

DEGENERACY AND WHERE TO FIND IT
A GENTLE INTRODUCTION TO QUANTUM GASES
PHY 301 – THERMAL PHYSICS
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Preface

Please note that this set of notes is **NOT** meant to be a substitute for any course material, and is instead complementary to it at best. This content is not endorsed by Bill or the other AIs in any way. The following review is mostly a transcription of some handwritten notes I kept as an undergraduate when I took my first and second statistical mechanics courses, as well as some advanced content that I wrote as a training guide for new students joining the Bakr Lab. It is hard for me to place exact citations throughout this, as I do not include those in my own notes. As far as possible, I have tried to compile a list of the references [1–4] which I used when writing these and taking my statistical mechanics course in the past. This document may be updated periodically, and the latest version will be put on Canvas as well as my [personal webpage](#).

I would argue that (aside from the canonical partition function being the most important takeaway from this class) the study of quantum gases is perhaps the most poignant and intriguing parts of an undergraduate statistical mechanics class. While it may seem that quantum gases are irrelevant to our experiences in everyday life, I aim to convince you that many fields of physics deal with them in some way¹.

¹As of publishing this first draft, this aim has not yet been fulfilled.

1 Statistical Mechanics of Ideal Gases

Having dealt with the formalism of statistical mechanics and the three primary ensembles in which most of the bookkeeping is done, we now turn to study the ideal gas in a more rigorous fashion. This will involve us making heavy use of the grand canonical ensemble, so it may be wise to familiarise yourself with it before embarking on this review.

1.1 The Classical Ideal Gas

In our previous study of the classical ideal gas (non-interacting particles in a box), we derived the Sackur-Tetrode equation in the canonical ensemble:

$$S(T, V, N) = Nk_B \left[\log \left(\frac{V}{N} \right) + \frac{3}{2} \log \left(\frac{mk_B T}{2\pi\hbar^2} \right) + \frac{5}{2} \right] \quad (1.1)$$

$$= Nk_B \left[\log \left(\frac{V}{N\Lambda^3} \right) + \frac{5}{2} \right] \quad (1.2)$$

where we have defined the **thermal de Broglie wavelength** (or simply **thermal wavelength**) Λ as:

$$\Lambda = \sqrt{\frac{2\pi\hbar^2\beta}{m}} = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad (1.3)$$

This is understood to be the typical de Broglie wavelength of a particle of mass m in the gas when it is held at temperature T . While the Sackur-Tetrode equation agrees with experimental data at sufficiently high temperatures, it breaks down when $V/N\Lambda^3 \lesssim 1$. Specifically, the entropy diverges to negative infinity (in direct contradiction with the Third Law) when the thermal wavelength becomes comparable to the inter-particle spacing $\sqrt[3]{V/N}$, implying that some form of interaction is occurring between the particles to produce this deviation. While an ideal gas is assumed to be devoid of inter-particle interactions (such as hard-sphere collisional interactions or attractive/repulsive electromagnetic interactions), we have neglected the fact that quantum mechanical symmetry requirements on the many-particle wavefunction of the system play a significant role at low temperatures.

1.2 Moving from Particles to Occupations

Given a system in thermodynamic equilibrium with its surroundings, we expect that the equilibrium state of the system implies that its observables do not change over time (or at least do not fluctuate to a significant extent). The Hamiltonian of the system can be written as a Hermitian matrix, whose hermiticity implies that it has strictly real eigenvalues, known as the energies of the corresponding eigenstates of the system. A system in any of these eigenstates $|\psi_j\rangle$ evolves according to the unitary operator $U = \exp(-iE_j t/\hbar)$, where E_j is the energy of the eigenstate $|\psi_j\rangle$. Since thermal equilibrium implies that the observables do not evolve over time, we expect that a system in thermal equilibrium should be either in an eigenstate of the Hamiltonian, or a statistical mixture thereof. This is typically represented by the system having a diagonal density matrix known as a **mixed thermal state**, comprised of a statistical mixture of pure eigenstates. Observables of this mixed thermal state then show no time evolution, simply obeying a statistical distribution given by the diagonal elements themselves. This view that eigenstates are thermal is known as the **eigenstate thermalization hypothesis**, and is a yet unproven conjecture (though stronger forms of this have been proven in a large class of systems).

As a great form of simplification, we assume that our classical ideal gas consists of a large number of non-interacting particles, each of which is in a single-particle eigenstate of the system. We further assume that the

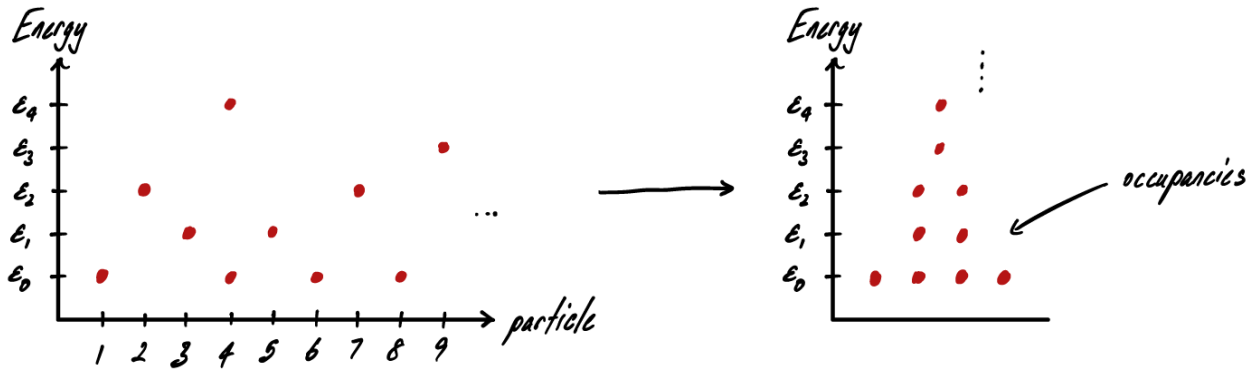


FIGURE 1: Counting Distinguishable vs. Indistinguishable Particles. (Left) When the constituent particles are distinguishable from one another, we can assign specific energies to each particle. (Right) When the particles are identical (or sufficiently indistinguishable), it is more justified to instead count the *number* of particles occupying each energy level.

single-particle eigenstates are labelled by a single quantum number $\{\epsilon\}$, so the total state of the system can be written as $|\epsilon_1, \epsilon_2, \dots, \epsilon_N\rangle$. Such a representation of the system's state is known as the particle-centric representation. The primary caveat of this approach is that it assumes all particles are distinguishable from one another – that is, it assumes that for any two particles in the same single-particle eigenstate ($\epsilon_i = \epsilon_j$ for $i \neq j$), we are able to tell them apart from one another. This statement is no longer true at the quantum mechanical level, where the constituent particles of a gas are fundamentally indistinguishable from one another. Furthermore, this indistinguishability places symmetry requirements on the state of the system depending on whether the constituent particles are bosons or fermions. Under the permutation operator $\Pi_{i,j}$ which swaps the particles in the i and j indices, we have the following requirements:

$$\Pi_{i,j} |\epsilon_1, \dots, \epsilon_i, \dots, \epsilon_j, \dots, \epsilon_N\rangle = |\epsilon_1, \dots, \epsilon_j, \dots, \epsilon_i, \dots, \epsilon_N\rangle \quad \text{for bosons} \quad (1.4)$$

$$\Pi_{i,j} |\epsilon_1, \dots, \epsilon_i, \dots, \epsilon_j, \dots, \epsilon_N\rangle = -|\epsilon_1, \dots, \epsilon_j, \dots, \epsilon_i, \dots, \epsilon_N\rangle \quad \text{for fermions} \quad (1.5)$$

where Eq. 1.5 is a manifestation of the Pauli exclusion principle obeyed by fermions. This symmetry requirement sets up incredibly convoluted wavefunctions for the many-particle system at equilibrium, with the state being either totally symmetrised or totally antisymmetrised using some appropriate sum or determinant² operation. For this reason, the particle-centric representation is undesirable when dealing with the quantum statistics of ideal gases and a new representation is needed.

Instead of asking which single-particle eigenstate any given particle is in, we flip the question to now ask how many particles n_i are in a given single-particle eigenstate $|\epsilon_i\rangle$. In this manner, we construct the occupation-centric representation of a system $|n_1, n_2, \dots, n_i, \dots\rangle$, where the symmetry requirements are assumed to be automatically taken care of. The translation from the particle-centric to occupation-centric picture is shown in Fig. 1. In this new representation, the canonical partition function is written as:

$$\begin{aligned} Z(T, V, N) &= \sum_{\{n_i\}} e^{-\beta \sum_j \epsilon_j n_j} \delta_{N, \sum_j n_j} \\ &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \sum_{n_j=0}^{\infty} \dots e^{-\beta \sum_j \epsilon_j n_j} \delta_{N, \sum_j n_j} \end{aligned} \quad (1.6)$$

²See the Slater determinant.

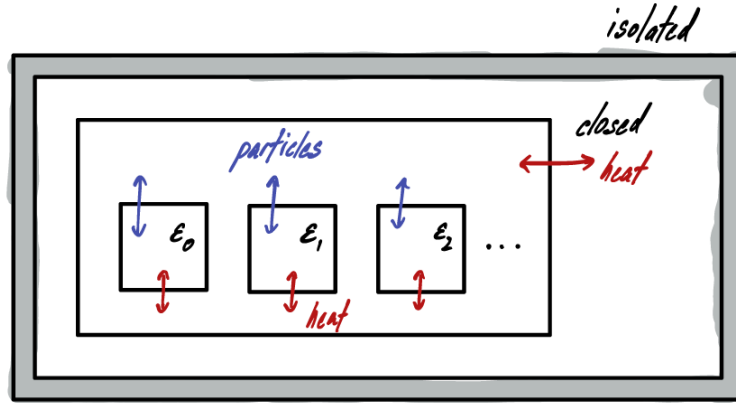


FIGURE 2: Closed Systems as Interacting Open Systems. When the constituent particles of a closed system are indistinguishable from one another, it is preferable to work in the basis of occupation numbers for the various energy levels. Here, we consider each energy level as an open system, able to exchange heat and particles with the closed system as a reservoir. In this manner, the partition function of the entire system is better studied by considering the grand partition functions of the constituent energy levels, rather than the single canonical partition function of the closed system.

In the first line, we construct the canonical partition as a sum over all possible states, weighted by the Boltzmann factor $e^{-\beta E}$ where E is the total energy of the state. Since the configuration of each state is specified by a set of occupancies $\{n_i\}$ of all single-particle eigenstates, the sum for the partition function is then written as a set of sums over each eigenstate's possible occupancies. However, since the canonical ensemble is constructed under the assumption of a conserved particle number, we must constrain the set of configurations through the imposition of an overall Kronecker delta $\delta_{N, \sum_j n_j}$, which ensures that the sum of all states' occupancies gives the total particle number N . This Kronecker delta is a painful and awkward demand which prevents us from factorising the partition function into a product of sums over the individual single-particle eigenstates, since it tells us that not all of the occupancies are independent of each other.

Let us consider looking at the closed system in a slightly different manner. Since each particle is assumed to be in a single-particle eigenstate $|\epsilon_i\rangle$, we can take our closed system and partition it into distinct regions corresponding to each single-particle eigenstate, as shown in Fig. 2. This construction must be done in a manner that ensures the partitions form a covering of the entire state space – that is, any given particle must be in one of the eigenstates at any given point in time. Assuming the partitions are constructed such that they are permeable (allowing particle exchange), the individual particles are free to roam around within the closed system, entering and leaving the regions corresponding to the various single-particle eigenstates. However, since two neighbouring regions are in thermal contact with one another, they are necessarily in thermodynamic equilibrium and (by the Zeroth Law), all partitions are in thermodynamic equilibrium. This implies that every partition corresponding to a single-particle eigenstate forms an open subsystem of the closed system, having the same values of temperature T , pressure p and chemical potential μ . Since these subsystems are not assumed to change in spatial volume, but are allowed to exchange heat and particles amongst each other, they are best described using the **grand potential** (or **Landau potential**):

$$\Phi = \langle E \rangle - TS - \mu \langle N \rangle = -pV \implies d\Phi = -S dT - p dV - N d\mu \quad (1.7)$$

Enacting the double Legendre transformation, the natural variables of the problem are thus (T, V, μ) , and we see that it is necessary to shift to the **grand canonical ensemble** for the statistical mechanics approach. We first recall that the **grand canonical partition function** (or simply **grand partition function**) for a system is

defined by:

$$\mathcal{Z}(T, V, \mu) = \sum_{\alpha} e^{-\beta E_{\alpha} + \beta \mu N_{\alpha}} \quad (1.8)$$

where N_{α} is the number of particles present in the microstate α and E_{α} is the total energy of all particles in said microstate. In our construction, each open subsystem has a fixed energy ϵ_i , so the grand partition function of each subsystem can be rewritten as:

$$\begin{aligned} \mathcal{Z}_i(T, V, \mu) &= \sum_{n_i} e^{-\beta \epsilon_i n_i + \beta \mu n_i} \\ &= \sum_{n_i} e^{-\beta n_i (\epsilon_i - \mu)} \end{aligned} \quad (1.9)$$

where the sum is now carried out over the number of particles n_i in the i -th open subsystem. This leads us to the total grand partition function of the closed system as:

$$\mathcal{Z}(T, V, \mu) = \prod_i \sum_{n_i} e^{-\beta n_i (\epsilon_i - \mu)} \quad (1.10)$$

In this formalism, the partition function avoids the awkward imposition of the Kronecker delta on the total particle number at the cost of introducing the chemical potential μ . Regardless, this makes it far easier to place constraints on the occupancies of any individual single-particle eigenstate (such as in the case of fermions due to the Pauli exclusion principle), as we will see soon. Another reason that the grand canonical ensemble is desirable here is that the probability of the system being in a given microstate $|\alpha\rangle \equiv |n_{1,\alpha}, n_{2,\alpha}, \dots, n_{i,\alpha}, \dots\rangle$ factorises easily as:

$$\begin{aligned} p_{\alpha} &= \frac{1}{\mathcal{Z}} e^{-\beta E_{\alpha} + \beta \mu N_{\alpha}} \\ &= \frac{1}{\mathcal{Z}} e^{-\beta \sum_i \epsilon_i n_{i,\alpha} + \beta \mu \sum_i n_{i,\alpha}} \\ &= \frac{\prod_i e^{-\beta \epsilon_i n_{i,\alpha} + \beta \mu n_{i,\alpha}}}{\prod_i \sum_{n_i} e^{-\beta n_i (\epsilon_i - \mu)}} \\ &= \prod_i \frac{e^{-\beta \epsilon_i n_{i,\alpha} + \beta \mu n_{i,\alpha}}}{\sum_{n_i} e^{-\beta n_i (\epsilon_i - \mu)}} \\ &= \prod_i \frac{e^{-\beta \epsilon_i n_{i,\alpha} + \beta \mu n_{i,\alpha}}}{\mathcal{Z}_i} \\ &= \prod_i p_{i,\alpha}(n_{i,\alpha}) \end{aligned} \quad (1.11)$$

where $p_{i,\alpha}(n_{i,\alpha})$ is the probability of there being n_i particles in the i -th single-particle eigenstate in the microstate α . This simple factorisation demonstrates how the shift to the grand canonical ensemble allows us to treat each single-particle eigenstate independently, and thus the only requirement to look at the system as a whole is to simply take a product of the individual probabilities or partition functions.

1.3 The Ideal Bose Gas

The spin-statistics theorem is a fundamental result from quantum field theory which tells us that all particles of integer spin (such as photons) obey a **canonical commutation relation** in their creation and annihilation operators of the form:

$$[\hat{a}_i, \hat{a}_j^\dagger] = \hat{a}_i \hat{a}_j^\dagger - \hat{a}_j^\dagger \hat{a}_i = \delta_{ij}, \quad [\hat{a}_i, \hat{a}_j] = [\hat{a}_i^\dagger, \hat{a}_j^\dagger] = 0 \quad (1.12)$$

Such particles are called **bosons**, and they are allowed to have unbounded occupancy (from above) in any single-particle eigenstate. Specifically, the successive application of \hat{a}_i^\dagger on the vacuum state n times will create n particles in the i -th eigenstate, with the requirement of symmetrisation automatically satisfied since all n particles are in the same single-particle eigenstate. Bosonic classification is not limited to elementary particles of integer spin, but rather can be applied to any composite particle with *total* integer spin³. Examples of this include hydrogen atoms (two up quarks, one down quark and an electron), larger atoms like ²³Na, ⁸⁷Rb and even molecules such as ⁴⁰Ca¹⁹F.

With an unbounded occupancy in each single-particle eigenstate (henceforth called **energy level**), the grand partition function from Eq. 1.10 is now written as a product over infinite sums:

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \prod_i \sum_{n_i=0}^{\infty} e^{-\beta n_i (\epsilon_i - \mu)} \\ &= \prod_i \underbrace{\frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}}}_{=\mathcal{Z}_{i,\text{BE}}} \end{aligned} \quad (1.13)$$

where we simply use the formula for the sum of an infinite geometric series. The fundamental relation now takes the form:

$$\beta\Phi = -\beta pV = -\log \mathcal{Z} = \sum_i \log \left[1 - e^{-\beta(\epsilon_i - \mu)} \right] \quad (1.14)$$

We can now compute the average number of bosons in a specific energy level ϵ_j by summing over all possible values for n_j weighted by the grand canonical probabilities:

$$\begin{aligned} \langle n_j \rangle &= \sum_{n_j} n_j p(n_j) \\ &= \sum_{n_j} n_j \frac{1}{\mathcal{Z}} e^{-\beta n_j (\epsilon_j - \mu)} \\ &= -\frac{\partial \log \mathcal{Z}}{\partial (\beta \epsilon_j)} \\ &= \frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}} e^{-\beta(\epsilon_j - \mu)} \\ &= \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1} = \bar{n}_{\text{BE}}(\epsilon_j) \end{aligned} \quad (1.15)$$

This derivative might seem strange, but it is a careful choice motivated by the fact that we only want to pull down a factor of n_j from the exponent. Furthermore, the log of the partition function from Eq. 1.14 is written as a sum over terms containing all possible ϵ_i 's, so the inclusion of ϵ_j in the derivative allows us to drop all terms except the one which contains the energy level of interest. The final result $\bar{n}_{\text{BE}}(\epsilon_j)$ is known as the **Bose-Einstein distribution**, which describes the occupancy of an energy level by an ideal gas of bosons.

³One must be careful to include all spin couplings, such as the fine and hyperfine structure. For instance, the ⁸⁷Rb atom has total electronic angular momentum $J = 1/2$ in its ground state, at the level of fine structure coupling. When the nuclear spin ($I = 3/2$) is coupled to the valence electron through hyperfine structure, this gives rise to the hyperfine splitting of the ground state and thus integer total angular momentum $F = 1, 2$.

Examining this result closer, we see that since $\langle n_j \rangle$ is itself an average of non-negative numbers, it must be non-negative itself. Thus, the chemical potential μ must be less than the ground state energy $\epsilon_0 = \min(\{\epsilon_i\})$. In this form, it is clear that the occupancy of the ground state $\langle n_0 \rangle$ exhibits singular behaviour in the limit $\mu \rightarrow \epsilon_0$. Physically, this implies that in this limit, the occupancy of the ground state presents a macroscopic (of order N) contribution to the gas, rather than the usual microscopic (of order 1) contribution expected in the thermodynamic limit. This is the phenomenon of **Bose-Einstein condensation**, and we will explore this further in a later section.

1.4 The Ideal Fermi Gas

In contrast to the canonical commutation relation obeyed by bosons, particles of half-integer spin (such as electrons) obey a **canonical anticommutation relation** of the form:

$$\{\hat{a}_i, \hat{a}_j^\dagger\} = \hat{a}_i \hat{a}_j^\dagger + \hat{a}_j^\dagger \hat{a}_i = \delta_{ij}, \quad \{\hat{a}_i, \hat{a}_j\} = \{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} = 0 \quad (1.16)$$

Particles of this sort are called **fermions**. The canonical anticommutation relation also encodes the Pauli exclusion principle in the last equality, where setting $i = j$ shows:

$$\hat{a}_i^\dagger \hat{a}_i^\dagger + \hat{a}_i^\dagger \hat{a}_i^\dagger = 2(\hat{a}_i^\dagger)^2 = 0$$

which tells us that it is not possible to create two fermions in the same single-particle eigenstate i using successive applications of \hat{a}_i^\dagger . We thus have to restrict each energy level's occupancy in the grand canonical ensemble to $n_i = 0, 1$ for all eigenstates. The grand partition function is then written:

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \prod_i \sum_{n_i=0}^1 e^{-\beta n_i (\epsilon_i - \mu)} \\ &= \prod_i \underbrace{\left[1 + e^{-\beta(\epsilon_i - \mu)} \right]}_{=\mathcal{Z}_{i,\text{FD}}} \end{aligned} \quad (1.17)$$

with the fundamental relation giving:

$$\beta\Phi = -\beta pV = -\log \mathcal{Z} = -\sum_i \log \left[1 + e^{-\beta(\epsilon_i - \mu)} \right] \quad (1.18)$$

In a similar manner to the bosonic case, we take the appropriate derivative to extract the average occupancy of the j -th energy level as:

$$\begin{aligned} \langle n_j \rangle &= -\frac{\partial \log \mathcal{Z}}{\partial(\beta\epsilon_j)} \\ &= \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1} = \bar{n}_{\text{FD}}(\epsilon_j) \end{aligned} \quad (1.19)$$

In contrast to the Bose-Einstein distribution, the **Fermi-Dirac distribution** $\bar{n}_{\text{FD}}(\epsilon_j)$ is regular for all values of the chemical potential μ , and is always constrained to lie in the interval $0 < \langle n_j \rangle < 1$. We will explore this distribution in greater detail later on.

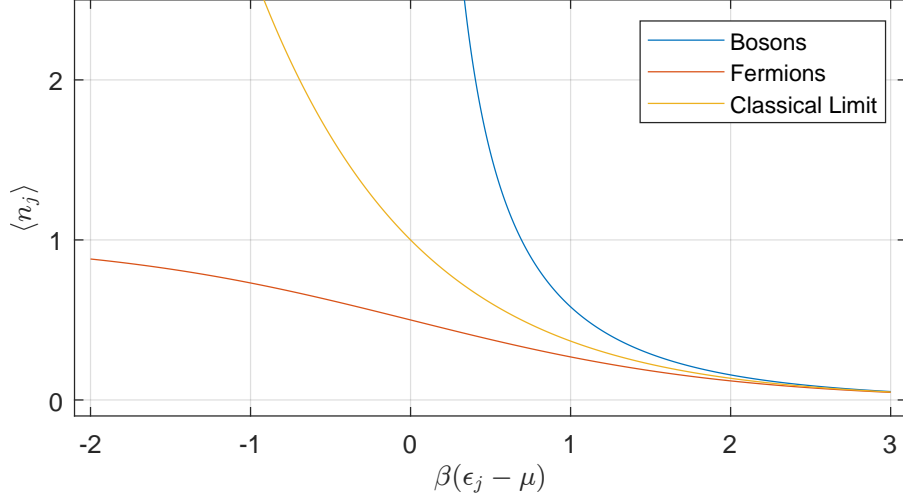


FIGURE 3: Number Distributions of Quantum and Classical Ideal Gases. The quantum Bose-Einstein (BE) and Fermi-Dirac (FD) distributions both converge to the classical behaviour obtained from the Maxwell-Boltzmann distribution at sufficiently dilute and high temperature settings. At low temperatures or high density, the fermions saturate at an occupancy of 1 for $\epsilon_j < \mu$, while the boson occupancy in the ground state $\epsilon_0 = \mu$ diverges.

1.5 The Dilute Gas Limit

The Bose-Einstein and Fermi-Dirac distributions look very similar, and we obtain the total particle number from them as:

$$\langle N \rangle = \sum_j \langle n_j \rangle = \sum_j \frac{1}{e^{\beta(\epsilon_j - \mu)} \mp 1} \quad (1.20)$$

with the upper sign chosen for bosons and the lower sign for fermions. To ensure that both of these are sensible distributions, we have to confirm that they recover the expected classical behaviour in the dilute gas limit where the inter-particle spacings become large (so quantum mechanical effects can be safely ignored). In this limit of low particle density $\langle N \rangle / V$ and high temperature T , there are far more single-particle eigenstates than there are particles, so we expect that each $\langle n_j \rangle$ must be incredibly small. This implies:

$$e^{\beta(\epsilon_j - \mu)} \gg 1 \implies \langle n_j \rangle \approx e^{-\beta(\epsilon_j - \mu)}$$

This is true for both bosons and fermions, since the difference between them is a term of $\mathcal{O}(1)$ that we drop in this limit. We then consider the total particle number in this limit to write:

$$\langle N \rangle = \sum_j \langle n_j \rangle = e^{\beta\mu} \sum_j e^{-\beta\epsilon_j} \implies \frac{\langle n_j \rangle}{\langle N \rangle} = \frac{e^{-\beta\epsilon_j}}{\sum_k e^{-\beta\epsilon_k}}$$

This is simply the result from the classical canonical partition function, which tells us the probability of a particle occupying the j -th energy level! Summarising these results, we easily see that this can be written concisely as:

$$n_j = \frac{1}{e^{\beta(\epsilon_j - \mu)} + \zeta}, \quad \text{with} \quad \begin{cases} \zeta = -1 & \text{for bosons (BE)} \\ \zeta = +1 & \text{for fermions (FD)} \\ \zeta = 0 & \text{for classical limit (MB)} \end{cases} \quad (1.21)$$

These are plotted in Fig. 3. We see that the Bose-Einstein distribution diverges to $+\infty$ as $\mu \rightarrow \epsilon_j$ (only possible for the ground state $j = 0$), while the Maxwell-Boltzmann distribution reaches unity. In contrast, the Fermi-Dirac distribution is always bounded between 0 and 1, and reaches exactly 1/2 when $\mu \rightarrow \epsilon_j$. While the plots in Fig. 3 make it look like the distributions converge for large values of the x -axis (and hence low T), we should bear in mind that μ is also being varied here, and so both dependencies need to be considered when taking the limit (by eye) on the plot.

2 Elementary Bose Gases

In this section, we now want to start studying some simple and familiar examples of Bose gases (gases of bosons). We will still assume that these gases are ideal, in that they are non-interacting.

2.1 The Photon Gas

Photons naturally have negligible interactions amongst themselves⁴, and they are constantly emitted and absorbed by the walls of any cavity confining them. The standard interaction for a photon γ comes in the form of its **vertex interaction** with fermions, such as the electron e^- :



Since this is a perfectly valid chemical reaction, we can apply the condition for chemical equilibrium ($\sum_j \mu_j \nu_j = 0$ where ν_j are the stoichiometric coefficients of the reaction) to obtain:

$$\mu_{e^-} = \mu_{e^-} + \mu_\gamma$$

This tells us that the chemical potential for a photon is identically $\mu = 0$, so it costs no energy to add or remove a photon from the system (in agreement with our intuition). With this in mind, we now wish to write a Hamiltonian for the non-interacting photon gas. Under the assumption that photons do not interact with one another, the Hamiltonian is simply:

$$H = \sum_j \hbar\omega_j n_j$$

where ω_j is the angular frequency of the j -th photon energy level, and n_j is the number of photons in said energy level. Plugging this into the Bose-Einstein distribution from Eq. 1.15 gives us the mean occupancy of the j -th energy level as:

$$\langle n_j \rangle = \frac{1}{e^{\beta\hbar\omega_j} - 1} \quad (2.2)$$

where we set $\mu = 0$. While this is valuable in determining the behaviour of the occupancies as a function of temperature, this is not the full picture. To proceed further, we need to consider the fact that photons not only have an energy given by $\hbar\omega_j$, but also a wavevector \mathbf{k}_j which determines their direction of travel. The two are not independent, but are rather linked by:

$$\omega_j = c|\mathbf{k}_j|$$

⁴While there is a nonzero photon-photon scattering cross section, it is incredibly small and only becomes appreciable for extremely high energy densities (such as those found in the early Universe). We will thus ignore any form of inter-photon interaction in our treatment of the photon gas.

This means that any given ω_j is highly degenerate, corresponding to all wavevectors \mathbf{k} with magnitude ω_j/c pointing in any direction. This degeneracy of the energy levels poses a nasty challenge without further assumptions, so we will have to proceed cautiously in computing this degeneracy. It turns out that borrowing some ideas from the microcanonical ensemble is the ideal method for unpacking this. We start by considering a cavity of volume V in the shape of a cube with side length $L = V^{1/3}$. We also further assume that L is much larger than the typical wavelength of the photons contained within it. Within this cavity, we then have photons propagating as plane waves of the form:

$$\mathbf{E}(\mathbf{r}, t) = \text{Re} \left\{ e^{i(\mathbf{k}_j \cdot \mathbf{r} - \omega_j t)} \hat{\mathbf{n}}_{j,s} \right\}$$

where $\hat{\mathbf{n}}$ is the unit polarisation vector of the plane wave (subject to $\mathbf{k}_j \cdot \hat{\mathbf{n}}_{j,s} = 0$ since electromagnetic waves are transverse), with two possible polarisations available for each \mathbf{k}_j . We thus see that a single photon mode is fully specified by its wavevector \mathbf{k}_j and its polarisation $\hat{\mathbf{n}}_{j,s}$. Demanding that the photons are strictly contained within the cavity (and thus the plane waves should vanish outside it), the wavevectors take on discrete values set by the boundary condition that $L = n\lambda/2$ for integer n along each axis:

$$\mathbf{k}_j = \frac{\pi}{L} \begin{pmatrix} n_{x,j} \\ n_{y,j} \\ n_{z,j} \end{pmatrix}, \quad n_{i,j} \in \mathbb{Z}$$

with the possible values for $(n_{x,j}, n_{y,j}, n_{z,j})$ situated at the discrete points on a cubic lattice (excluding the point $(0, 0, 0)$ since there are no photons of zero energy, though this is a negligible correction to the later computation). In this space of wavevectors, henceforth called k -space (or reciprocal space), we identify with each state a cubic cell of volume $(\pi/L)^3 = \pi^3/V$ surrounding its point in the discrete lattice.

We started this discussion with the problem that each ω_i is degenerate since there are multiple possible wavevectors \mathbf{k}_j that give rise to the same ω_i . Thus, the idea of computing the total energy by summing over the energies indexed by their frequencies ω_i must be carefully treated to include the degeneracy. In statistical mechanics, this is commonly known as computing the **density of states**. Knowing that the photon energies are only dependent on the magnitude of the wavevector according to $\omega = c|\mathbf{k}|$, we can see that the region of k -space associated with all photons lying in some energy (ignoring the factor of \hbar) interval $\omega < c|\mathbf{k}| < \omega + d\omega$ is the first octant of a spherical shell of radius ω/c and thickness $d\omega$. The number of wavevectors contained within this shell is then:

$$2 \times \underbrace{\frac{1}{8} \times 4\pi \left(\frac{\omega}{c}\right)^2 \frac{d\omega}{c}}_{\text{volume of the shell}} \times \underbrace{\frac{1}{\pi^3/V}}_{\text{unit cell volume}}$$

where the first factor of 2 is from the degeneracy in the polarisation. It is perhaps important to clarify why we only consider the first octant here. We constructed our photon gas in a box by imposing closed boundary conditions on all modes, which dictates that the photons must vanish outside the box and thus the value of the photon field on the boundaries of the box must vanish. Consider now the following two photon modes:

$$\mathbf{k}_1 = \frac{\pi}{L} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{k}_2 = \frac{\pi}{L} \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix}$$

whose index vectors are $(1, 0, 0)^\top$ and $(-1, 0, 0)^\top$ respectively. These are valid wavevectors which obey the boundary conditions, but in order for them to do so over a full oscillation in time, they must be standing waves (such that the two endpoints are nodes). Thus, their physical behaviour over a full oscillation turns out

to be exactly the same and we should only include one of these wavevectors when counting over modes. This argument can be applied independently to each of the x , y and z axes, returning a factor of $(1/2)^3 = 1/8$ to account for the overcounting.

Another way to approach the problem is to instead impose periodic boundary conditions rather than closed boundary conditions. Here, we demand that the value and derivative of the photon field at any boundary must be equal to its value under translation by any integer multiple of L in any of the three axes. Under these conditions, we instead find that the allowed wavevectors are given by:

$$\mathbf{k}_j = \frac{2\pi}{L} \begin{pmatrix} n_{x,j} \\ n_{y,j} \\ n_{z,j} \end{pmatrix}, \quad n_{i,j} \in \mathbb{Z}$$

Now, we also find that k -space is divided into cells of volume $(2\pi/L)^3 = 8\pi^3/V$ each, identified with each point in the lattice of allowed wavevectors. With periodic boundary conditions, we observe that wavevectors differing by a sign in any of its components (like the above example) are now completely distinct in their behaviour over a full oscillation cycle, since they correspond to forward and backward moving plane waves along those axes. Thus, we do not need to include any overcounting factor and instead arrive at:

$$2 \times \underbrace{4\pi \left(\frac{\omega}{c}\right)^2 \frac{d\omega}{c}}_{\text{volume of the shell}} \times \underbrace{\frac{1}{8\pi^3/V}}_{\text{unit cell volume}}$$

which is the exact same result as the one we obtained with closed boundary conditions! Thus, it does not matter which set of boundary conditions we choose, as long as we remain consistent in the logic and inclusion of any overcounting factors. Upon simplifying this, we obtain the density of states $g(\omega)$:

$$g(\omega) d\omega = \frac{V}{\pi^2 c^3} \omega^2 d\omega \quad (2.3)$$

which counts the number of unique states in k -space contained within a shell of radius ω/c and of thickness $d\omega$. We further assume that the cavity is sufficiently large so the density of states is effectively a continuous function of ω , since the spacings between the individual states in k -space become small in the limit of large V . This allows us to turn any discrete sum over the density of states into a continuous integral with well-defined support. Finally, we have all the pieces in place and can start computing meaningful observables of the photon gas, such as its internal energy. We combine Eqs. 2.2 and 2.3 to write:

$$\begin{aligned} \langle E \rangle &= \sum_j g(\epsilon_j) \epsilon_j \langle n_j \rangle \\ &= \int_0^\infty d\omega g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \\ &= \frac{V\hbar}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \\ &= \frac{V}{\pi^2 c^3} \frac{1}{\hbar^3 \beta^4} \underbrace{\int_0^\infty dx \frac{x^3}{e^x - 1}}_{=\zeta(3)\Gamma(3)} \end{aligned} \quad (2.4)$$

$$= \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3} V \quad (2.5)$$

In the fourth line, we use a relation more generally known as the **Bose-Einstein integral** which we will explore later. This result is known as the **Stefan-Boltzmann law**, which specifically tells us that the energy

of a photon gas is related to its temperature as T^4 . We can also compute the pressure exerted by this gas on the walls of the cavity using an appropriate derivative (easily checked by finding the equations of state for the grand potential):

$$p = \frac{1}{\beta} \left(\frac{\partial \log \mathcal{Z}}{\partial V} \right)_{\beta} = -\frac{1}{\beta} \frac{\partial}{\partial V} \sum_j \log (1 - e^{-\beta \hbar \omega_j})$$

While it looks like there is no appearance of V on the right, we should note that the confinement of the photons to the cavity forces the modes to be restricted in some way by L , and hence encodes some dependence on V . To enact the partial derivative, we make use of the fact that for a function $f(x) \sim x^\alpha$, the action of the derivative simply brings down a power of α and divides through by x to give $f'(x) \sim \alpha x^{\alpha-1}$. In our expression, it then suffices to determine the power dependence of the right hand side on V . Note that β has no V dependence, since it only depends on T (which is varied independently of V). As for ω_j , we see that $\omega_j = c|\mathbf{k}_j| \sim L^{-1} = V^{-1/3}$. This tells us that:

$$\frac{\partial \omega_j}{\partial V} = -\frac{\omega_j}{3V}$$

which leads to the expression for the pressure as:

$$\begin{aligned} p &= -\frac{1}{\beta} \frac{\partial}{\partial V} \sum_j \log (1 - e^{-\beta \hbar \omega_j}) \\ &= \frac{1}{1 - e^{-\beta \hbar \omega_j}} \frac{1}{\beta} \sum_j \frac{\partial}{\partial V} e^{-\beta \hbar \omega_j} \\ &= \frac{e^{-\beta \hbar \omega_j}}{1 - e^{-\beta \hbar \omega_j}} \sum_j \frac{1}{3V} \hbar \omega_j \\ &= \sum_j \frac{1}{3V} \langle n_j \rangle \hbar \omega_j \\ &= \frac{1}{3} \frac{\langle E \rangle}{V} \end{aligned} \tag{2.6}$$

This is the celebrated result that the pressure of a photon gas is equal to a third of its energy density! Interestingly, one can also obtain this same result from purely classical arguments in electrodynamics. We recall that the Maxwell stress tensor is given by:

$$\sigma_{ij} = \varepsilon_0 \left(E_i E_j - \frac{1}{2} \delta_{ij} E^2 \right) + \frac{1}{\mu_0} \left(B_i B_j - \frac{1}{2} \delta_{ij} B^2 \right)$$

Since a photon gas is considered to be an isotropic and uniform radiation field, the Maxwell stress tensor in the cavity should be diagonal (since the off-diagonal elements represent shear forces which break the spherical symmetry). Furthermore, the diagonal elements are defined to be the pressure exerted by the electromagnetic field on a surface element, so it should be equal to $\sigma_{ij} = p \delta_{ij}$. Taking the trace of both these expressions for the stress tensor, we see that:

$$3p = \frac{1}{2} \left(\varepsilon E^2 + \frac{1}{\mu_0} B^2 \right) = u_{\text{EM}}$$

where u_{EM} is the electromagnetic energy density (energy in the field per unit volume). This returns the same result obtained from statistical mechanics above.

2.2 The Phonon Gas

We now turn our attention to a simplified model of solids, and the vibrations of the atoms contained within them. The atoms making up a bulk solid typically form some sort of lattice structure, with their equilibrium positions regularly spaced. Consider such a lattice of N atoms in 3D, so we have a set of $3N$ displacement coordinates $\{q_i\}$ for the displacement of each atom along each dimension. Expanding around the equilibrium positions (take this to be $\{q_i\} = 0$), we have the potential energy:

$$V(\{q\}) = V_0 + \frac{1}{2} \sum_{i,j=1}^{3N} \left. \frac{\partial^2 V}{\partial q_i \partial q_j} \right|_{\{q\}=0} q_i q_j \quad (2.7)$$

in terms of the elements of the elastic matrix \mathbf{V} (matrix of mixed second partial derivatives of V). We also have the kinetic energy:

$$T(\{\dot{q}\}) = \frac{1}{2} \sum_{i,j=1}^{3N} \dot{q}_i M_{ij} \dot{q}_j \quad (2.8)$$

in terms of the mass matrix \mathbf{M} . Since the elastic matrix and mass matrix are symmetric positive-definite, they can be simultaneously diagonalised to give an eigenbasis spanned by the normal coordinates $\{\eta\}$. In terms of these new coordinates, the energy is then written:

$$E = V_0 + \frac{1}{2} \sum_{j=1}^{3N} \mu_j (\dot{\eta}_j^2 + \omega_j^2 \eta_j^2) \quad (2.9)$$

where μ_j is the effective mass of the j -th normal mode and ω_j is its corresponding angular frequency. It should also be noted that since we began with exactly $3N$ degrees of freedom in the coordinates $\{q\}$, we must still have $3N$ corresponding normal coordinates $\{\eta\}$. This treatment is true for sufficiently small oscillations (small compared to the scale of any anharmonicity in the potential term), and thus we see that the vibrations of the solid are well described by a set of coupled harmonic oscillators. The quantum mechanical treatment is trivial to carry out from here, by performing a canonical quantisation step on this new Hamiltonian (Eq. 2.9) to introduce discrete quanta of energy as **phonons**. The energy of a state with n_j phonons in the j -th mode is then written:

$$E_{\{n\}} = \sum_{j=1}^{3N} \hbar \omega_j n_j \quad (2.10)$$

In a similar argument to the photon gas case, we find that the emission and absorption of phonons through collisions leads to the conclusion that $\mu = 0$ for the phonon gas. Thus, we have the same Hamiltonian as the photon gas and the same imposition of vanishing chemical potential and can apply the same treatment as before, up to the fact that there are a finite number ($3N$) of phonon modes (as opposed to an infinite number of photon modes). We thus write the density of states for phonons as:

$$g(\omega) d\omega = \frac{3}{2} \frac{V}{\pi^2 c^3} \omega^2 d\omega \quad (2.11)$$

where c here is now the speed of sound in the solid medium, and the prefactor of $3/2$ accounts for the fact that we now have two transverse polarisations and one longitudinal polarisation (compared to the two transverse polarisations for photons). Furthermore, this density of states is only true up to some cutoff frequency ω_D , known as the **Debye frequency**. This *hard cutoff* can be argued from the perspective of the smallest possible oscillation wavelength – the shortest possible wavelength that can be realised in a lattice of spacing a is

of the order a , since any shorter wavelengths would be aliased. Thus, we expect there to be a cutoff lower wavelength, corresponding to an upper bound on the frequency of allowed phonon excitations. The Debye frequency is then easily found by normalising the density of states:

$$\int_0^{\omega_D} d\omega g(\omega) = 3N \implies \omega_D = \left(\frac{6N\pi^2 c^3}{V} \right)^{1/3} \quad (2.12)$$

To make things simpler, we include this hard cutoff in the density of states itself using a Heaviside theta function:

$$g(\omega) d\omega = \frac{3}{2} \frac{V}{\pi^2 c^3} \omega^2 \theta(\omega_D - \omega) d\omega$$

This gives us all we need to start computing the observables for a phonon gas, so we begin as usual with the internal energy:

$$\begin{aligned} \langle E \rangle &= \sum_{j=1}^{3N} \langle n_j \rangle \hbar \omega_j \\ &= \int_0^{\omega_D} d\omega g(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \\ &= \frac{9N}{\omega_D^3} \int_0^{\omega_D} d\omega \omega^2 \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \\ &= 9N k_B \frac{T^4}{T_D^3} \int_0^{T_D/T} dx \frac{x^3}{e^x - 1} \end{aligned} \quad (2.13)$$

where in the last line, I have introduced the **Debye temperature** $T_D = \hbar \omega_D / k_B$. This integral is nearly of the form from before where we used the result of the Bose-Einstein integral, but it has a finite upper limit of integration so it needs to be treated carefully. For low temperatures $T \ll T_D$, the upper limit becomes large so we can approximate it by $+\infty$ to obtain:

$$\langle E \rangle \approx \frac{3\pi^4}{5} N k_B \frac{T^4}{T_D^3}, \quad \text{for } T \ll T_D \quad (2.14)$$

For high temperatures $T \gg T_D$, all values of x being integrated over are small so we can expand the integrand as:

$$\frac{x^3}{e^x - 1} \approx \frac{x^3}{x + \frac{1}{2}x + \frac{1}{6}x^3} \approx x^2 - \frac{1}{2}x^3 + \frac{1}{12}x^4$$

This becomes a trivial integral over a polynomial function, so we obtain the high-temperature limit as:

$$\langle E \rangle \approx 3N k_B T \left[1 - \frac{3}{8} \frac{T_D}{T} + \frac{1}{20} \left(\frac{T_D}{T} \right)^2 \right], \quad \text{for } T \gg T_D \quad (2.15)$$

At intermediate temperatures $T \sim T_D$, one will have to numerically evaluate the integral, but this is not of concern to us. We can also use this expression for the internal energy to obtain the constant-volume heat capacity C_V as:

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = \begin{cases} \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D} \right)^3 & \text{for } T \ll T_D \\ 3N k_B \left[1 - \frac{1}{20} \left(\frac{T_D}{T} \right)^2 \right] & \text{for } T \gg T_D \end{cases} \quad (2.16)$$

This implies that for sufficiently high temperatures, the heat capacity saturates at $C_V \approx 3N k_B$, while for low temperatures it behaves as $C_V \sim T^3$. These predictions from the simple Debye model work surprisingly well when fit to experimental measurements of the heat capacity of solids.

3 Bose-Einstein Condensation

Now that we have studied some of the simpler behaviours of Bose gases, we turn to the fundamentally quantum mechanical phenomenon of Bose-Einstein condensation. As we saw earlier, the occupancy of the ground state for a Bose gas diverges in the limit of $\mu \rightarrow \epsilon_0$, producing a macroscopic (order N) contribution to the particle number from a single state, which is not typically expected for a classical ideal gas. To study this phenomenon, we need to deal with this divergence in a mathematically justified manner, which will require us to go back to the log of the partition function.

3.1 Condensation of the Free 3D Bose Gas

To quantify the approach of a Bose gas towards condensation, we define the **fugacity** z of a gas as [2]:

$$z = e^{\beta\mu} \quad (3.1)$$

We now consider the case of a free Bose gas, where the potential energy vanishes and so the single-particle Hamiltonian is simply that of a free particle: $E_j = p^2/2m$. This restricts the fugacity to the range $0 < z < 1$, since the energy is bounded below by 0 while being unbounded above. The singular behaviour of the ground state occupancy thus occurs in the limit of $z \rightarrow 1$. To study the thermodynamics of the free Bose gas, we have to convert the summation over energy eigenstates into a continuous integral over phase space. For this, we write:

$$-\beta\Phi = \log \mathcal{Z} = - \int \frac{d\mathbf{r} d\mathbf{p}}{(2\pi\hbar)^3} \log \left(1 - ze^{-\frac{\beta}{2m}p^2} \right) - \log(1-z) \quad (3.2)$$

where the second term represents the contribution from $\mathbf{p} = 0$, which needs to be dealt with separately. The justification for this can also be seen from the perspective of integrating over phase space using the energy parametrisation. Such an integral would have to be scaled by the density of states for a free 3D gas, which scales as $\rho(\epsilon) \sim \epsilon^{1/2}$, and thus vanishes at the point $\epsilon = 0$. This is incorrect, since we know that there is exactly one state for which $\epsilon = 0$, so it is justified to bring that state out of the integral when studying the singular behaviour at that point.

The spatial integral is now trivially evaluated to produce the volume V of the gas. For the momentum integral, we make the following substitution:

$$\begin{aligned} y &= \frac{\beta}{2m} p^2 \Rightarrow p = |\mathbf{p}| = \sqrt{\frac{2my}{\beta}} \\ \Rightarrow dy &= \frac{\beta}{m} dp p \\ \Rightarrow \frac{d\mathbf{p}}{(2\pi\hbar)^3} &= \frac{4\pi dp p^2}{(2\pi\hbar)^3} = \frac{2}{\Lambda^3} \sqrt{\frac{y}{\pi}} dy \end{aligned} \quad (3.3)$$

where Λ is the thermal de Broglie wavelength from Eq. 1.3. The remainder of the integral is then evaluated as follows:

$$\begin{aligned}
\log \mathcal{Z} &= -\frac{2}{\sqrt{\pi}} \frac{V}{\Lambda^3} \int_0^\infty dy y^{1/2} \log(1 - ze^{-y}) - \log(1 - z) \\
&= \frac{2}{\sqrt{\pi}} \frac{V}{\Lambda^3} \int_0^\infty dy y^{1/2} \sum_{k=1}^\infty \frac{1}{k} (ze^{-y})^k - \log(1 - z) \\
&= \frac{V}{\Lambda^3} \sum_{k=1}^\infty \frac{z^k}{k} \frac{2}{\sqrt{\pi}} \int_0^\infty dy y^{1/2} e^{-ky} - \log(1 - z)
\end{aligned}$$

This is nearly in calculable form, and we simply make the substitution $t = ky$ to convert the integral into the form of the gamma function as:

$$\begin{aligned}
\log \mathcal{Z} &= \frac{V}{\Lambda^3} \sum_{k=1}^\infty \frac{z^k}{k^{5/2}} \frac{2}{\sqrt{\pi}} \int_0^\infty dt t^{1/2} e^{-t} - \log(1 - z) \\
&= \frac{V}{\Lambda^3} \sum_{k=1}^\infty \frac{z^k}{k^{5/2}} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}\right) - \log(1 - z) \\
&= \frac{V}{\Lambda^3} \sum_{k=1}^\infty \frac{z^k}{k^{5/2}} - \log(1 - z) \\
&= \frac{V}{\Lambda^3} \text{Li}_{5/2} - \log(1 - z) \tag{3.4}
\end{aligned}$$

where we have invoked the **polylogarithm** function $\text{Li}_s(z)$. This constitutes a class of infinite power series expansions parametrised by s , generally written as:

$$\text{Li}_s(z) = \sum_{k=1}^\infty \frac{z^k}{k^s} \tag{3.5}$$

The polylogarithms are related by the recurrence relations:

$$\text{Li}_{s-1}(z) = z \frac{\partial}{\partial z} \text{Li}_s(z) \tag{3.6}$$

$$\text{Li}_{s+1}(z) = \int_0^z dz' \frac{\text{Li}_s(z')}{z'} \tag{3.7}$$

They also converge to a finite value for $s > 1$ in the limit $z \rightarrow 1$ since:

$$\text{Li}_s(1) = \sum_{k=1}^\infty \frac{1}{k^s} = \zeta(s) \tag{3.8}$$

The properties of the polylogarithm function then imply that the expression for the grand potential in Eq. 3.4 consists of a convergent term and a logarithmically divergent term. Physically, this manifests most notably in the occupancies of the various microstates of the gas. We obtain the total particle number as:

$$\begin{aligned}
\langle N \rangle &= \left(z \frac{\partial}{\partial z} \log \mathcal{Z} \right)_{\beta, V} \\
&= \underbrace{\frac{V}{\Lambda^3} \text{Li}_{3/2}(z)}_{N_{\text{excited}}} + \underbrace{\frac{z}{1-z}}_{N_{\text{ground}}} \tag{3.9}
\end{aligned}$$

$$\stackrel{z \rightarrow 1}{=} \frac{V}{\Lambda^3} \zeta\left(\frac{3}{2}\right) + \lim_{z \rightarrow 1} \frac{z}{1-z} \tag{3.10}$$

Thus, we see that as a Bose gas approaches the limit of $z \rightarrow 1$, the total number of particles in the excited states converges to a finite number, while the occupancy of the ground state theoretically diverges. This means that the addition of new particles into such a system will force them to occupy the ground state, pushing a significant fraction of the gas *en masse* into the ground state. This is the mathematical argument behind the phenomenon of Bose-Einstein condensation. Clearly, the sudden onset of condensation must occur due to the change in some parameter which pushes the fugacity z toward the value of unity. For a given particle number N and fixed volume V of the gas, the formation of the condensate occurs at a critical temperature $T_c = (k_B \beta_c)^{-1}$ determined by:

$$\begin{aligned} \Lambda^3 \Big|_{T=T_c} &= \left(\hbar \sqrt{\frac{2\pi\beta_c}{m}} \right)^3 = \frac{V}{N} \zeta\left(\frac{3}{2}\right) \\ \implies T_c &= \frac{2\pi\hbar^2}{mk_B} \left[\frac{V}{N} \zeta\left(\frac{3}{2}\right) \right]^{-2/3} \end{aligned} \quad (3.11)$$

We can thus write the occupancy fraction of the ground state, also known as the **condensate fraction**, in terms of the critical temperature as:

$$\frac{N_0}{N} = \begin{cases} 1 - \left(\frac{T}{T_c}\right)^{3/2} & \text{for } T < T_c \\ 0 & \text{for } T > T_c \end{cases} \quad (3.12)$$

Alternatively, we can also force the fugacity to approach the limit of unity by keeping the gas at a fixed temperature while increasing its density. Defining the density $\rho = N/V$ and specific volume $v = V/N = \rho^{-1}$, we can see that condensation occurs at the critical values:

$$\rho_c = \frac{1}{\Lambda^3} \zeta\left(\frac{3}{2}\right) \iff v_c = \frac{\Lambda^3}{\zeta\left(\frac{3}{2}\right)} \quad (3.13)$$

This gives us an expression for the condensate fraction in terms of the specific volume as:

$$\frac{N_0}{N} = \begin{cases} 1 - \frac{v}{v_c} & \text{for } v < v_c \\ 0 & \text{for } v > v_c \end{cases} \quad (3.14)$$

The condensation behaviours as a function of temperature and volume are shown in Fig. 4, with the appearance of the condensate clearly demonstrated below the critical temperature and volume.

3.2 Free Bose Gases in Lower Dimensions

In our previous derivation of the condensation behaviour, we assumed the gas was in 3D, specifically using the 3D Hamiltonian for a free Bose gas. We can now perform the same analysis in 1D and 2D to study the behaviour of such gases as they approach the $z \rightarrow 1$ limit. In 2D, we proceed with a similar expression for the grand potential:

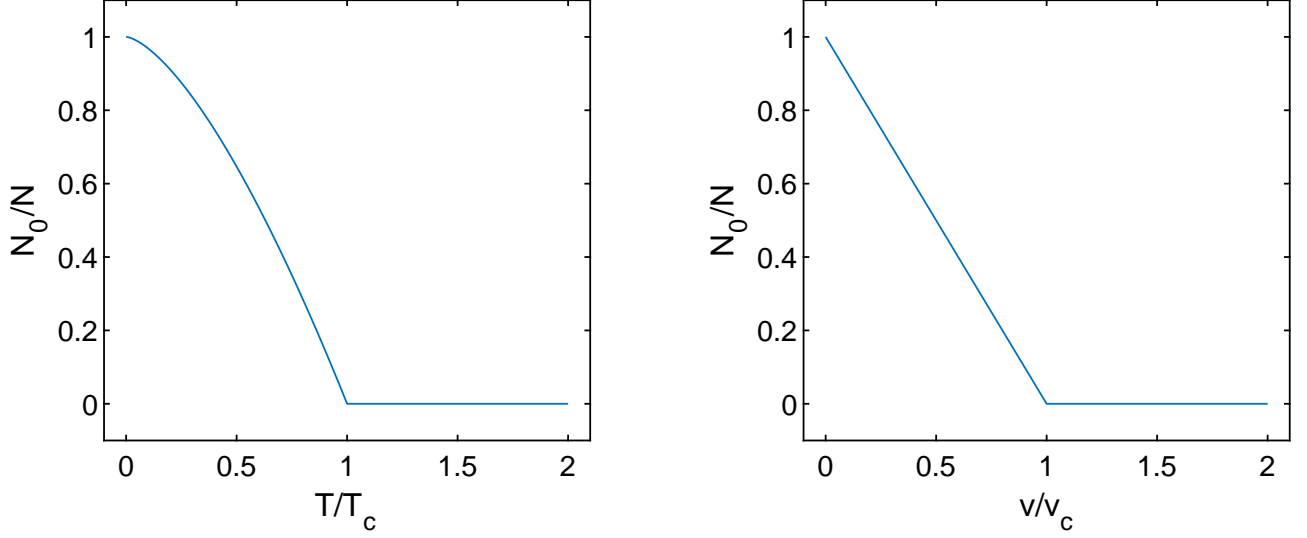


FIGURE 4: Condensate fraction as a function of temperature and specific volume. (Left): As the temperature is decreased below the critical temperature T_c , the ground occupancy takes on a macroscopic value and eventually attains unity at zero temperature. **(Right):** As the specific volume is decreased (at constant temperature), the condensate appears once the critical volume is crossed, and increases linearly to unity in the limit of zero volume.

$$\begin{aligned}
-\beta\Phi &= - \int \frac{d\mathbf{r} d\mathbf{p}}{(2\pi\hbar)^2} \log \left(1 - ze^{-\frac{\beta}{2m}p^2} \right) - \log(1-z) \\
&= - \frac{A}{\Lambda^2} \int_0^\infty dy \log(1 - ze^{-y}) - \log(1-z) \\
&= \frac{A}{\Lambda^2} \sum_{k=1}^\infty z^k e^{-ky} - \log(1-z) \\
&= \frac{A}{\Lambda} \sum_{k=1}^\infty \frac{z^k}{k^2} - \log(1-z) \\
&= \frac{A}{\Lambda^2} \text{Li}_2(z) - \log(1-z)
\end{aligned} \tag{3.15}$$

where we use the fact that $\int d\mathbf{r} = A$ is the area of the two-dimensional Bose gas. We can now evaluate the mean particle number as:

$$\begin{aligned}
\langle N \rangle_{2D} &= \left(z \frac{\partial}{\partial z} \log \mathcal{Z} \right)_{\beta, V} \\
&= \frac{A}{\Lambda^2} \text{Li}_1(z) + \frac{z}{1-z} \\
&\stackrel{z \rightarrow 1}{\equiv} \frac{A}{\Lambda^2} \zeta(1) + \lim_{z \rightarrow 1} \frac{z}{1-z}
\end{aligned} \tag{3.16}$$

Interestingly, the number of excited states does not converge here, since $\zeta(1)$ diverges. This implies that there is no macroscopic occupancy of the ground state, and hence no condensate forms. The same logic can be extended to a Bose gas in one dimension, where we obtain:

$$\langle N \rangle_{1D} \stackrel{z \rightarrow 1}{\equiv} \frac{L}{\Lambda} \zeta\left(\frac{1}{2}\right) + \lim_{z \rightarrow 1} \frac{z}{1-z} \tag{3.17}$$

where L is the length of the one-dimensional Bose gas. Once again, the excited state occupancy does not converge⁵, and so Bose-Einstein condensation does not occur in homogeneous one-dimensional Bose gases. This runs counter to intuition, since we know for a fact that BECs in 1D and 2D have been observed and studied, and in fact pretty much every quantum gas microscope experiment uses BECs in 2D. It turns out that condensation occurs in these lower dimensions when the gas is trapped in a suitable potential, which increases the energy dependency of the density of states to a sufficient extent such that the excited state occupancy converges to a finite value.

4 Degenerate Fermi Gases

We now shift our focus to the other type of fundamental quantum gas – the Fermi gas. In this case, the bounded occupancy of a state due to the Pauli exclusion principle gives rise to vastly different behaviours from the Bose gas. For one, there is no analog of condensation for a non-interacting Fermi gas since we can never have more than one fermion in a given state. We will also see that this gives rise to a type of pressure not observed for bosons.

4.1 Fermi Gases at Zero Temperature

We start by considering a gas of free (no potential energy) fermions at zero temperature ($\beta \rightarrow \infty$). In this limit, we notice that the Fermi-Dirac distribution from Eq. 1.19 trivially becomes:

$$\bar{n}_{\text{FD}}(\epsilon_j) \xrightarrow{T=0} \begin{cases} 1 & \text{for } \epsilon_j < \mu \\ 0 & \text{for } \epsilon_j > \mu \end{cases} \quad (4.1)$$

The chemical potential μ thus sets a hard cutoff at zero temperature for the energy levels which are occupied. If we consider an ordered list of all the energy levels available for the fermions to occupy, the chemical potential is the highest occupied level at zero temperature. This is so special that we have a name for it – the **Fermi energy** E_F (sometimes also called the **Fermi level**). We now want to compute the Fermi energy and explore how it appears in our primary observables of interest.

In a similar fashion to the photon gas, we once again consider the confinement of the Fermi gas to a volume V , and impose closed boundary conditions which demand that the wavefunctions for the fermions vanish outside the volume. This returns us a set of allowed wavevectors \mathbf{k} according to:

$$\mathbf{k}_j = \frac{\pi}{L} \begin{pmatrix} n_{x,j} \\ n_{y,j} \\ n_{z,j} \end{pmatrix}, \quad n_{i,j} \in \mathbb{Z}^+$$

Since we have a quadratic dispersion in energy (instead of the linear dispersion in the photon gas) due to the finite mass of the fermions⁶, we turn to the expression of the energies as: $\epsilon = \hbar^2 |\mathbf{k}|^2 / 2m$. Knowing that all states below E_F are occupied at zero temperature, we first count the number of states in k -space contained within the first octant of a sphere of radius $\sqrt{2m\epsilon}/\hbar$:

⁵While it is true that the Riemann zeta function has a finite value at $1/2$, this is obtained through analytic continuation and is not physically justified in the situation considered here. The physical result must be obtained as the **limit** of the polylogarithm as $z \rightarrow 1$, which is always diverging for $s \leq 1$.

⁶This should be your first hint that the results we obtain here for the massive Fermi gas ($m > 0$) should resemble (up to the difference in occupancy distribution) the results of the photon gas in the ultrarelativistic regime ($p \gg mc$). This is true in the case of neutrinos, where their rest mass is so small that they can be treated as a massless fermion.

$$\Sigma(\epsilon) = 2 \times \underbrace{\frac{1}{8} \times \frac{4}{3} \pi \left(\frac{\sqrt{2m\epsilon}}{\hbar} \right)^3}_{\text{volume of the octant}} \times \underbrace{\frac{1}{\pi^3/V}}_{\text{unit cell volume}} = \frac{2\sqrt{2}}{3} \frac{m^{3/2} \epsilon^{3/2} V}{\pi^2 \hbar^3} \quad (4.2)$$

where the prefactor of 2 arises from the spin degeneracy⁷. Then, when this sphere is of radius equal to the Fermi energy (before converting to k), the total number of states must equal the total number of fermions present in the gas! This allows us to easily solve for E_F :

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \quad (4.3)$$

Interestingly, while the Fermi energy has the dimensions of energy, it is an intensive quantity since any dependence on system size from N is cancelled out by that of V . This tells us that the Fermi energy is a material property of the system, independent of its size rather than a variable that depends on the scale at which the measurement is performed. It should also be noted that while this derivation was done at zero temperature, the Fermi energy of this non-interacting Fermi gas does not change at higher temperatures⁸. We now attempt to compute the internal energy of the Fermi gas, which is easily done with the density of states:

$$g(\epsilon) d\epsilon = \frac{\partial \Sigma(\epsilon)}{\partial \epsilon} d\epsilon = \frac{\sqrt{2}}{\pi^2} \frac{m^{3/2} \epsilon^{1/2}}{V \hbar^3} \quad (4.4)$$

We then evaluate the total energy in the usual fashion:

$$\begin{aligned} \langle E \rangle &= \int_0^\infty d\epsilon g(\epsilon) \bar{n}_{\text{FD}}(\epsilon) \epsilon \\ &= \frac{\sqrt{2}}{\pi^2} \int_0^{E_F} d\epsilon \frac{m^{3/2} \epsilon^{1/2}}{V \hbar^3} \epsilon \\ &= \frac{3\hbar^2}{10m} N \left(\frac{3\pi^2 N}{V} \right)^{2/3} \\ &= \frac{3}{5} N E_F \end{aligned} \quad (4.5)$$

From the total internal energy (in its natural variables), we can compute the pressure of the Fermi gas at zero temperature using the equation of state:

$$\begin{aligned} p &= - \left(\frac{\partial \langle E \rangle}{\partial V} \right)_N \\ &= \frac{\hbar^2}{5m} N \frac{N}{V} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \\ &= \frac{2}{3} \frac{\langle E \rangle}{V} \end{aligned} \quad (4.6)$$

which tells us that the Fermi gas has a pressure of two-thirds its energy density, even at absolute zero temperature. This is rather wild, since we would expect no significant contribution to pressure when all thermal motion is suppressed at low temperatures, but it turns out that this pressure originates not from a thermal sense but from a quantum mechanical one. The Pauli exclusion principle prevents any two fermions of the

⁷Recall that these are fermions with half-integer spin, so there is no analog like in the bosonic case where the spin can be ignored. For higher spin- s fermions, we simply replace the factor of 2 by $2s + 1$.

⁸This is no longer the case in interacting Fermi gases, such as those found in semiconductors. It is the change of the Fermi energy with temperature that gives them their interesting properties of changing conductance as a function of temperature.

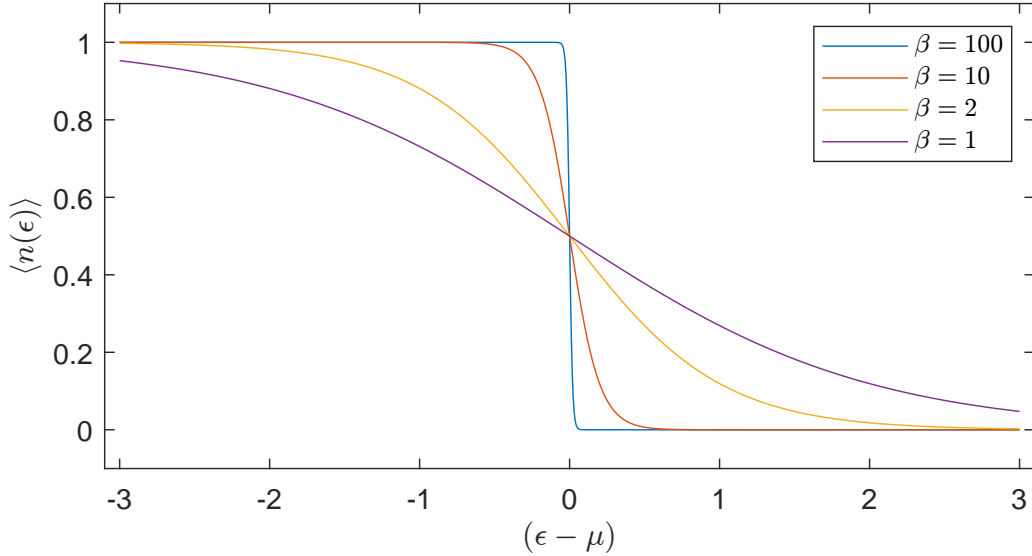


FIGURE 5: Fermi-Dirac distribution as a function of temperature. In the limit of zero temperature, the Fermi-Dirac distribution is a step function which has a hard cutoff at the Fermi energy. As the temperature is increased, this step function *smoothens out* over an energy range of several $k_B T$.

same species from occupying the same state, which precludes the occupation of more than two fermions at a given spatial position (if they have opposite spin). This means that as more particles are introduced into the gas, the volume of the gas must increase in a manner that prevents any overlap between the particles, resulting in what is known as **degeneracy pressure**.

4.2 Fermi Gases at Finite Temperature

All of the analyses carried out in the preceding section were done under the assumption of zero temperature, which is the limit that turns the Fermi-Dirac number distribution into a step function. At finite⁹ nonzero temperatures, this distribution function smooths out in a manner that allows some small occupancy above the Fermi energy E_F , with some reduced occupancy just below E_F . Regardless of the temperature, the function always crosses the point of half-occupancy $\langle n(\epsilon) \rangle = 1/2$ at the Fermi energy. This is plotted for various values of β in Fig. 5.

It is important to note the density of state $g(\epsilon)$ that we derived earlier is valid at all temperatures, since it is simply a statement on the single-particle eigenstates of the system rather than one that depends on the state of the system itself. Despite this, the chemical potential μ at finite temperature is no longer equal to the Fermi energy E_F , and this is easily seen from the density of states itself. Since the Fermi-Dirac distribution is symmetric about the Fermi energy, the probability of a state at some Δ above E_F being occupied is the same as the probability of a state at Δ below E_F being unoccupied. If μ were to remain constant at finite $T > 0$, the density of states being greater at higher ϵ implies that we could increase the number of fermions in the system by simply increasing the temperature, which violates total particle number conservation. Thus, the chemical potential must decrease slightly with T to keep the particle number balanced. In fact, the chemical potential is now set by:

⁹It's strange that the term *finite temperature* in the condensed matter community implies nonzero temperature, even though zero is finite by any measure of cardinality. Then again, I don't make the rules.

$$N = \int_0^\infty d\epsilon g(\epsilon) \bar{n}_{\text{FD}}(\epsilon) = \int_0^\infty d\epsilon g(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \quad (4.7)$$

By solving this integral for μ , we would then be able to compute the total internal energy of the Fermi gas for $T > 0$ using:

$$\langle E \rangle = \int_0^\infty d\epsilon g(\epsilon) \bar{n}_{\text{FD}}(\epsilon) \epsilon = \int_0^\infty d\epsilon g(\epsilon) \frac{\epsilon}{e^{\beta(\epsilon-\mu)} + 1} \quad (4.8)$$

These integrals have no algebraic solution in general, and must be treated using approximations in the regime of interest.

4.2.1 The Sommerfeld Expansion

In order to treat the integrals in Eqs. 4.7 and 4.8 for general $T \ll T_F$ (equivalently, $\beta \gg \beta_F$), we resort to an expansion technique developed by Arnold Sommerfeld. I believe the treatment provided in Schroeder is sufficiently well written to understand how to obtain the corrections to first order. Here, I will instead provide a more general approach from [3] which gives us the full expansion, and connects things back to the polylogarithm. We first note that both integrals are of the general form:

$$I = \int_0^\infty d\epsilon f(\epsilon) \bar{n}_{\text{FD}}(\epsilon) \quad (4.9)$$

where $f(\epsilon)$ contains the density of states $g(\epsilon)$, along with some other smoothly varying function of ϵ . We first use the variable change¹⁰ $(\epsilon - \mu)/k_B T = x$:

$$\begin{aligned} I &= \int_{-\mu/k_B T}^\infty dx k_B T \frac{f(k_B T x + \mu)}{e^x + 1} \\ &= k_B T \int_{-\mu/k_B T}^0 dx \frac{f(k_B T x + \mu)}{e^x + 1} + k_B T \int_0^\infty dx \frac{f(k_B T x + \mu)}{e^x + 1} \\ &= k_B T \int_0^{\mu/k_B T} dx \frac{f(\mu - k_B T x)}{e^{-x} + 1} + k_B T \int_0^\infty dx \frac{f(k_B T x + \mu)}{e^x + 1} \end{aligned}$$

In these steps, I have simply split up the integral over its limits and flipped the first term so the lower limit is always 0 (since we don't have a well-defined density of states for negative energies, by the definition of the ground state being $\epsilon_0 = 0$). We now split the first integral using:

$$\frac{1}{e^{-x} + 1} = \frac{e^x}{e^x + 1} = 1 - \frac{1}{e^x + 1}$$

This gives:

$$\begin{aligned} I &= k_B T \int_0^{\mu/k_B T} dx f(\mu - k_B T x) - k_B T \int_0^{\mu/k_B T} dx \frac{f(\mu - k_B T x)}{e^x + 1} + k_B T \int_0^\infty dx \frac{f(k_B T x + \mu)}{e^x + 1} \\ &= \int_0^\mu d\epsilon f(\epsilon) - k_B T \int_0^{\mu/k_B T} dx \frac{f(\mu - k_B T x)}{e^x + 1} + k_B T \int_0^\infty dx \frac{f(k_B T x + \mu)}{e^x + 1} \end{aligned}$$

where in the second line I have transformed the first integral back to ϵ . All steps so far have been exact, and were merely to massage the integral into a form more suitable for approximation. We now replace the upper

¹⁰While we have been using the inverse temperature β most of the time, it is wiser to use T in this context since it is a small variable that can be used as an expansion parameter, as opposed to β which is large and thus must be treated asymptotically.

limit in the second integral with $+\infty$, which is justified since $\mu/k_B T \approx E_F/k_B T = T_F/T \gg 1$. Furthermore, the denominator rapidly grows for large x so the integrand quickly goes to zero past the upper limit $\mu/k_B T$. This allows us to combine the last two terms:

$$I = \int_0^\mu d\epsilon f(\epsilon) + k_B T \int_0^\infty dx \frac{f(\mu - k_B T x) - f(\mu + k_B T x)}{e^x + 1}$$

We now expand $f(\mu \pm k_B T x)$ in the second term around μ , with the perturbative parameter $k_B T x$:

$$\begin{aligned} I &= \int_0^\mu d\epsilon f(\epsilon) + k_B T \int_0^\infty dx \frac{1}{e^x + 1} \sum_{n=0}^{\infty} \left[\frac{\partial^n f(y)}{\partial y^n} \Big|_{y=\mu} \frac{(k_B T x)^n}{n!} - \frac{\partial^n f(y)}{\partial y^n} \Big|_{y=\mu} \frac{(-k_B T x)^n}{n!} \right] \\ &= \int_0^\mu d\epsilon f(\epsilon) + k_B T \sum_{n=1}^{\infty} \int_0^\infty dx \frac{2}{e^x + 1} \frac{\partial^{2n-1} f(y)}{\partial y^{2n-1}} \Big|_{y=\mu} \frac{x^{2n-1}}{(2n-1)!} \\ &= \int_0^\mu d\epsilon f(\epsilon) + \sum_{n=1}^{\infty} \frac{\partial^{2n-1} f(y)}{\partial y^{2n-1}} \Big|_{y=\mu} \frac{2(k_B T)^{2n}}{(2n-1)!} \underbrace{\int_0^\infty dx \frac{x^{2n-1}}{e^x + 1}}_{I_{2n}} \end{aligned} \quad (4.10)$$

In the first line, we simply perform a Taylor expansion on each of the two terms in the second integral. In this form, it is clear that even powers of the expansion vanish since the two terms are equal in magnitude and opposite in sign, so we regroup this in the second line by re-expressing the sum index to only capture the odd terms from the previous line. In the last line, we pull all terms independent of x out of the integral, leaving us with a dimensionless integral I_{2n} to be evaluated. This integral should look familiar, and in fact it is nothing more than a polylogarithm with a little modification. In a similar manner to Eq. ??, we can write this as:

$$\begin{aligned} I_\alpha &= \int_0^\infty dx \frac{x^{\alpha-1}}{e^x + 1} \\ &= \int_0^\infty dx \frac{x^{\alpha-1}}{e^x} (1 + e^{-x})^{-1} \\ &= \int_0^\infty dx \frac{x^{\alpha-1}}{e^x} \sum_{n=0}^{\infty} (-e^{-nx}) \\ &= \sum_{n=0}^{\infty} \int_0^\infty dx (-1)^n x^{\alpha-1} e^{-(n+1)x} \\ &= \sum_{n=0}^{\infty} (-1)^n \frac{1}{(n+1)^\alpha} \int_0^\infty dy y^{\alpha-1} e^{-y} \\ &= \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\Gamma(\alpha)}{n^\alpha} = \eta(\alpha) \Gamma(\alpha) = (1 - 2^{1-\alpha}) \zeta(\alpha) \Gamma(\alpha) \end{aligned} \quad (4.11)$$

where $\eta(\alpha)$ is the Dirichlet eta function, and the last equality uses the relation between the Dirichlet eta and Riemann zeta functions. Plugging this into the Sommerfeld expansion, we obtain:

$$I = \int_0^\mu d\epsilon f(\epsilon) + \sum_{n=1}^{\infty} \frac{\partial^{2n-1} f(y)}{\partial y^{2n-1}} \Big|_{y=\mu} \frac{2(k_B T)^{2n}}{(2n-1)!} (1 - 2^{1-2n}) \zeta(2n) \Gamma(2n) \quad (4.12)$$

$$= \int_0^\mu d\epsilon f(\epsilon) + \frac{\pi^2}{6} (k_B T)^2 f'(\mu) + \frac{7\pi^4}{360} (k_B T)^4 f'''(\mu) + \dots \quad (4.13)$$

In the second line, I have explicitly evaluated the first two perturbative terms of the expansion using the known values of $\zeta(2n)$, which returns the same result as seen in textbooks to $\mathcal{O}(T^2)$. With the expansion in place, we can now determine the behaviour of μ for finite temperatures by evaluating Eq. 4.7:

$$\begin{aligned}
N &= N \left(\frac{\mu}{E_F} \right)^{3/2} + \frac{\pi^2}{8} \left(\frac{k_B T}{E_F} \right)^2 \left(\frac{\mu}{E_F} \right)^{-1/2} + \mathcal{O}(T^4) \\
\implies \frac{\mu}{E_F} &\approx 1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F} \right)^2 + \mathcal{O}(T^4)
\end{aligned} \tag{4.14}$$

Finally, this provides us with a characterisation of the chemical potential at finite temperatures that we can insert into any other results we obtain from the Sommerfeld expansion. This gives us temperature dependence in our integral quantity I , which is useful for taking derivatives. For instance, explicit evaluation of Eq. 4.8 for the internal energy returns:

$$\begin{aligned}
\langle E \rangle(T, V, N) &= \frac{3}{5} N E_F \left(\frac{\mu}{E_F} \right)^{5/2} + \frac{3\pi^2}{8} N k_B \frac{T^2}{T_F} \left(\frac{\mu}{E_F} \right)^{1/2} + \mathcal{O}(T^4) \\
&\approx \frac{3}{5} N E_F + \frac{\pi^2}{4} N \frac{(k_B T)^2}{E_F} + \mathcal{O}(T^4)
\end{aligned} \tag{4.15}$$

It is trivial to obtain a heat capacity from here:

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = \frac{\pi^2}{2} N k_B \frac{T}{T_F} \tag{4.16}$$

4.3 A More General Framework

In the previous section on Bose-Einstein condensation, we seemed to do everything in terms of polylogarithms which kept things looking a little simpler. We can do the same for the Fermi gas, just with a slight modification that we will see soon. Returning to the grand potential from Eq. 1.18, we turn the sum over states into a continuous integral but with no isolation of the $\mathbf{p} = 0$ term this time since there is no irregularity to deal with:

$$\begin{aligned}
-\beta\Phi &= \beta pV = - \int \frac{d\mathbf{r} d\mathbf{p}}{(2\pi\hbar)^3} \log \left(1 + z e^{-\frac{\beta}{2m} p^2} \right) \\
&= \frac{2}{\sqrt{\pi}} \frac{V}{\Lambda^3} \int_0^\infty dy y^{1/2} \log(1 + z e^{-y}) \\
&= \frac{V}{\Lambda^3} \sum_{k=1}^\infty \frac{(-1)^{k+1} z^k}{k} \frac{2}{\sqrt{\pi}} \int_0^\infty dy y^{1/2} e^{-ky} \\
&= - \frac{V}{\Lambda^3} \sum_{k=1}^\infty \frac{(-z)^k}{k^{5/2}} \\
&= - \frac{V}{\Lambda^3} \text{Li}_{5/2}(-z)
\end{aligned} \tag{4.17}$$

where I have used the same tricks as before in the case of the Bose gas (Eq. 3.4), and we arrive once again at the usual polylogarithm! The only difference now is that its argument is negative, so convergence only occurs in the range $z > -1$ ¹¹. The particle number is similarly obtained using a derivative (Eq. 3.9):

$$\begin{aligned}
\langle N \rangle &= \left(z \frac{\partial}{\partial z} \log \mathcal{Z} \right)_{\beta, V} \\
&= - \frac{V}{\Lambda^3} \text{Li}_{3/2}(-z)
\end{aligned} \tag{4.18}$$

¹¹This will be trivially satisfied for the Fermi gas, since $z = e^{\beta\mu}$ is always positive.

We can use this to write an equation of state for the Fermi gas (in terms of polylogarithms):

$$\beta p = -\frac{1}{\Lambda^3} \text{Li}_{5/2}(-z) \Big|_{z=-\text{Li}_{3/2}^{-1}(-\langle N \rangle \Lambda^3/V)} \implies \frac{pV}{Nk_B T} = \frac{\text{Li}_{5/2}(z)}{\text{Li}_{3/2}(z)} \Big|_{z=-\text{Li}_{3/2}^{-1}(-\langle N \rangle \Lambda^3/V)} \quad (4.19)$$

where $\text{Li}_\alpha^{-1}(x) = y$ is to be read as the solution to $\text{Li}_\alpha(y) = x$. Knowing that the leading term in each polylogarithm is simply z , we see that this returns us the classical ideal gas equation of state in the $z \rightarrow 0$ limit ($\mu \ll -1$).

At this point, I could write more about the approach to degeneracy for a Fermi gas, but I am not familiar enough with the subject matter to do so (my experience is almost exclusively with Bose gases and BECs). These details can be found in references on quantum gases [1], or in more recent literature.

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