Bc. Jaroslav Zůda

Statistical physics and Thermodynamics

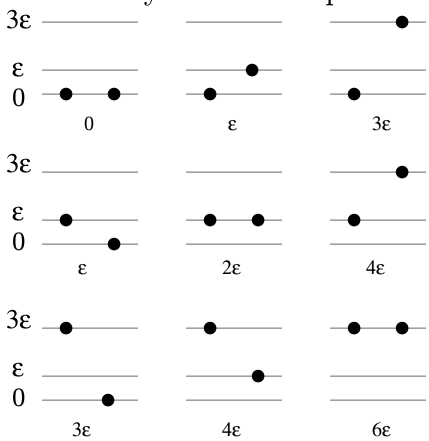
Problem 1: Consider a system consisting of two particles, each ow which can be in any one of three quantum states of respective energies, $0, \epsilon, 3\epsilon$. The system is in contact with a heat reservoir at temperature T.

1. Write an expression for the particion function Z if the particles obey classical MB statistics and are considered distinguishable.
2. What is Z if the particles obey BE statistics?
3. What is Z if the particles obey FD statistics?

The partition function can be write as

$$Z = \sum_n \mathrm{e}^{-\frac{E_n}{T}}.$$

In the next pictures there are all possible states with respective energies. Then it is easy to find the partition function.



For MB statistics and distinguishable particles I have to count all states in the picture. Finally I have

$$Z_{MB} = \mathrm{e}^{-\frac{0}{T}} + 2\mathrm{e}^{-\frac{\epsilon}{T}} + \mathrm{e}^{-\frac{2\epsilon}{T}} + 2\mathrm{e}^{-\frac{3\epsilon}{T}} + 2\mathrm{e}^{-\frac{4\epsilon}{T}} + \mathrm{e}^{-\frac{6\epsilon}{T}}$$

The partition function in BE statistics is similar to partition function in MB statistics, but particles are not distinguishable here. It means that total energy levels, which were counted twice, are counted only once here.

$$Z_{BE} = \mathrm{e}^{-\frac{0}{T}} + \mathrm{e}^{-\frac{\epsilon}{T}} + \mathrm{e}^{-\frac{2\epsilon}{T}} + \mathrm{e}^{-\frac{3\epsilon}{T}} + \mathrm{e}^{-\frac{4\epsilon}{T}} + \mathrm{e}^{-\frac{6\epsilon}{T}}$$

In fermions case, there should be only one particle in each energy level, so the states where are two particles are forbidden. Partition function is then

$$Z_{FD} = \mathrm{e}^{-\frac{\epsilon}{T}} + \mathrm{e}^{-\frac{3\epsilon}{T}} + \mathrm{e}^{-\frac{4\epsilon}{T}}$$

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Statistical physics and thermodynamics

Problem 2: A simple harmonic one-dimensional oscillator has energy levels given by $E_n = (n+\frac{1}{2})\hbar\omega$, where ω is the characteristic frequency of the oscillator and the quantum number n can assume the possible integral values $n = 0, 1, 2, \ldots$. Suppose that such an oscillator is in thermal contact with a heat reservoir at temperature T.

1. Find the ratio of the probability of the oscillator being in the first excited state to the probability of its being in the ground state.

2. Find the mean energy of the oscillator as a function of the temperature T.

Basic assumption: In equilibrium, all states are equally probable. This means that entropy S is maximal. From definition I have

$$S = \ln \Gamma(E),$$

where $\Gamma(E)$ is density of states. There should be Boltzmann constant, but I can choose its value.

There is a heat reservoir and our system, so density of states in our system is

$$\Gamma(E_1) = \Gamma_1(E_1)\Gamma_2(E_0 - E_1).$$

Entropy is

$$S = \ln \Gamma_1(E_1) + \ln \Gamma_2(E_0 - E_1).$$

I know that entropy should be maximal in equilibrium:

$$\frac{\mathrm{d}S}{\mathrm{d}E} = 0 \Rightarrow \frac{\mathrm{d}S_1}{\mathrm{d}E_1} - \frac{\mathrm{d}S_2}{\mathrm{d}E_1} = 0 \Rightarrow \frac{\mathrm{d}S_1}{\mathrm{d}E_1} = \frac{\mathrm{d}S_2}{\mathrm{d}E_1} = \frac{1}{T}$$

In equilibrium, the temperatures of heat reservoir and our system are equal.

Now I have necessary theorems to calculate probability to find system in the state with energy E_n.

$$\begin{aligned} \Gamma'(E_0 - E_r) &= \mathrm{e}^{S'(E_0 - E_r)} \sim \mathrm{e}^{S'(E_0) - \frac{\partial S}{\partial E_0} E_r} = K\mathrm{e}^{-\frac{E_r}{T}} \\ \Rightarrow P_r &= C\mathrm{e}^{-\frac{E_r}{T}}, \end{aligned}$$

where

$$\sum_r P_r = 1 \Rightarrow C = \frac{1}{\sum_k \mathrm{e}^{-\frac{E_k}{T}}} = \frac{1}{Z},$$

where Z is the partition function. Now I can compute the ratio of probability of being in the first excited state ($n = 1$) to the probability of being in the ground state ($n = 0$):

$$\begin{aligned}\frac{P_1}{P_0} &= \frac{C\mathrm{e}^{-\frac{\left(1+\frac{1}{2}\right)\hbar\omega}{T}}}{C\mathrm{e}^{-\frac{\left(0+\frac{1}{2}\right)\hbar\omega}{T}}} \\ &= \mathrm{e}^{\frac{\hbar\omega}{T}}\end{aligned}$$

For the mean value of any quantity X holds the equation

$$\langle X \rangle = \sum_r X_r P_r$$

I will compute the mean value of energy:

$$\begin{aligned}\langle E \rangle &= \sum_r E_r C\mathrm{e}^{-\frac{E_r}{T}} \\ &= \frac{T^2}{Z}\frac{\mathrm{d}}{\mathrm{d}T}\sum_r \mathrm{e}^{-\frac{E_r}{T}} = \frac{T^2}{Z}\frac{\mathrm{d}Z}{\mathrm{d}T} \\ &= T^2\frac{\mathrm{d}\ln Z}{\mathrm{d}T}\end{aligned}$$

Definition of free energy F: $Z = \mathrm{e}^{-\frac{F}{T}} \Rightarrow F = -T\ln Z$ The free energy can be used to compute the mean value of energy in easier way.

$$\langle E \rangle = -T^2\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{F}{T}\right) = F - T\frac{\mathrm{d}F}{\mathrm{d}T}$$

I will use this equation later, because I have to find the free energy. For this I will compute the partition function.

$$\begin{aligned}Z &= \sum_{r=0}^{\infty}\mathrm{e}^{-\frac{\left(r+\frac{1}{2}\right)\hbar\omega}{T}} = \mathrm{e}^{-\frac{\hbar\omega}{2T}}\sum_{r=0}^{\infty}\mathrm{e}^{-\frac{r\hbar\omega}{T}} \\ &= \frac{\mathrm{e}^{-\frac{\hbar\omega}{2T}}}{1-\mathrm{e}^{-\frac{\hbar\omega}{T}}} = \frac{1}{\mathrm{e}^{\frac{\hbar\omega}{2T}}-\mathrm{e}^{-\frac{\hbar\omega}{2T}}} = \frac{1}{2\sinh\frac{\hbar\omega}{2T}} \\ \Rightarrow F &= T\ln 2\sinh\frac{\hbar\omega}{2T} \\ \Rightarrow \langle E \rangle &= T\ln 2\sinh\frac{\hbar\omega}{2T} - T\left(\ln 2\sinh\frac{\hbar\omega}{2T} + T\frac{2\cosh\frac{\hbar\omega}{2T}}{2\sinh\frac{\hbar\omega}{2T}}\left(-\frac{\hbar\omega}{2T^2}\right)\right) \\ &= \frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2T}\end{aligned}$$

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Statistical physics and Thermodynamics

Problem 3: For ideal gases in two dimensions, find

1. The heat capacity at constant area in the high-temperature limit for both the Fermi and Bose cases.
2. The heat capacity at constant area in the low-temperature limit for the Fermi case

For quantum ideal gas I have

$$Z = e^{-\frac{\Omega}{T}} = \sum_r e^{-\frac{E_r - \mu N_r}{T}},$$

where Ω is Landau potential for systems, where the number of particles N is not fixed.

I have ideal gas, so the approximation by 1-particle states is applicable. There can be any number of particles for bosons and maximum of 1 particle for fermions. For both cases the partition function is different. In this approximation, each state is specified by saying how many particles are in each of 1-particle levels. The energy of state is given by

$$\begin{aligned} E_r &= n_1\epsilon_1 + n_2\epsilon_2 + \dots \\ N_r &= n_1 + n_2 + \dots . \end{aligned}$$

Now I can compute the partition function and then Landau potential.

$$\begin{aligned} Z &= \sum_r e^{-\frac{E_r - \mu N_r}{T}} = \sum_r e^{-\frac{n_1\epsilon_1 + n_2\epsilon_2 + \dots - \mu n_1 - \mu n_2 - \dots}{T}} \\ &= \sum_r e^{-\frac{n_1(\epsilon_1 - \mu)}{T}} e^{-\frac{n_2(\epsilon_2 - \mu)}{T}} \dots \\ &= \sum_{n_1=0}^{\infty \vee 1} \sum_{n_2=0}^{\infty \vee 1} \dots e^{-\frac{n_1(\epsilon_1 - \mu)}{T}} e^{-\frac{n_2(\epsilon_2 - \mu)}{T}} \dots \\ &= \prod_{i=1}^{\infty} \sum_{n_i=0}^{\infty \vee 1} e^{-\frac{n_i(\epsilon_i - \mu)}{T}} \\ &= \prod_{i=1}^{\infty} \frac{1}{1 - e^{-\frac{\epsilon_i - \mu}{T}}} \qquad \text{for bosons} \end{aligned}$$

$$
\begin{aligned}
&= \prod_{i=1}^{\infty}\left(1+\mathrm{e}^{-\frac{\epsilon_i-\mu}{T}}\right) \qquad \text{for fermions} \\
\Rightarrow \Omega_B &= -T\ln\prod_{i=1}^{\infty}\frac{1}{1-\mathrm{e}^{-\frac{\epsilon_i-\mu}{T}}} = T\sum_{i=1}^{\infty}\ln\left(1-\mathrm{e}^{-\frac{\epsilon_i-\mu}{T}}\right) \\
\Omega_F &= -T\ln\prod_{i=1}^{\infty}\left(1+\mathrm{e}^{-\frac{\epsilon_i-\mu}{T}}\right) = -T\sum_{i=1}^{\infty}\ln\left(1+\mathrm{e}^{-\frac{\epsilon_i-\mu}{T}}\right) \\
\Rightarrow \Omega &= \pm T\sum_{i=1}^{\infty}\ln\left(1\mp\mathrm{e}^{-\frac{\epsilon_i-\mu}{T}}\right)
\end{aligned}
$$

The upper signs are for bosons, the lower signs are for fermions.

I use the 1-particle approximation so it is necessary to compute the time independent Schroedinger equation.

$$
\begin{aligned}
E\psi &= \frac{\vec{p}^2}{2m}\psi + V\psi \\
\Rightarrow \frac{2mE}{\hbar^2}\psi &= -\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi \\
\Rightarrow E &= \frac{\hbar^2\pi^2}{2mL^2}(n_x^2+n_y^2) \\
&= \frac{\hbar^2k^2}{2m}
\end{aligned}
$$

I will approximate the sum over energies with integral over states. 1 state is in $\frac{\pi^2}{L^2}$ area, so the density of states is $\rho(k)=\frac{S}{\pi^2}$. In the next will be used V instead of S because of possible collision with entropy, which has same symbol S.

$$
\begin{aligned}
\Omega &= \pm T\int_{\text{1st quadrant}}\mathrm{d}^2k\frac{V}{\pi^2}\ln\left(1\mp\mathrm{e}^{-\frac{\frac{\hbar^2k^2}{2m}-\mu}{T}}\right) \\
&= \pm T\int_0^{\infty}\mathrm{d}kk\int_{\text{1st quadrant}}\mathrm{d}\varphi\frac{V}{\pi^2}\ln\left(1\mp\mathrm{e}^{-\frac{\frac{\hbar^2k^2}{2m}-\mu}{T}}\right) \\
&= \pm T\int_0^{\infty}\mathrm{d}k\frac{\pi}{2}k\frac{V}{\pi^2}\ln\left(1\mp\mathrm{e}^{-\frac{\frac{\hbar^2k^2}{2m}-\mu}{T}}\right) \\
&= \pm T\frac{V}{\pi}\int_0^{\infty}\mathrm{d}kk\ln\left(1\mp\mathrm{e}^{-\frac{\frac{\hbar^2k^2}{2m}-\mu}{T}}\right) \\
&\left| E=\frac{\hbar^2k^2}{2m}\Rightarrow \mathrm{d}E=\frac{\hbar^2k}{m}\mathrm{d}k \right.
\end{aligned}
$$

$$
\begin{aligned}
&= \pm T\frac{V}{\pi}\int_0^\infty \mathrm{d}E\frac{m}{\hbar^2}\ln\left(1\mp \mathrm{e}^{-\frac{E-\mu}{T}}\right)\\
&= \pm\frac{TVm}{\pi\hbar^2}\int_0^\infty \mathrm{d}E\ln\left(1\mp \mathrm{e}^{-\frac{E-\mu}{T}}\right)\\
&\quad \Big| x=\frac{E}{T}\Rightarrow \mathrm{d}x=\frac{1}{T}\mathrm{d}E\\
&= \pm\underbrace{\frac{T^2Vm}{\pi\hbar^2}}_{C}\int_0^\infty \mathrm{d}x\ln\left(1\mp \mathrm{e}^{-x}\underbrace{\mathrm{e}^{\frac{\mu}{T}}}_{K}\right)\\
&= \pm C\int_0^\infty \mathrm{d}x\ln\left(1\mp K\mathrm{e}^{-x}\right)\\
&\quad \Big| u=\ln\left(1\mp K\mathrm{e}^{-x}\right)\Rightarrow u'=\frac{\pm K\mathrm{e}^{-x}}{1\mp K\mathrm{e}^{-x}}\\
&\quad | v'=1\Rightarrow v=x\\
&= C\left(\left[x\ln\left(1\mp K\mathrm{e}^{-x}\right)\right]_0^\infty-\int_0^\infty \mathrm{d}x\frac{Kx\mathrm{e}^{-x}}{1\mp K\mathrm{e}^{-x}}\right)\\
&\quad \big|\left[x\ln\left(1\mp K\mathrm{e}^{-x}\right)\right]_0^\infty=0\\
&= -C\int_0^\infty \mathrm{d}x\frac{x}{\mathrm{e}^{x-\frac{\mu}{T}}\mp 1}\\
&= -\frac{T^2Vm}{\pi\hbar^2}(B,F)_1\left(\frac{\mu}{T}\right)
\end{aligned}
$$

The equation above is Landau potential for quantum ideal gas. I have to compute the low and high temperature limits of heat capacity. Heat capacity is defined as $c_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$, so I need to compute entropy.

$$
\begin{aligned}
S=-\frac{\partial\Omega}{\partial T} &= \frac{2TVm}{\pi\hbar^2}(B,F)_1\left(\frac{\mu}{T}\right)+\frac{T^2Vm}{\pi\hbar^2}(B,F)_0\left(\frac{\mu}{T}\right)\left(-\frac{\mu}{T^2}\right)\\
&= \frac{2TVm}{\pi\hbar^2}(B,F)_1\left(\frac{\mu}{T}\right)-\frac{Vm\mu}{\pi\hbar^2}(B,F)_0\left(\frac{\mu}{T}\right)
\end{aligned}
$$

I need to find the chemical potential μ and boson and fermion function. I will use the number of particles defined with $N=-\frac{\partial\Omega}{\partial\mu}$.

$$
N = \frac{TVm}{\pi\hbar^2}(B,F)_0\left(\frac{\mu}{T}\right)
$$

The limit for temperature in the high temperature approximation is infinity and $\frac{N}{V}\rightarrow 0\Rightarrow\frac{\mu}{T}\rightarrow-\infty$.

From class I have

$$
\lim_{y\rightarrow-\infty}(B,F)_N(y)=\Gamma(N+1)\left(\mathrm{e}^y\pm\frac{\mathrm{e}^{2y}}{2^N}\right)
$$

In this case $N = 0$, so

$$\begin{aligned}
(B,F)_0\left(\frac{\mu}{T}\right) &= \Gamma(1)\left(\mathrm{e}^{\frac{\mu}{T}} \pm \frac{1}{2^0}\mathrm{e}^{\frac{2\mu}{T}}\right) \\
&= \frac{N\pi\hbar^2}{TVm} \\
\Rightarrow \mathrm{e}^{\frac{\mu}{T}} \pm \mathrm{e}^{\frac{2\mu}{T}} &= \frac{N\pi\hbar^2}{TVm}
\end{aligned}$$

I will use the expansion to the second order.

$$\begin{aligned}
\mathrm{e}^y &= x + f(x) \\
\Rightarrow x &= x + f(x) \pm (x + f(x))^2 \\
\Rightarrow \mp x^2 &= f(x)(1 \pm 2x) \\
\Rightarrow f(x) &= \mp\frac{x^2}{1 \pm 2x} \sim \mp x^2 \\
\Rightarrow \mathrm{e}^y &= x \mp x^2 \\
\Rightarrow \mathrm{e}^{\frac{\mu}{T}} &= \frac{N\pi\hbar^2}{TVm} \mp \left(\frac{N\pi\hbar^2}{TVm}\right)^2 \\
\Rightarrow (B,F)_1\left(\frac{\mu}{T}\right) &= \frac{N\pi\hbar^2}{TVm} \mp \left(\frac{N\pi\hbar^2}{TVm}\right)^2 \pm \frac{1}{2}\left(\frac{N\pi\hbar^2}{TVm} \mp \left(\frac{N\pi\hbar^2}{TVm}\right)^2\right)^2
\end{aligned}$$

In the next will be μ computed. I do not have to compute $(B,F)_0$ because after comparing the equation for entropy to equation for number of particles we can see that the second part of the entropy can be written as $\frac{N\mu}{T}$.

$$\begin{aligned}
\mathrm{e}^y &= x \mp x^2 \\
\Rightarrow y &= \ln\left(x \mp x^2\right) \\
&= \ln x + \ln(1 \mp x) \\
&= \ln x \mp x \\
\Rightarrow \mu &= T\left(\ln\frac{N\pi\hbar^2}{TVm} \mp \frac{N\pi\hbar^2}{TVm}\right)
\end{aligned}$$

With these equations the entropy has the following expression:

$$\begin{aligned}
S = {} & \frac{2TVm}{\pi\hbar^2}\left(\frac{N\pi\hbar^2}{TVm} \mp \left(\frac{N\pi\hbar^2}{TVm}\right)^2 \pm \frac{1}{2}\left(\frac{N\pi\hbar^2}{TVm} \mp \left(\frac{N\pi\hbar^2}{TVm}\right)^2\right)^2\right) \\
& -\frac{N}{T}T\left(\ln\frac{N\pi\hbar^2}{TVm} \mp \frac{N\pi\hbar^2}{TVm}\right)
\end{aligned}$$

$$
\begin{aligned}
&= \frac{2TVmN\pi\hbar^2}{TVm\pi\hbar^2}\left(1 \mp \frac{N\pi\hbar^2}{TVm} \pm \frac{N\pi\hbar^2}{2TVm}\right) - \underbrace{N\ln\frac{N\pi\hbar^2}{Vm}}_{K} + N\ln T \pm \frac{N^2\pi\hbar^2}{TVm} \\
&= 2N\left(1 \mp \frac{N\pi\hbar^2}{2TVm}\right) - K + N\ln T \pm \frac{N^2\pi\hbar^2}{2TVm} \\
&= 2N - K + N\ln T \mp \frac{N^2\pi\hbar^2}{2TVm} \\
\Rightarrow c_V &= T\left(\frac{N}{T} \pm \frac{N^2\pi\hbar^2}{2T^2Vm}\right) \\
&= N \pm \frac{N^2\pi\hbar^2}{2TVm} = N\left(1 \pm \frac{N\pi\hbar^2}{2TVm}\right)
\end{aligned}
$$

The result is different from the classical model due to quantum corrections.

The low temperature approximation will be computed only for fermions. In this case $T \to 0 \wedge \frac{N}{V} \to \infty \Rightarrow \frac{\mu}{T} \to \infty$. From class I have

$$
\begin{aligned}
\lim_{y\to\infty} F_n(y) &= \frac{y^{n+1}}{n+1} + 2ny^{n-1}F_1(0) \\
F_1(0) &= \frac{1}{2}\Gamma(2)\zeta(2) = \frac{\pi^2}{12} \\
\Rightarrow F_0(y) &= y \\
F_1(y) &= \frac{y^2}{2} + \frac{\pi^2}{6} \\
\Rightarrow F_0\left(\frac{\mu}{T}\right) &= \frac{\mu}{T} \\
&= \frac{N\pi\hbar^2}{TVm} \\
\Rightarrow \mu &= \frac{N\pi\hbar^2}{Vm} \\
F_1\left(\frac{\mu}{T}\right) &= \frac{1}{2}\left(\frac{N\pi\hbar^2}{TVm}\right)^2 + \frac{\pi^2}{6} \\
\Rightarrow S &= \frac{2TVm}{\pi\hbar^2}\left(\frac{1}{2}\left(\frac{N\pi\hbar^2}{TVm}\right)^2 + \frac{\pi^2}{6}\right) - \frac{Vm}{\pi\hbar^2}\frac{N\pi\hbar^2}{Vm}\frac{\frac{N\pi\hbar^2}{Vm}}{T} \\
&= \frac{TVmN^2\pi^2\hbar^4}{\pi\hbar^2T^2V^2m^2} + \frac{2TVm\pi^2}{6\pi\hbar^2} - \frac{N^2\pi\hbar^2}{TVm} \\
&= \frac{N^2\pi\hbar^2}{TVm} + \frac{TVm\pi}{3\hbar^2} - \frac{N^2\pi\hbar^2}{TVm} \\
&= \frac{TVm\pi}{3\hbar^2}
\end{aligned}
$$

$$\Rightarrow c_V = T\left(\frac{Vm\pi}{3\hbar^2}\right) = \frac{TVm\pi}{3\hbar^2}$$

This is the low temperature limit for Fermi gas.

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Statistical physics and Thermodynamics

Problem 4: Find the high- and low-temperature limits of the heat capacity of a Debye solid in two dimensions.

In the Debye model the states are influenced by all atoms. Low lying excitations are collective oscilations of the crystal and they are called phonons. The partition function can be then write as

$$Z = \mathrm{e}^{-\frac{F}{T}} = \sum_{\text{1st state}} \left(\mathrm{e}^{-\frac{E_1}{T}}\right)^{n_1} \sum_{\text{2nd state}} \left(\mathrm{e}^{-\frac{E_2}{T}}\right)^{n_2} \dots \sum_{2N} \left(\mathrm{e}^{-\frac{E_{3N}}{T}}\right)^{n_{2N}}$$

There are $2N$ sums because the problem is in two dimensions. Now is the problem to find the energies of oscillations. I will use mechanical model with springs. Lagrangian of this problem is

$$\begin{aligned} L &= \sum_i \left(\frac{1}{2}m\dot{x}_i^2 - \frac{1}{2}k\left(x_{i+1}-x_i\right)^2\right) \\ \Rightarrow m\ddot{x}_i &= k\left(x_{i+1}-x_i\right) + k\left(x_i - x_{i-1}\right) \end{aligned}$$

Assumption of solution: $x_i(t) = A\sin\left(\frac{i}{N}2\pi r - \omega_r t\right)$, where r denotes the mode of the oscillation.

$$\begin{aligned} x_{i+1}-x_i &= A\left(\sin\left(\frac{i+1}{N}2\pi r - \omega_r t\right) - \sin\left(\frac{i}{N}2\pi r - \omega_r t\right)\right) \\ &= A\left(\sin\left(\frac{i}{N}2\pi r - \omega_r t\right) + \frac{2\pi r}{N}\cos\left(\frac{i}{N}2\pi r - \omega_r t\right)\right) \\ &\quad -A\sin\left(\frac{i}{N}2\pi r - \omega_r t\right) \\ &= A\frac{2\pi r}{N}\cos\left(\frac{i}{N}2\pi r - \omega_r t\right) \end{aligned}$$

Analogically for $x_i - x_{i-1}$ I have $A\frac{2\pi r}{N}\cos\left(\frac{i-1}{N}2\pi r - \omega_r t\right)$. Then the force equation is

$$\begin{aligned} -m\omega_r^2 x_i &= Ak\frac{2\pi r}{N}\left(\cos\left(\frac{i-1}{N}2\pi r - \omega_r t\right) - \cos\left(\frac{i}{N}2\pi r - \omega_r t\right)\right) \\ &= Ak\frac{2\pi r}{N}\left(\cos\left(\frac{i}{N}2\pi r - \omega_r t\right) - \left(-\frac{2\pi r}{N}\right)\sin\left(\frac{i}{N}2\pi r - \omega_r t\right)\right) \\ &\quad -Ak\frac{2\pi r}{N}\cos\left(\frac{i}{N}2\pi r - \omega_r t\right) \end{aligned}$$

$$
\begin{aligned}
&= Ak\left(\frac{2\pi r}{N}\right)^2 \sin\left(\frac{i}{N}2\pi r - \omega_r t\right) \\
\Rightarrow m\omega_r^2 &= k\left(\frac{2\pi r}{N}\right)^2 \\
\Rightarrow \omega_r &= \sqrt{\frac{k}{m}}\frac{2\pi r}{N} \\
&= \sqrt{\frac{a^2 k}{m}}\frac{2\pi}{L}r = \sqrt{\frac{a^2 k}{m}}k_r
\end{aligned}
$$

The energy of the state is then

$$
\begin{aligned}
E_r &= \hbar\omega_r \\
\Rightarrow Z &= \sum_{n_1=0}^{\infty}\left(\mathrm{e}^{-\frac{\hbar\omega_1}{T}}\right)^{n_1}\sum_{n_2=0}^{\infty}\left(\mathrm{e}^{-\frac{\hbar\omega_2}{T}}\right)^{n_2}\dots \\
&= \frac{1}{1-\mathrm{e}^{-\frac{\hbar\omega_1}{T}}}\frac{1}{1-\mathrm{e}^{-\frac{\hbar\omega_2}{T}}}\dots\frac{1}{1-\mathrm{e}^{-\frac{\hbar\omega_{2N}}{T}}} \\
\Rightarrow F &= T\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega_1}{T}}\right)\left(1-\mathrm{e}^{-\frac{\hbar\omega_2}{T}}\right)\dots \\
&= T\sum_{n=1}^{2N}\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega_n}{T}}\right) \\
&= T\int_0^{k_{max}}\mathrm{d}^2\vec{k}\rho(k)\ln\left(1-\mathrm{e}^{-\frac{\hbar k v}{T}}\right)
\end{aligned}
$$

The density of states is $\rho(k) = \left(\frac{L}{2\pi}\right)^2$. Then for free energy I have

$$
\begin{aligned}
F &= T\int_0^{k_{max}}\mathrm{d}^2\vec{k}\left(\frac{L}{2\pi}\right)^2\ln\left(1-\mathrm{e}^{-\frac{\hbar k v}{T}}\right) \\
&= T\int_0^{k_{max}}\mathrm{d}k k 2\pi\frac{L^2}{4\pi^2}\ln\left(1-\mathrm{e}^{-\frac{\hbar k v}{T}}\right) \\
&\quad |\omega = vk \Rightarrow \mathrm{d}\omega = v\mathrm{d}k \\
&= \frac{TL^2}{2\pi}\int_0^{\omega_{max}}\mathrm{d}\omega\frac{1}{v^2}\omega\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega}{T}}\right) \\
&\quad \left|\int_0^{\omega_D}\frac{L^2\omega}{2\pi v^2}\mathrm{d}\omega = \frac{V\omega_D^2}{4\pi v^2} = N\right. \\
&\quad \left|\Rightarrow \omega_D = 2v\sqrt{\frac{\pi N}{V}}\right. \\
&= \frac{TV}{2\pi v^2}\int_0^{\omega_D}\mathrm{d}\omega\omega\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega}{T}}\right)
\end{aligned}
$$

$$
\begin{aligned}
&\left| x = \frac{\hbar\omega}{T} \Rightarrow \mathrm{d}x = \frac{\hbar}{T}\mathrm{d}\omega \right. \\
= \quad & \frac{TV}{2\pi v^2}\frac{T}{\hbar}\frac{T}{\hbar}\int_0^{\frac{\hbar\omega_D}{T}} \mathrm{d}x x \ln\left(1 - \mathrm{e}^{-x}\right) \\
= \quad & \frac{T^3 V}{2\pi v^2 \hbar^2}\int_0^{\frac{\hbar\omega_D}{T}} \mathrm{d}x x \ln\left(1 - \mathrm{e}^{-x}\right) \\
&\left| u = \ln\left(1 - \mathrm{e}^{-x}\right) \Rightarrow u' = \frac{\mathrm{e}^{-x}}{1 - \mathrm{e}^{-x}} \right. \\
&\left| v' = x \Rightarrow v = \frac{x^2}{2} \right. \\
= \quad & \frac{T^3 V}{2\pi v^2 \hbar^2}\left(\left[\frac{x^2}{2}\ln\left(1 - \mathrm{e}^{-x}\right)\right]_0^{\frac{T_D}{T}} - \frac{1}{2}\int_0^{\frac{T_D}{T}} \frac{x^2 \mathrm{e}^{-x}}{1 - \mathrm{e}^{-x}}\right) \\
= \quad & \frac{T^3 V}{4\pi v^2 \hbar^2}\left(\frac{T_D^2}{T^2}\ln\left(1 - \mathrm{e}^{-\frac{T_D}{T}}\right) - \int_0^{\frac{T_D}{T}} \mathrm{d}x \frac{x^2}{\mathrm{e}^x - 1}\right) \\
= \quad & \frac{T T_D^2 V}{4\pi v^2 \hbar^2}\left(\ln\left(1 - \mathrm{e}^{-\frac{T_D}{T}}\right) - \frac{T^2}{T_D^2}\int_0^{\frac{T_D}{T}} \mathrm{d}x \frac{x^2}{\mathrm{e}^x - 1}\right) \\
&\left| T_D^2 = \hbar^2\omega_D^2 = \hbar^2 \frac{4v^2\pi N}{V} \right. \\
= \quad & \frac{TV}{4\pi v^2 \hbar^2}\hbar^2\frac{4v^2\pi N}{V}\left(\ln\left(1 - \mathrm{e}^{-\frac{T_D}{T}}\right) - \frac{T^2}{T_D^2}\int_0^{\frac{T_D}{T}} \mathrm{d}x \frac{x^2}{\mathrm{e}^x - 1}\right) \\
= \quad & NT\left(\ln\left(1 - \mathrm{e}^{-\frac{T_D}{T}}\right) - \frac{T^2}{T_D^2}\int_0^{\frac{T_D}{T}} \mathrm{d}x \frac{x^2}{\mathrm{e}^x - 1}\right)
\end{aligned}
$$

This is the free energy for Debye solid in two dimensions. Now I will compute the high-temperature limit of heat capacity.

$$
\begin{aligned}
\lim_{T\to\infty} F \quad &= \quad NT\left(\ln\left(1 - \left(1 - \frac{T_D}{T}\right)\right) - \frac{T^2}{T_D^2}\int_0^{\frac{T_D}{T}} \mathrm{d}x x\right) \\
&= \quad NT\left(\ln\frac{T_D}{T} - \frac{1}{2}\right) \\
&= \quad NT\ln\frac{T_D}{T} - \frac{1}{2}NT \\
\Rightarrow S = -\frac{\partial F}{\partial T} \quad &= \quad \frac{N}{2} - N\ln\frac{T_D}{T} + NT\frac{T}{T_D}\frac{T_D}{T^2}
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{N}{2} + NT_D - N\ln\frac{T_D}{T} \\
\Rightarrow c_V = T\frac{\partial S}{\partial T} &= NT\frac{T}{T_D}\frac{T_D}{T^2} = N
\end{aligned}
$$

Now I will compute the low-temperature limit of heat capacity.

$$
\begin{aligned}
\lim_{T\to 0} F &= NT\left(-\mathrm{e}^{-\frac{T_D}{T}} - \frac{T^2}{T_D^2}B_2(0)\right) \\
&= -NT\mathrm{e}^{-\frac{T_D}{T}} - \frac{NT^3}{T_D^2}B_2(0) \\
&\quad |B_N(0) = \Gamma(N+1)\zeta(N+1) \Rightarrow B_2(0) = 2\zeta(3) \\
&= -NT\mathrm{e}^{-\frac{T_D}{T}} - 2\frac{NT^3}{T_D^2}\zeta(3) \\
\Rightarrow S &= N\mathrm{e}^{-\frac{T_D}{T}} + NT\mathrm{e}^{-\frac{T_D}{T}}\frac{T_D}{T^2} + \frac{6NT^2\zeta(3)}{T_D^2} \\
&= N\mathrm{e}^{-\frac{T_D}{T}} + N\frac{T_D}{T}\mathrm{e}^{-\frac{T_D}{T}} + \frac{6NT^2\zeta(3)}{T_D^2} \\
\Rightarrow c_V &= T\left(\frac{NT_D}{T^2}\mathrm{e}^{-\frac{T_D}{T}} - \frac{NT_D}{T^2}\mathrm{e}^{-\frac{T_D}{T}} + \frac{NT_D^2}{T^3}\mathrm{e}^{-\frac{T_D}{T}} + \frac{12NT\zeta(3)}{T_D^2}\right) \\
&= \frac{NT_D^2}{T^2}\mathrm{e}^{-\frac{T_D}{T}} + \frac{12NT^2\zeta(3)}{T_D^2} \approx \frac{12NT^2\zeta(3)}{T_D^2}
\end{aligned}
$$

Bc. Jaroslav Zůda

Statistical physics and Thermodynamics

Problem 5: A system consist of N very weakly interacting particles at a temperature T sufficiently high so that classical statistical mechanics is applicable. Each particle has mass m and is free to perform one-dimensional oscillations about its equilibrium position. Calculate the heat capacity of this system or particles at this temperature in each of the following cases:

1. The force effective in restoring each particle to its equilibrium position is proportional to its displacement x from this position.
2. The restoring force is proportional to x^2.

The energy of the oscillators is given by equation

$$E = \frac{p^2}{2m} + U,$$

where U is the potential energy given by equation

$$U = \int F \mathrm{d}s$$

In this problem F is the force effective in restoring particles and is proportional to x, respectively x^2. Then the potential energy is

$$U_1 = \frac{1}{2}\alpha x^2$$
$$U_2 = \frac{1}{3}\beta x^3$$

and total energy

$$E_1 = \frac{p^2}{2m} + \frac{\alpha x^2}{2}$$
$$E_2 = \frac{p^2}{2m} + \frac{\beta x^3}{3}$$

The partition function for the first problem is

$$Z = \mathrm{e}^{-\frac{F}{T}} = \sum_r \mathrm{e}^{-\frac{E_r}{T}}$$

$$
\begin{aligned}
&= \int \frac{\mathrm{d}p_i \mathrm{d}x_i}{(2\pi\hbar)^N} \mathrm{e}^{-\frac{\sum_i \left(\frac{p_i^2}{2m} + \frac{\alpha x_i^2}{2}\right)}{T}} \\
&= \prod_{i=1}^{N} \int \frac{\mathrm{d}p_i \mathrm{d}x_i}{2\pi\hbar} \mathrm{e}^{-\frac{\frac{p_i^2}{2m} + \frac{\alpha x_i^2}{2}}{T}} \\
&= \prod_{i=1}^{N} \frac{1}{2\pi\hbar} \int \mathrm{d}p_i \mathrm{e}^{-\frac{p_i^2}{2mT}} \int \mathrm{d}x_i \mathrm{e}^{-\frac{\alpha x^2}{2T}} \\
&= \left(\frac{1}{2\pi\hbar} \int \mathrm{d}p \mathrm{e}^{-\frac{p^2}{2mT}} \int \mathrm{d}x \mathrm{e}^{-\frac{\alpha x^2}{2T}} \right)^N \\
&= \left(\frac{1}{2\pi\hbar} \sqrt{2\pi m T} \sqrt{\frac{2\pi T}{\alpha}} \right)^N \\
&= \left(\frac{2\pi T \sqrt{m}}{2\pi\hbar\sqrt{\alpha}} \right)^N \\
&= \left(\frac{T}{\hbar} \sqrt{\frac{m}{\alpha}} \right)^N \\
\Rightarrow F &= -NT \ln \frac{T}{\hbar} \sqrt{\frac{m}{\alpha}} \\
&= -NT \ln T + NT \ln \hbar \sqrt{\frac{\alpha}{m}} \\
\Rightarrow S = -\frac{\partial F}{\partial T} &= N \ln T + N - N \ln \hbar \sqrt{\frac{\alpha}{m}} \\
\Rightarrow c_V = T\frac{\partial S}{\partial T} &= T\frac{N}{T} = N
\end{aligned}
$$

This is the heat capacity for the system where the restoring force is proportional to x.

The partition function for the second problem is

$$
\begin{aligned}
Z = \mathrm{e}^{-\frac{F}{T}} &= \sum_r \mathrm{e}^{-\frac{E_r}{T}} \\
&= \int \frac{\mathrm{d}p_i \mathrm{d}x_i}{(2\pi\hbar)^N} \mathrm{e}^{-\frac{\sum_i \left(\frac{p_i^2}{2m} + \frac{\beta x_i^3}{3}\right)}{T}} \\
&= \prod_{i=1}^{N} \int \frac{\mathrm{d}p_i \mathrm{d}x_i}{2\pi\hbar} \mathrm{e}^{-\frac{\frac{p_i^2}{2m} + \frac{\beta x_i^3}{3}}{T}}
\end{aligned}
$$

$$
\begin{aligned}
&= \prod_{i=1}^{N} \frac{1}{2\pi\hbar} \int \mathrm{d}p_i \mathrm{e}^{-\frac{p_i^2}{2mT}} \int \mathrm{d}x_i \mathrm{e}^{-\frac{\beta x^3}{3T}} \\
&= \left(\frac{1}{2\pi\hbar} \int \mathrm{d}p \mathrm{e}^{-\frac{p^2}{2mT}} \int \mathrm{d}x \mathrm{e}^{-\frac{\beta x^3}{3T}} \right)^N \\
&\quad \left| \int_0^\infty \mathrm{d}x \mathrm{e}^{-\alpha x^s} = \frac{1}{s} \alpha^{-\frac{1}{s}} \Gamma\left(\frac{1}{s}\right) \right. \\
&= \left(\frac{1}{2\pi\hbar} \sqrt{2\pi m T} \frac{2}{3} \left(\frac{3T}{\beta} \right)^{\frac{1}{3}} \Gamma\left(\frac{1}{3}\right) \right)^N \\
&= \left(\frac{T^{\frac{5}{6}} m^{\frac{1}{2}} \Gamma\left(\frac{1}{3}\right)}{3^{\frac{2}{3}} \left(2\pi\hbar^2\right)^{\frac{1}{2}} \beta^{\frac{1}{3}}} \right)^N \\
\Rightarrow F &= -NT \ln T^{\frac{5}{6}} - NT \underbrace{\ln \frac{m^{\frac{1}{2}} \Gamma\left(\frac{1}{3}\right)}{3^{\frac{2}{3}} \left(2\pi\hbar^2\right)^{\frac{1}{2}} \beta^{\frac{1}{3}}}}_{C} \\
&= -\frac{5}{6} NT \ln T - NTC \\
\Rightarrow S &= \frac{5}{6} N \ln T + \frac{5}{6} N + NC \\
\Rightarrow c_V &= \frac{5N}{6}
\end{aligned}
$$

This is the heat capacity for the system where the restoring force is proportional to x^2.

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Statistical physics and Thermodynamics

Problem 6: Assume the following highly simplified model for calculating the specific heat of graphite, which has a highly anisotropic crystalline structure. Each carbom atom in this structure can be regarded as performing simple harmonic oscillations in three dimensions. The restoring forces in directions parallel to a layer are very large; hence the natural frequencies of oscillations in the x and y directions lying within the plane of a layer are both equal to a value $\omega_{\parallel}$ which is so large that $\hbar\omega_{\parallel}$ is much greater than the temperature corresponding to $300\,\mathrm{K}$. On the other hand, the restoring force perpendicular to a layer is quite small; hence the frequency of oscillation $\omega_{\perp}$ of an atom in the z direction perpendicular to a layer is so small that $\hbar\omega_{\perp}$ is much smaller than the energy corresponding to $300\,\mathrm{K}$. On the basis of this model, what is the molar specific heat (at constant volume) of graphite at $300\,\mathrm{K}$.

According to the formulation of the problem I will use the Einstein quantum model. This model assume that all atoms perform harmonic oscillations at the same frequency.

The energy of quantum oscillator is

$$\begin{aligned}
E_n &= \left(n+\frac{1}{2}\right)\hbar\omega \\
\Rightarrow \sum_n \mathrm{e}^{-\frac{E_n}{T}} &= \sum_{n=0}^{\infty} \mathrm{e}^{-\frac{\left(n+\frac{1}{2}\right)\hbar\omega}{T}} \\
&= \mathrm{e}^{-\frac{\hbar\omega}{2T}} \sum_{n=0}^{\infty} \left(\mathrm{e}^{-\frac{\hbar\omega}{T}}\right)^n \\
&= \mathrm{e}^{-\frac{\hbar\omega}{2T}} \frac{1}{1-\mathrm{e}^{-\frac{\hbar\omega}{T}}} \\
&= \frac{1}{2\sinh\frac{\hbar\omega}{2T}}
\end{aligned}$$

The partition function of the whole system in one dimension is

$$\begin{aligned}
Z &= \prod_{i=1}^{N} \frac{1}{2\sinh\frac{\hbar\omega_i}{2T}} \\
&= \left(\frac{1}{2\sinh\frac{\hbar\omega}{2T}}\right)^N
\end{aligned}$$

There are two different frequencies of oscillations so then

$$\begin{aligned}
Z &= \left(\frac{1}{2\sinh\frac{\hbar\omega_\parallel}{2T}}\right)^{2N}\left(\frac{1}{2\sinh\frac{\hbar\omega_\perp}{2T}}\right)^{N} \\
\Rightarrow F &= 2NT\ln 2\sinh\frac{\hbar\omega_\parallel}{2T} + NT\ln 2\sinh\frac{\hbar\omega_\perp}{2T} \\
\Rightarrow S &= -2N\ln 2\sinh\frac{\hbar\omega_\parallel}{2T} + 2NT\frac{\hbar\omega_\parallel\coth\frac{\hbar\omega_\parallel}{2T}}{2T^2} \\
& -N\ln 2\sinh\frac{\hbar\omega_\perp}{2T} + NT\frac{\hbar\omega_\perp\coth\frac{\hbar\omega_\perp}{2T}}{2T^2} \\
\Rightarrow c_V &= 2NT\frac{\hbar\omega_\parallel\coth\frac{\hbar\omega_\parallel}{2T}}{2T^2} - NT\frac{\hbar\omega_\parallel\coth\frac{\hbar\omega_\parallel}{2T}}{T^2} + NT\frac{\hbar\omega_\parallel}{T\sinh^2\frac{\hbar\omega_\parallel}{2T}}\frac{\hbar\omega_\parallel}{2T^2} \\
& +NT\frac{\hbar\omega_\perp\coth\frac{\hbar\omega_\perp}{2T}}{2T^2} - NT\frac{\hbar\omega_\perp\coth\frac{\hbar\omega_\perp}{2T}}{2T^2} + NT\frac{\hbar\omega_\perp}{2T\sinh^2\frac{\hbar\omega_\perp}{2T}}\frac{\hbar\omega_\perp}{2T^2} \\
&= \frac{N\hbar^2\omega_\parallel^2}{2T^2\sinh^2\frac{\hbar\omega_\parallel}{2T}} + \frac{N\hbar^2\omega_\perp^2}{4T^2\sinh^2\frac{\hbar\omega_\perp}{2T}} \\
&= N\left(2\left(\frac{\hbar\omega_\parallel}{2T\sinh\frac{\hbar\omega_\parallel}{2T}}\right)^2 + \left(\frac{\hbar\omega_\perp}{2T\sinh\frac{\hbar\omega_\perp}{2T}}\right)^2\right) \\
& \left|\alpha = \frac{\hbar\omega_\parallel}{2T} \gg 1\right. \\
& \left|\beta = \frac{\hbar\omega_\perp}{2T} \ll 1\right. \\
&= N\left(2\left(\frac{\alpha}{\sinh\alpha}\right)^2 + \left(\frac{\beta}{\sinh\beta}\right)^2\right) \\
\Rightarrow C_V &= 2\left(\frac{\alpha}{\sinh\alpha}\right)^2 + \left(\frac{\beta}{\sinh\beta}\right)^2
\end{aligned}$$

This is the general equation for molar specific heat. Now I will compute the low and high temperature approximations. The high temperature approximation is applicable when $\beta \leq 1$ and the low temperature is for $\alpha \geq 1$.

The low temperature approximation:

$$\begin{aligned}
\frac{\alpha}{\sinh\alpha} &= \frac{2\alpha}{e^\alpha - e^{-\alpha}} \\
&= \frac{2\alpha e^{-\alpha}}{1 - e^{-2\alpha}}
\end{aligned}$$

$$
\begin{aligned}
& \Big| \alpha \to \infty \Rightarrow \mathrm{e}^{-2\alpha} \to 0 \\
= \; & 2\alpha \mathrm{e}^{-\alpha}
\end{aligned}
$$

The high temperature approximation:

$$
\begin{aligned}
\frac{\beta}{\sinh\beta} &= \frac{\beta}{\beta + \frac{\beta^3}{6} + \dots} \\
&= \frac{1}{1+\frac{\beta^2}{6}}
\end{aligned}
$$

The molar specific heat of graphite is then

$$
\begin{aligned}
C_V &= 2\left(2\alpha \mathrm{e}^{-\alpha}\right)^2 + \frac{1}{\left(1+\frac{\beta^2}{6}\right)^2} \\
&= 8\alpha^2 \mathrm{e}^{-2\alpha} + \frac{1}{1+\frac{\beta^2}{3}} \\
&= 8\left(\frac{\hbar\omega_{\|}}{2T}\right)^2 \mathrm{e}^{-2\frac{\hbar\omega_{\|}}{2T}} + \frac{1}{1+\frac{\left(\frac{\hbar\omega_{\perp}}{2T}\right)^2}{3}} \\
&= 2\frac{\hbar^2\omega_{\|}^2}{T^2}\mathrm{e}^{-\frac{\hbar\omega_{\|}}{T}} + \frac{1}{1+\frac{\hbar^2\omega_{\perp}^2}{12T^2}}
\end{aligned}
$$

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Statistical physics and Thermodynamics

Problem 7: Electromagnetic radiation at temperature T_i fills a cavity of volume V. If the volume of the thermally insulated cavity is expanded quasi statically to a volume $8V$, what is the final temperature T_f?

The basic assumption: In equilibrium, all states are equally probable. If the system is expanded quasi statically, it means that the system is in equilibrium in every time of the change. The system is also thermally insulated, so there is no change of heat. It also means that there is no change of entropy.

Now I will compute the entrophy for electromagnetic radiation using the equation for Landau potential of bosons from Problem 3. The dispersion relation in the foton case is $E = \hbar kc$.

$$
\begin{aligned}
\Omega &= T\sum_{i=1}^{\infty}\ln\left(1-\mathrm{e}^{-\frac{\epsilon_i-\mu}{T}}\right) \\
&= T\int_{1stoctant}\mathrm{d}^3k\frac{V}{\pi^3}\ln\left(1-\mathrm{e}^{-\frac{\hbar kc-\mu}{T}}\right) \\
&= T\int\mathrm{d}kk^2\frac{V}{2\pi^2}\ln\left(1-\mathrm{e}^{-\frac{\hbar kc-\mu}{T}}\right) \\
&\quad |E=\hbar kc\Rightarrow\mathrm{d}E=\hbar c\mathrm{d}k \\
&= \frac{TV}{2\pi^2}\int_0^{\infty}\frac{1}{\hbar c}\mathrm{d}E\frac{E^2}{\hbar^2c^2}\ln\left(1-\mathrm{e}^{-\frac{E-\mu}{T}}\right) \\
&= \frac{TV}{2\pi^2\hbar^3c^3}\int_0^{\infty}\mathrm{d}EE^2\ln\left(1-\mathrm{e}^{-\frac{E-\mu}{T}}\right) \\
&\quad \left|x=\frac{E}{T}\Rightarrow\mathrm{d}x=\frac{\mathrm{d}E}{T}\right. \\
&= \frac{TV}{2\pi^2\hbar^3c^3}\int_0^{\infty}T\mathrm{d}xT^2x^2\ln\left(1-\mathrm{e}^{-x+\frac{\mu}{T}}\right) \\
&= \frac{VT^4}{2\pi^2\hbar^3c^3}\int_0^{\infty}\mathrm{d}xx^2\ln\left(1-\mathrm{e}^{-x+\frac{\mu}{T}}\right) \\
&\quad \left|u=\ln\left(1-\mathrm{e}^{-x+\frac{\mu}{T}}\right)\Rightarrow u'=\frac{1}{\mathrm{e}^{x-\frac{\mu}{T}}-1}\right. \\
&\quad \left|v'=x^2\Rightarrow v=\frac{x^3}{3}\right. \\
&= \frac{VT^4}{2\pi^2\hbar^3c^3}\left(\left[\frac{x^3}{3}\ln\left(1-\mathrm{e}^{-x+\frac{\mu}{T}}\right)\right]_0^{\infty}-\frac{1}{3}\int_0^{\infty}\mathrm{d}x\frac{x^3}{\mathrm{e}^{x-\frac{\mu}{T}}-1}\right)
\end{aligned}
$$

$$
\begin{aligned}
&= -\frac{VT^4}{6\pi^2\hbar^3c^3}B_3\left(\frac{\mu}{T}\right) \\
\Rightarrow S &= \frac{2VT^3}{3\pi^2\hbar^3c^3}B_3\left(\frac{\mu}{T}\right) - \frac{VT^2\mu}{2\pi^2\hbar^3c^3}B_2\left(\frac{\mu}{T}\right)
\end{aligned}
$$

This is the general equation for ultrarelativistic bosons. The system is in equilibrium and then the free energy is minimal.

$$\frac{\partial F}{\partial N} = 0 \quad \Rightarrow \quad \mu = 0$$

The the entropy is

$$S = \frac{2VT^3}{3\pi^2\hbar^3c^3}B_3\left(0\right)$$

As was said above, the entropy is constant during the quasi statical process.

$$
\begin{aligned}
VT^3 &= K \\
\Rightarrow V_1T_1^3 &= V_2T_2^3 \\
\Rightarrow T_f &= T_i\sqrt[3]{\frac{V_i}{V_f}} \\
&= T_i\sqrt[3]{\frac{V_i}{8V_i}} \\
&= \frac{1}{2}T_i
\end{aligned}
$$

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Statistical physics and Thermodynamics

Problem 8: Use the Debye approximation to find the equation of state for a solid; i. e. find the pressure p as a function of V and T. What are the limiting cases valid when $T \ll \theta_D$ and when $T \gg \theta_D$? Express your answer in terms of the quantity

$$\gamma \equiv -\frac{V}{\theta_D}\frac{\mathrm{d}\theta_D}{\mathrm{d}V}.$$

Assume that γ is a constant, independent of temperature. (It is called the Grüneisen constant.) Show that the coefficient of thermal expansion α is then related to γ by the relation

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \kappa\left(\frac{\partial p}{\partial T}\right)_V = \kappa\gamma\frac{c_V}{V},$$

where c_V is the heat capacity of the solid and κ is the compressibility.

As was derived in Problem 4, the free energy is

$$\begin{aligned} F &= T\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega_1}{T}}\right)\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega_2}{T}}\right)\dots \\ &= T\sum_{i=1}^{3N}\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega_i}{T}}\right) \\ &= T\int_0^{k_{max}}\mathrm{d}^3k\rho(k)\ln\left(1-\mathrm{e}^{-\frac{\hbar kv}{T}}\right) \end{aligned}$$

There are some changes caused by adding third dimmension. The density of states is then $\rho(k) = \left(\frac{L}{2\pi}\right)^3$. Then I have

$$\begin{aligned} F &= T\int_0^{k_{max}}\mathrm{d}kk^2 4\pi\frac{V}{8\pi^3}\ln\left(1-\mathrm{e}^{-\frac{\hbar kv}{T}}\right) \\ &= \frac{TV}{2\pi^2}\int_0^{k_{max}}\mathrm{d}kk^2\ln\left(1-\mathrm{e}^{-\frac{\hbar kv}{T}}\right) \\ &\quad |k=\omega v \Rightarrow \mathrm{d}k = v\mathrm{d}\omega \\ &= \frac{3TV}{2\pi^2}\int_0^{\omega_{max}}\frac{1}{v}\mathrm{d}\omega\frac{\omega^2}{v^2}\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega}{T}}\right) \\ &= \frac{3TV}{2\pi^2 v^3}\int_0^{\omega_{max}}\mathrm{d}\omega\omega^2\ln\left(1-\mathrm{e}^{-\frac{\hbar\omega}{T}}\right) \\ &\quad \left|\int_0^{\omega_{max}}\mathrm{d}\omega\frac{\omega^2 V}{2\pi^2 v^3} = N\right. \end{aligned}$$

$$\left|\Rightarrow \frac{V\omega^3}{6\pi^2 v^3} = N \Rightarrow \omega_{max} = v\sqrt[3]{\frac{6N\pi^2}{V}} = \omega_D\right.$$

$$\left|x = \frac{\hbar\omega}{T} \Rightarrow \mathrm{d}x = \frac{\hbar}{T}\mathrm{d}\omega\right.$$

$$\begin{aligned}
&= \frac{3TV}{2\pi^2 v^3}\int_0^{\frac{T_D}{T}} \frac{T}{\hbar}\mathrm{d}x\frac{T^2 x^2}{\hbar^2}\ln\left(1-\mathrm{e}^{-x}\right) \\
&= \frac{3VT^4}{2\pi^2\hbar^3 v^3}\int_0^{\frac{T_D}{T}} \mathrm{d}x x^2\ln\left(1-\mathrm{e}^{-x}\right)
\end{aligned}$$

$$\left|u = \ln\left(1-\mathrm{e}^{-x}\right) \Rightarrow u' = \frac{\mathrm{e}^{-x}}{1-\mathrm{e}^{-x}} = \frac{1}{\mathrm{e}^x - 1}\right.$$

$$\left|v' = x^2 \Rightarrow v = \frac{x^3}{3}\right.$$

$$\begin{aligned}
&= \frac{3VT^4}{2\pi^2\hbar^3 v^3}\left(\left[\frac{x^3}{3}\ln\left(1-\mathrm{e}^{-x}\right)\right]_0^{\frac{T_D}{T}} - \frac{1}{3}\int_0^{\frac{T_D}{T}} \mathrm{d}x\frac{x^3}{\mathrm{e}^x-1}\right) \\
&= \frac{VTT_D^3}{2\pi^2\hbar^3 v^3}\left(\ln\left(1-\mathrm{e}^{-\frac{T_D}{T}}\right) - \frac{T^3}{T_D^3}\int_0^{\frac{T_D}{T}} \mathrm{d}x\frac{x^3}{\mathrm{e}^x-1}\right) \\
&= \frac{VT\hbar^3 v^3 6N\pi^2}{V2\pi^2 v^3\hbar^3}\left(\ln\left(1-\mathrm{e}^{-\frac{T_D}{T}}\right) - \frac{T^3}{T_D^3}\int_0^{\frac{T_D}{T}} \mathrm{d}x\frac{x^3}{\mathrm{e}^x-1}\right) \\
&= 3NT\left(\ln\left(1-\mathrm{e}^{-\frac{T_D}{T}}\right) - \frac{T^3}{T_D^3}\int_0^{\frac{T_D}{T}} \mathrm{d}x\frac{x^3}{\mathrm{e}^x-1}\right)
\end{aligned}$$

This is the free energy of Debye solid. The pressure is then

$$\begin{aligned}
p &= -\frac{\partial F}{\partial V} = -\frac{\partial F}{\partial T_D}\frac{\partial T_D}{\partial V} \\
\frac{\partial F}{\partial T_D} &= 3NT\left(\frac{1}{T\left(\mathrm{e}^{\frac{T_D}{T}}-1\right)} + \frac{3T^3}{T_D^4}\int_0^{\frac{T_D}{T}} \mathrm{d}x\frac{x^3}{\mathrm{e}^x-1} - \frac{T^3}{T_D^3}\frac{T_D^3}{T^4}\frac{1}{\mathrm{e}^{\frac{T_D}{T}}-1}\right) \\
&= \frac{9NT^4}{T_D^4}\int_0^{\frac{T_D}{T}} \mathrm{d}x\frac{x^3}{\mathrm{e}^x-1} \\
\Rightarrow p &= \frac{9NT^4\gamma}{T_D^3 V}D\left(\frac{T_D}{T}\right)
\end{aligned}$$

The high temperature approximation ($T \gg T_D$):

$$\begin{aligned} D\left(\frac{T_D}{T}\right) &= \int_0^{\frac{T_D}{T}} \mathrm{d}x \frac{x^3}{\mathrm{e}^x - 1} = \int_0^{\frac{T_D}{T}} \mathrm{d}x \frac{x^3}{1 + x - 1} \\ &= \left[\frac{x^3}{3}\right]_0^{\frac{T_D}{T}} = \frac{T_D^3}{3T^3} \\ \Rightarrow p &= \frac{9NT^4\gamma}{T_D^3 V} \frac{T_D^3}{3T^3} = \frac{3NT\gamma}{V} \end{aligned}$$

The low temperature approximation ($T \ll T_D$):

$$\begin{aligned} D\left(\frac{T_D}{T}\right) &= B_3(0) = \Gamma(4)\zeta(4) = \frac{\pi^4}{15} \\ \Rightarrow p &= \frac{3NT^4\gamma\pi^4}{5T_D^3 V} \end{aligned}$$

Now I will compute the heat capacity and $\frac{\partial p}{\partial T}$ and compare the results.

$$\begin{aligned} \frac{\partial F}{\partial T} &= 3N \ln\left(1 - \mathrm{e}^{-\frac{T_D}{T}}\right) - 3NT \frac{1}{\mathrm{e}^{\frac{T_D}{T}} - 1} \frac{T_D}{T^2} \\ &\quad - \frac{12NT^3}{T_D^3} D\left(\frac{T_D}{T}\right) - \frac{3NT^4}{T_D^3} \frac{T_D^3}{T^3} \frac{1}{\mathrm{e}^{\frac{T_D}{T}} - 1} \frac{T_D}{T^2} \\ &= 3N \ln\left(1 - \mathrm{e}^{-\frac{T_D}{T}}\right) - \frac{12NT^3}{T_D^3} D\left(\frac{T_D}{T}\right) \\ \Rightarrow c_V &= T\left(\frac{3NT_D}{T^2\left(\mathrm{e}^{\frac{T_D}{T}} - 1\right)} + \frac{36NT^2}{T_D^3} D\left(\frac{T_D}{T}\right) - \frac{12NT^3}{T_D^3} \frac{T_D^4}{T^5\left(\mathrm{e}^{\frac{T_D}{T}} - 1\right)}\right) \\ &= \frac{36NT^3}{T_D^3} D\left(\frac{T_D}{T}\right) - \frac{9NT_D}{T\left(\mathrm{e}^{\frac{T_D}{T}} - 1\right)} \\ \frac{\partial p}{\partial T} &= \frac{36NT^3\gamma}{VT_D^3} D\left(\frac{T_D}{T}\right) - \frac{9NT^4\gamma}{VT_D^3} \frac{T_D^4}{T^5\left(\mathrm{e}^{\frac{T_D}{T}} - 1\right)} \\ \Rightarrow \frac{\partial p}{\partial T} &= \frac{\gamma c_V}{V} \end{aligned}$$

The results are as expected and then the coefficient of thermal expansion is related to γ by equation $\alpha = \frac{\kappa\gamma c_V}{V}$.

Bc. Jaroslav Zůda

Statistical physics and Thermodynamics

Problem 9: Assume the existence of a Bose gas with dispresion relation $E = A|k|^n$ where n is any natural number. If the number of particles is not conserved, comptute the dependence of the specific heat c_V on the temperature T.

As was derived in problem 3, the Landau potential for quantum Bose gas has formula

$$\begin{aligned}
\Omega &= T\sum_{i=1}^{\infty}\ln\left(1-\mathrm{e}^{-\frac{\epsilon_i-\mu}{T}}\right)\\
&= T\int_{1stoctant}\mathrm{d}^3k\frac{V}{\pi^3}\ln\left(1-\mathrm{e}^{-\frac{Ak^n-\mu}{T}}\right)\\
&= \frac{TV}{\pi^3}\int\mathrm{d}kk^2\frac{\pi}{2}\ln\left(1-\mathrm{e}^{-\frac{Ak^n-\mu}{T}}\right)\\
&= \frac{TV}{2\pi^2}\int\mathrm{d}kk^2\ln\left(1-\mathrm{e}^{-\frac{Ak^n-\mu}{T}}\right)\\
&\quad \Big| E = Ak^n \Rightarrow \mathrm{d}E = nAk^{n-1}\mathrm{d}k\\
&= \frac{TV}{2\pi^2}\int\mathrm{d}E\frac{1}{nA\frac{E^{\frac{n-1}{n}}}{A^{\frac{n-1}{n}}}}\frac{E^{\frac{2}{n}}}{A^{\frac{2}{n}}}\ln\left(1-\mathrm{e}^{-\frac{E-\mu}{T}}\right)\\
&= \frac{TV}{2n\pi^2A^{\frac{3}{n}}}\int\mathrm{d}EE^{\frac{3-n}{n}}\ln\left(1-\mathrm{e}^{-\frac{E-\mu}{T}}\right)\\
&\quad \Big| x = \frac{E}{T} \Rightarrow \mathrm{d}x = \frac{1}{T}\mathrm{d}E\\
&= \frac{TV}{2n\pi^2A^{\frac{3}{n}}}\int T\mathrm{d}xT^{\frac{3-n}{n}}x^{\frac{3-n}{n}}\ln\left(1-\mathrm{e}^{-x+\frac{\mu}{T}}\right)\\
&= \frac{VT^{\frac{n+3}{n}}}{2n\pi^2A^{\frac{3}{n}}}\int\mathrm{d}xx^{\frac{3-n}{n}}\ln\left(1-K\mathrm{e}^{-x}\right)\\
&\quad \Big| u = \ln\left(1-K\mathrm{e}^{-x}\right) \Rightarrow u' = \frac{1}{K^{-1}\mathrm{e}^x-1}\\
&\quad \Big| v' = x^{\frac{3-n}{n}} \Rightarrow v = \frac{n}{3}x^{\frac{3}{n}}\\
&= \frac{VT^{\frac{n+3}{n}}}{2n\pi^2A^{\frac{3}{n}}}\left(\left[\frac{nx^{\frac{3}{n}}}{3}\ln\left(1-K\mathrm{e}^{-x}\right)\right]_0^{\infty}-\frac{n}{3}\int\mathrm{d}x\frac{x^{\frac{3}{n}}}{\mathrm{e}^{x-\frac{\mu}{T}}-1}\right)\\
&= \frac{VT^{\frac{n+3}{n}}}{6\pi^2A^{\frac{3}{n}}}B_{\frac{3}{n}}\left(\frac{\mu}{T}\right)
\end{aligned}$$

$$
\begin{aligned}
\Rightarrow S &= -\frac{(n+3)\,VT^{\frac{3}{n}}}{6n\pi^2 A^{\frac{3}{n}}} B_{\frac{3}{n}}\left(\frac{\mu}{T}\right) + \frac{V\mu T^{\frac{3-n}{n}}}{2n\pi^2 A^{\frac{3}{n}}} B_{\frac{3-n}{n}}\left(\frac{\mu}{T}\right) \\
\Rightarrow c_{V,\mu} &= T\left(-\frac{3\,(n+3)\,VT^{\frac{3-n}{n}}}{6n^2\pi^2 A^{\frac{3}{n}}} B_{\frac{3}{n}}\left(\frac{\mu}{T}\right) + \frac{(n+3)\,\mu VT^{\frac{3-2n}{n}}}{2n^2\pi^2 A^{\frac{3}{n}}} B_{\frac{3-n}{n}}\left(\frac{\mu}{T}\right)\right) \\
&\quad +T\left(\frac{(3-n)\,\mu VT^{\frac{3-2n}{n}}}{2n^2\pi^2 A^{\frac{3}{n}}} B_{\frac{3-n}{n}}\left(\frac{\mu}{T}\right) - \frac{(3-n)\,\mu^2 VT^{\frac{3-3n}{n}}}{2n^2\pi^2 A^{\frac{3}{n}}} B_{\frac{3-2n}{n}}\left(\frac{\mu}{T}\right)\right) \\
&= \frac{V}{2n^2\pi^2 A^{\frac{3}{n}}}\left(-(n+3)\,T^{\frac{3}{n}} B_{\frac{3}{n}}\left(\frac{\mu}{T}\right) + 6\mu T^{\frac{3-n}{n}} B_{\frac{3-n}{n}}\left(\frac{\mu}{T}\right)\right. \\
&\quad \left. -(3-n)\,\mu^2 T^{\frac{3-2n}{n}} B_{\frac{3-2n}{n}}\left(\frac{\mu}{T}\right)\right)
\end{aligned}
$$

Bc. Jaroslav Zůda

Statistical physics and Thermodynamics

Problem 10: Assume that we have a classical ideal gas where the particles also carry an internal degree of freedom. So apart from carrying kinetic energy $\frac{p^2}{2m}$ they also carry internal energy $\pm\Delta$. Show how one can measure delta by measuring the heat capacity.

The partition function for classical ideal das is

$$\begin{aligned}
Z &= \sum_r \mathrm{e}^{-\frac{E_r-\mu N_r}{T}} \\
&= \sum_{N=0}^{\infty} \mathrm{e}^{\frac{\mu N}{T}} \mathrm{e}^{-\frac{E_N}{T}} \\
&= \sum_{N=0}^{\infty} \mathrm{e}^{\frac{\mu N}{T}} \frac{1}{N!} \prod_{i=1}^{N} \int \mathrm{d}^3p\mathrm{d}^3x \frac{1}{8\pi^3\hbar^3} \mathrm{e}^{-\frac{p^2}{2mT}\pm\frac{\Delta}{T}} \\
&= \sum_{N=0}^{\infty} \left(\mathrm{e}^{\frac{\mu\pm\Delta}{T}}\right)^N \frac{V^N}{N!8^N\pi^{3N}\hbar^{3N}} \left(\prod_{i=1}^{N} \int \mathrm{d}p\mathrm{e}^{-\frac{p^2}{2mT}}\right)^3 \\
&= \sum_{N=0}^{\infty} \left(\mathrm{e}^{\frac{\mu\pm\Delta}{T}}\right)^N \frac{V^N}{N!8^N\pi^{3N}\hbar^{3N}} \left(\prod_{i=1}^{N} \int \mathrm{d}p\mathrm{e}^{-\frac{p^2}{2mT}}\right)^3 \\
&= \sum_{N=0}^{\infty} \left(\mathrm{e}^{\frac{\mu\pm\Delta}{T}}\right)^N \frac{V^N (2\pi mT)^{\frac{3N}{2}}}{N!8^N\pi^{3N}\hbar^{3N}} \\
&= \sum_{N=0}^{\infty} \frac{1}{N!} \left(\mathrm{e}^{\frac{\mu\pm\Delta}{T}} \frac{Vm^{\frac{3}{2}}T^{\frac{3}{2}}}{2^{\frac{5}{2}}\pi^{\frac{5}{2}}\hbar^3}\right)^N \\
&= \mathrm{e}^{\mathrm{e}^{\frac{\mu\pm\Delta}{T}} \frac{Vm^{\frac{3}{2}}T^{\frac{3}{2}}}{2^{\frac{5}{2}}\pi^{\frac{5}{2}}\hbar^3}} \\
\Rightarrow \Omega &= -T\mathrm{e}^{\frac{\mu\pm\Delta}{T}} \frac{Vm^{\frac{3}{2}}T^{\frac{3}{2}}}{2^{\frac{5}{2}}\pi^{\frac{5}{2}}\hbar^3} \\
&= -\mathrm{e}^{\frac{\mu\pm\Delta}{T}} \alpha V T^{\frac{5}{2}}
\end{aligned}$$

The coefficient α is constant. The total Landau potential is sum of potential with $+\Delta$ and with $-\Delta$.

$$\begin{aligned}
\Omega &= -\alpha V T^{\frac{5}{2}} \left(\mathrm{e}^{\frac{\mu+\Delta}{T}} + \mathrm{e}^{\frac{\mu-\Delta}{T}}\right) \\
&= -\alpha V T^{\frac{5}{2}} \mathrm{e}^{\frac{\mu}{T}} \left(\mathrm{e}^{\frac{\Delta}{T}} + \mathrm{e}^{-\frac{\Delta}{T}}\right)
\end{aligned}$$

$$
\begin{aligned}
&= -\underbrace{2\alpha V}_{K} T^{\frac{5}{2}} \mathrm{e}^{\frac{\mu}{T}} \cosh \frac{\Delta}{T} \\
\Rightarrow N &= K T^{\frac{3}{2}} \mathrm{e}^{\frac{\mu}{T}} \cosh \frac{\Delta}{T} \\
\Rightarrow \mathrm{e}^{\frac{\mu}{T}} &= \frac{N}{K T^{\frac{3}{2}} \cosh \frac{\Delta}{T}} \\
\Rightarrow \mu &= T \ln \frac{N}{K T^{\frac{3}{2}} \cosh \frac{\Delta}{T}}
\end{aligned}
$$

Now I can compute the entropy and add the expression for the chemical potential. Finally I will derive the entropy and get the heat capacity and compare the result to the classical result, which is $\frac{3}{2}N$.

$$
\begin{aligned}
S &= \frac{5}{2} K T^{\frac{3}{2}} \mathrm{e}^{\frac{\mu}{T}} \cosh \frac{\Delta}{T} - K T^{\frac{1}{2}} \mu \mathrm{e}^{\frac{\mu}{T}} \cosh \frac{\Delta}{T} - K T^{\frac{1}{2}} \Delta \mathrm{e}^{\frac{\mu}{T}} \sinh \frac{\Delta}{T} \\
&= K T^{\frac{3}{2}} \mathrm{e}^{\frac{\mu}{T}} \cosh \frac{\Delta}{T} \left(\frac{5}{2} - \frac{\mu}{T} - \frac{\Delta}{T} \tanh \frac{\Delta}{T} \right) \\
&= \frac{K T^{\frac{3}{2}} N \cosh \frac{\Delta}{T}}{K T^{\frac{3}{2}} \cosh \frac{\Delta}{T}} \left(\frac{5}{2} - \ln \frac{N}{K T^{\frac{3}{2}} \cosh \frac{\Delta}{T}} - \frac{\Delta}{T} \tanh \frac{\Delta}{T} \right) \\
&= N \left(\frac{5}{2} - \ln \frac{N}{K} + \ln T^{\frac{3}{2}} + \ln \cosh \frac{\Delta}{T} - \frac{\Delta}{T} \tanh \frac{\Delta}{T} \right) \\
\Rightarrow c_V &= T \left(\frac{3N}{2T} - \frac{N\Delta}{T^2} \tanh \frac{\Delta}{T} + \frac{N\Delta}{T^2} \tanh \frac{\Delta}{T} + \frac{N\Delta^2}{T^3 \cosh^2 \frac{\Delta}{T}} \right) \\
&= \frac{3}{2} N + \frac{N\Delta^2}{T^2 \cosh^2 \frac{\Delta}{T}}
\end{aligned}
$$

If the classical gas carry internal degree of freedom, the heat capacity will increase by factor $\frac{x^2}{\cosh^2 x}$, where $x = \frac{\Delta}{T}$.

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Statistical physics and Thermodynamics

Problem 11: Calculate the magnetic susceptibility of a free electron gas! In a electron gas there are two competing effects that will decide how the induced magnetic field will be when one applies an external magnetic field. The electrons themselves carry spin to which there is a magnetic moment associated. The magnetic moments tend to align with the magnetic field thus creating an induce magnetic moment in the same direction as the applied magnetic field. This is paramagnetic behavior. However, since the electrons are themselves charged they will move in circles in the magnetic field which will create a current that tends to reduce the applied external magnetic field. This is diamagnetic behavior. Calculate the Landau potential for these two problems independently and calculate the susceptibility χ it gives rise to according formula

$$M = -\left(\frac{\partial \Omega}{\partial H}\right)_{T,V,\mu}$$

$$\chi = \frac{\partial M}{\partial H} = -\frac{\partial^2 \Omega}{\partial H^2}$$

Start from the formula for the Landau potential using the ideal gas approximation

$$\Omega = -T \sum_a \ln\left(1 + \mathrm{e}^{-\frac{E_a - \mu}{T}}\right)$$

In the paramagnetic case, the states have different energy according to if the spin is up or down

$$E_a = \frac{p^2}{2m} \pm \beta H$$

where $\beta = \frac{|e|\hbar}{2mc}$ is the Bohr magneton and H is the external magnetic field. In the diamagnetic case, as was shown in class, the sum over states can be exchanged with

$$\sum_a \rightarrow \sum_{n=0}^{\infty} \int \mathrm{d}p_z 2 \frac{V}{(2\pi\hbar)^2} \frac{|e|H}{c}$$

where the energy of the states is given by

$$E = \hbar\omega\left(n + \frac{1}{2}\right) + \frac{p_z^2}{2m}$$

To get explicit results, use the high temperature approximation to lowest order and use what you know for the free electron gas without a magnetic field. Is the gas paramagnetic or diamagnetic?

I found that free electron gas is paramagnetic in the literature.

The Landau potential of free electron gas is

$$\Omega = -T\sum_a \ln\left(1+\mathrm{e}^{-\frac{E_a-\mu}{T}}\right)$$

and energy of the states is given by equation

$$E_a = \frac{p^2}{2m} \pm \beta H$$

I will integrate the Landau potential instead of summing.

$$\begin{aligned}
\Omega &= -2T\int \mathrm{d}^3x\mathrm{d}^3p\frac{1}{8\pi^3\hbar^3}\ln\left(1+\mathrm{e}^{-\frac{E-\mu}{T}}\right)\\
&= -\frac{TV}{4\pi^3\hbar^3}\int \mathrm{d}p4\pi p^2\ln\left(1+\mathrm{e}^{-\frac{E-\mu}{T}}\right)\\
&= -\frac{TV}{\pi^2\hbar^3}\int \mathrm{d}pp^2\ln\left(1+\mathrm{e}^{-\frac{E-\mu}{T}}\right)\\
&\quad \left| E=\frac{p^2}{2m}\Rightarrow \mathrm{d}E=\frac{p}{m}\mathrm{d}p \right.\\
&= -\frac{TV}{\pi^2\hbar^3}\int m\mathrm{d}E2^{\frac{1}{2}}m^{\frac{1}{2}}E^{\frac{1}{2}}\ln\left(1+\mathrm{e}^{-\frac{E\pm\beta H-\mu}{T}}\right)\\
&= -\frac{2^{\frac{1}{2}}TVm^{\frac{3}{2}}}{\pi^2\hbar^3}\int \mathrm{d}EE^{\frac{1}{2}}\ln\left(1+\mathrm{e}^{-\frac{E\pm\beta H-\mu}{T}}\right)\\
&\quad \left| x=\frac{E}{T}\Rightarrow \mathrm{d}x=\frac{1}{T}\mathrm{d}E \right.\\
&= -TC\int T\mathrm{d}xT^{\frac{1}{2}}x^{\frac{1}{2}}\ln\left(1+K\mathrm{e}^{-x}\right)\\
&= -CT^{\frac{5}{2}}\int \mathrm{d}xx^{\frac{1}{2}}\ln\left(1+K\mathrm{e}^{-x}\right)\\
&\quad \left| u=\ln\left(1+K\mathrm{e}^{-x}\right)\Rightarrow u'=\frac{-K\mathrm{e}^{-x}}{1+K\mathrm{e}^{-x}}=-\frac{1}{K^{-1}\mathrm{e}^{x}+1} \right.\\
&\quad \left| v'=x^{\frac{1}{2}}\Rightarrow v=\frac{2}{3}x^{\frac{3}{2}} \right.\\
&= -CT^{\frac{5}{2}}\left(\left[\frac{2x^{\frac{3}{2}}}{3}\ln\left(1+K\mathrm{e}^{-x}\right)\right]_0^\infty+\frac{2}{3}\int \mathrm{d}x\frac{x^{\frac{3}{2}}}{\mathrm{e}^{x-\frac{\mu\pm\beta H}{T}}+1}\right)
\end{aligned}$$

$$= -\frac{2^{\frac{3}{2}} T^{\frac{5}{2}} V m^{\frac{3}{2}}}{3\pi^2 \hbar^3} F_{\frac{3}{2}} \left(\frac{\mu \pm \beta H}{T} \right)$$

This is the Landau potential for free paramagnetic electron gas. The susceptibility is defined for constant temperature, volume and chemical potential, so I can derivate the potential twice and make the high temperature approximation. But I will use another method.

$$\begin{aligned}
\Omega &= -\alpha \left(F_{\frac{3}{2}} \left(\frac{\mu - \beta H}{T} \right) + F_{\frac{3}{2}} \left(\frac{\mu + \beta H}{T} \right) \right) \\
F_{\frac{3}{2}} \left(\frac{\mu - \beta H}{T} \right) &= \int_0^\infty \mathrm{d}x \frac{x^{\frac{3}{2}}}{\mathrm{e}^{x - \frac{\mu - \beta H}{T}} + 1} \\
&= T^{-\frac{5}{2}} \int_0^\infty \mathrm{d}E \frac{E^{\frac{3}{2}}}{\mathrm{e}^{\frac{E - \mu + \beta H}{T}} + 1} \\
\int_0^\infty \mathrm{d}E \frac{E^{\frac{3}{2}}}{\mathrm{e}^{\frac{E - \mu + \beta H}{T}} + 1} &= T \int_{-\frac{\mu - \beta H}{T}}^\infty \mathrm{d}z \frac{(\mu - \beta H + zT)^{\frac{3}{2}}}{\mathrm{e}^z + 1} \\
&= T \int_{-\frac{\mu - \beta H}{T}}^0 \mathrm{d}z \frac{(\mu - \beta H + zT)^{\frac{3}{2}}}{\mathrm{e}^z + 1} + T \int_0^\infty \mathrm{d}z \frac{(\mu - \beta H + zT)^{\frac{3}{2}}}{\mathrm{e}^z + 1} \\
&= T \int_0^{\frac{\mu - \beta H}{T}} \mathrm{d}z \frac{(\mu - \beta H - zT)^{\frac{3}{2}}}{\mathrm{e}^{-z} + 1} + T \int_0^\infty \mathrm{d}z \frac{(\mu - \beta H + zT)^{\frac{3}{2}}}{\mathrm{e}^z + 1} \\
&= T \int_0^{\frac{\mu - \beta H}{T}} \mathrm{d}z \, (\mu - \beta H - zT)^{\frac{3}{2}} - T \int_0^{\frac{\mu - \beta H}{T}} \mathrm{d}z \frac{(\mu - \beta H - zT)^{\frac{3}{2}}}{\mathrm{e}^{-z} + 1} \\
&\quad + T \int_0^\infty \mathrm{d}z \frac{(\mu - \beta H + zT)^{\frac{3}{2}}}{\mathrm{e}^z + 1} \\
&= \int_0^{\mu - \beta H} \mathrm{d}E E^{\frac{3}{2}} + T \int_0^\infty \mathrm{d}z \frac{(\mu - \beta H + zT)^{\frac{3}{2}} - (\mu - \beta H - zT)^{\frac{3}{2}}}{\mathrm{e}^z + 1} \\
&= \int_0^{\mu - \beta H} \mathrm{d}E E^{\frac{3}{2}} + 2T \frac{\partial f}{\partial \nu} \int_0^\infty \mathrm{d}z \frac{z}{\mathrm{e}^z + 1} \\
&\quad \Big| f = x^{\frac{3}{2}}, \nu = \mu - \beta H \\
&\quad \Big| \int_0^\infty \mathrm{d}z \frac{z}{\mathrm{e}^z + 1} = F_1(0) = \frac{1}{2} \Gamma(2) \zeta(2) = \frac{\pi^2}{12} \\
&= \frac{2}{5} (\mu - \beta H)^{\frac{5}{2}} + \frac{\pi^2 T}{4} (\mu - \beta H)^{\frac{1}{2}}
\end{aligned}$$

Then I have

$$\begin{aligned}
I_1+I_2 &= \frac{2}{5}(\mu-\beta H)^{\frac{5}{2}}+\frac{\pi^2 T}{4}(\mu-\beta H)^{\frac{1}{2}}+\frac{2}{5}(\mu+\beta H)^{\frac{5}{2}}+\frac{\pi^2 T}{4}(\mu+\beta H)^{\frac{1}{2}} \\
&\quad \Big|(1\pm x)^n = 1\pm nx+\binom{n}{2}x^2\pm\ldots \\
&= \frac{2}{5}\mu^{\frac{5}{2}}\left(\left(1-\frac{\beta H}{\mu}\right)^{\frac{5}{2}}+\left(1+\frac{\beta H}{\mu}\right)^{\frac{5}{2}}\right)+\frac{\pi^2\mu^{\frac{1}{2}}T}{4}\left(\left(1-\frac{\beta H}{\mu}\right)^{\frac{1}{2}}+\left(1+\frac{\beta H}{\mu}\right)^{\frac{1}{2}}\right) \\
&= \frac{2\mu^{\frac{5}{2}}}{5}\left(1-\frac{5\beta H}{2\mu}+\frac{15\beta^2H^2}{8\mu^2}+1+\frac{5\beta H}{2\mu}+\frac{15\beta^2H^2}{8\mu^2}\right) \\
&\quad +\frac{\pi^2\mu^{\frac{1}{2}}T}{4}\left(1-\frac{\beta H}{2\mu}-\frac{\beta^2H^2}{8\mu^2}+1+\frac{\beta H}{2\mu}-\frac{\beta^2H^2}{8\mu^2}\right) \\
&= \frac{4\mu^{\frac{5}{2}}}{5}+\frac{\pi^2 T\mu^{\frac{1}{2}}}{2}+\frac{3\mu^{\frac{1}{2}}\beta^2H^2}{2}-\frac{\pi^2T\beta^2H^2}{16\mu^{\frac{3}{2}}} \\
&\approx \frac{4}{5}\mu^{\frac{5}{2}}+\frac{\pi^2 T\mu^{\frac{1}{2}}}{2}+\frac{3\mu^{\frac{1}{2}}\beta^2H^2}{2} \\
\Rightarrow \Omega &= -\alpha T^{-\frac{5}{2}}\left(\frac{4}{5}\mu^{\frac{5}{2}}+\frac{\pi^2 T\mu^{\frac{1}{2}}}{2}+\frac{3\mu^{\frac{1}{2}}\beta^2H^2}{2}\right) \\
&= -\alpha\Omega_0-\frac{3\alpha\mu^{\frac{1}{2}}\beta^2H^2}{2T^{\frac{5}{2}}} \\
\Rightarrow M &= \frac{3\alpha\mu^{\frac{1}{2}}\beta^2 H}{T^{\frac{5}{2}}} \\
\Rightarrow \chi &= \frac{3\alpha\mu^{\frac{1}{2}}\beta^2}{T^{\frac{5}{2}}}=\frac{3\mu^{\frac{1}{2}}\beta^2}{T^{\frac{5}{2}}}\frac{2^{\frac{3}{2}}T^{\frac{5}{2}}Vm^{\frac{3}{2}}}{3\pi^2\hbar^3}=\frac{2^{\frac{3}{2}}\mu^{\frac{1}{2}}\beta^2Vm^{\frac{3}{2}}}{\pi^2\hbar^3}
\end{aligned}$$

This is the magnetic susceptibility for paramagnetic case of free electron gas. Now I will compute the diamagnetic case.

$$\begin{aligned}
\Omega &= -T\sum_{n=0}^{\infty}\frac{VeH}{2\pi^2\hbar^2c^2}\int \mathrm{d}p_z\ln\left(1+\mathrm{e}^{-\frac{\hbar\omega\left(n+\frac{1}{2}\right)+\frac{p_z^2}{2m}-\mu}{T}}\right) \\
&= -\alpha\sum_{n=0}^{\infty}\int \mathrm{d}p_z\ln\left(1+\mathrm{e}^{-\frac{\hbar\omega\left(n+\frac{1}{2}\right)+\frac{p_z^2}{2m}-\mu}{T}}\right) \\
\int \mathrm{d}p_z\ln\left(1+K\mathrm{e}^{-\frac{p_z^2}{2mT}}\right) &= \frac{m^{\frac{1}{2}}T^{\frac{1}{2}}}{2^{\frac{1}{2}}}\int \mathrm{d}x\, x^{-\frac{1}{2}}\ln\left(1+K\mathrm{e}^{-x}\right)
\end{aligned}$$

$$
\begin{aligned}
&= (2mT)^{\frac{1}{2}} F_{\frac{1}{2}}\left(\frac{\mu-\hbar\omega\left(n+\frac{1}{2}\right)}{T}\right)\\
\Rightarrow \Omega &= -\frac{eVHT^{\frac{3}{2}}m^{\frac{1}{2}}}{2^{\frac{1}{2}}\pi^2\hbar^2c^2}\sum_{n=0}^{\infty}F_{\frac{1}{2}}\left(\frac{\mu-\hbar\omega\left(n+\frac{1}{2}\right)}{T}\right)
\end{aligned}
$$

I have to compute the infinite sum of fermion functions. I will use the approximation to integral. Then for the infinite sum I have

$$
\begin{aligned}
\sum_{n=0}^{\infty}F_{\frac{1}{2}}\left(\frac{\mu-\hbar\omega\left(n+\frac{1}{2}\right)}{T}\right) &= \frac{T}{\hbar\omega}\int_0^{\infty}\mathrm{d}nF_{\frac{1}{2}}\left(\frac{\mu-\hbar\omega\left(n+\frac{1}{2}\right)}{T}\right)\\
&= -\frac{2T}{3\hbar\omega}\left(F_{\frac{3}{2}}\left(\frac{\mu}{T}-\frac{\hbar\omega}{2T}\right)-F_{\frac{3}{2}}\left(-\infty\right)\right)\\
&= -\frac{2T}{3\hbar\omega}F_{\frac{3}{2}}\left(\frac{\mu}{T}-\frac{\hbar\omega}{2T}\right)\\
\Rightarrow \Omega &= \frac{2^{\frac{1}{2}}eVHT^{\frac{5}{2}}m^{\frac{1}{2}}}{3\pi^2\hbar^3\omega c^2}F_{\frac{3}{2}}\left(\frac{\mu}{T}-\frac{\hbar\omega}{2T}\right)\\
&= \beta F_{\frac{3}{2}}\left(\frac{\mu}{T}-\frac{\hbar\omega}{2T}\right)
\end{aligned}
$$

In the paramagnetic case I had similar fermion function. The solution is same.

$$
\begin{aligned}
F_{\frac{3}{2}}\left(\frac{\mu-\beta H}{T}\right) &= T^{-\frac{5}{2}}\left(\frac{2}{5}\left(\mu-\beta H\right)^{\frac{5}{2}}+\frac{\pi^2T}{4}\left(\mu-\beta H\right)^{\frac{1}{2}}\right)\\
\Rightarrow F_{\frac{3}{2}}\left(\frac{\mu}{T}-\frac{\hbar\omega}{2T}\right) &= T^{-\frac{5}{2}}\left(\frac{2}{5}\left(\mu-\frac{\hbar\omega}{2}\right)^{\frac{5}{2}}+\frac{\pi^2T}{4}\left(\mu-\frac{\hbar\omega}{2}\right)^{\frac{1}{2}}\right)\\
&= T^{-\frac{5}{2}}\frac{2\mu^{\frac{5}{2}}}{5}\left(1-\frac{5\hbar\omega}{4\mu}+\frac{15\hbar^2\omega^2}{32\mu^2}\right)\\
&\quad +T^{-\frac{5}{2}}\frac{\pi^2T\mu^{\frac{1}{2}}}{4}\left(1-\frac{\hbar\omega}{4\mu}-\frac{\hbar^2\omega^2}{32\mu^2}\right)\\
&= \frac{2\mu^{\frac{5}{2}}}{5T^{\frac{5}{2}}}+\frac{\hbar\omega\mu^{\frac{3}{2}}}{2T^{\frac{5}{2}}}+\frac{\pi^2\mu^{\frac{1}{2}}}{4T^{\frac{3}{2}}}+\frac{3\hbar^2\omega^2\mu^{\frac{1}{2}}}{16T^{\frac{5}{2}}}
\end{aligned}
$$

From quantum mechanics I have $\omega=\frac{eH}{m}$. Then for Landau potential I have

$$
\Omega = \frac{2^{\frac{1}{2}}eVHT^{\frac{5}{2}}m^{\frac{1}{2}}}{3\pi^2\hbar^3\omega c^2}\left(\frac{2\mu^{\frac{5}{2}}}{5T^{\frac{5}{2}}}+\frac{\hbar\omega\mu^{\frac{3}{2}}}{2T^{\frac{5}{2}}}+\frac{\pi^2\mu^{\frac{1}{2}}}{4T^{\frac{3}{2}}}+\frac{3\hbar^2\omega^2\mu^{\frac{1}{2}}}{16T^{\frac{5}{2}}}\right)
$$

$$
\begin{aligned}
&= \frac{2^{\frac{1}{2}}VT^{\frac{5}{2}}m^{\frac{3}{2}}}{3\pi^2\hbar^3c^2}\left(\frac{2\mu^{\frac{5}{2}}}{5T^{\frac{5}{2}}}+\frac{\hbar eH\mu^{\frac{3}{2}}}{2mT^{\frac{5}{2}}}+\frac{\pi^2\mu^{\frac{1}{2}}}{4T^{\frac{3}{2}}}+\frac{3\hbar^2e^2H^2\mu^{\frac{1}{2}}}{16m^2T^{\frac{5}{2}}}\right)\\
\Rightarrow M &= -\frac{2^{\frac{1}{2}}VT^{\frac{5}{2}}m^{\frac{3}{2}}}{3\pi^2\hbar^3c^2}\left(\frac{\hbar e\mu^{\frac{3}{2}}}{2mT^{\frac{5}{2}}}+\frac{3\hbar^2e^2H\mu^{\frac{1}{2}}}{8m^2T^{\frac{5}{2}}}\right)\\
\Rightarrow \chi &= -\frac{2^{\frac{1}{2}}VT^{\frac{5}{2}}m^{\frac{3}{2}}}{3\pi^2\hbar^3c^2}\frac{3\hbar^2e^2\mu^{\frac{1}{2}}}{8m^2T^{\frac{5}{2}}}\\
&= -\frac{Vm^{-\frac{1}{2}}e^2\mu^{\frac{1}{2}}}{2^{\frac{5}{2}}\pi^2\hbar c^2}\\
&= -\frac{V\mu^{\frac{1}{2}}m^{\frac{3}{2}}\beta^2}{2^{\frac{1}{2}}\pi^2\hbar^3}
\end{aligned}
$$

The total susceptibility is then

$$
\begin{aligned}
\chi &= \frac{2^{\frac{3}{2}}\mu^{\frac{1}{2}}\beta^2Vm^{\frac{3}{2}}}{\pi^2\hbar^3}-\frac{V\mu^{\frac{1}{2}}m^{\frac{3}{2}}\beta^2}{2^{\frac{1}{2}}\pi^2\hbar^3}\\
&= \frac{3Vm^{\frac{3}{2}}\mu^{\frac{1}{2}}\beta^{\frac{1}{2}}}{2^{\frac{1}{2}}\pi^2\hbar^3}\geq 0
\end{aligned}
$$

The free electron gas is paramagnetic.