Problem 1

Classical statistics

The grand canonical ensemble fixes the temperature $T$ and the chemical potential of each species of particle $\mu_\alpha$. The grand partition function is given by summing over all indistinguishable single-particle states:

$$Z = \sum_{n_\alpha} \frac{1}{n_\alpha!} e^{-\beta \epsilon_\alpha n_\alpha} e^{\beta \mu n_\alpha},$$

where we included the Gibbs factor. The series can be summed:

$$Z(T, \mu) = \exp e^{\beta (\mu - \epsilon_\alpha)}.$$  \hfill (2)

The probability of the single-particle state to have occupation $n_\alpha$ is then

$$P_\alpha(n_\alpha; T, \mu) = Z^{-1} e^{\beta n_\alpha (\mu - \epsilon_\alpha)}.$$  \hfill (3)

The grand partition defines the grand potential

$$\Omega(T, \mu) = -k_B T \ln Z(T, \mu).$$  \hfill (4)

To express the probability $P_\alpha(n_\alpha; T, \mu)$ in terms of the expected particle number $\langle n_\alpha \rangle$, we use the relation

$$\langle n_\alpha \rangle = -\frac{\partial \Omega}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = e^{\beta (\mu - \epsilon_\alpha)}.$$  \hfill (5)

This gives chemical potential as

$$\mu = \epsilon_\alpha + k_B T \ln \langle n_\alpha \rangle.$$  \hfill (6)

Therefore, the probability can be written as

$$P_\alpha(n_\alpha; T, \langle n_\alpha \rangle) = \frac{\langle n_\alpha \rangle^{n_\alpha}}{e^{\langle n_\alpha \rangle}}.$$  \hfill (7)
The fluctuations are found as usual:

\[
(\Delta n_\alpha)^2 = \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial \mu^2} = e^{\beta(\mu - \epsilon_\alpha)} = \langle n_\alpha \rangle, \tag{8}
\]

so the fractional fluctuation in particle number is

\[
\frac{\Delta n_\alpha}{\langle n_\alpha \rangle^2} = \frac{1}{\langle n_\alpha \rangle}. \tag{9}
\]

**Quantum statistics**

For the case of bosons/fermions (upper/lower sign), the expression for the probability is still

\[
P_\alpha(n_\alpha; T, \mu) = e^{\beta(\mu - \epsilon_\alpha)n_\alpha} \frac{Z(T, \mu)}{\langle n_\alpha \rangle} \tag{10}
\]

The grand partition function is different:

\[
Z(T, \mu) = \left(1 \mp e^{\beta(\mu - \epsilon_\alpha)}\right) \mp 1. \tag{11}
\]

This gives the expected number of bosons/fermions as

\[
\langle n_\alpha \rangle = \frac{1}{\beta} \frac{\partial Z}{\partial \mu} = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} \mp 1}. \tag{12}
\]

This relation can be inverted to obtain

\[
\mu = \epsilon_\alpha - k_B T \ln \left(\frac{1 \pm \langle n_\alpha \rangle}{\langle n_\alpha \rangle}\right). \tag{13}
\]

For dilute systems \(\langle n_\alpha \rangle \ll 1\), this gives the same chemical potential as the classical case. We can compute the probability using this expression:

\[
P_\alpha(n_\alpha; T, \langle n_\alpha \rangle) = e^{\beta(\mu - \epsilon_\alpha)n_\alpha} \frac{Z}{\langle n_\alpha \rangle} = \left(\frac{\langle n_\alpha \rangle}{1 \pm \langle n_\alpha \rangle}\right)^{\langle n_\alpha \rangle} \left(\frac{1}{1 \pm \langle n_\alpha \rangle}\right)^{\langle n_\alpha \rangle}. \tag{14}
\]

The fluctuations are found in the same way:

\[
\frac{\Delta n_\alpha^2}{\langle n_\alpha \rangle^2} = \frac{1}{\langle n_\alpha \rangle^2} \frac{\partial^2 \ln Z}{\partial \mu^2} = \frac{1}{\beta\langle n_\alpha \rangle} \frac{\partial \ln \langle n_\alpha \rangle}{\partial \mu} = \frac{1}{\langle n_\alpha \rangle^2} \left(\frac{e^{\beta(\epsilon_\alpha - \mu)}}{(e^{\beta(\epsilon_\alpha - \mu)} \mp 1)}\right)^2 = \frac{1 \pm \langle n_\alpha \rangle}{\langle n_\alpha \rangle}. \tag{15}
\]

At large occupations at fixed \(T\), or, equivalently, at low enough \(k_B T\) for a fixed occupation, fluctuations in the occupation numbers do not match the classical result, and the condition \(e^{\beta(\mu - \epsilon)} \gg 1\) is no longer satisfied.
Problem 2

(a)
As in the previous problem, the grand partition function for electrons is

\[ Z = \prod_{\alpha} \left[ 1 + e^{-\beta(\epsilon_{\alpha} - \mu)} \right]. \]  

(16)

The total number of electrons is given by

\[ N = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = \sum_{\alpha} \frac{1}{e^{\beta(\epsilon_{\alpha} - \mu)} + 1} = \frac{g_s V}{(2\pi)^d} \int d^d k \frac{1}{e^{\beta(\epsilon - \mu)} + 1}, \]  

(17)

where we converted the sum over states to an integral over wavenumbers and assumed that the energy depends only on the wavenumber \( \vec{k} \), and every state has degeneracy \( g_s \). For free electrons, \( g_s = 2 \) comes from the spin. If the energy of the single-particle states depends only on \( k = |\vec{k}| \) as \( \epsilon_k = \frac{\hbar^2 k^2}{2m} \), then the integral can be converted to one over \( \epsilon \):

\[ \rho = \frac{N}{V} = \frac{g_s \Omega_d}{(2\pi)^d} \frac{m}{\hbar^2} \left( \frac{2m}{\hbar^2} \right)^{d/2} \int_0^\infty d\epsilon \frac{e^{\epsilon^{d/2} - 1}}{e^{\beta(\epsilon - \mu)} + 1}, \]  

(18)

so that the density of states is

\[ D(\epsilon) = \Theta(\epsilon) \frac{g_s \Omega_d}{2(2\pi)^d} \frac{2m}{\hbar^2} \epsilon^{d/2} e^{d/2 - 1}, \]  

(19)

where \( \Omega_d \) is the \( d \)-dimensional solid angle, given by

\[ \Omega_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}. \]  

(20)

The expression for \( P \) is:

\[ P = -\frac{\Omega}{V} = \frac{k_B T}{V} \int_0^\infty d\epsilon \ln \left[ 1 + e^{-\beta(\epsilon - \mu)} \right] D(\epsilon). \]  

(21)

(b)
As \( T \to 0 \), the Fermi function becomes \( \Theta(\mu - \epsilon) \). This is because the ground state for a free fermionic system completely fills up the lowest energy levels up to the energy it takes to add another particle, which is the definition of the chemical potential \( \mu(T = 0) = \epsilon_F \). Therefore, the density is

\[ \rho = g_s \int_0^{\mu(T=0)} d\epsilon D(\epsilon) = \frac{g_s \pi^{d/2}}{\Gamma(d/2 + 1)(2\pi)^d} \left( \frac{2m \epsilon_F}{\hbar^2} \right)^{d/2}. \]  

(22)

The relation can be inverted to write Fermi energy in terms of density:

\[ \epsilon_F = \frac{\hbar^2}{2m} \left( \frac{d\rho(2\pi)^d}{\Omega_d g_s} \right)^{2/d}. \]  

(23)

To find pressure at low temperature, note that the logarithm in Eq. (21) has the following behavior as
\[ \beta \to \infty: \]

\[ \ln \left[ 1 + e^{\beta(\mu - \varepsilon)} \right] \approx \mu - \varepsilon \text{ if } \varepsilon < \mu, \]

\[ \ln \left[ 1 + e^{\beta(\mu - \varepsilon)} \right] \approx e^{-\beta(\varepsilon - \mu)} \text{ if } \varepsilon > \mu. \]

Neglecting the exponentially small term for \( \mu < \varepsilon \) and replacing \( \mu(T = 0) = \varepsilon_F \), the pressure is:

\[ P = \frac{1}{V} \int_0^{\varepsilon_F} d\varepsilon \left( \varepsilon_F - \varepsilon \right) D(\varepsilon) = \frac{g_s \Omega_d}{2(2\pi)^d} \left( \frac{2m}{\hbar^2} \right)^{d/2} \ell_F^d \frac{4}{d+2} \frac{1}{d+2} \rho \varepsilon_F. \]  

(c)

To find compressibility, we can first find the derivative in terms of the density and Fermi energy of the system. We can use Eq. (22) to see that \( \varepsilon_F \propto \rho^{2/d} \), so \( P(V) \) is a function of a power of \( V \): \( P(V) \propto V^{-2/d-1} \):

\[ -\left( \frac{\partial P}{\partial V} \right)_{N, T} = -\frac{2}{d+2} \frac{\partial (\rho \varepsilon_F)}{\partial V} = \frac{2 \rho \varepsilon_F}{dV}. \]

The compressibility is

\[ \kappa_T = -\frac{1}{V} \left( \frac{\partial P}{\partial V} \right)^{-1} = \frac{d}{2 \rho \varepsilon_F}. \]

Problem 3

(a)

Due to the presence of the external field \( H \), the energy of the single-particle state will now depend on the spin of the particle. In particular, the single-particle \( \mathcal{Z} \) is different for parallel(anti-parallel) spins:

\[ \mathcal{Z}_\pm(\varepsilon_k) = 1 + e^{-\beta(\varepsilon_k^0 \mp \mu_B H - \mu)}, \varepsilon_k^0 = \frac{\hbar^2 k^2}{2m}, \]

so the grand potentials are

\[ \Omega_\pm = -k_B TV \int \frac{d^d k}{(2\pi)^d} \ln \mathcal{Z}_\pm(\varepsilon_k). \]

The number of particles is

\[ \langle N_\pm \rangle = -\frac{\partial \Omega_\pm}{\partial \mu} = \int_0^\infty d\varepsilon \frac{D(\varepsilon)}{e^{\beta(\varepsilon \mp \mu_B H - \mu)} + 1}, \]

where

\[ D(\varepsilon) = \Theta(\varepsilon) \frac{V \Omega_d}{(2\pi)^d} \frac{m}{\hbar^2} \left( \sqrt{\frac{2m}{\hbar^2}} \right)^{d-2} \varepsilon^{d/2-1}. \]

is the density of states. Notice that the factor of \( g_s \) is missing because the two spin states have different energies and are counted separately.
(b) 

The magnetization is

\[ \langle M \rangle = \frac{\mu_B \Omega_d}{2(2\pi)^d} \left( \frac{2m}{\hbar^2} \right)^{d/2} \int_0^\infty dy y^{d/2-1} \left[ \frac{1}{e^{\frac{y}{B}}+1} - \frac{1}{e^{\frac{y}{B}}-1} \right]. \]  

(32)

Above, we made the substitution \( y = \beta \epsilon \) and defined variables \( x_\pm = \beta(\mu \pm \mu_B H) \). Using the Sommerfeld expansion

\[ I = \int_0^\infty dy \frac{H(y)}{e^{y\beta}+1} \approx \int_0^\infty dy \frac{\pi^2}{6} H'(y), \]

we obtain

\[ \langle M \rangle = \frac{\mu_B \Omega_d}{2(2\pi)^d} \left( \frac{2m k_B T}{\hbar^2} \right)^{d/2} \left[ \frac{2}{d} (\mu + \mu_B H)^{d/2} - \frac{2}{d} (\mu - \mu_B H)^{d/2} + \frac{(d-2)\pi^2 k_B^2 T^2}{12} \left( (\mu + \mu_B H)^{d/2-2} - (\mu - \mu_B H)^{d/2-2} \right) \right]. \]

(34)

After a few steps of algebra, we obtain

\[ \langle M \rangle = \frac{\mu_B \Omega_d}{2(2\pi)^d} \left( \frac{2m}{\hbar^2} \right)^{d/2} \left[ \frac{2}{d} (\mu + \mu_B H)^{d/2} - \frac{2}{d} (\mu - \mu_B H)^{d/2} + \frac{(d-2)\pi^2 k_B^2 T^2}{12} \left( (\mu + \mu_B H)^{d/2-2} - (\mu - \mu_B H)^{d/2-2} \right) \right]. \]

(35)

(c) 

As \( H \rightarrow 0 \), we can expand the terms inside the square brackets in the above equation:

\[ \langle M \rangle \approx \frac{\mu_B^2 k_B T}{(2\pi)^d} \left( \frac{2m}{\hbar^2} \right)^{d/2} \mu^{d/2-1} \left( 1 + \frac{(d-2)(d-4)\pi^2 k_B^2 T^2}{24\mu^2} \right). \]

(36)

The resulting susceptibility is

\[ \chi = \frac{\mu_B^2 \Omega_d}{(2\pi)^d} \left( \frac{2m}{\hbar^2} \right)^{d/2} \mu^{d/2-1} \left( 1 + \frac{(d-2)(d-4)\pi^2 k_B^2 T^2}{24\mu^2} \right). \]

(37)

We can eliminate \( \mu \) to in favor of the total number of electrons \( N \):

\[ N = g_s \int_0^\infty d\epsilon \frac{D(\epsilon)}{e^{\beta(\epsilon - \mu)} + 1}, \]

(38)

where we restored the spin degeneracy \( g_s = 2 \) in the absence of the magnetic field. Using the Sommerfeld expansion once more, we find

\[ N = g_s V \Omega_d \left( \frac{2m}{\hbar^2} \right)^{d/2} \mu^{d/2} \left( 1 + \frac{d(d-2)\pi^2 k_B^2 T^2}{24e_F^2} \right), \]

(39)

where we replaced \( \mu \approx \epsilon_F \) in the second term, which is accurate to order \( k_B T^2/\epsilon_F^2 \). Rearranging terms gives

\[ \frac{N d(2\pi)^d}{g_s V \Omega_d} \left( \frac{\hbar^2}{2m} \right)^{d/2} = \mu^{d/2} \left( 1 + \frac{d(d-2)\pi^2 k_B^2 T^2}{24e_F^2} \right), \]

(40)
Taking both side to the $2/d$ power and using the binomial theorem, the relation between $N$ and $\mu$ is

$$\mu = \frac{\hbar^2}{2m} \left( \frac{dN(2\pi)^d}{g_s V \Omega_d} \right)^{2/d} \left( 1 - \frac{(d-2)\pi^2 k_B^2 T^2}{12\epsilon_F^2} \right),$$

(41)

where the first term outside the parentheses is the Fermi energy $\epsilon_F = \mu(T = 0)$. Returning to the magnetization, using the expression for $\mu = \mu(T, \epsilon_F)$ and the binomial theorem, the susceptibility is

$$\chi = \frac{\mu^2 B \Omega_d}{2(2\pi)^d} \left( \frac{2m}{\hbar^2} \right)^{d/2} \left( 1 - \frac{(d-2)\pi^2 k_B^2 T^2}{12\epsilon_F^2} \right).$$

(42)

**Problem 4**

(a) The total number of states per momentum volume $d^3 p$ is

$$g_s V \frac{d^3 p}{(2\pi \hbar)^3} = d\epsilon D(\epsilon),$$

(43)

where $g_s = 2$ accounts for both possible polarizations of the photon. Given the single-particle Hamiltonian $\epsilon = pc$, we find the density of states:

$$D(\epsilon) = \frac{g_s V \epsilon^2}{2\pi^2 \hbar^2 c^3} \Theta(\epsilon).$$

(44)

(b) Since the free energy must be at a minimum for photons since their number is determined by the condition of thermal equilibrium, $\mu = 0$ for photons and any other non-conserved particles. The grand potential for a non-interacting phonon gas is

$$\Omega = -k_B T \ln Z = \frac{k_B T g_s V}{2\pi^2 \hbar^2 c^3} \int_0^\infty d\epsilon \epsilon^2 \ln \left( 1 - e^{-\beta \epsilon} \right).$$

(45)

By changing to the dimensionless variable $y = \beta \epsilon$, we obtain

$$\Omega = \frac{(k_B T)^4 g_s V}{2\pi^2 \hbar^2 c^3} \int_0^\infty dy y^2 \ln \left( 1 - e^{-y} \right).$$

(46)

The integral is equal to $-\frac{\pi^4}{45}$.

(c) The pressure the gas exerts is proportional to the grand potential:

$$P = -\frac{\Omega}{V} = -\frac{\pi^2 g_s (k_B T)^4}{90 \hbar^2 c^3}.$$  

(47)

The energy can be found by using the fact that $\mu = 0$ and $\Omega = F = E - TS$:

$$S(T) = -\frac{\partial \Omega}{\partial T} = -\frac{4\Omega}{T},$$

(48)
so
\[ u = \frac{E}{V} = 3P. \] (49)

**Problem 5**

(a)
The density of states for a two-dimensional gas is
\[ g_s \frac{d^2k}{(2\pi)^2} = g_s \frac{k}{2\pi} dk = D(|\vec{k}|) dk. \] (50)

For spin 0 bosons, \( g_s = 1 \). Further simplification requires assuming that the dispersion is parabolic:
\[ \varepsilon(k) = \frac{\hbar^2 k^2}{2m}, \] in which case we can use the group velocity \( v_g = \frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{m} \) to write
\[ D(\varepsilon) d\varepsilon = D(\varepsilon) \frac{1}{v_g(\varepsilon)} d\varepsilon = mg_s V \frac{d\varepsilon}{2\pi\hbar^2}. \] (51)

This is the well-known result for a two-dimensional electron gas: its DOS is independent of energy \( \varepsilon \).

(b)
To obtain the pressure of the Bose gas as a function of fugacity \( f = \exp(\beta\mu) \), we will introduce the grand canonical ensemble. Since the particle number \( N \) is fixed, we will need an auxiliary condition to ensure that conjugate variables \( \mu, N \) are mutually consistent. In other words, we will require the condition \( N = -\left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} \) with \( N \) being the actual (as opposed to the average) particle number. To obtain the grand canonical partition function \( Z \), we will begin with the canonical partition function \( Z \) and sum over all possible occupations:
\[ Z(T, V, \mu) = \sum_{N=0}^{\infty} f^N Z(T, V, N) = \sum_{N=0}^{\infty} \sum_k f^N e^{-N\beta\varepsilon_k}, \] (52)
where \( \varepsilon_k \) are the energy levels of the single-particle states at wavevector \( k \). For bosons, there can be an arbitrary filling of each state \( k \), so the sum over \( N \) becomes a geometric series:
\[ Z = \sum_k \left( 1 - f e^{-\beta\varepsilon_k} \right)^{-1}, \] (53)
and the grand potential becomes
\[ \Omega = -k_B T \ln Z = k_B T \sum_k \ln \left( 1 - f e^{-\beta\varepsilon_k} \right). \] (54)

The auxiliary condition to fix particle number is found as before:
\[ N = -\left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} = \sum_k \frac{1}{f^{-1} e^{\beta\varepsilon_k} - 1}. \] (55)

In this form, it is particularly obvious that \( f < 1 \), since the occupation of each level has to be positive. In other words, the boson chemical potential \( \mu \) is always negative.

In the special case where none of the levels has a macroscopic degeneracy, these sums can be transformed into integrals over energy with the substitution \( \sum_k F(\varepsilon_k) \rightarrow \int_{-\infty}^{\infty} D(\varepsilon) F(\varepsilon) d\varepsilon \). Here, \( D(\varepsilon) \) is
the density of states, and $F(\epsilon)$ is any function. Using this substitution, the expression for the number of particles $N$ becomes

$$N = \int_{0}^{\infty} d\epsilon \, \frac{D(\epsilon)}{f^{-1}e^{\beta \epsilon} - 1} = \frac{k_B T m \gamma_s V}{2\pi \hbar^2} \int_{0}^{\infty} dx \, \frac{1}{f^{-1}e^{\beta x} - 1}. \quad (56)$$

The pressure can be found as before:

$$P = -\frac{\Omega}{V} = -\frac{k_B T}{V} \int_{0}^{\infty} d\epsilon D(\epsilon) \ln \left(1 - f e^{-\beta \epsilon}\right). \quad (57)$$

Here, the volume $V$ is defined as $V = L^d$ with $d$ being the dimensionality ($d = 2$). As for the particle number, we substitute $D(\epsilon) = \frac{mg_s V}{2\pi \hbar^2}$ and change to dimensionless variable $x = \beta \epsilon$, so the pressure becomes

$$P = -\frac{mg_s (k_B T)^2}{2\pi \hbar^2} \int_{0}^{\infty} dx \, x f^{-1}e^{-x} \ln(1 - f e^{-x}). \quad (58)$$

(c) To the leading order, we expect to recover the ideal gas law at high temperatures and low densities, when the effects of quantum statistics are absent. First, we rewrite Eq. (58) using integration by parts:

$$P = \frac{mg_s (k_B T)^2}{2\pi \hbar^2} \int_{0}^{\infty} dx \, x f^{-1}e^{-x} \left(1 + f e^{-x}\right) = \frac{mg_s (k_B T)^2 f}{2\pi \hbar^2} \left(1 + \frac{f}{4}\right). \quad (59)$$

In the same limit, we can reduce Eq. (56) to

$$\frac{N}{V} \approx \frac{k_B T m \gamma_s f}{2\pi \hbar^2} \left(1 + \frac{f}{2}\right) \quad (61)$$

to first order in $f$. To leading non-linear order in $f$, we find

$$P = \frac{N k_B T}{V} \left(1 - \frac{\pi \hbar^2 N}{2V k_B T \gamma_s}\right). \quad (62)$$

(d) The condition for Bose-Einstein condensation is the vanishing of the chemical potential $\mu$ at a finite temperature $T_{BEC}$. We typically obtain $T_{BEC}$ from Eq. (56) with $f = 1$:

$$\frac{N}{V} = \frac{k_B T_{BEC} m \gamma_s}{2\pi \hbar^2} \int_{0}^{\infty} dx \, \frac{1}{e^{x} - 1}. \quad (63)$$

This integral does not converge, since, at small $x$, the integrand has the behavior $\frac{1}{e^{x} - 1} \approx \frac{1}{x}$, resulting in a logarithmic divergence. This means that our assumption that condensation occurs at some finite temperature was flawed and there is no temperature such that $\mu = 0$. To determine the scaling of $T_{BEC}$ with various parameters, consider Eq. (56). Notice that since the integral diverges logarithmically, the number of particles in the excited states can never saturate, unlike in the 3D (or linearly dispersing)
case, when the integral converges. Therefore, we expect $\beta_{\text{BEC}} \sim \ln N$. This can be shown rigorously by performing the integral Eq. (56) exactly: $\frac{N}{V} \sim -\ln(1-f) \approx f$. For small $f = e^{\beta \mu} \ll 1$, which happens as we lower temperature, we obtain $\beta_{\text{BEC}} \sim \ln f \sim \ln N$. 
