Mandatory Assignement 4 - Ivar Haugerud - FYS2160

1.1) To find the entropy we will first find the multiplicity for a given number of N_+ and N_-, with $N_+ + N_- = N$.

The multiplicity of this system is calculated through the binomial formula

$$\Omega = \binom{N}{N_+} = \frac{N!}{(N-N_+)!\,N_+!} = \frac{N!}{N_-!\,N_+!}$$

Let's find the logarithm of Ω, and use Stirlings approximation

$$\ln \Omega = \ln(N!) - \ln(N_-!) - \ln(N_+!)$$

$$\approx N\ln(N) - N - N_-\ln(N_-) + N_- - N_+\ln(N_+) + N_+$$

$N_+ + N_-$ cancels $-N$, and we put in $N_\pm = \frac{N}{2}(1 \pm x)$ where $x = \frac{U}{N\varepsilon}$. We then get

$$= N\ln(N) - \frac{N}{2}(1-x)\ln\left(\frac{N}{2}(1-x)\right) - \frac{N}{2}(1+x)\ln\left(\frac{N}{2}(1+x)\right)$$

$$= N\ln N - \frac{N}{2}(1-x)\left(\ln\left(\frac{N}{2}\right) + \ln(1-x)\right) - \frac{N}{2}(1+x)\left(\ln\left(\frac{N}{2}\right) + \ln(1+x)\right)$$

$$\approx N\ln N - \frac{N}{2}(1-x)\left(\ln(N) - \ln(2) + \ln(1-x)\right)$$
$$- \frac{N}{2}(1+x)\left(\ln(N) - \ln(2) + \ln(1+x)\right)$$

$$= N\ln N - \frac{N}{2}\left(2\ln(N) - 2\ln(2) + \ln(1-x) + \ln(1+x)\right) - \frac{Nx}{2}\left(\ln N - \ln 2 + \ln(1+x) - \ln N + \ln 2 - \ln(1-x)\right)$$

$$= N\ln N - N\ln N + N\ln 2 - \frac{N}{2}\left(\ln(1-x) + \ln(1+x)\right) - \frac{Nx}{2}\left(\ln(1+x) - \ln(1-x)\right)$$

1.1)

$$= N\ln(2) - \frac{N}{2}\left(\ln(1-x) + \ln(1+x)\right) - \frac{Nx}{2}\left(\ln(1+x) - \ln(1-x)\right)$$

$$\approx N\ln(2) - \frac{N}{2}\left(-x - \frac{x^2}{2} + x - \frac{x^2}{2}\right) - \frac{Nx}{2}\left(x - \frac{x^2}{2} + x + \frac{x^2}{2}\right)$$

$$= N\ln(2) - \frac{N}{2}(-x^2) - \frac{Nx}{2}(2x)$$

$$= N\ln(2) + \frac{Nx^2}{2} - Nx^2$$

$$= N\ln(2) - \frac{Nx^2}{2}$$

$\ln(1+x) \approx x - \frac{x^2}{2}$
$\ln(1-x) \approx -x - \frac{x^2}{2}$
for small x

This means that

$$S = k\ln(\Omega) = kN\ln(2) - \frac{Nkx^2}{2}$$

This means that the entropy per particle is

$$S_m = \frac{S}{N} = k\ln(2) - \frac{kx^2}{2}$$

$$= k\ln(2) - \frac{k}{2}\left(\frac{U}{N\varepsilon}\right)^2$$

In the thermodynamic limit $N \to \infty$ we get that the last term vanishes, and we are left with

$$\underline{S_m = k\ln(2)}$$

1.2) When the system is in a thermal ~~bath~~ the partition function for one particle is

$$Z_1 = \sum_s e^{-\cancel{\varepsilon} E_s \beta} = e^{-\varepsilon_+ \beta} + e^{-\varepsilon_- \beta} = e^{-\varepsilon\beta} + e^{\varepsilon\beta}$$

$$= \underline{2\cosh(\varepsilon\beta)}$$

1.3) Since we are working with identicle, distinguishable particles we have

$$Z_N = Z_1 Z_2 Z_3 \dots Z_N.$$

Since all particles have the same ~~energy~~ possible states we get

$$Z_N = Z_1^N = \underline{2^N \cosh^N(\varepsilon\beta)}$$

1.4) With this expression we can find the Helmholtzfree energy

$$F = -kT\ln(Z_N) = -kT\ln\left(2^N\cosh^N(\varepsilon\beta)\right)$$

$$= -kT\left[\ln(2^N) + \cosh^N(\varepsilon\beta)\right]$$

$$= \underline{-NkT\left[\ln(2) + \ln(\cosh(\varepsilon\beta))\right]}$$

1.5) We can also calculate the average energy for the N particles:

$$U = -\frac{1}{Z}\frac{\partial}{\partial \beta} Z = -\frac{\partial}{\partial \beta}\ln(Z)$$

$$= -\frac{\partial}{\partial \beta}\left(\ln\left(2^N \cosh^N(\varepsilon\beta)\right)\right)$$

$$= -\frac{\partial}{\partial \beta}\left(N\ln 2 + N\ln(\cosh(\varepsilon\beta))\right)$$

$$= -N\frac{\partial}{\partial \beta}\left(\ln(\cosh(\varepsilon\beta))\right)$$

$$= -N\frac{1}{\cosh(\varepsilon\beta)}\sinh(\varepsilon\beta)\cdot\varepsilon$$

$$= -N\varepsilon\tanh(\varepsilon\beta)$$

We can continue with this expression to find $\varepsilon\beta$ as a function of x

$$-N\varepsilon\tanh(\varepsilon\beta) = U$$

$$\tanh(\varepsilon\beta) = -\frac{U}{N\varepsilon} = -x$$

$$\varepsilon\beta = \operatorname{arctanh}(-x)$$

We use this expression for $\varepsilon\beta$ and put it in for $\varepsilon\beta$ in the Helmholtz free energy

1.5) $F = -Nk T[\ln(2) + \ln(\cosh(\varepsilon\beta))]$

$= -NkT[\ln(2) + \ln(\cosh(\operatorname{arcsinh}(-x)))]$

$= -NkT[\ln(2) + \ln(\sqrt{1+\sinh^2(\operatorname{arcsinh}(-x))})]$

$= -NkT[\ln(2) + \ln(\sqrt{1+x^2})]$

$= -NkT[\ln(2) + \frac{1}{2}\ln(1+x^2)]$

1.6) Knowing F and U we can find the entropy:

$$S = \frac{U-F}{T} = \frac{-N\varepsilon\tanh(\varepsilon\beta) + NkT[\ln(2) + \frac{1}{2}\ln(1+x^2)]}{T}$$

$$S = -\frac{N\varepsilon}{T}\tanh(\varepsilon\beta) + Nk[\ln(2) + \frac{1}{2}\ln(1+x^2)]$$

The energy per particle is then:

$$S_M = \frac{S}{N} = -\frac{\varepsilon}{T}\tanh(\varepsilon\beta) + k[\ln(2) + \frac{1}{2}\ln(1+x^2)]$$

$$= -\frac{\varepsilon}{T}\tanh(\operatorname{arctanh}(-x)) + k[\ln(2) + \frac{1}{2}\ln(1+x^2)]$$

$$= \frac{\varepsilon}{T}x + k[\ln(2) + \frac{1}{2}\ln(1+x^2)]$$

$$= \frac{U}{NT} + k[\ln(2) + \frac{1}{2}\ln(1 + \frac{U^2}{N^2\varepsilon^2})]$$

$N \to \infty$: $S_M \approx k\ln(2)$ since $\frac{1}{N} \approx 0$ and $\ln(1) = 0$

1.8) Using two different methods we achieve the same answer, in the thermodynamic limit. With the first method we used combinatorics, ignoring the thermal bath. In the other method we used the partition function for a thermal bath.

The reason for why these two methods result in the same answer is, I believe the thermodynamic ~~[illegible]~~ limit.
When $N \to \infty$ the effect of the thermal bath is not important for the entropy of each particle which has two possible states: $+\varepsilon$ and $-\varepsilon$.
$\Rightarrow \Omega = 2^N \Rightarrow S = k N \ln(2)$, which is what we found.

2) For the harmonic oscillator we have no degeneracy, and $E_n = \hbar\omega(n+\frac{1}{2}) = \varepsilon(n+\frac{1}{2})$.

We know that shifting the energies by a constant does not effect the probabilities. Therefore we will use $E_n = \hbar\omega n = \varepsilon n$

2.1) $$Z = \sum_S e^{-E_S \beta} = \sum_{n=0}^{\infty} e^{-\varepsilon n \beta}$$

$$= 1 + e^{-\varepsilon\beta} + e^{-2\varepsilon\beta} + e^{-3\varepsilon\beta} + e^{-4\varepsilon\beta} + \dots$$

$$= 1 + x + x^2 + x^3 + x^4 + \dots, \quad x = e^{-\varepsilon\beta}$$

$$= \frac{1}{1-x} = \frac{1}{1-e^{-\varepsilon\beta}}$$

2.2) Since we are working with independent distinguishable particles we have

$Z_N = Z_1 Z_2 Z_3 \dots Z_N$, and since all Z's are the same

$$Z_N = Z_1^N = \frac{1}{(1-e^{-\varepsilon\beta})^N}$$

$$\Rightarrow F = -kT\ln(Z) = -kT\ln\left((1-e^{-\varepsilon\beta})^{-N}\right)$$

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

2.3) We can compute the energy as well:

$$\langle E_N \rangle = -\frac{\partial}{\partial \beta} \ln(Z) = -\frac{\partial}{\partial \beta} \ln\left((1-e^{-\varepsilon\beta})^{-N} \right)$$

$$= N \frac{\partial}{\partial \beta} \ln(1-e^{-\varepsilon\beta})$$

$$= N \frac{1}{1-e^{-\varepsilon\beta}} \cdot \frac{\partial}{\partial \beta}(-e^{-\varepsilon\beta})$$

$$= \frac{N}{1-e^{-\varepsilon\beta}} \cdot \varepsilon e^{-\varepsilon\beta} = \underline{\frac{N\varepsilon e^{-\varepsilon\beta}}{1-e^{-\varepsilon\beta}}}$$

In the low T limit:

$$T \to 0,\ \beta \to \infty : \langle E_N \rangle = \frac{N\varepsilon}{e^{\varepsilon\beta}-1} \approx \frac{N\varepsilon}{e^{\varepsilon\beta}} \to 0$$

In the low T limit the energy will go towards zero, makes sense:

$$T \to \infty,\ \beta \to 0 : \langle E_N \rangle = \frac{N\varepsilon}{e^{\varepsilon\beta}-1} \approx \frac{N\varepsilon}{1+\varepsilon\beta-1}$$

$$= \frac{N\varepsilon}{\varepsilon\beta} = \frac{N}{\beta} = \underline{NkT}$$

The energy will behave linearly with N and go towards infinity.

2.4| We can also compute the heatcapacity c_V

$$c_V = \frac{\partial U}{\partial T} = k \frac{\partial}{\partial \beta} \left(\frac{N\varepsilon}{e^{\varepsilon\beta}-1} \right)$$

$$\boxed{\begin{aligned} \beta &= kT \\ \Rightarrow T &= \frac{\beta}{k} \end{aligned}}$$

$$= kN\varepsilon \frac{\partial}{\partial \beta}\left(\left(e^{\varepsilon\beta}-1\right)^{-1} \right)$$

$$= -Nk\varepsilon \frac{1}{\left(e^{\varepsilon\beta}-1\right)^2} \cdot \varepsilon e^{\varepsilon\beta}$$

$$= \frac{-Nk\varepsilon^2 e^{\varepsilon\beta}}{\left(e^{\varepsilon\beta}-1\right)^2}$$

High T limit: $T \to \infty$, $\beta \to 0$, $e^{\varepsilon\beta} \simeq 1 + \varepsilon\beta$

$$c_V = \frac{-Nk\varepsilon^2(1+\varepsilon\beta)}{\left(1+\varepsilon\beta-1\right)^2} = \frac{-Nk\varepsilon^2(1+\varepsilon\beta)}{\varepsilon^2\beta^2}$$

$$= \frac{-Nk}{\beta^2}(1+\varepsilon\beta)$$

$$= -Nk\left(\frac{1}{\beta^2} + \frac{\varepsilon}{\beta}\right) \to \infty$$

Increasing T in the high T limit results in large changes of internal energy

2.4) the low T limit:

$T \to 0, \ \beta \to \infty$

$$C_V = \frac{Nk\varepsilon^2 e^{\varepsilon\beta}}{(e^{\varepsilon\beta}-1)^2} \approx \frac{Nk\varepsilon^2 e^{\varepsilon\beta}}{e^{2\varepsilon\beta}}$$

$$= \frac{Nk\varepsilon^2}{e^{\varepsilon\beta}} \longrightarrow \underline{0}$$

As $T \to 0$ the heat capacity goes towards 0, ~~does not make~~

By increasing T in the low T limit the change in internal energy is very small.

(Have to be careful since this is no longer true for large changes in T since we assumed T = small)

3.1) $$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}$$

$$Z = \sum_{n=1}^{\infty} e^{-E_n\beta} = \sum_{n=1}^{\infty} e^{-\frac{n^2\hbar^2\pi^2}{2mL^2}\beta}$$

In the high T limit ~~#~~ each term is close and we can approximate the sum with an integral

$$Z \approx \int_0^{\infty} e^{-\varepsilon n^2\beta}\,dn = \frac{1}{2}\sqrt{\frac{\pi}{\varepsilon\beta}} = \frac{\sqrt{\pi}}{2}\sqrt{\frac{2mL^2}{\hbar^2\pi^2\beta}}$$

$$= \sqrt{\frac{\pi}{2}}\frac{L}{\pi\hbar}\sqrt{\frac{m}{\beta}} = \frac{L}{\hbar}\sqrt{\frac{m}{2\beta\pi}}$$

$$= \sqrt{\frac{mkT}{2\pi}}\frac{L}{\hbar}$$, where $Z \propto \sqrt{T}$

In the low T limit we have few accesible states an $e^{-\frac{\varepsilon n^2}{kT}}$ becoming very small as n increases. We will therefore approximate the sum with two terms

$$Z \approx \sum_{n=1}^{2} e^{-\varepsilon\beta n^2} = e^{-\varepsilon\beta} + e^{-4\varepsilon\beta}$$

$$= e^{-\frac{\hbar^2\pi^2}{2mL^2}\beta} + e^{-4\frac{\hbar^2\pi^2}{2mL^2}\beta}$$

which is approximately correct in the low T limit.

3.2) We can compute the average energy for both cases

$$U = -\frac{\partial}{\partial\beta} \ln(Z)$$

High T:

$$U = -\frac{\partial}{\partial\beta} \ln\left(\sqrt{\frac{mL^2}{2\pi\beta\hbar^2}}\right)$$

$$= -\frac{1}{2}\frac{\partial}{\partial\beta} \ln\left(\frac{mL^2}{2\pi\beta\hbar^2}\right)$$

$$= -\frac{1}{2}\frac{1}{\frac{mL^2}{2\pi\beta\hbar^2}} \cdot \left(-\frac{mL^2}{2\pi\beta^2\hbar^2}\right)$$

$$= \frac{1}{4}\frac{\cancel{mL^2 2\pi\beta\hbar^2}}{\cancel{mL^2 2\pi\beta^2\hbar^2}}$$

$$= \frac{1}{4\beta} = \underline{\underline{\frac{kT}{4}}}$$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\left(\frac{kT}{4}\right) = \underline{\underline{\frac{k}{4}}}$$

The heat capacity becomes a constant

3.2) <u>Low T:</u>

$$U = -\frac{\partial}{\partial \beta} \ln(Z)$$

$$= \cancel{\frac{\partial}{\partial \beta}} - \frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= -\frac{1}{e^{-\frac{\hbar^2\pi^2}{2mL^2}\beta} + e^{-\frac{4\hbar^2\pi^2}{2mL^2}\beta}} \cdot \left(-\frac{\hbar^2\pi^2}{2mL^2} e^{-\frac{\hbar^2\pi^2}{2mL^2}\beta} - \frac{4\hbar^2\pi^2}{2mL^2} \cdot e^{-\frac{4\hbar^2\pi^2\beta}{2mL^2}}\right)$$

$$= \frac{\hbar^2\pi^2(e^{-\gamma} + 4e^{-\gamma 4})}{2mL^2(e^{-\gamma} + e^{-4\gamma})}, \quad \gamma = \frac{\hbar^2\pi^2\beta}{2mL^2}$$

In the low T limit γ is very large, and we can approximate even further

$$U \simeq \frac{\hbar^2\pi^2}{2mL^2}\frac{e^{-\gamma}}{e^{-\gamma}} = \frac{\hbar^2\pi^2}{2mL^2}$$

$$C_V = \frac{\partial U}{\partial T} = 0$$

Heat capacity goes towards 0

3.3) The internal energy of ideal gas is $U = \frac{3}{2}NkT$, (We use ideal gas since we only have 1 particle, and is therefore exact)

$$NkT = \frac{2U}{3}$$

$$\Rightarrow PV = \frac{2U}{3},$$ For our case in 1D we will change to

$$FL = \frac{2U}{3},$$ where F is force

3.3) In the high T limit we get

$$FL = \frac{2U}{3} = \frac{2}{3} \cdot \frac{kT}{4}$$

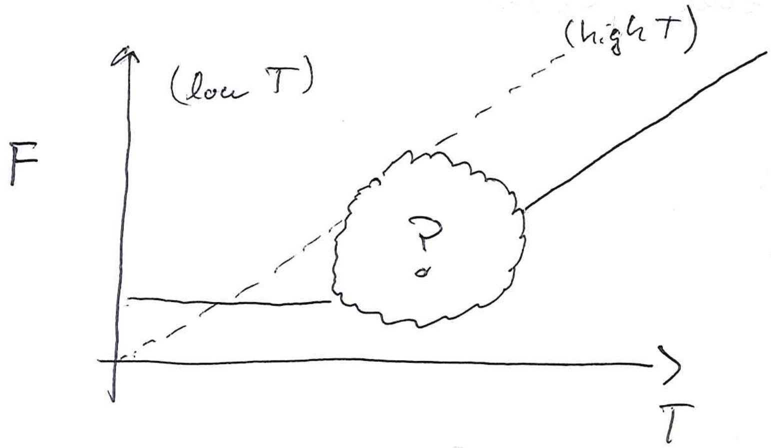
$$\underline{FL = \frac{kT}{6}}$$

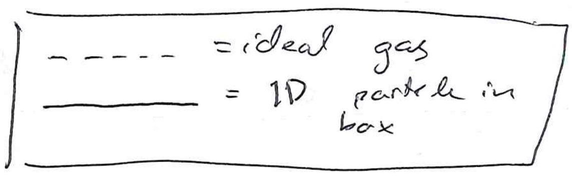
In the low T limit we get

$$FL = \frac{2}{3} U = \frac{2}{3} \frac{\hbar^2 \pi^2}{2mL^2}$$

$$\underline{FL^3 = \frac{\hbar^2 \pi^2}{6m}}$$

If we plot this we get, for constant L.





We see that for the 1D case we will never get zero energy, which is true in QM since the wavefunction needs to satisfy the boundary conditions. In the high T case they behave the same way (linear with T), with a slope of $\frac{Nk}{V}$ and $\frac{k}{6L}$.