = k \ln N! - k \ln(N - N_1)! - k \ln N_1!
\]

\[
\approx kN \ln N - kN - k(N - N_1) \ln(N - N_1) + k(N - N_1) - kN_1 \ln N_1 + N_1
\]

\[
= kN \ln N - k(N - N_1) \ln(N - N_1) - kN_1 \ln N_1
\]

\[
= kN \ln N - k(N - U/E) \ln(N - U/E) - k(U/E) \ln(U/E)
\]

7b. In the microcanonical ensemble \( n_1 = U/E N \) and \( n_0 = 1 - U/E N \) are the most probable, indeed the only possible values, since \( U \) is fixed. Thus there are no fluctuations.

7c. We have that

\[
\frac{1}{T} = \left( \frac{T}{U} \frac{\partial S}{\partial U} \right)_N = \frac{k}{E} \ln \left( \frac{EN}{U} - 1 \right).
\]

This is negative if
\[
\frac{EN}{U} - 1 < 1
\]

or

\[
\frac{U}{EN} = n_1 > \frac{1}{2}.
\]

This is a case of negative absolute temperature. The point here is that even though the energy of the system continues to increase after \( n_1 \) passes \( 1/2 \), the entropy decreases because the number of configurations is decreasing. If all the particles are in the upper state, there is only one configuration and the entropy vanishes.

7d. Energy will flow from the negative temperature system \( \tilde{N} \) to the positive temperature system \( P \). This increases the total entropy since the addition of energy to \( P \) increases its entropy while the subtraction of energy from \( \tilde{N} \) also increases its entropy! Negative temperatures are hotter than positive!

**Discussion problem**

You were asked to compute, as a function of \( x \), the Helmholtz free energy of an ideal gas of fixed total volume \( V \) and a moveable partition that separates the total volume into a fraction \( xV \) and a fraction \( (1-x)V \).

For an ideal gas, we have \( dA = -S \, dT - P \, dV \). Thus at fixed temperature

\[
dA = -\frac{NkT}{V} \, dV
\]

and

\[
A = -NkT \ln V,
\]

up to a constant (which might be a function of temperature but does not depend on the volume). The free energy is additive, so for the whole system we have

\[
A = A_1 + A_2 = -N_1kT \ln V_1 - N_2kT \ln V_2
\]

\[
= -N_1kT \ln(xV) - N_2kT \ln[(1-x)V]
\]

Note that

\[
\frac{dA}{dx} = -N_1kT \frac{1}{x} + N_2kT \frac{1}{1-x}
\]

and setting this equal to zero gives the equilibrium value of \( x \) :

\[
x_{eq} = \frac{N_1}{N_1 + N_2}.
\]