Homework #5

6.1 ONE-DIMENSIONAL LATTICE

For a one-dimensional lattice completely filled by \( N_A \) particles of type A and \( N_B \) particles of type B, so \( N_A + N_B \) total sites, we have the following properties.

(a) For the entropy, \( S = k_B \ln W \)

\[
W(N_A, N_B) = \frac{(N_A + N_B)!}{N_A! N_B!} \quad \text{A and B distinguishable}
\]

so that if \( N_A \gg 1 \) and \( N_B \gg 1 \) we can say

\[
S = k_B \ln W = k_B \left[ (N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B \right]
\]

as the linear terms cancel (as in our mixing entropy problem).

(b) To determine the relationship of the chemical potential and the entropy, we know the total differential

\[
ds = \frac{1}{T} \, dU + \frac{P}{T} \, dV - \frac{M_A}{T} \, dN_A - \frac{M_B}{T} \, dN_B
\]

where \( M_A \) and \( M_B \) are the chemical potentials of A and B, respectively.

From the property of the total differential

\[
M_A = -T \left( \frac{\partial S}{\partial N_A} \right)_{N_B, U, V} \quad M_B = -T \left( \frac{\partial S}{\partial N_B} \right)_{N_A, U, V}
\]

(c) From the results above

\[
\left( \frac{\partial S}{\partial N_A} \right)_{N_B, U, V} = k_B \left[ \ln(N_A + N_B) + X - \ln N_A - X \right] = -k_B \ln \left[ \frac{N_A}{N_A + N_B} \right]
\]
so that the chemical potential

$$\mu_A = T \left( \frac{\partial S}{\partial N_A} \right)_{N \neq N_B} = \frac{N_A}{N_A + N_B}$$

where \( \frac{N_A}{N_A + N_B} \) = \( x_A \) is the mole fraction of species A.

6.2 THE ENTROPY OF AN IDEAL GAS

Let's start from the relation

$$\left( \frac{\partial S}{\partial V} \right)_{u,n} = \frac{P}{T} = \frac{N k_B}{V}$$

where we have used the general relation \( \left( \frac{\partial S}{\partial V} \right)_{u,n} = \frac{P}{T} \) and the special result that for an ideal gas

$$\frac{P}{T} = \frac{N k_B}{V}$$

Rearranging we have

$$dS = \frac{N k_B}{V} dV$$

and we can integrate that as

$$S_2 - S_1 = \int_{1}^{2} dS = \Delta S = \int_{V_1}^{V_2} \frac{N k_B}{V} dV = N k_B \ln \left( \frac{V_2}{V_1} \right)$$

and we can say that for an ideal gas

$$S(N, V) = N k_B \ln V$$
6.3 Entropy changes don't depend on a process pathway

(a) We can write for an ideal gas at fixed number
\[ \Delta S_N = S_2(V_2) - S_1(V_1) = N k_B \ln \left( \frac{V_2}{V_1} \right) \]

(b) That (a) was at fixed number but at fixed volume
\[ \Delta S_V = S_2(N_2) - S(N_1) = (N_2 - N_1) k_B \ln V \]

(c) For the two-step process
\[ (V_1, N_1) \rightarrow (V_2, N_1) \rightarrow (V_2, N_2) \]
the total entropy change will be
\[ \Delta S = N_1 k_B \ln \left( \frac{V_2}{V_1} \right) + (N_2 - N_1) k_B \ln \left( \frac{V_2}{V_1} \right) \]
starting entropy \( (N_1, V_1) \rightarrow (N_2, V_1) \) change in second step
\[ = N_1 k_B \ln V_2 - N_1 k_B \ln V_1 + N_2 k_B \ln V_2 - N_2 k_B \ln V_1 \]
\[ = N_2 k_B \ln V_2 - N_1 k_B \ln V_1 = S(V_2, N_2) - S(V_1, N_1) \]

(d) For (c) but in the reverse order
\[ (V_1, N_1) \rightarrow (V_1, N_2) \rightarrow (V_2, N_2) \]
we have
\[ \Delta S = (N_2 - N_1) k_B \ln V_1 + N_2 k_B \ln \left( \frac{V_2}{V_1} \right) \]
\[ = N_2 k_B \ln V_1 - N_1 k_B \ln V_1 + N_2 k_B \ln V_2 - N_2 k_B \ln V_1 \]
\[ = N_2 k_B \ln V_2 - N_1 k_B \ln V_1 = S(V_2, N_2) - S(V_1, N_1) \]
as expected for a state function.
6.4 COMPUTE $\Delta S(V)$ FOR AN IDEAL GAS

Suppose we double the volume of an ideal gas from $V$ to $2V$ in a quasi-static isothermal process (constant $T$). The change in entropy will be

$$\Delta S = S_{2V} - S_V = Nk_B \ln(2V) - Nk_B \ln V = Nk_B \ln 2$$
7.1 THE WORK OF COMPRESSION

We have explored the quasistatic isothermal compression of an ideal gas. The van der Waals equation of state improves on the ideal gas law by including attraction between gas particles, through coefficient $a$, and repulsion between gas particles, through coefficient $b$.

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

(a) The work done in an isothermal compression from $V_1$ to $V_2$, where we can take $P_{ext} = P_{gas}$, is

$$W = -\int_{V_1}^{V_2} P_{ext} \, dV = -\int_{V_1}^{V_2} \left[ \frac{RT}{V-b} - \frac{a}{V^2} \right] \, dV$$

$$= -RT \ln \left( \frac{V_2 - b}{V_1 - b} \right) - a \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

(b) In the low density limit, we can take the particle number to be fixed while the volume becomes LARGE. In that case $V \gg b$ and the log term gets close to $W_{ideal}$. So as $V_2 < V_1$ in compression

$$\Delta W \approx -a \left( \frac{1}{V_2} - \frac{1}{V_1} \right) < 0 \quad \Delta W = W_{real} - W_{ideal}$$

and less work is required to compress the real gas.
For the high density limit, the volumes become small and approach the order of 6, leading to dominance of the logarithmic term in the work. Due to repulsions between particles, the $p_{\text{real}} > p_{\text{ideal}}$ and more work is done to compress the real gas.

### 7.3 The Work of Expansion in Freezing an Ice Cube

We have a 2cm x 2cm x 2cm cube of liquid water freezing

\[
\begin{array}{c}
\text{latex} \\
0^\circ \text{C}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{liquid} \\
\rho = 1.000 \text{ g/cm}^3
\end{array} \quad \begin{array}{c}
\text{ice} \\
\rho = 0.915 \text{ g/cm}^3
\end{array}
\]

all at 4 atm and 0°C. The work done will be

\[
W = -P_{\text{ext}} (V_{\text{ice}} - V_{\text{liquid}})
\]

\[
= -P_{\text{ext}} \left[ \frac{M_{\text{ice}}}{\rho_{\text{ice}}} - \frac{M_{\text{liq}}}{\rho_{\text{liq}}} \right]
\]

We have 8 cm$^3$ of liquid so we have 8 cm$^3 \cdot (1.000 \text{ g/cm}^3) = 8 \text{ g}$ of ice or liquid.

\[
W = -(1 \text{ atm})(8 \text{ g}) \left[ \frac{1}{0.915 \text{ g/cm}^3} - \frac{1}{1.000 \text{ g/cm}^3} \right]
\]

\[
\times (10^{-3} \text{ L}) \left( \frac{8.315 \text{ J}}{0.08205 \text{ L atm}} \right) = -0.075 \text{ J}
\]

which is $W = -0.018 \text{ cal}$. Work is done by the system.
7.4 THE WORK OF EXPANDING A GAS

To expand a gas from a volume \( V \) to a volume \( 2V \) we use at constant \( T \)

\[
W = -RT \ln \left( \frac{V_2}{V_1} \right) = -RT \ln \left( \frac{2V}{V} \right)
\]

\[
= -RT \ln 2 = -0.693 RT
\]

where the gas does work on the environment and negative work is done on the gas.

7.6 THE WORK IN A THERMODYNAMIC CYCLE

We have a thermodynamic cycle

![Diagram of a thermodynamic cycle](image)

We can compute the total work performed in the cycle by computing the sum of the work in each of the four steps

\[
W = W_1 + W_2 + W_3 + W_4
\]

We can see that the volume change in steps (1) and (3) is zero so that \( W_1 = W_3 = 0 \). In each of the other steps

\[
W = -\int P_{\text{ext}} \, dV
\]
where the external pressure is constant. We find

\[ W_2 = -\int_{V_B}^{V_C} 300 \text{ atm} \, dV = -300 \text{ atm} \left( 2 \text{ m}^3 - 1 \text{ m}^3 \right) \]

\[ = -300 \text{ atm cm}^3 \]

\[ W_B = -\int_{V_D}^{V_A} 100 \text{ atm} \, dV = -100 \text{ atm} \left( 1 \text{ cm}^3 - 2 \text{ cm}^3 \right) \]

\[ = +100 \text{ atm cm}^3 \]

The overall total work done is

\[ W = -300 \text{ atm cm}^3 + 100 \text{ atm cm}^3 = -200 \text{ atm cm}^3 \]

\[ = -200 \text{ cm}^3 \left( 0.101 \frac{\text{J}}{\text{atm cm}^3} \right) = -20.3 \text{ J} \]

So that overall negative work is done on the system.

7.7 ENGINE EFFICIENCIES

For a Carnot cycle, we know that the engine efficiency is

\[ \eta = \frac{W}{q_H} = 1 - \frac{q_c}{q_H} = 1 - \frac{T_c}{T_H} \]

where \( T_c \) and \( T_H \) are the temperatures of the cold and hot, i.e., temperatures of bringing in the heat (\( T_H \)) and putting out exhaust (\( T_c \)).

(a) For

\[ \eta = 1 - \frac{T_c}{T_H} = 1 - \frac{273 \text{ K}}{380 \text{ K}} = 28\% \]

(b) For

\[ \eta = 1 - \frac{T_c}{T_H} = 1 - \frac{323 \text{ K}}{380 \text{ K}} = 15\% \rightarrow \text{ almost } \frac{1}{2}! \]
For our Hadley cycle

we will consider an imaginary balloon with 1 m$^3$ of an ideal gas.

(a) At 1 atm and 300 K, the number of moles of gas in the balloon will be

$$
n = \frac{PV}{RT} = \frac{(1 \text{ atm})(1 \text{ m}^3)(10^5 \text{ L/m}^3)}{(0.08205 \text{ L atm/mol K})(300 \text{ K})} = 40.6 \text{ mol}
$$

(b) The balloon air is heated to 330 K. If the surrounding atmosphere is at 1 atm, the volume will increase to

$$
V = 1 \text{ m}^3 \left(\frac{330 \text{ K}}{300 \text{ K}}\right) = 1.1 \text{ m}^3
$$

and the density will decrease to

$$
\rho = \frac{40.6 \text{ mol}}{1.1 \text{ m}^3} = 36.9 \text{ mol/m}^3
$$

(c) If the balloon rises adiabatically, it will rise to a height we are asked to estimate using Figure 10.2.
Now in mbar our pressure is determined using:

\[
1 \text{ atm} = 1,013.25 \text{ mbar}
\]

but Dill says we can assume \( 1 \text{ atm} \equiv 1 \text{ bar} \). Where is the atmosphere's pressure equal to the pressure in our expanded balloon:

\[
p = 1 \text{ atm} \left( \frac{300K}{330K} \right) = 0.91 \text{ atm}
\]

I can't read that height off the figure, but we can use:

\[
\frac{p(\ell)}{p(0)} = \exp \left[ -\frac{mg \ell}{R T} \right] = \exp \left[ -0.00011 \frac{1}{m} \ell \right]
\]

\[
p(0) = 1 \text{ atm} = 0.08205 \text{ atm} \text{ L atm/mol K}
\]

\[
0.08205 \text{ L atm/mol K} \times 330K = 8.615 \text{ kg m}^2 \text{ s}^{-2} \text{ mol} \text{ K}^{-1}
\]

Solving for \( \ell \) gives:

\[
\ell = \frac{1}{-0.00011} \ln \left( \frac{0.91}{1.0} \right) = 670 \text{ m} \quad \text{about a kilometer!}
\]
7.9 STIRLING ENGINE

A Stirling engine follows a thermodynamic cycle of an ideal gas that is quasistatic.

(a) In the constant volume isochoric legs of the cycle the volume is constant so that

\[ W_{12} = W_{34} = 0 \]

(b) We can find the total energy change around the cycle to be zero since the total energy \( U \) is a state function.

\[ \Delta U = 0 \]

(c) The total work performed in the cycle is

\[ W_{\text{tot}} = W_{23} + W_{41} \]

where

\[ W_{23} = - \int_{V_1}^{V_2} p \, dV = -NRT \int_{V_1}^{V_2} \frac{1}{V} \, dV = -NRT \ln \left( \frac{V_2}{V_1} \right) \]

and

\[ W_{41} = - \int_{V_2}^{V_1} p \, dV = -NRT \int_{V_2}^{V_1} \frac{1}{V} \, dV = -NRT \ln \left( \frac{V_1}{V_2} \right) \]
for the total work done

\[ W = -NRT_2 \ln \left( \frac{V_2}{V_1} \right) - NRT_1 \ln \left( \frac{V_1}{V_2} \right) \]

\[ = -N \ln \left( \frac{V_2}{V_1} \right) (T_2 - T_1) \]

and since \( T_2 > T_1 \) and \( V_2 > V_1 \) the work done BY the engine is \( T_1 \), which is what we like for an engine!

(d) If we take for \( N = 0.1 \) mol of the ideal gas and

\[ T_2 = 2000 \text{ K} \quad V_2 = 1 \text{ L} \]
\[ T_1 = 300 \text{ K} \quad V_1 = 0.01 \text{ L} \]

the work done ON the engine is

\[ W = -N \ln \left( \frac{V_2}{V_1} \right) (T_2 - T_1) = -6.5 \text{ kJ} \]

so that the engine, with a volume ratio of 100:1 and \( T \) ratio

\[ \frac{T_c}{T_H} = \frac{300 \text{ K}}{2000 \text{ K}} = 0.15 \]

does -6.5 kJ of work in a cycle. The efficiency would be

\[ \eta = 1 - \frac{T_c}{T_H} = 85 \% \]
We take our car engine to have a volume ratio
\[
\frac{V_2}{V_1} = 8
\]

If we imagine using a diatomic gas, \( C_v = \frac{5}{2} Nk_B \) and for ethane, \( C_v = 5 Nk_B \).

(a) With a diatomic gas, our engine efficiency is expected to be
\[
\eta = 1 - \left( \frac{V_1}{V_2} \right)^{\frac{Nk_B}{C_v}}
\]
which is the result for the Otto cycle.

For our engine
\[
\eta = 1 - \left( \frac{1}{8} \right)^{\frac{Nk_B}{C_v}} = 0.86
\]
with a diatomic gas.

(b) For our engine using a gas of ethane
\[
\eta = 1 - \left( \frac{1}{8} \right)^{\frac{5}{5}} = 0.34
\]
less efficient turn with a diatomic gas.

(c) We could enhance the efficiency with a higher compression ratio.