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Chapter 5

Noninteracting Quantum Systems

5.1 References

- F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1987)
This has been perhaps the most popular undergraduate text since it first appeared in 1967, and with good reason.
- A. H. Carter, *Classical and Statistical Thermodynamics* (Benjamin Cummings, 2000)
A very relaxed treatment appropriate for undergraduate physics majors.
- D. V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, 2000)
This is the best undergraduate thermodynamics book I've come across, but only 40% of the book treats statistical mechanics.
- C. Kittel, *Elementary Statistical Physics* (Dover, 2004)
Remarkably crisp, though dated, this text is organized as a series of brief discussions of key concepts and examples. Published by Dover, so you can't beat the price.
- R. K. Pathria, *Statistical Mechanics* (2nd edition, Butterworth-Heinemann, 1996)
This popular graduate level text contains many detailed derivations which are helpful for the student.
- M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* (3rd edition, World Scientific, 2006)
An excellent graduate level text. Less insightful than Kardar but still a good modern treatment of the subject. Good discussion of mean field theory.
- E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics* (part I, 3rd edition, Pergamon, 1980)
This is volume 5 in the famous Landau and Lifshitz *Course of Theoretical Physics*. Though dated, it still contains a wealth of information and physical insight.

5.2 Statistical Mechanics of Noninteracting Quantum Systems

5.2.1 Bose and Fermi systems in the grand canonical ensemble

The quantum mechanical Hamiltonian for a many particle but non-interacting system may be written as

$$\hat{H} = \sum_{\alpha} \varepsilon_{\alpha} \hat{n}_{\alpha} \quad , \quad (5.1)$$

where \hat{n}_{α} is the number of particles in the single particle quantum state $|\alpha\rangle$ with energy ε_{α} . This form is called the *second quantized representation* of the Hamiltonian. The number eigenbasis is therefore also an energy eigenbasis. Any eigenstate of \hat{H} may be labeled by the integer eigenvalues of the \hat{n}_{α} number operators, and written as $|n_1, n_2, \dots\rangle$. We then have

$$\hat{n}_{\alpha} |\mathbf{n}\rangle = n_{\alpha} |\mathbf{n}\rangle \quad (5.2)$$

and

$$\hat{H} |\mathbf{n}\rangle = \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha} |\mathbf{n}\rangle \quad . \quad (5.3)$$

The eigenvalues n_{α} take on different possible values depending on whether the constituent particles are *bosons* or *fermions*, viz.

$$\begin{aligned} \text{bosons} : n_{\alpha} &\in \{0, 1, 2, 3, \dots\} \\ \text{fermions} : n_{\alpha} &\in \{0, 1\} \quad . \end{aligned} \quad (5.4)$$

In other words, for bosons, the occupation numbers are nonnegative integers. For fermions, the occupation numbers are either 0 or 1 due to the *Pauli principle*, which says that at most one fermion can occupy any single particle quantum state. There is no Pauli principle for bosons.

The N -particle partition function $Z(T, N)$ is then

$$Z(T, N) = \sum_{\{n_{\alpha}\}} e^{-\beta \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha}} \delta_{N, \sum_{\alpha} n_{\alpha}} \quad , \quad (5.5)$$

where the sum is over all allowed values of the set $\{n_{\alpha}\}$, which depends on the *statistics* of the particles. Bosons satisfy *Bose-Einstein* (BE) statistics, in which $n_{\alpha} \in \{0, 1, 2, \dots\}$. Fermions satisfy *Fermi-Dirac* (FD) statistics, in which $n_{\alpha} \in \{0, 1\}$.

The OCE partition sum is difficult to perform, owing to the constraint $\sum_{\alpha} n_{\alpha} = N$ on the total number of particles. This constraint is relaxed in the GCE, where

$$\begin{aligned} \Xi(T, \mu) &= \sum_N e^{\beta \mu N} Z(T, N) \\ &= \sum_{\{n_{\alpha}\}} e^{-\beta \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha}} e^{\beta \mu \sum_{\alpha} n_{\alpha}} = \prod_{\alpha} \left(\sum_{n_{\alpha}} e^{-\beta(\varepsilon_{\alpha} - \mu) n_{\alpha}} \right) \quad . \end{aligned} \quad (5.6)$$

Note that the grand partition function Ξ takes the form of a product over contributions from the individual single particle states. Recall that the grand potential Ω is given by $\Omega = -k_B T \log \Xi$, i.e. $\Xi = \exp(-\Omega/k_B T)$.

By the way, our notation here is a bit loose and possibly misleading. Formally we should write $Z = Z(T, N, \{X_j\})$ where each X_j is an independent extensive variable changes in which under equilibrium conditions result in thermodynamic work. Similarly, $\Xi = \Xi(T, \mu, \{X_j\})$.

We now perform the single particle sums:

$$\begin{aligned} \sum_{n=0}^{\infty} e^{-\beta(\varepsilon-\mu)n} &= \frac{1}{1 - e^{-\beta(\varepsilon-\mu)}} && \text{(bosons)} \\ \sum_{n=0}^1 e^{-\beta(\varepsilon-\mu)n} &= 1 + e^{-\beta(\varepsilon-\mu)} && \text{(fermions)} \end{aligned} \quad (5.7)$$

Therefore we have¹

$$\begin{aligned} \Xi^{\text{BE}} &= \prod_{\alpha} \frac{1}{1 - e^{-(\varepsilon_{\alpha}-\mu)/k_{\text{B}}T}} \\ \Omega^{\text{BE}} &= -k_{\text{B}}T \log \Xi^{\text{BE}} = k_{\text{B}}T \sum_{\alpha} \log \left(1 - e^{-(\varepsilon_{\alpha}-\mu)/k_{\text{B}}T} \right) \end{aligned} \quad (5.8)$$

for Bose-Einstein statistics and

$$\begin{aligned} \Xi^{\text{FD}} &= \prod_{\alpha} \left(1 + e^{-(\varepsilon_{\alpha}-\mu)/k_{\text{B}}T} \right) \\ \Omega^{\text{FD}} &= -k_{\text{B}}T \log \Xi^{\text{FD}} = -k_{\text{B}}T \sum_{\alpha} \log \left(1 + e^{-(\varepsilon_{\alpha}-\mu)/k_{\text{B}}T} \right) \end{aligned} \quad (5.9)$$

for Fermi-Dirac statistics. We can combine these expressions into one, writing

$$\Omega^{\text{B/F}}(T, V, \mu) = \pm k_{\text{B}}T \sum_{\alpha} \log \left(1 \mp e^{-(\varepsilon_{\alpha}-\mu)/k_{\text{B}}T} \right) \quad , \quad (5.10)$$

where we take the upper sign for Bose-Einstein statistics and the lower sign for Fermi-Dirac statistics. Note that the average occupancy of single particle state α is

$$\langle \hat{n}_{\alpha} \rangle = \frac{\partial \Omega^{\text{B/F}}}{\partial \varepsilon_{\alpha}} = \frac{1}{e^{(\varepsilon_{\alpha}-\mu)/k_{\text{B}}T} \mp 1} \quad , \quad n_{\varepsilon}^{\text{B/F}}(T, \mu) = \frac{1}{e^{(\varepsilon-\mu)/k_{\text{B}}T} \mp 1} \quad . \quad (5.11)$$

Thus $n_{\varepsilon}^{\text{B/F}}(T, \mu)$ is the average occupation of single particle states of energy ε for bosons (B) and fermions (F) at temperature T and chemical potential μ . The total particle number is then

$$N^{\text{B/F}}(T, V, \mu) = \sum_{\alpha} \frac{1}{e^{(\varepsilon_{\alpha}-\mu)/k_{\text{B}}T} \mp 1} \quad . \quad (5.12)$$

We will henceforth write $n_{\alpha}(\mu, T) = \langle \hat{n}_{\alpha} \rangle$ for the thermodynamic average of this occupancy.

¹Note that convergence of the partition sum for bosons requires $\exp((\mu - \varepsilon_{\alpha})/k_{\text{B}}T) < 1$, which is to say that $\mu < \min_{\alpha} \varepsilon_{\alpha}$ for all α .

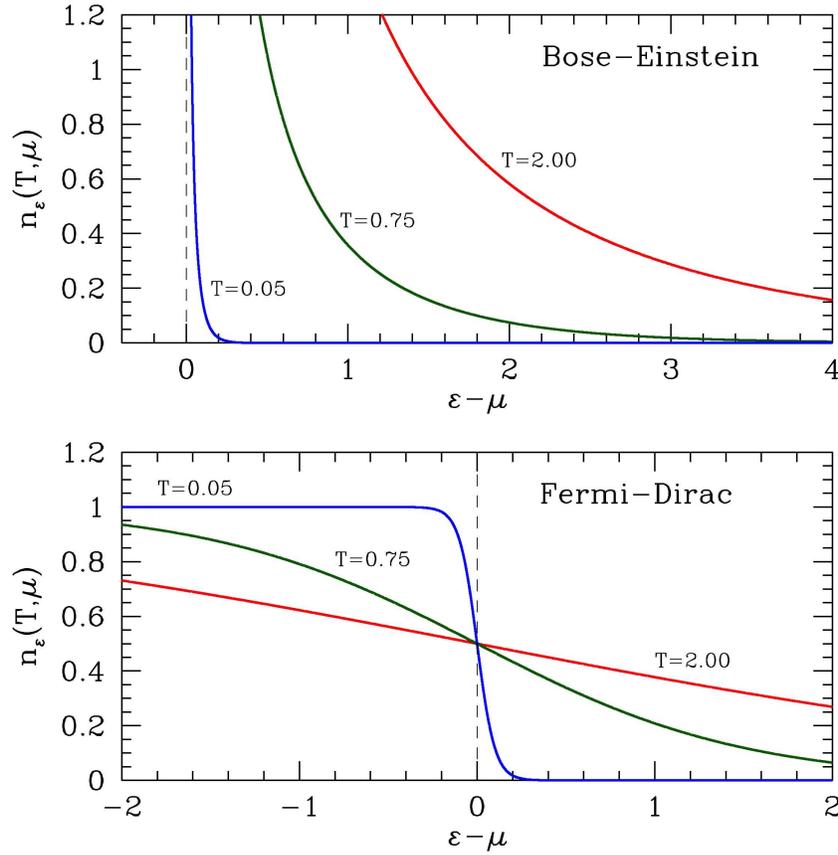


Figure 5.1: Occupation number *versus* $\epsilon - \mu$ for Bose and Fermi distributions.

5.2.2 Quantum statistics and the Maxwell-Boltzmann limit

Consider a system composed of N noninteracting particles. The Hamiltonian is

$$\hat{H} = \sum_{j=1}^N \hat{h}_j \quad . \quad (5.13)$$

The single particle Hamiltonian \hat{h} has eigenstates $|\alpha\rangle$ with corresponding energy eigenvalues ϵ_α . What is the partition function? Is it

$$Z \stackrel{?}{=} \sum_{\alpha_1} \dots \sum_{\alpha_N} e^{-\beta(\epsilon_{\alpha_1} + \epsilon_{\alpha_2} + \dots + \epsilon_{\alpha_N})} = \zeta^N \quad , \quad (5.14)$$

where ζ is the single particle partition function, $\zeta = \sum_{\alpha} e^{-\beta\epsilon_\alpha}$. For systems where the individual particles are *distinguishable*, such as spins on a lattice which have fixed positions, this is indeed correct. But for particles free to move in a gas, this equation is *wrong*. The reason is that for *indistinguishable particles* the many particle quantum mechanical states are specified by a collection of *occupation numbers* n_α , which tell us how many particles are in the single-particle state $|\alpha\rangle$. The energy is $E = \sum_{\alpha} n_\alpha \epsilon_\alpha$ and

the total number of particles is $N = \sum_{\alpha} n_{\alpha}$. That is, each collection of occupation numbers $\{n_{\alpha}\}$ labels a unique many particle state $|\{n_{\alpha}\}\rangle$. In the product ζ^N , the collection $\{n_{\alpha}\}$ occurs many times. We have therefore *overcounted* the contribution to Z_N due to this state. By what factor have we overcounted? It is easy to see that the overcounting factor is

$$\text{degree of overcounting} = \frac{N!}{\prod_{\alpha} n_{\alpha}!} ,$$

which is the number of ways we can rearrange the labels α_j to arrive at the same collection $\{n_{\alpha}\}$. This follows from the multinomial theorem,

$$\left(\sum_{\alpha=1}^K x_{\alpha} \right)^N = \sum_{n_1} \sum_{n_2} \cdots \sum_{n_K} \frac{N!}{n_1! n_2! \cdots n_K!} x_1^{n_1} x_2^{n_2} \cdots x_K^{n_K} \delta_{N, n_1 + \cdots + n_K} . \quad (5.15)$$

Thus, the correct expression for Z_N is

$$\begin{aligned} Z_N &= \sum_{\{n_{\alpha}\}} e^{-\beta \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha}} \delta_{N, \sum_{\alpha} n_{\alpha}} \\ &= \sum_{\alpha_1} \sum_{\alpha_2} \cdots \sum_{\alpha_N} \left(\frac{\prod_{\alpha} n_{\alpha}!}{N!} \right) e^{-\beta(\varepsilon_{\alpha_1} + \varepsilon_{\alpha_2} + \cdots + \varepsilon_{\alpha_N})} . \end{aligned} \quad (5.16)$$

In the high temperature limit, almost all the n_{α} are either 0 or 1, hence $Z_N \approx \zeta^N / N!$. This is the classical *Maxwell-Boltzmann limit* of quantum statistical mechanics. We now see the origin of the $1/N!$ term which is so important in the thermodynamics of entropy of mixing.

Finally, starting with the expressions for the grand partition function for Bose-Einstein or Fermi-Dirac particles, and working in the low density limit where $n_{\alpha}(\mu, T) \ll 1$, we have $\varepsilon_{\alpha} - \mu \gg k_B T$, which is to say $\mu \ll \varepsilon_0 - k_B T$ where ε_0 is the minimum single particle energy. Consequently,

$$\begin{aligned} \Omega^{B/F} &= \pm k_B T \sum_{\alpha} \log \left(1 \mp e^{-(\varepsilon_{\alpha} - \mu)/k_B T} \right) \\ &\approx -k_B T \sum_{\alpha} e^{-(\varepsilon_{\alpha} - \mu)/k_B T} \equiv \Omega^{MB} . \end{aligned} \quad (5.17)$$

This is the Maxwell-Boltzmann limit of quantum statistical mechanics. The occupation number average in the Maxwell-Boltzmann limit is then

$$\langle \hat{n}_{\alpha} \rangle = e^{-(\varepsilon_{\alpha} - \mu)/k_B T} . \quad (5.18)$$

5.2.3 Single particle density of states

The *single particle density of states per unit volume* $g(\varepsilon)$ is defined as

$$g(\varepsilon) = \frac{1}{V} \sum_{\alpha} \delta(\varepsilon - \varepsilon_{\alpha}) . \quad (5.19)$$

The concept of density of states is an important one and the student should develop some facility with it. Note that the dimensions of $g(\varepsilon)$ and $[g(\varepsilon)] = E^{-1}L^{-d}$, where E stands for energy and L for length. We may now write

$$\Omega^{\text{B/F}}(T, V, \mu) = \pm V k_{\text{B}} T \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \log\left(1 \mp e^{-(\varepsilon-\mu)/k_{\text{B}}T}\right) . \quad (5.20)$$

For particles with a dispersion $\varepsilon(\mathbf{k})$, with $\mathbf{p} = \hbar\mathbf{k}$, we have

$$g(\varepsilon) = \mathbf{g} \int \frac{d^d k}{(2\pi)^d} \delta(\varepsilon - \varepsilon(\mathbf{k})) = \frac{\mathbf{g} \Omega_d}{(2\pi)^d} \frac{k^{d-1}}{d\varepsilon/dk} . \quad (5.21)$$

Here, $\mathbf{g} = 2S + 1$ is the spin degeneracy, and $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the surface area of a unit sphere in d dimensions, with $\Gamma(z)$ the gamma function. Furthermore, we assume that $\varepsilon(\mathbf{k})$ is both isotropic and monotonically increasing function in k . Then we have

$$g_{d=1}(\varepsilon) = \frac{\mathbf{g}}{\pi} \frac{dk}{d\varepsilon} , \quad g_{d=2}(\varepsilon) = \frac{\mathbf{g}}{2\pi} k \frac{dk}{d\varepsilon} , \quad g_{d=3}(\varepsilon) = \frac{\mathbf{g}}{2\pi^2} k^2 \frac{dk}{d\varepsilon} . \quad (5.22)$$

In order to obtain $g(\varepsilon)$ as a function of the energy ε one must invert the dispersion relation $\varepsilon = \varepsilon(k)$ to obtain $k = k(\varepsilon)$. A quick way to derive the result in eqn. 5.21 is to write

$$g(\varepsilon) d\varepsilon = \mathbf{g} \frac{d^d k}{(2\pi)^d} = \frac{\mathbf{g} \Omega_d}{(2\pi)^d} k^{d-1} dk . \quad (5.23)$$

For a general isotropic power law dispersion $\varepsilon(\mathbf{k}) = A|\mathbf{k}|^\sigma$, this yields

$$\varepsilon(\mathbf{k}) = A k^\sigma \quad \Rightarrow \quad g(\varepsilon) = \frac{\mathbf{g} \Omega_d}{(2\pi)^{d\sigma}} A^{-d/\sigma} \varepsilon^{\frac{d}{\sigma}-1} \Theta(\varepsilon) . \quad (5.24)$$

For a ballistic dispersion $\varepsilon(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m$, we have²

$$g(\varepsilon) = \frac{\mathbf{g}}{\Gamma(d/2)} \left(\frac{m}{2\pi\hbar^2} \right)^{d/2} \varepsilon^{(d-2)/2} \Theta(\varepsilon) , \quad (5.25)$$

where $\Theta(\varepsilon)$ is the step function, which takes the value 0 for $\varepsilon < 0$ and 1 for $\varepsilon \geq 0$. The appearance of $\Theta(\varepsilon)$ simply says that all the single particle energy eigenvalues are nonnegative.

Note that

$$n_\varepsilon^{\text{B/F}}(T, \mu) = \frac{1}{e^{(\varepsilon-\mu)/k_{\text{B}}T} \mp 1} . \quad (5.26)$$

This result is valid independent of the form of $g(\varepsilon)$. The average total number of particles is then

$$N^{\text{B/F}}(T, V, \mu) = V \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \overbrace{\frac{n_\varepsilon^{\text{B/F}}(T, \mu)}{1}} , \quad (5.27)$$

which does depend on $g(\varepsilon)$.

²Throughout, we assume a box of volume V , but we assume that the separation $\delta\varepsilon$ between successive quantized single particle energy eigenvalues is negligible so that $g(\varepsilon)$ can be replaced by its energy average over a small window $\Delta\varepsilon \gg \delta\varepsilon$.

5.3 Expansion in Powers of the Density

5.3.1 Expansion in powers of the fugacity

From eqn. 5.27, we have that the number density $n = N/V$ is

$$n(T, z) = \int_{-\infty}^{\infty} d\varepsilon \frac{g(\varepsilon)}{z^{-1} e^{\varepsilon/k_B T} \mp 1} = \sum_{j=1}^{\infty} C_j(T) z^j \quad , \quad (5.28)$$

where $z = \exp(\mu/k_B T)$ is the *fugacity* and

$$C_j(T) = (\pm 1)^{j-1} \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) e^{-j\varepsilon/k_B T} \quad . \quad (5.29)$$

Note that $[C_j] = V^{-1}$ for all j . From $\Omega = -pV$ and our expression above for $\Omega(T, V, \mu)$, we have

$$p(T, z) = \mp k_B T \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \log\left(1 \mp z e^{-\varepsilon/k_B T}\right) = \int_{-\infty}^{\infty} d\varepsilon \frac{H(\varepsilon)}{z^{-1} e^{\varepsilon/k_B T} \mp 1} \quad , \quad (5.30)$$

where in the second expression we have integrated by parts, defining

$$H(\varepsilon) = \int_{-\infty}^{\varepsilon} d\varepsilon' g(\varepsilon') \quad , \quad (5.31)$$

which is the integral of the density of states, *i.e.* $g(\varepsilon) = H'(\varepsilon)$. We then obtain

$$p(T, z) = k_B T \sum_{j=1}^{\infty} j^{-1} C_j(T) z^j \quad . \quad (5.32)$$

Eqns. 5.28 and 5.32 express $n(T, z)$ and $p(T, z)$ as power series in the fugacity z , with T -dependent coefficients. In principal, we can eliminate z using eqn. 5.28, writing $z = z(T, n)$ as a power series in the number density n , and substitute this into eqn. 5.32 to obtain an equation of state $p = p(T, n)$ of the form

$$p(T, n) = n k_B T \left(1 + B_2(T) n + B_3(T) n^2 + \dots \right) \quad . \quad (5.33)$$

Note that the low density limit $n \rightarrow 0$ yields the ideal gas law independent of the density of states $g(\varepsilon)$. This follows from expanding $n(T, z)$ and $p(T, z)$ to lowest order in z , yielding $n = C_1 z + \mathcal{O}(z^2)$ and $p = k_B T C_1 z + \mathcal{O}(z^2)$. Dividing the second of these equations by the first yields $p = n k_B T + \mathcal{O}(n^2)$, which is the ideal gas law. Note that $z = n/C_1 + \mathcal{O}(n^2)$ can formally be written as a power series in n .

Unfortunately, there is no general analytic expression for the virial coefficients $B_j(T)$ in terms of the expansion coefficients $n_j(T)$. One can grind through in an order-by-order calculation, with increasing labor at each successive order. Proceeding thusly, the first few virial coefficients are given by

$$B_1 = 1 \quad , \quad B_2 = -\frac{C_2}{2C_1^2} \quad , \quad B_3 = \frac{C_2^2}{C_1^4} - \frac{2C_3}{3C_1^3} \quad . \quad (5.34)$$

It is easy to see that, in general, $B_j^F = (-1)^{j-1} B_j^B$, where the superscripts denote Fermi (F) or Bose (B) statistics.

We remark that the equation of state for classical (and quantum) *interacting* systems also can be expanded in terms of virial coefficients. Consider, for example, the van der Waals equation of state,

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T \quad . \quad (5.35)$$

This may be recast as

$$\begin{aligned} p &= \frac{nk_B T}{1 - bn} - an^2 \\ &= nk_B T + (bk_B T - a)n^2 + k_B T b^2 n^3 + k_B T b^3 n^4 + \dots \quad , \end{aligned} \quad (5.36)$$

where $n = N/V$. Thus, for the van der Waals system, we have $B_2 = b - \frac{a}{k_B T}$ and $B_k = b^{k-1}$ for all $k \geq 3$.

5.3.2 Ballistic dispersion

For the ballistic dispersion $\varepsilon(\mathbf{p}) = \mathbf{p}^2/2m$ we computed the density of states in eqn. 5.25. One finds

$$C_j(T) = (\pm 1)^{j-1} \frac{g \lambda_T^{-d}}{\Gamma(d/2)} \int_0^\infty dt t^{\frac{d}{2}-1} e^{-jt} = (\pm 1)^{j-1} j^{-d/2} g \lambda_T^{-d} \quad , \quad (5.37)$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$ is the thermal wavelength.

We may also write

$$n(T, z) = \pm g \lambda_T^{-d} \text{Li}_{\frac{d}{2}}(\pm z) \quad (5.38)$$

and

$$p(T, z) = \pm g k_B T \lambda_T^{-d} \text{Li}_{\frac{d}{2}+1}(\pm z) \quad , \quad (5.39)$$

where

$$\text{Li}_s(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^s} \quad (5.40)$$

is the *polylogarithm function*. Note that $\text{Li}_s(z)$ obeys a recursion relation in its index, *viz.*

$$z \frac{\partial}{\partial z} \text{Li}_s(z) = \text{Li}_{s-1}(z) \quad , \quad (5.41)$$

and that

$$\zeta(s) = \text{Li}_s(1) = \sum_{n=1}^{\infty} \frac{1}{n^s} \quad (5.42)$$

is the Riemann zeta function.

5.4 Photon Statistics

5.4.1 Thermodynamics of the photon gas

There exists a certain class of particles, including photons and certain elementary excitations in solids such as phonons (*i.e.* lattice vibrations) and magnons (*i.e.* spin waves) which obey bosonic statistics but with zero chemical potential. This is because their overall number is not conserved (under typical conditions) – photons can be emitted and absorbed by the atoms in the wall of a container, phonon and magnon number is also not conserved due to various processes, *etc.* In such cases, the free energy attains its minimum value with respect to particle number when

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = 0 \quad . \quad (5.43)$$

The number distribution, from eqn. 5.11, is then

$$n_\varepsilon(T) = \frac{1}{e^{\varepsilon/k_B T} - 1} \quad . \quad (5.44)$$

The grand partition function for a system of particles with $\mu = 0$ is

$$\Omega(T, V) = V k_B T \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \log(1 - e^{-\varepsilon/k_B T}) \quad , \quad (5.45)$$

where $g(\varepsilon)$ is the density of states per unit volume.

Suppose a particle with $\mu = 0$ exhibits a power law dispersion $\varepsilon(\mathbf{k}) = A |\mathbf{k}|^\sigma$. We can compute the density of states $g(\varepsilon)$, *viz.*

$$g(\varepsilon) = \frac{\mathbf{g} \Omega_d}{(2\pi)^d} \frac{k^{d-1}}{d\varepsilon/dk} = \left(\frac{\mathbf{g} \Omega_d}{(2\pi)^d \sigma A^{d/\sigma}} \right) \varepsilon^{\frac{d}{\sigma}-1} \Theta(\varepsilon) \quad . \quad (5.46)$$

Recall that $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the total solid angle in d dimensions. The step function $\Theta(\varepsilon)$ enforces that the energy spectrum is bounded from below by $\varepsilon = 0$, *i.e.* there are no negative energy states. For a general power law density of states $g(\varepsilon) = C \varepsilon^{r-1} \Theta(\varepsilon)$ and $\mu = 0$, we have

$$n(T) = C \int_0^{\infty} d\varepsilon \frac{\varepsilon^{r-1}}{e^{\varepsilon/k_B T} - 1} = C \zeta(r) \Gamma(r) (k_B T)^r \quad (5.47)$$

and

$$p(T) = -C \int_0^{\infty} d\varepsilon \varepsilon^{r-1} \log(1 - e^{-\varepsilon/k_B T}) = C \zeta(r+1) \Gamma(r) (k_B T)^{r+1} \quad . \quad (5.48)$$

To work out the above integrals, first change variables to $t = \varepsilon/k_B T$, then expand in powers of $\exp(-t)$, integrate over t , and express the sums in terms of Riemann zeta (see eqn. 5.42). Dividing these two equations, we obtain the equation of state

$$p = \frac{\zeta(r+1)}{\zeta(r)} n k_B T \quad . \quad (5.49)$$

To find the entropy, we use Gibbs-Duhem:

$$d\mu = 0 = -s dT + v dp \implies s = v \frac{dp}{dT} \quad , \quad (5.50)$$

where s is the entropy per particle and $v = n^{-1}$ is the volume per particle. In d space dimensions,

$$s(T) = (r+1) \frac{\zeta(r+1)}{\zeta(r)} k_B \quad . \quad (5.51)$$

The entropy per particle is constant. The internal energy is

$$E = -\frac{\partial \log \Xi}{\partial \beta} = -\frac{\partial}{\partial \beta} (\beta p V) = r p V \quad , \quad (5.52)$$

and hence the energy per particle is

$$\varepsilon = \frac{E}{N} = r p v = \frac{r \zeta(r+1)}{\zeta(r)} k_B T \quad . \quad (5.53)$$

For the photon gas, we have $\varepsilon(\mathbf{k}) = \hbar c k$, whence $\sigma = 1$, $r = d$, $A = \hbar c$, and

$$g(\varepsilon) = \left(\frac{2g \pi^{d/2}}{\Gamma(d/2) (\hbar c)^d} \right) \varepsilon^{d-1} \Theta(\varepsilon) \quad . \quad (5.54)$$

In $d = 3$ dimensions the degeneracy is $g = 2$, which is the number of independent polarization states. Thus, for the photon gas in $d = 3$ dimensions, we have $g = 2$ and $C = 1/\pi^2 \hbar^3 c^3$, and

$$n(T) = \frac{2 \zeta(3)}{\pi^2} \frac{(k_B T)^3}{(\hbar c)^3} \quad , \quad p(T) = \frac{2 \zeta(4)}{\pi^2} \frac{(k_B T)^4}{(\hbar c)^3} \quad . \quad (5.55)$$

It turns out that $\zeta(3) = 1.20206$ and $\zeta(4) = \pi^4/90$. We also have $\hbar c/k_B = 0.2290 \text{ cm} \cdot \text{K}$, and thus $k_B T/\hbar c = 4.3755 T[\text{K}] \text{ cm}^{-1}$. We then obtain

$$p = 0.90039 n k_B T \quad , \quad n(T) = 20.286 \times T^3 [\text{K}^3] \text{ cm}^{-3} \quad . \quad (5.56)$$

5.4.2 Classical arguments for the photon gas

A number of thermodynamic properties of the photon gas can be determined from purely classical arguments. Here we recapitulate a few important ones.

1. Suppose our photon gas is confined to a rectangular box of dimensions $L_x \times L_y \times L_z$. Suppose further that the dimensions are all expanded by a factor $\lambda^{1/3}$, *i.e.* the volume is isotropically expanded by a factor of λ . The cavity modes of the electromagnetic radiation have quantized wavevectors, even within classical electromagnetic theory, given by

$$\mathbf{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right) \quad . \quad (5.57)$$

Since the energy for a given mode is $\varepsilon(\mathbf{k}) = \hbar c|\mathbf{k}|$, we see that the energy changes by a factor $\lambda^{-1/3}$ under an adiabatic volume expansion $V \rightarrow \lambda V$, where the distribution of different electromagnetic mode occupancies remains fixed. Thus,

$$V \left(\frac{\partial E}{\partial V} \right)_S = \lambda \left(\frac{\partial E}{\partial \lambda} \right)_S = -\frac{1}{3}E \quad . \quad (5.58)$$

Thus,

$$p = - \left(\frac{\partial E}{\partial V} \right)_S = \frac{E}{3V} \quad , \quad (5.59)$$

as we found in eqn. 5.52. Since $E = E(T, V)$ is extensive, we must have $p = p(T)$ alone.

2. Since $p = p(T)$ alone, we have

$$\begin{aligned} \left(\frac{\partial E}{\partial V} \right)_T &= \left(\frac{\partial E}{\partial V} \right)_p = 3p \\ &= T \left(\frac{\partial p}{\partial T} \right)_V - p \quad , \end{aligned} \quad (5.60)$$

where the second line follows the Maxwell relation $\left(\frac{\partial S}{\partial V} \right)_p = \left(\frac{\partial p}{\partial T} \right)_V$, after invoking the First Law $dE = TdS - pdV$. Thus,

$$T \frac{dp}{dT} = 4p \quad \implies \quad p(T) = AT^4 \quad , \quad (5.61)$$

where A is a constant. Thus, we recover the temperature dependence found microscopically in eqn. 5.48.

3. Given an energy density E/V , the differential energy flux emitted in a direction θ relative to a surface normal is

$$dj_\varepsilon = c \cdot \frac{E}{V} \cdot \cos \theta \cdot \frac{d\Omega}{4\pi} \quad , \quad (5.62)$$

where $d\Omega$ is the differential solid angle. Thus, the power emitted per unit area is

$$\frac{dP}{dA} = \frac{cE}{4\pi V} \int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \sin \theta \cdot \cos \theta = \frac{cE}{4V} = \frac{3}{4} cp(T) \equiv \sigma T^4 \quad , \quad (5.63)$$

where $\sigma = \frac{3}{4}cA$, with $p(T) = AT^4$ as we found above. From quantum statistical mechanical considerations, we have

$$\sigma = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3} = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4} \quad (5.64)$$

is *Stefan's constant*.

5.4.3 Surface temperature of the earth

We derived the result $P = \sigma T^4 \cdot A$ where $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$ for the power emitted by an electromagnetic ‘black body’. Let’s apply this result to the earth-sun system. We’ll need three lengths: the radius of the sun $R_\odot = 6.96 \times 10^8 \text{ m}$, the radius of the earth $R_e = 6.38 \times 10^6 \text{ m}$, and the radius of the earth’s orbit $a_e = 1.50 \times 10^{11} \text{ m}$. Let’s assume that the earth has achieved a steady state temperature of T_e . We balance the total power incident upon the earth with the power radiated by the earth. The power incident upon the earth is

$$P_{\text{incident}} = \frac{\pi R_e^2}{4\pi a_e^2} \cdot \sigma T_\odot^4 \cdot 4\pi R_\odot^2 = \frac{R_e^2 R_\odot^2}{a_e^2} \cdot \pi \sigma T_\odot^4 . \quad (5.65)$$

The power radiated by the earth is

$$P_{\text{radiated}} = \sigma T_e^4 \cdot 4\pi R_e^2 . \quad (5.66)$$

Setting $P_{\text{incident}} = P_{\text{radiated}}$, we obtain

$$T_e = \left(\frac{R_\odot}{2 a_e} \right)^{1/2} T_\odot . \quad (5.67)$$

Thus, we find $T_e = 0.04817 T_\odot$, and with $T_\odot = 5780 \text{ K}$, we obtain $T_e = 278.4 \text{ K}$. The mean surface temperature of the earth is $\bar{T}_e = 287 \text{ K}$, which is only about 10 K higher. The difference is due to the fact that the earth is not a perfect blackbody, *i.e.* an object which absorbs all incident radiation upon it and emits radiation according to Stefan’s law. As you know, the earth’s atmosphere retraps a fraction of the emitted radiation – a phenomenon known as the *greenhouse effect*.

5.4.4 Distribution of blackbody radiation

Recall that the frequency of an electromagnetic wave of wavevector \mathbf{k} is $\nu = c/\lambda = ck/2\pi$. Therefore the number of photons $\mathcal{N}(\nu, T)$ per unit frequency in thermodynamic equilibrium is (recall there are two polarization states)

$$\mathcal{N}(\nu, T) d\nu = \frac{2V}{8\pi^3} \cdot \frac{d^3k}{e^{hck/k_B T} - 1} = \frac{V}{\pi^2} \cdot \frac{k^2 dk}{e^{hck/k_B T} - 1} . \quad (5.68)$$

We therefore have

$$\mathcal{N}(\nu, T) = \frac{8\pi V}{c^3} \cdot \frac{\nu^2}{e^{h\nu/k_B T} - 1} . \quad (5.69)$$

Since a photon of frequency ν carries energy $h\nu$, the energy per unit frequency $\mathcal{E}(\nu)$ is

$$\mathcal{E}(\nu, T) = \frac{8\pi hV}{c^3} \cdot \frac{\nu^3}{e^{h\nu/k_B T} - 1} . \quad (5.70)$$

Note what happens if Planck’s constant h vanishes, as it does in the classical (Maxwell-Boltzmann) limit. The denominator can then be written

$$e^{h\nu/k_B T} - 1 = \frac{h\nu}{k_B T} + \mathcal{O}(h^2) \quad (5.71)$$

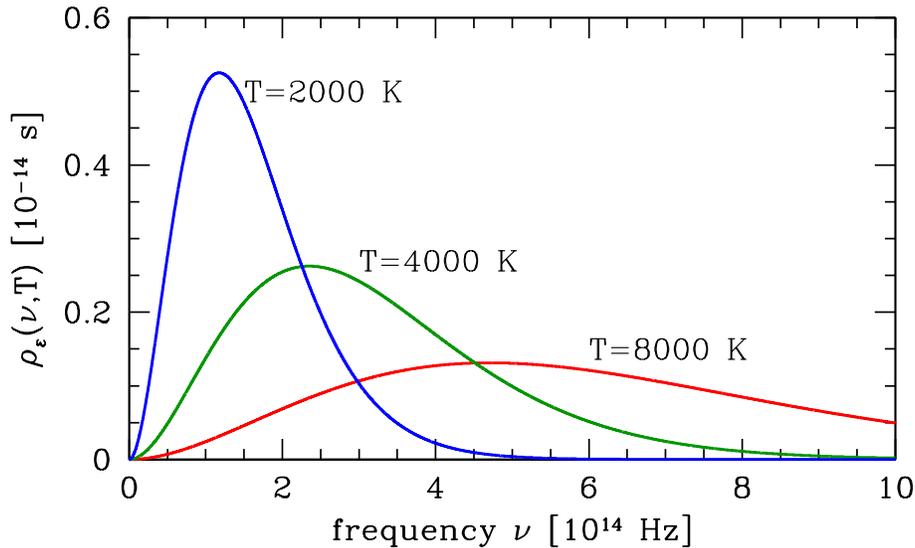


Figure 5.2: Spectral density $\rho_\varepsilon(\nu, T)$ for blackbody radiation at three temperatures.

and

$$\mathcal{E}_{\text{MB}}(\nu, T) = \lim_{h \rightarrow 0} \mathcal{E}(\nu) = V \cdot \frac{8\pi k_B T}{c^3} \nu^2 \quad . \quad (5.72)$$

In classical electromagnetic theory, then, the total energy integrated over all frequencies *diverges*. This is known as the *ultraviolet catastrophe*, since the divergence comes from the large ν part of the integral, which in the optical spectrum is the ultraviolet portion. With quantization, the Bose-Einstein factor imposes an effective ultraviolet cutoff $k_B T/h$ on the frequency integral, and the total energy, as we found above, is finite:

$$E(T) = \int_0^\infty d\nu \mathcal{E}(\nu) = 3pV = V \cdot \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3} \quad . \quad (5.73)$$

We can define the spectral density $\rho_\varepsilon(\nu)$ of the radiation as

$$\rho_\varepsilon(\nu, T) \equiv \frac{\mathcal{E}(\nu, T)}{E(T)} = \frac{15}{\pi^4} \frac{h}{k_B T} \frac{(h\nu/k_B T)^3}{e^{h\nu/k_B T} - 1} \quad (5.74)$$

so that $\rho_\varepsilon(\nu, T) d\nu$ is the fraction of the electromagnetic energy, under equilibrium conditions, between frequencies ν and $\nu + d\nu$, i.e. $\int_0^\infty d\nu \rho_\varepsilon(\nu, T) = 1$. In fig. 5.2 we plot this for three different temperatures. The maximum occurs at a frequency $\nu^* = s k_B T/h$, where

$$\frac{d}{ds} \left(\frac{s^3}{e^s - 1} \right) = 0 \quad \implies \quad \frac{s}{1 - e^{-s}} = 3 \quad \implies \quad s = 2.82144 \quad . \quad (5.75)$$

Thus $\nu^* = 58.8 \text{ GHz} \cdot T[\text{K}]$.

5.4.5 What if the sun emitted ferromagnetic spin waves?

We saw in eqn. 5.62 that the power emitted per unit surface area by a blackbody is σT^4 . The power law here follows from the ultrarelativistic dispersion $\varepsilon = \hbar ck$ of the photons. Suppose that we replace this dispersion with the general form $\varepsilon = \varepsilon(\mathbf{k})$. Now consider a large box in equilibrium at temperature T . The *energy current* incident on a differential area dA of surface normal to \hat{z} is

$$dP = dA \cdot \int \frac{d^3k}{(2\pi)^3} \Theta(\cos\theta) \cdot \varepsilon(\mathbf{k}) \cdot \frac{1}{\hbar} \frac{\partial \varepsilon(\mathbf{k})}{\partial k_z} \cdot \frac{1}{e^{\varepsilon(\mathbf{k})/k_B T} - 1} . \quad (5.76)$$

Let us assume an isotropic power law dispersion of the form $\varepsilon(\mathbf{k}) = Ck^\alpha$. Then after a straightforward calculation we obtain

$$\frac{dP}{dA} = \tilde{\sigma} T^{2+2\alpha-1} , \quad (5.77)$$

where the expression for $\tilde{\sigma}$ is left as an exercise to the reader. One can check that for $g = 2$, $C = \hbar c$, and $\alpha = 1$ that this result reduces to that of eqn. 5.64. For the case of ferromagnetic spin waves, $\alpha = 2$, in which case $P = \tilde{\sigma} T^3 A$. What would be the surface temperature of the earth if the photon dispersion were $\varepsilon = Ck^\alpha$? Generalizing the results from §5.4.3, we find

$$T_e = \left(\frac{R_\odot}{2a_e} \right)^{\alpha/(1+\alpha)} T_\odot . \quad (5.78)$$

With $R_\odot/2a_e = 2.32 \times 10^{-3}$, assuming the same value for $T_\odot = 5780$ K, and with $\alpha = 2$, we obtain $T_e = 101$ K.

5.5 The Ideal Bose Gas

5.5.1 General formulation for noninteracting systems

Recall that the grand partition function for noninteracting bosons is given by

$$\Xi(T, V, \mu) = \prod_\alpha \left(\sum_{n_\alpha=0}^{\infty} e^{\beta(\mu-\varepsilon_\alpha)n_\alpha} \right) = \prod_\alpha \left(1 - e^{\beta(\mu-\varepsilon_\alpha)} \right)^{-1} , \quad (5.79)$$

In order for the sum to converge to the RHS above, we must have $\mu < \varepsilon_\alpha$ for all single-particle states $|\alpha\rangle$. The density of particles is then

$$n(T, \mu) = -\frac{1}{V} \left(\frac{\partial \Omega}{\partial \mu} \right)_{T, V} = \frac{1}{V} \sum_\alpha \frac{1}{e^{\beta(\varepsilon_\alpha - \mu)} - 1} = \int_{\varepsilon_0}^{\infty} d\varepsilon g(\varepsilon) \overbrace{\frac{1}{e^{(\varepsilon - \mu)/k_B T} - 1}}^{n_\varepsilon^B(T, \mu)} , \quad (5.80)$$

where $g(\varepsilon) = V^{-1} \sum_\alpha \delta(\varepsilon - \varepsilon_\alpha)$ is the density of single particle states per unit volume. We must have that $g(\varepsilon) = 0$ for $\varepsilon < \varepsilon_0$ since ε_0 is the ground state energy of the single particle system. Typically we

will have $\varepsilon_0 = 0$, as is the case for any dispersion of the form $\varepsilon(\mathbf{k}) = A|\mathbf{k}|^\theta$, where θ is an exponent ($\theta = 2$ for ballistic particles), for example. However, in the presence of a magnetic field, we could have $\varepsilon(\mathbf{k}, \sigma) = A|\mathbf{k}|^\theta - g\mu_0 H\sigma$, in which case $\varepsilon_0 = -g\mu_0|H|$. The equation $n = n(T, \mu)$ is an equation of state relating the three intensive quantities n , T , and μ .

For fixed T and $\mu < 0$, it is easy to see that $n(T, \mu)$ is a monotonically increasing function of μ ,³ and the maximum possible value for $n(T, \mu)$, called the *critical density* $n_c(T)$, is achieved for $\mu = \varepsilon_0$, *i.e.*

$$n_c(T) = \int_{\varepsilon_0}^{\infty} d\varepsilon \frac{g(\varepsilon)}{e^{(\varepsilon - \varepsilon_0)/k_B T} - 1} . \quad (5.81)$$

If $g(\varepsilon_0) > 0$, then setting $\varepsilon = \varepsilon_0 + \delta\varepsilon$ and analyzing the integrand in the vicinity of $\delta\varepsilon = 0$, we conclude that $n_c(T)$ diverges. In this case, we can always invert eqn. 5.80 to obtain $\mu = \mu(T, n)$. This is the case for power law dispersions $\varepsilon(\mathbf{k}) = Ak^\theta$ with $\theta \geq d$, since, as we've seen, $g(\varepsilon) = C\varepsilon^{r-1}$ with $r = d/\theta$. But if $g(\varepsilon_0) = 0$, assuming $g(\varepsilon)$ is continuous (*e.g.*, whenever $\theta < d$), $n_c(T)$ is finite⁴. In this case, for $n > n_c(T)$, there is no allowed value of the chemical potential for which eqn. 5.80 can be satisfied. What happens then?

When $n_c(T)$ is finite, we can equivalently restate the problem in terms of a *critical temperature* $T_c(n)$, defined by the equation $n_c(T_c) = n$. For $T < T_c$, we apparently can no longer invert to obtain $\mu(T, n)$, so clearly something has gone wrong. The remedy is to recognize that the single particle energy levels are discrete, and separate out the contribution from the lowest energy state ε_0 . The number density of particles in the one-body ground state, *i.e.* the single particle state with energy ε_0 , is

$$n_0 = \frac{1}{V} \frac{g_0}{e^{-\beta\delta\mu} - 1} \quad (5.82)$$

To make up for the missing density, we must have that n_0 is finite. This entails that $\delta\mu$ is infinitesimal in the thermodynamic limit, and solving for $\delta\mu$ we obtain

$$\delta\mu = \mu - \varepsilon_0 = -k_B T \log\left(1 + \frac{g_0}{n_0 V}\right) \approx -\frac{g_0 k_B T}{N_0} , \quad (5.83)$$

where g_0 is the degeneracy of the single particle state with energy ε_0 . Thus, for $T < T_c(n)$, the chemical potential μ lies below ε_0 by an infinitesimal amount. The total density is then a sum of contributions:

$$n = n_0 + n_c(T) . \quad (5.84)$$

What has happened is this: At fixed density n , for $T < T_c(n)$, the number of bosons $N_0 = n_0 V$ in the one-body ground state $|\psi_0\rangle$ with energy ε_0 is *extensive*, and we say that these particles have *condensed*. A macroscopic number of particles occupy a single quantum state, which is allowed according to the rules of Bose-Einstein statistics. The quantity $n_0 = N_0/V$ is the *condensate number density*. The remaining particles, with number density $n_c(T)$, are said to comprise the *overcondensate*. The relation $n = n_0 + n_c(T)$ may be regarded as an equation of state relating the three intensive quantities T , n , and n_0 .

³At fixed $\mu < 0$, $n(T, \mu)$ is a monotonically increasing function of T .

⁴Well, that isn't quite true. For example, if $g(\varepsilon) \sim 1/\log(1/\varepsilon)$ as $\varepsilon \rightarrow 0^+$, then $\lim_{\varepsilon \rightarrow 0^+} g(\varepsilon) = 0$ yet the integral has a very weak $\log \log(1/\eta)$ divergence, where η is the lower cutoff. But for any power law density of states where $g(\varepsilon) \propto \varepsilon^{r-1}$ with $r > 1$ as $\varepsilon \rightarrow 0^+$, the integral converges.

To reiterate, in the thermodynamic limit, when $T < T_c(n)$ we have $\mu = \varepsilon_0$ and $n_0 \in [0, n]$, with

$$n(T, n_0) = n_0 + \overbrace{\int_{\varepsilon_0}^{\infty} d\varepsilon \frac{g(\varepsilon)}{e^{(\varepsilon-\varepsilon_0)/k_B T} - 1}}^{n_c(T)} \quad , \quad (5.85)$$

an equation of state relating T , n , and n_0 . For $T > T_c(n)$, we have $\mu < \varepsilon_0$ and $n_0 = 0$, with

$$n(T, \mu) = \int_{\varepsilon_0}^{\infty} d\varepsilon \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/k_B T} - 1} \quad , \quad (5.86)$$

an equation of state relating T , n , and μ . The critical temperature $T_c(n)$ is determined by simultaneously setting $T = T_c$ and $n_0 = 0$ in eqn. 5.85, or, equivalently, by setting $T = T_c$ and $\mu = \varepsilon_0$ in eqn. 5.86, yielding the condition $n = n_c(T_c)$. In the condensed phase, the *condensate fraction* is defined to be

$$f_0(T, n) \equiv \frac{n_0(T, n)}{n} = 1 - \frac{n_c(T)}{n} \quad . \quad (5.87)$$

Note that $f_0(T, n)$ at fixed n is a monotonically decreasing function of T with $f_0(T = 0, n) = 1$ and $f_0(T = T_c(n), n) = 0$.

Incidentally, why are we allowed to ignore $\delta\mu$ in the expression for $n_c(T)$ in eqn. 5.84? Suppose our particles have a dispersion $\varepsilon(\mathbf{k}) \propto k^\theta$ as $k \rightarrow 0$, i.e. at low energies. With box quantization, the first excited state energy will be $\varepsilon_1 \sim L^{-\theta}$ since its wavevector is $k_1 \sim L^{-1}$. Since $\delta\mu \sim V^{-1} \sim L^{-d}$, we see that $\delta\mu$ is negligible compared with ε_1 provided $\theta < d$, which, as we have seen, is precisely the condition for the existence of a condensate.

5.5.2 Ballistic dispersion

We already derived, in §5.3.2, expressions for $n(T, z)$ and $p(T, z)$ for the ideal Bose gas (IBG) with ballistic dispersion $\varepsilon(\mathbf{p}) = \mathbf{p}^2/2m$. We found

$$\begin{aligned} n(T, z) &= g \lambda_T^{-d} \text{Li}_{\frac{d}{2}}(z) \\ p(T, z) &= g k_B T \lambda_T^{-d} \text{Li}_{\frac{d}{2}+1}(z), \end{aligned} \quad (5.88)$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$ is the thermal wavelength, and where g is the internal (e.g. spin) degeneracy of each single particle energy level. Here $z = \exp(\mu/k_B T)$ is the fugacity and $\text{Li}_s(z) = \sum_{m=1}^{\infty} z^m/m^s$ is the polylogarithm function. For bosons with a spectrum bounded below by $\varepsilon_0 = 0$, the fugacity takes values on the interval $z \in [0, 1]$ ⁵. Note that $\text{Li}_s(z = 1) = \zeta(s)$, which is Riemann's zeta function; $\zeta(s)$ is finite for $s > 1$.

⁵It is easy to see that the chemical potential for noninteracting bosons can never exceed the minimum value ε_0 of the single particle dispersion.

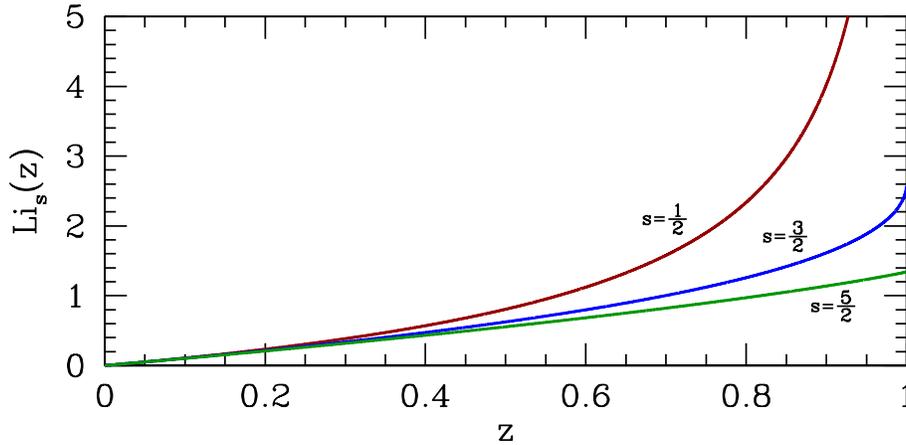


Figure 5.3: The polylogarithm function $\text{Li}_s(z)$ versus z for $s = \frac{1}{2}$, $s = \frac{3}{2}$, and $s = \frac{5}{2}$. Note that $\text{Li}_s(1) = \zeta(s)$ diverges for $s \leq 1$.

Clearly $n(T, z) = g \lambda_T^{-d} \text{Li}_{d/2}(z)$ is an increasing function of z for fixed T . In fig. 5.3 we plot the function $\text{Li}_s(z)$ versus z for three different values of s . We note that the maximum value $\text{Li}_s(z = 1)$ is finite if $s > 1$. Thus, for $d > 2$, there is a maximum density $n_{\text{max}}(T) = g \zeta(d/2) \lambda_T^{-d}$ which is an increasing function of temperature T . Put another way, if we fix the density n , then there is a critical temperature T_c below which there is no solution to the equation $n = n(T, z)$. The critical temperature $T_c(n)$ is then determined by the relation

$$n = g \zeta\left(\frac{d}{2}\right) \lambda_{T_c}^{-d/2} = g \zeta\left(\frac{d}{2}\right) \left(\frac{m k_B T_c}{2\pi \hbar^2}\right)^{d/2} \implies k_B T_c = \frac{2\pi \hbar^2}{m} \left(\frac{n}{g \zeta\left(\frac{d}{2}\right)}\right)^{2/d}. \quad (5.89)$$

What happens for $T < T_c$?

As shown above in §5.5.1, we must separate out the contribution from the lowest energy single particle mode, which for ballistic dispersion lies at $\varepsilon_0 = 0$. Thus writing

$$n = \frac{1}{V} \frac{1}{z^{-1} - 1} + \frac{1}{V} \sum_{(\varepsilon_\alpha > 0)} \frac{1}{z^{-1} e^{\varepsilon_\alpha/k_B T} - 1}, \quad (5.90)$$

where we have taken $g = 1$. Now V^{-1} is of course very small, since V is thermodynamically large, but if $\mu \rightarrow 0$ then $z^{-1} - 1$ is also very small and their ratio can be finite, as we have seen. Indeed, if the density of $\mathbf{k} = 0$ bosons n_0 is finite, then their total number N_0 satisfies

$$N_0 = V n_0 = \frac{1}{z^{-1} - 1} \implies z = \frac{1}{1 + N_0^{-1}}. \quad (5.91)$$

The chemical potential is given by

$$\mu = k_B T \log z = -k_B T \log(1 + N_0^{-1}) \approx -\frac{k_B T}{N_0} \rightarrow 0^- \quad (5.92)$$

In other words, the chemical potential is infinitesimally negative, because N_0 is assumed to be thermodynamically large. According to eqn. 5.10, the contribution to the pressure from the $\mathbf{k} = 0$ states

is

$$p_0 = -\frac{k_B T}{V} \log(1 - z) = \frac{k_B T}{V} \log(1 + N_0) \rightarrow 0^+ . \quad (5.93)$$

So the $\mathbf{k} = 0$ bosons, which we identify as the *condensate*, contribute nothing to the pressure.

Having separated out the $\mathbf{k} = 0$ mode, we can now replace the remaining sum over α by the usual integral over \mathbf{k} . We then have

$$T < T_c \quad : \quad n = n_0 + \mathbf{g} \zeta\left(\frac{d}{2}\right) \lambda_T^{-d} \quad , \quad p = \mathbf{g} \zeta\left(\frac{d}{2} + 1\right) k_B T \lambda_T^{-d} \quad (5.94)$$

and

$$T > T_c \quad : \quad n = \mathbf{g} \text{Li}_{\frac{d}{2}}(z) \lambda_T^{-d} \quad , \quad p = \mathbf{g} \text{Li}_{\frac{d}{2} + 1}(z) k_B T \lambda_T^{-d} . \quad (5.95)$$

The *condensate fraction* n_0/n is unity at $T = 0$, when all particles are in the condensate with $\mathbf{k} = 0$, and decreases with increasing T until $T = T_c$, at which point it vanishes. Explicitly, we have

$$\frac{n_0(T, n)}{n} = 1 - \frac{\mathbf{g} \zeta\left(\frac{d}{2}\right)}{n \lambda_T^d} = 1 - \left(\frac{T}{T_c(n)}\right)^{d/2} . \quad (5.96)$$

5.5.3 Energy, entropy and heat capacity

Energy

Let us compute the internal energy E for the ideal Bose gas. We have

$$\frac{\partial}{\partial \beta} (\beta \Omega) = \Omega + \beta \frac{\partial \Omega}{\partial \beta} = \Omega - T \frac{\partial \Omega}{\partial T} = \Omega + TS \quad (5.97)$$

and therefore

$$\begin{aligned} E = \Omega + TS + \mu N &= \mu N + \frac{\partial}{\partial \beta} (\beta \Omega) \\ &= V \left(\mu n - \frac{\partial}{\partial \beta} (\beta p) \right) = \frac{1}{2} d \mathbf{g} V k_B T \lambda_T^{-d} \text{Li}_{\frac{d}{2} + 1}(z) . \end{aligned} \quad (5.98)$$

This expression is valid at all temperatures, both above and below T_c . Note that the condensate particles do not contribute to E , because the $\mathbf{k} = 0$ condensate particles carry no energy.

Entropy

Working along similar lines, it is left as an exercise to the reader to obtain the following formulae for the entropy per particle of the ideal Bose gas in d dimensions:

$$\begin{aligned} \frac{S(T < T_c, V, N)}{N k_B} &= \left(\frac{d}{2} + 1\right) \zeta\left(\frac{d}{2} + 1\right) \cdot \frac{\mathbf{g}}{n \lambda_T^d} \\ \frac{S(T > T_c, V, N)}{N k_B} &= \left(\frac{d}{2} + 1\right) \frac{\text{Li}_{\frac{d}{2} + 1}(z)}{\text{Li}_{\frac{d}{2}}(z)} - \log z \quad , \end{aligned} \quad (5.99)$$

with $n = N/V$. In the second equation above, one must invert $n\lambda_T^d = g \text{Li}_{\frac{d}{2}}(z)$ to obtain $z(T, n)$. Note that the above equations agree at $T = T_c$, where $z = 1$.

Let us contrast these results with those for the classical nonrelativistic ideal gas, for which

$$Z_{\text{ClG}}(T, V, N) = \frac{1}{N!} \left(\frac{gV}{\lambda_T^d} \right)^N \quad \Rightarrow \quad \frac{S_{\text{ClG}}(T, V, N)}{Nk_B} = \log(n\lambda_T^d/g) + \frac{d}{2} + 1 \quad . \quad (5.100)$$

For the ideal Bose gas in the Maxwell-Boltzmann limit, where $z \rightarrow 0$ and $\text{Li}_s(z) = z + 2^{-s}z^2 + \dots$, we have $z = n\lambda_T^d/g$, and the classical and quantum entropies agree to lowest nontrivial order in the dimensionless quantity $n\lambda_T^3$. But as $T \rightarrow 0^+$, the classical entropy per particle $s(T, n)$ diverges logarithmically toward negative infinity. On the other hand, in the low temperature (condensed) phase of the ideal Bose gas, we have $z = 1$ and $s(T, n) \propto n^{-1}T^{d/2}$, which vanishes as $T \rightarrow 0$.

Heat capacity

We now investigate the heat capacity $C_{V,N} = \left(\frac{\partial E}{\partial T} \right)_{V,N}$. Since we have been working in the GCE, it is very important to note that N is held constant when computing $C_{V,N}$. We'll also restrict our attention to the case $d = 3$ since the ideal Bose gas does not condense at finite T for $d \leq 2$ and $d > 3$ is unphysical. While we're at it, we'll also set $g = 1$.

The number of particles is

$$N = \begin{cases} N_0 + \zeta(3/2) V \lambda_T^{-3} & (T < T_c) \\ V \lambda_T^{-3} \text{Li}_{3/2}(z) & (T > T_c) \end{cases} \quad , \quad (5.101)$$

and the energy is

$$E = \frac{3}{2} k_B T \frac{V}{\lambda_T^3} \text{Li}_{5/2}(z) = \frac{3}{2} pV \quad . \quad (5.102)$$

For $T < T_c$, we have $z = 1$ and

$$C_{V,N} = \left(\frac{\partial E}{\partial T} \right)_{V,N} = \frac{15}{4} \zeta(5/2) \frac{V}{\lambda_T^3} k_B \quad . \quad (5.103)$$

The molar heat capacity is therefore

$$c_{V,N}(T, n) = N_A \cdot \frac{C_{V,N}}{N} = \frac{15}{4} \zeta(5/2) (n \lambda_T^3)^{-1} R \quad . \quad (5.104)$$

For $T > T_c$, we have

$$dE|_V = \frac{15}{4} k_B T \text{Li}_{5/2}(z) \frac{V}{\lambda_T^3} \cdot \frac{dT}{T} + \frac{3}{2} k_B T \text{Li}_{3/2}(z) \frac{V}{\lambda_T^3} \cdot \frac{dz}{z} \quad , \quad (5.105)$$

where we have invoked eqn. 5.41. Taking the differential of N , we have

$$dN|_V = \frac{3}{2} \text{Li}_{3/2}(z) \frac{V}{\lambda_T^3} \cdot \frac{dT}{T} + \text{Li}_{1/2}(z) \frac{V}{\lambda_T^3} \cdot \frac{dz}{z} \quad . \quad (5.106)$$

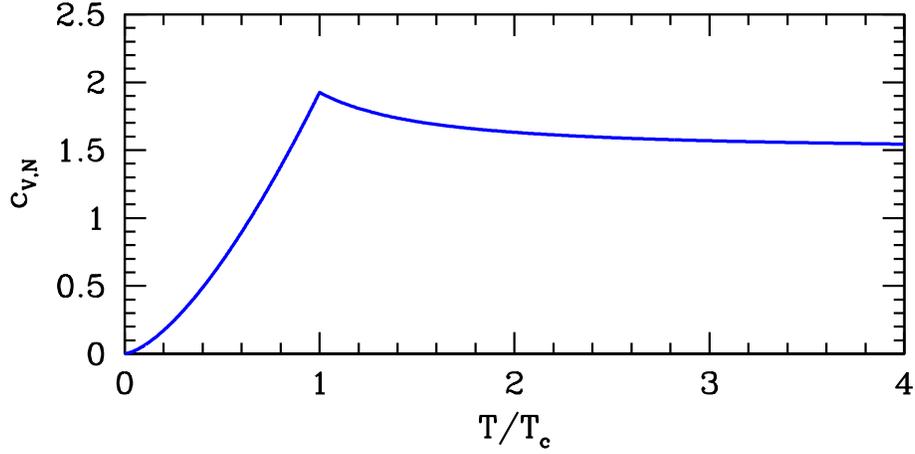


Figure 5.4: Molar heat capacity of the ideal Bose gas (units of R). Note the cusp at $T = T_c$.

We set $dN = 0$, which fixes dz in terms of dT , resulting in

$$c_{V,N}(T, z) = \frac{3}{2}R \cdot \left[\frac{\frac{5}{2} \text{Li}_{5/2}(z)}{\text{Li}_{3/2}(z)} - \frac{\frac{3}{2} \text{Li}_{3/2}(z)}{\text{Li}_{1/2}(z)} \right] . \quad (5.107)$$

To obtain $c_{V,N}(T, n)$, we must then invert the relation

$$n(T, z) = \lambda_T^{-3} \text{Li}_{3/2}(z) \quad (5.108)$$

in order to obtain $z(T, n)$, and then insert this into eqn. 5.107. The results are shown in fig. 5.4. There are several noteworthy features of this plot. First of all, by dimensional analysis the function $c_{V,N}(T, n)$ is R times a function of the dimensionless ratio $T/T_c(n) \propto T n^{-2/3}$. Second, the high temperature limit is $\frac{3}{2}R$, which is the classical value. Finally, there is a *cusp* at $T = T_c(n)$. At the cusp, we have

$$R^{-1} c_{V,N}(T_c(n), n) = \frac{15 \zeta(5/2)}{4 \zeta(3/2)} = 1.92567 \dots \quad (5.109)$$

5.5.4 Isotherms for the ideal Bose gas

Let a be some length scale and define

$$v_a = a^3 \quad , \quad p_a = \frac{2\pi\hbar^2}{ma^5} \quad , \quad T_a = \frac{2\pi\hbar^2}{ma^2k_B} \quad (5.110)$$

Then we have

$$\frac{v_a}{v} = \left(\frac{T}{T_a} \right)^{3/2} \text{Li}_{3/2}(z) + v_a n_0 \quad , \quad \frac{p}{p_a} = \left(\frac{T}{T_a} \right)^{5/2} \text{Li}_{5/2}(z) \quad , \quad (5.111)$$

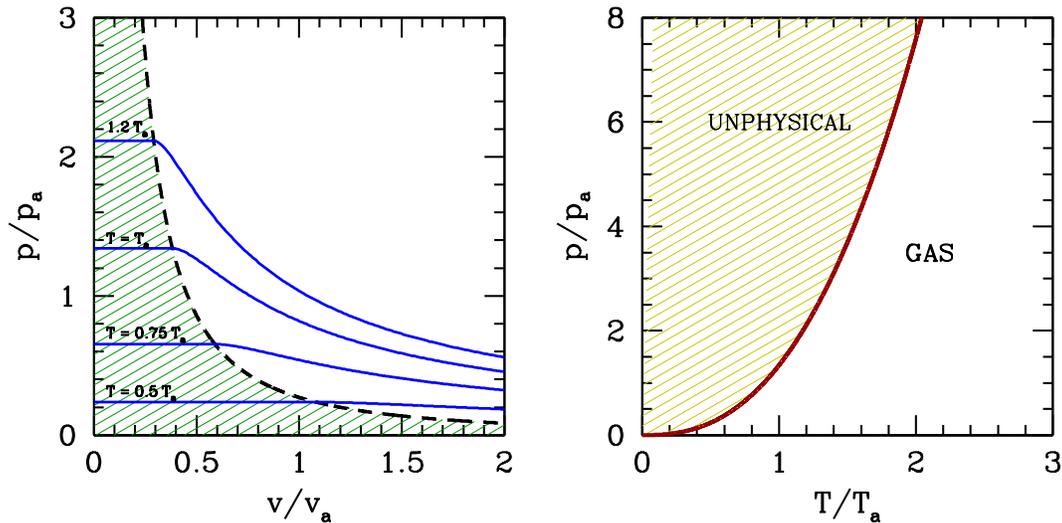


Figure 5.5: Phase diagrams for the ideal Bose gas. Left panel: (p, v) plane. The solid blue curves are isotherms, and the green hatched region denotes $v < v_c(T)$, where the system is partially condensed. Right panel: (p, T) plane. The solid red curve is the coexistence curve $p_c(T)$, along which Bose condensation occurs. No distinct thermodynamic phase exists in the yellow hatched region above $p = p_c(T)$.

where $v = V/N$ is the volume per particle⁶ and n_0 is the condensate number density; n_0 vanishes for $T \geq T_c$, where $z = 1$. One identifies a critical volume $v_c(T)$ by setting $z = 1$ and $n_0 = 0$, leading to $v_c(T) = v_a (T/T_a)^{3/2}$. For $v < v_c(T)$, we set $z = 1$ in eqn. 5.111 to find a relation between v , T , and n_0 . For $v > v_c(T)$, we set $n_0 = 0$ in eqn. 5.111 to relate v , T , and z . Note that the pressure is independent of volume for $T < T_c$. The isotherms in the (p, v) plane are then flat for $v < v_c$. This resembles the coexistence region familiar from our study of the thermodynamics of the liquid-gas transition. The situation is depicted in fig. 5.5. In the (T, p) plane, we identify $p_c(T) = p_a (T/T_a)^{5/2}$ as the critical temperature at which condensation starts to occur.

Recall the Gibbs-Duhem equation, $d\mu = -s dT + v dp$. Along a coexistence curve, we have the Clausius-Clapeyron relation,

$$\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T \Delta v} \quad , \quad (5.112)$$

where $\ell = T(s_2 - s_1)$ is the latent heat per mole, and $\Delta v = v_2 - v_1$. For ideal gas Bose condensation, the coexistence curve resembles the red curve in the right hand panel of fig. 5.5. There is no meaning to the shaded region where $p > p_c(T)$. Nevertheless, it is tempting to associate the curve $p = p_c(T)$ with the coexistence of the $\mathbf{k} = 0$ condensate and the remaining uncondensed ($\mathbf{k} \neq 0$) bosons.

The entropy in the coexistence region is given by

$$s = -\frac{1}{N} \left(\frac{\partial \Omega}{\partial T}\right)_V = \frac{5}{2} \zeta(5/2) k_B v \lambda_T^{-3} = \frac{5}{2} \frac{\zeta(5/2)}{\zeta(3/2)} k_B \left(1 - \frac{n_0}{n}\right) \quad . \quad (5.113)$$

All the entropy is thus carried by the uncondensed bosons, and the condensate carries zero entropy. The Clausius-Clapeyron relation can then be interpreted as describing a phase equilibrium between the

⁶Note that in the thermodynamics chapter we used v to denote the molar volume, $N_A V/N$.

condensate, for which $s_0 = v_0 = 0$, and the uncondensed bosons, for which $s' = s(T)$ and $v' = v_c(T)$. So this identification forces us to conclude that the specific volume of the condensate is zero. This is certainly false in an interacting Bose gas!

While one can identify, by analogy, a ‘latent heat’ $\ell = T \Delta s = T s$ in the Clapeyron equation, it is important to understand that there is no distinct thermodynamic phase associated with the region in which $p > p_c(T)$. Ideal Bose gas condensation is a second order transition, and not a first order transition.

5.5.5 Properties of liquid ^4He

The λ -transition

Helium has two stable isotopes. ^4He is a boson, consisting of two protons, two neutrons, and two electrons (hence an even number of fermions). ^3He is a fermion, with one less neutron than ^4He . Each ^4He atom can be regarded as a tiny hard sphere of mass $m = 6.65 \times 10^{-24}$ g and diameter $a = 2.65$ Å. The gas-liquid transition is first order, as usual. However, as one continues to cool, a second transition sets in at $T = T_\lambda = 2.17$ K (at $p = 1$ atm). The λ -transition, so named for the λ -shaped anomaly in the specific heat in the vicinity of the transition, as shown in fig. 5.7, is continuous (*i.e.* second order). A sketch of the low temperature phase diagram is shown in fig. 5.6. At atmospheric pressure, helium liquefies at $T_1 = 4.2$ K.

If we pretend that ^4He is a noninteracting Bose gas, then from a density of $n = 2.2 \times 10^{22}$ cm $^{-3}$, we obtain a Bose-Einstein condensation temperature $T_c(n) = \frac{2\pi\hbar^2}{m} (n/\zeta(3/2))^{2/3} = 3.16$ K, which is in the right ballpark. The specific heat $C_p(T)$ is found to be singular at $T = T_\lambda$, with

$$C_p(T) = A |T - T_\lambda(p)|^{-\alpha} \quad . \quad (5.114)$$

α is an example of a *critical exponent*. We shall study the physics of critical phenomena later on in this

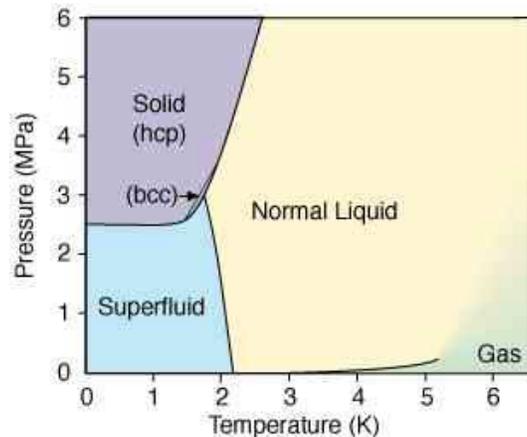


Figure 5.6: Phase diagram of ^4He . All phase boundaries are first order transition lines, with the exception of the normal liquid-superfluid transition, which is second order. (Source: University of Helsinki)

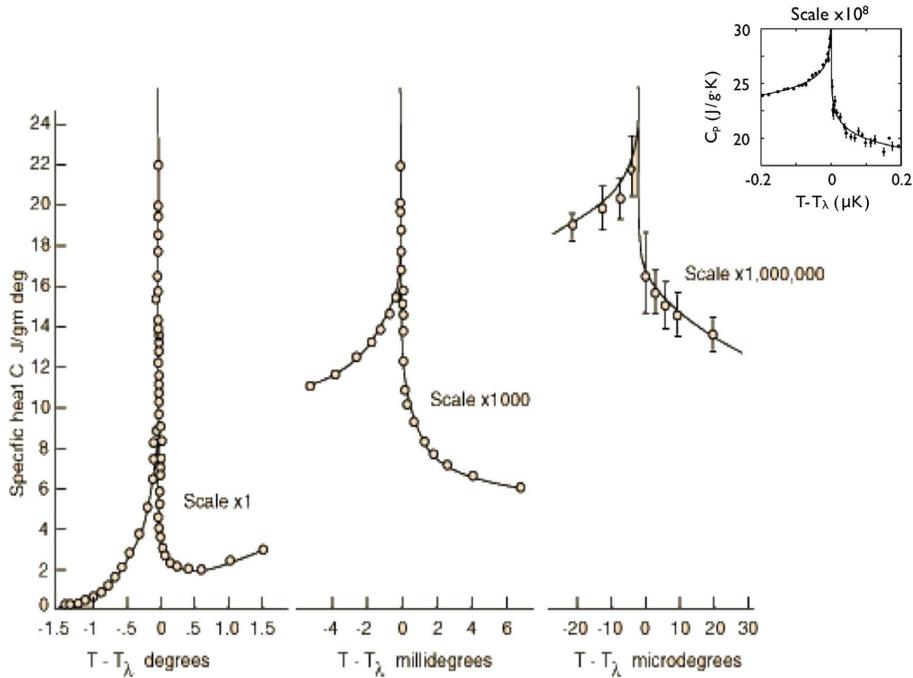


Figure 5.7: Specific heat of liquid ${}^4\text{He}$ in the vicinity of the λ -transition. Data from M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, C. J. Gortner, ed. (North-Holland, 1961). Inset at upper right: more recent data of J. A. Lipa *et al.*, *Phys. Rev. B* **68**, 174518 (2003) performed in zero gravity earth orbit, to within $\Delta T = 2$ nK of the transition.

course. For the ideal nonrelativistic Bose gas, the cusp singularity found in fig. 5.4 for $C_{V,N}(T)$ corresponds to $\alpha = -1$. Perhaps surprisingly, for $C_{p,N}(T)$ one finds instead $\alpha = \frac{1}{2}$ (see the calculation in §??). The observed behavior of $C_p(T)$ in ${}^4\text{He}$ is very nearly logarithmic in $|T - T_\lambda|$. In fact, both theory (renormalization group on the $O(2)$ model) and experiment concur that α is almost zero but in fact slightly negative, with $\alpha = -0.0127 \pm 0.0003$ in the best experiments (Lipa *et al.*, 2003). The λ transition is most definitely *not* an ideal Bose gas condensation. Theoretically, in the parlance of critical phenomena, IBG condensation and the λ -transition in ${}^4\text{He}$ lie in different *universality classes*⁷. Unlike the IBG, the condensed phase in ${}^4\text{He}$ is a distinct thermodynamic phase, known as a *superfluid*. Note that $C_p(T < T_c)$ for the IBG is not even defined, since for $T < T_c$ we have $p = p(T)$ and therefore $dp = 0$ requires $dT = 0$.

Fountain effect in superfluid ${}^4\text{He}$

At temperatures $T < T_\lambda$, liquid ${}^4\text{He}$ has a superfluid component which is a type of Bose condensate. In fact, there is an important difference between condensate fraction $N_{k=0}/N$ and superfluid density, which is denoted by the symbol ρ_s . In ${}^4\text{He}$, for example, at $T = 0$ the condensate fraction is only about

⁷IBG condensation is in the universality class of the spherical model. The λ -transition is in the universality class of the XY model.

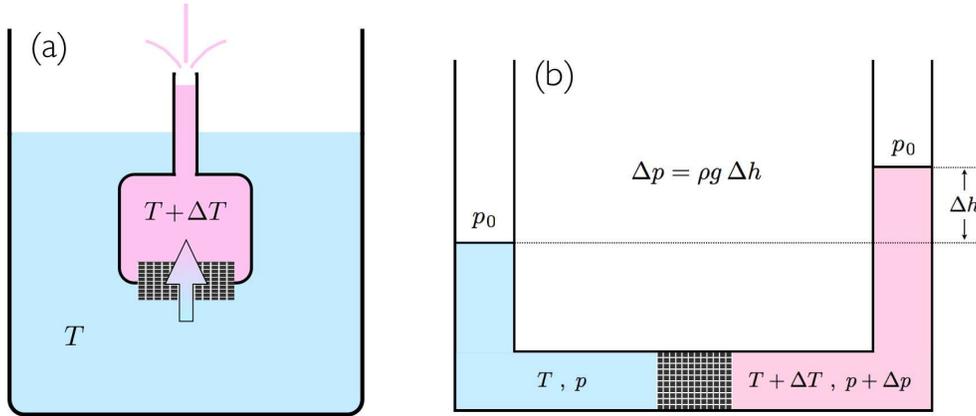


Figure 5.8: The fountain effect. In each case, a temperature gradient is maintained across a porous plug through which only superfluid can flow. This results in a pressure gradient which can result in a fountain or an elevated column in a U-tube.

8%, while the superfluid fraction $\rho_s/\rho = 1$. The distinction between N_0 and ρ_s is very interesting but lies beyond the scope of this course.

One aspect of the superfluid state is its complete absence of viscosity. For this reason, superfluids can flow through tiny cracks called *microleaks* that will not pass normal fluid. Consider then a porous plug which permits the passage of superfluid but not of normal fluid. The key feature of the superfluid component is that it has zero energy density. Therefore even though there is a transfer of particles across the plug, there is no energy exchange, and therefore a temperature gradient across the plug can be maintained⁸. In the U-tube experiment depicted in fig. 5.8, this results in a height difference between the two arms of the U-tube.

The elementary excitations in the superfluid state are sound waves called *phonons*. They are compressional waves, just like longitudinal phonons in a solid, but here in a liquid. Their dispersion is acoustic, given by $\omega(k) = ck$ where $c = 238$ m/s.⁹ They have no internal degrees of freedom, hence $g = 1$. Like phonons in a solid, the phonons in liquid helium are not conserved. Hence their chemical potential vanishes and these excitations are described by photon statistics. Appealing to the quantum thermodynamics of phonons, we may compute the height difference Δh in the U-tube.

Clearly $\Delta h = \Delta p/\rho g$. so we must find $p(T)$ for the helium. In the grand canonical ensemble, we have

$$\begin{aligned}
 p &= -\Omega/V = -k_B T \int \frac{d^3k}{(2\pi)^3} \log(1 - e^{-\hbar ck/k_B T}) \\
 &= -\frac{(k_B T)^4}{(\hbar c)^3} \frac{4\pi}{8\pi^3} \int_0^\infty du u^2 \log(1 - e^{-u}) = \frac{\pi^2}{90} \frac{(k_B T)^4}{(\hbar c)^3} .
 \end{aligned} \tag{5.115}$$

⁸Recall that two bodies in thermal equilibrium will have identical temperatures if they are free to exchange energy.

⁹The phonon velocity c is slightly temperature dependent.

Let's assume $T = 1$ K. We'll need the density of liquid helium, $\rho = 148 \text{ kg/m}^3$. We thus obtain

$$\begin{aligned} \frac{dh}{dT} &= \frac{2\pi^2}{45} \left(\frac{k_B T}{\hbar c} \right)^3 \frac{k_B}{\rho g} \\ &= \frac{2\pi^2}{45} \left(\frac{(1.38 \times 10^{-23} \text{ J/K})(1 \text{ K})}{(1.055 \times 10^{-34} \text{ J} \cdot \text{s})(238 \text{ m/s})} \right)^3 \times \frac{(1.38 \times 10^{-23} \text{ J/K})}{(148 \text{ kg/m}^3)(9.8 \text{ m/s}^2)} \simeq 32 \text{ cm/K} \end{aligned} \quad (5.116)$$

a very noticeable effect!

Andronikashvili experiment, superfluid density, and condensate fraction

At temperatures below T_λ , the superfluid component of liquid ^4He has zero viscosity. This entails several remarkable properties. For example, the superfluid can climb the walls of an open vessel in which it is contained and leak out, seemingly defying gravity, as depicted in panels (a), (b), and (c) of fig. 5.9. Panel (d) depicts the famous Andronikashvili experiment (1946) in which a set of metallic plates is immersed in a vat of liquid ^4He and used as a torsional oscillator. The restoring torque of a torsional fiber twisted by an angle θ is $\tau = -K\theta$, where K is the torsion elastic modulus. If the fiber is connected to

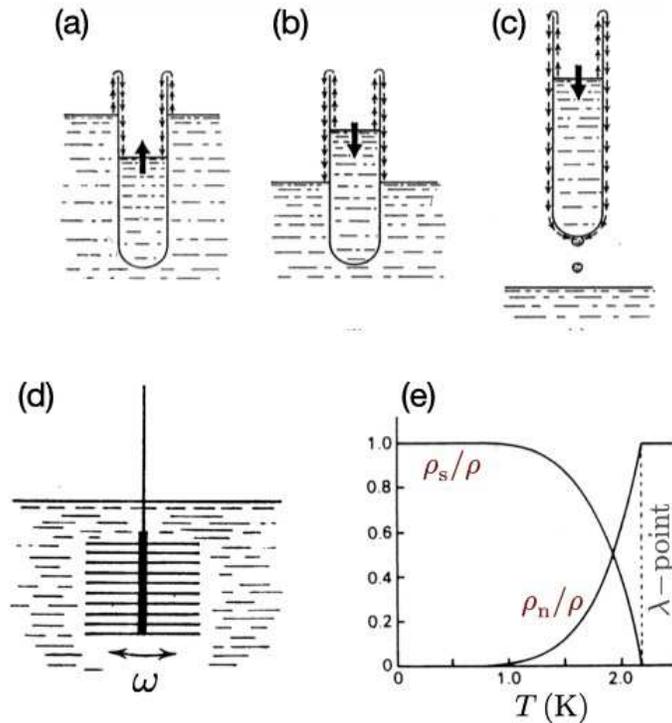


Figure 5.9: Strange properties of superfluid ^4He : (a)-(c) Driven by van der Waals forces, superfluid ^4He can climb walls and a container of superfluid can empty itself. (d) Andronikashvili's experiment (1946), in which a set of metallic disks immersed in a fluid is used as a torsional oscillator. Below T_λ , the period of the oscillations depends on temperature. (e) Normal and superfluid density fractions as a function of temperature.

an element of inertial moment I , then $I\ddot{\theta} = -K\theta$ and the frequency of oscillations (neglecting damping) is $\omega = \sqrt{K/I}$. In Andronikashvili's experiment, $I = I_{\text{app}} + I_{\text{He}}$, where I_{app} is the moment of inertia of the apparatus and I_{He} that of the ^4He which is dragged along due to frictional forces exerted on the fluid by the plates. In viscous liquids there is a length scale $\xi(\omega) \propto \sqrt{\nu/\omega}$, where ν is the viscosity such that if the distance between the plates is less than $\xi(\omega)$, then all the normal fluid between the plates is dragged along with the apparatus as it oscillates. Any superfluid, however, remains decoupled from the oscillation of the plates. Thus,

$$I_{\text{He}}(T) \approx \frac{1}{2}\pi R^4 h_{\text{eff}} \rho_n(T) \quad , \quad (5.117)$$

where $\rho_n(T)$ is the mass density of the normal component (with $\rho_n(T > T_\lambda) = \rho$, the total helium mass density), and R and h_{eff} are the radius and height of the helium liquid between the plates. The experimental results are sketched in panel (e) of fig. 5.9. As the temperature T decreases below T_λ , the moment of inertia $I_{\text{He}}(T)$ decreases in proportion to the normal fluid fraction. At $T = 0$, 100% of the helium is in the superfluid state and there is no contribution from the fluid to the moment of inertia I .

The many-body wavefunction

It is important to apprehend that there is a difference between *superfluid fraction* ρ_s/ρ , which is measured in the Andronikashvili experiment, and *condensate fraction* $f_0 = N_{k=0}/N$, which can be measured in scattering experiments. Theoretically, f_0 is a property of the many-body ground state wavefunction.

The ground state wavefunction of an N -particle system of point particles with no internal degrees of freedom is written as $\Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_N)$. For bosons, Ψ_0 is completely symmetric under any permutation of the labels $\mathbf{x}_i \rightarrow \mathbf{x}_{\sigma(i)}$ for all i , where $\sigma \in S_N$ is an element of the N object permutation group. The wavefunction is also assumed to be normalized, *i.e.*

$$\int \prod_{i=1}^N d^3x_i |\Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 = 1 \quad . \quad (5.118)$$

The condensate fraction f_0 can be expressed in terms of Ψ_0 as the following integral:

$$f_0 = \frac{N_0}{N} = \lim_{|\mathbf{x}-\mathbf{x}'| \rightarrow \infty} \frac{n_1(\mathbf{x}, \mathbf{x}')}{n} \quad , \quad (5.119)$$

where $n_1(\mathbf{x}, \mathbf{x}')$ is the off-diagonal one-body density matrix in the ground state¹⁰ and n is the total ^4He number density

$$n_1(\mathbf{x}, \mathbf{x}') = \int \prod_{i=2}^N d^3x_i \Psi_0^*(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi_0(\mathbf{x}', \mathbf{x}_2, \dots, \mathbf{x}_N) \quad . \quad (5.120)$$

Theoretically, an estimate of f_0 requires an accurately approximated ground state wavefunction Ψ_0 . The simplest trial wavefunctions for ^4He are of the Jastrow pair product form,

$$\Psi_0^{\text{var}}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \prod_{j < k} f(|\mathbf{x}_j - \mathbf{x}_k|) \quad , \quad (5.121)$$

¹⁰See S. Moroni and M. Boninsegni, *J. Low Temp. Phys.* **136**, 129 (2004).

where the pair function $f(r)$ is roughly constant for $r > d$, and rapidly decays to zero for $r < d$, with $d \approx 4.2 \text{ \AA}$ the diameter of a helium atom. Its precise functional form is then determined by minimizing the energy $E = \langle \hat{H} \rangle$. Accurate numerical work requires much more sophisticated techniques, such as Diffusion Monte Carlo or, at finite temperature, Path Integral Monte Carlo. Moroni and Boninsegni (2004) obtained $f_0 = 0.069 \pm 0.005$ and an equilibrium density of $\rho_0 = 0.02186 \text{ \AA}^{-3}$. In dilute atomic gases, discussed in the next section, the interactions are weak, $f_0 \approx 1$, and the condensate may be imaged experimentally. In ^4He f_0 can be ascertained experimentally from deep inelastic neutron scattering, and at the lowest temperatures under saturated vapor pressure measurements values from $f_0 \approx 0.06$ to $f_0 \approx 0.14$ have been reported.

5.6 The Ideal Fermi Gas

5.6.1 Grand potential and particle number

The grand potential of the ideal Fermi gas is, per eqn. 5.10,

$$\begin{aligned} \Omega(T, V, \mu) &= -k_B T \sum_{\alpha} \log \left(1 + e^{\mu/k_B T} e^{-\varepsilon_{\alpha}/k_B T} \right) \\ &= -V k_B T \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \log \left(1 + e^{(\mu-\varepsilon)/k_B T} \right) . \end{aligned} \quad (5.122)$$

The average number of particles in a state with energy ε is

$$n_{\varepsilon}^{\text{F}}(T, \mu) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} , \quad (5.123)$$

hence the total number of particles is

$$N(T, V, \mu) = V \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) n_{\varepsilon}^{\text{F}}(T, \mu) = V \int_{-\infty}^{\infty} d\varepsilon \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/k_B T} + 1} . \quad (5.124)$$

5.6.2 The Fermi distribution

We define the function

$$f_T(\omega) \equiv \frac{1}{e^{\omega/k_B T} + 1} , \quad (5.125)$$

known as the *Fermi distribution* (with T implicit). In the $T \rightarrow \infty$ limit, $f_T(\omega) \rightarrow \frac{1}{2}$ for all finite values of ω . As $T \rightarrow 0$, $f_T(\omega)$ approaches a step function $\Theta(-\omega)$. The average number of particles in a state of energy ε in a system at temperature T and chemical potential μ is $n_{\varepsilon}^{\text{F}}(T, \mu) = f_T(\varepsilon - \mu)$. In fig. 5.1 we plot $f_T(\varepsilon - \mu)$ versus ε for three representative temperatures. Oftentimes we will drop the subscript and write the Fermi distribution simply as $f(\varepsilon - \mu)$, with an implicit T -dependence.

5.6.3 $T = 0$ and the Fermi surface

At $T = 0$, we have $n_\varepsilon(T = 0, \mu) = \Theta(\mu - \varepsilon)$, which says that all single particle energy states up to $\varepsilon = \mu$ are filled, and all energy states above $\varepsilon = \mu$ are empty. We call $\mu(T = 0)$ the *Fermi energy*: $\varepsilon_F = \mu(T = 0)$. If the single particle dispersion $\varepsilon(\mathbf{k})$ depends only on the wavevector \mathbf{k} , then the locus of points in \mathbf{k} -space for which $\varepsilon(\mathbf{k}) = \varepsilon_F$, is called the *Fermi surface*. Thus, a Fermi surface is a $(d - 1)$ -dimensional *level set* of the function $\varepsilon(\mathbf{k})$, labeled by the value ε_F . For isotropic systems, $\varepsilon(\mathbf{k}) = \varepsilon(k)$ is a function only of the wavevector magnitude $k = |\mathbf{k}|$, and the Fermi surface is a sphere in $d = 3$ or a circle in $d = 2$. The radius of this circle is the *Fermi wavevector*, k_F . When there is internal (e.g. spin) degree of freedom, there is a Fermi surface and Fermi wavevector (for isotropic systems) for each polarization state of the internal degree of freedom.

Let's compute the Fermi wavevector k_F and Fermi energy ε_F for the IFG with a ballistic dispersion $\varepsilon(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m$. The number density is

$$n = g \int \frac{d^d k}{(2\pi)^d} \Theta(k_F - k) = \frac{g \Omega_d}{(2\pi)^d} \cdot \frac{k_F^d}{d} \quad (5.126)$$

and thus

$$n^{(d=1)} = g k_F / \pi \quad , \quad n^{(d=2)} = g k_F^2 / 4\pi \quad , \quad n^{(d=3)} = g k_F^3 / 6\pi^2 \quad , \quad (5.127)$$

where $\Omega_d = 2\pi^{d/2} / \Gamma(d/2)$ is the area of the unit sphere in d space dimensions. Note that the form of $n(k_F)$ is independent of the dispersion relation, so long as it remains isotropic. Inverting the above expressions, we obtain $k_F(n) = 2\pi(dn/g\Omega_d)^{1/d}$:

$$k_F^{(d=1)} = \pi n / g \quad , \quad k_F^{(d=2)} = (4\pi n / g)^{1/2} \quad , \quad k_F^{(d=3)} = (6\pi^2 n / g)^{1/3} \quad . \quad (5.128)$$

The Fermi energy in each case, for ballistic dispersion, is given by

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{2\pi^2 \hbar^2}{m} \left(\frac{dn}{g\Omega_d} \right)^{2/d} \quad , \quad (5.129)$$

and so

$$\varepsilon_F^{(d=1)} = \frac{\pi^2 \hbar^2 n^2}{2g^2 m} \quad , \quad \varepsilon_F^{(d=2)} = \frac{2\pi \hbar^2 n}{g m} \quad , \quad \varepsilon_F^{(d=3)} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 n}{g} \right)^{2/3} \quad . \quad (5.130)$$

Another useful result for the ballistic dispersion, which follows from the above, is that the density of states at the Fermi level is given by

$$g(\varepsilon_F) = \frac{g \Omega_d}{(2\pi)^d} \cdot \frac{m k_F^{d-2}}{\hbar^2} = \frac{d}{2} \cdot \frac{n}{\varepsilon_F} \quad . \quad (5.131)$$

That $g(\varepsilon_F)$ must be a numerical factor multiplied by n/ε_F is obvious on dimensional grounds.

For the electron gas, we have $g = 2$. In a metal, one typically has $k_F \sim 0.5 \text{ \AA}^{-1}$ to 2 \AA^{-1} , and $\varepsilon_F \sim 1 \text{ eV} - 10 \text{ eV}$. Due to the effects of the crystalline lattice, electrons in a solid behave as if they have an *effective mass* m^* which is typically on the order of the electron mass but very often about an order of magnitude smaller, particularly in semiconductors.

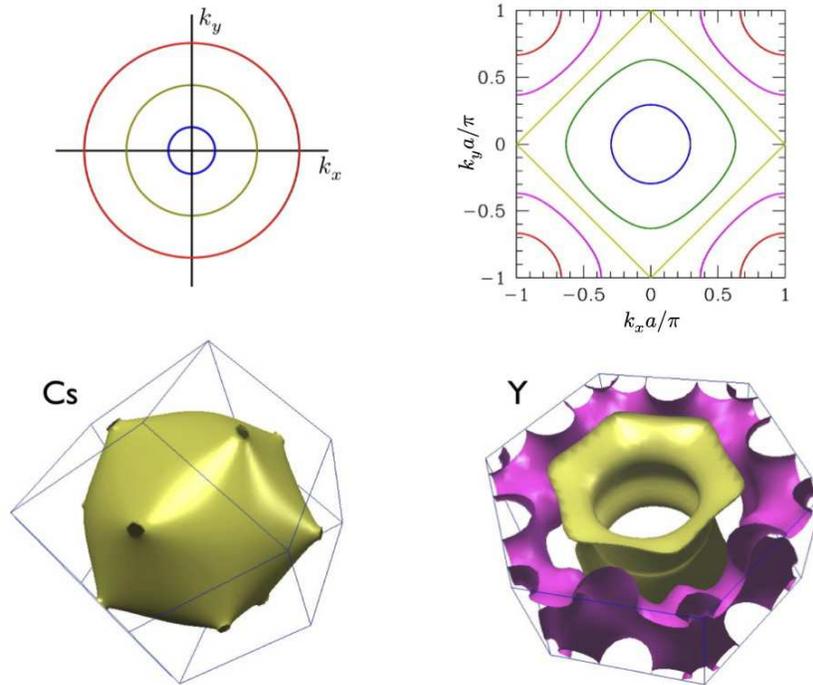


Figure 5.10: Fermi surfaces for two and three-dimensional structures. The wavevector \mathbf{k} ranges over the first Brillouin zone in each case. Upper left: free particles in two dimensions. Upper right: ‘tight binding’ electrons on a square lattice. Lower left: Fermi surface for cesium, which is predominantly composed of electrons in the $6s$ orbital shell. Lower right: the Fermi surface of yttrium has two parts. One part (yellow) is predominantly due to $5s$ electrons, while the other (pink) is due to $4d$ electrons. (Source: www.phys.ufl.edu/fermisurface/)

Nonisotropic dispersions $\varepsilon(\mathbf{k})$ are more interesting in that they give rise to non-spherical Fermi surfaces. The simplest example is that of a two-dimensional ‘tight-binding’ model of electrons hopping on a square lattice, as may be appropriate in certain layered materials. The dispersion relation is then

$$\varepsilon(k_x, k_y) = -2t \cos(k_x a) - 2t \cos(k_y a) \quad , \quad (5.132)$$

where k_x and k_y are confined to the interval $[-\frac{\pi}{a}, \frac{\pi}{a}]$. The quantity t has dimensions of energy and is known as the *hopping integral*. The Fermi surface is the set of points (k_x, k_y) which satisfies $\varepsilon(k_x, k_y) = \varepsilon_F$. When ε_F achieves its minimum value of $\varepsilon_F^{\min} = -4t$, the Fermi surface collapses to a point at $(k_x, k_y) = (0, 0)$. For energies just above this minimum value, we can expand the dispersion in a power series, writing

$$\varepsilon(k_x, k_y) = -4t + ta^2 (k_x^2 + k_y^2) - \frac{1}{12} ta^4 (k_x^4 + k_y^4) + \dots \quad . \quad (5.133)$$

If we only work to quadratic order in k_x and k_y , the dispersion is isotropic, and the Fermi surface is a circle, with $k_F^2 = (\varepsilon_F + 4t)/ta^2$. As the energy increases further, the continuous $O(2)$ rotational invariance is broken down to the discrete group of rotations of the square, C_{4v} . The Fermi surfaces distort and eventually, at $\varepsilon_F = 0$, the Fermi surface is itself a square. As ε_F increases further, the square turns back into a circle, but centered about the point $(\frac{\pi}{a}, \frac{\pi}{a})$. Note that everything is periodic in k_x and k_y modulo $\frac{2\pi}{a}$. The Fermi surfaces for this model are depicted in the upper right panel of fig. 5.10.

Fermi surfaces in three dimensions can be very interesting indeed, and of great importance in understanding the electronic properties of solids. Two examples are shown in the bottom panels of fig. 5.10. The electronic configuration of cesium (Cs) is $[\text{Xe}] 6s^1$. The $6s$ electrons ‘hop’ from site to site on a body centered cubic (BCC) lattice, a generalization of the simple two-dimensional square lattice hopping model discussed above. The elementary unit cell in k space, known as the *first Brillouin zone*, turns out to be a dodecahedron. In yttrium, the electronic structure is $[\text{Kr}] 5s^2 4d^1$, and there are two electronic energy bands at the Fermi level, meaning two Fermi surfaces. Yttrium forms a hexagonal close packed (HCP) crystal structure, and its first Brillouin zone is shaped like a hexagonal pillbox.

Spin-split Fermi surfaces

Consider an electron gas in an external magnetic field H . The single particle Hamiltonian is then¹¹

$$\hat{H} = \frac{\mathbf{p}^2}{2m} + \mu_B H \sigma \quad , \quad (5.134)$$

where μ_B is the *Bohr magneton*, $\mu_B = e\hbar/2mc = 5.788 \times 10^{-9}$ eV/G. It is convenient to keep in mind the ratio $\mu_B/k_B = 6.717 \times 10^{-5}$ K/G. where m is the electron mass. What happens at $T = 0$ to a noninteracting electron gas in a magnetic field?

Electrons of each spin polarization form their own Fermi surfaces. That is, there is an up spin Fermi surface, with Fermi wavevector $k_{F\uparrow}$, and a down spin Fermi surface, with Fermi wavevector $k_{F\downarrow}$. The individual Fermi energies, on the other hand, must be equal, hence

$$\frac{\hbar^2 k_{F\uparrow}^2}{2m} + \mu_B H = \frac{\hbar^2 k_{F\downarrow}^2}{2m} - \mu_B H \quad , \quad (5.135)$$

which says

$$k_{F\downarrow}^2 - k_{F\uparrow}^2 = \frac{2eH}{\hbar c} \quad . \quad (5.136)$$

The total density is

$$n = \frac{k_{F\uparrow}^3}{6\pi^2} + \frac{k_{F\downarrow}^3}{6\pi^2} \quad \Longrightarrow \quad k_{F\uparrow}^3 + k_{F\downarrow}^3 = 6\pi^2 n \quad . \quad (5.137)$$

Clearly the down spin Fermi surface grows and the up spin Fermi surface shrinks with increasing H . Eventually, the minority spin Fermi surface vanishes altogether. This happens for the up spins when $k_{F\uparrow} = 0$. Solving for the critical field, we obtain

$$H_c = \frac{\hbar c}{2e} \cdot (6\pi^2 n)^{2/3} \quad . \quad (5.138)$$

In real magnetic solids, like cobalt and nickel, the spin-split Fermi surfaces are not spheres, just like the case of the (spin degenerate) Fermi surfaces for Cs and Y shown in fig. 5.10.

¹¹Sorry about the notational resemblance between the Hamiltonian \hat{H} and the magnetic field H . The Hamiltonian is adorned with a stylish hat to obviate any potential confusion.

5.6.4 The Sommerfeld expansion

In dealing with the ideal Fermi gas, we will repeatedly encounter integrals of the form

$$\mathcal{I}(T, \mu) \equiv \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon - \mu) \phi(\varepsilon) \quad . \quad (5.139)$$

The Sommerfeld expansion provides a systematic way of expanding these expressions in powers of T and is an important analytical tool in analyzing the low temperature properties of the ideal Fermi gas (IFG).

We start by defining

$$\Phi(\varepsilon) \equiv \int_{-\infty}^{\varepsilon} d\varepsilon' \phi(\varepsilon') \quad (5.140)$$

so that $\phi(\varepsilon) = \Phi'(\varepsilon)$. We then have

$$\mathcal{I}(T, \mu) = \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon - \mu) \frac{d\Phi}{d\varepsilon} = - \int_{-\infty}^{\infty} d\varepsilon f'(\varepsilon) \Phi(\mu + \varepsilon) \quad , \quad (5.141)$$

where we assume $\Phi(-\infty) = 0$. Next, we invoke Taylor's theorem, to write

$$\Phi(\mu + \varepsilon) = \sum_{n=0}^{\infty} \frac{\varepsilon^n}{n!} \frac{d^n \Phi}{d\mu^n} = \exp\left(\varepsilon \frac{d}{d\mu}\right) \Phi(\mu) \quad . \quad (5.142)$$

This last expression involving the exponential of a differential operator may appear overly formal but it proves extremely useful. Since

$$f'(\varepsilon) = -\frac{1}{k_B T} \frac{e^{\varepsilon/k_B T}}{(e^{\varepsilon/k_B T} + 1)^2} \quad , \quad (5.143)$$

we define

$$\tilde{\mathcal{I}}(T, \mu) = \int_{-\infty}^{\infty} dv \frac{e^{vD}}{(e^v + 1)(e^{-v} + 1)} \Phi(\mu) \quad , \quad (5.144)$$

with $v = \varepsilon/k_B T$, where $D = k_B T \frac{d}{d\mu}$ is a dimensionless differential operator. The integral can now be done using the methods of complex integration:¹²

$$\begin{aligned} \int_{-\infty}^{\infty} dv \frac{e^{vD}}{(e^v + 1)(e^{-v} + 1)} &= 2\pi i \sum_{n=1}^{\infty} \text{Res} \left[\frac{e^{vD}}{(e^v + 1)(e^{-v} + 1)} \right]_{v=(2n+1)i\pi} \\ &= -2\pi i \sum_{n=0}^{\infty} D e^{(2n+1)i\pi D} = -\frac{2\pi i D e^{i\pi D}}{1 - e^{2\pi i D}} = \pi D \csc \pi D \quad . \end{aligned} \quad (5.145)$$

¹²Note that writing $v = (2n + 1) i\pi + \varepsilon$ we have $e^{\pm v} = -1 \mp \varepsilon - \frac{1}{2}\varepsilon^2 + \dots$, so $(e^v + 1)(e^{-v} + 1) = -\varepsilon^2 + \dots$. We then expand $e^{vD} = e^{(2n+1)i\pi D} (1 + \varepsilon D + \dots)$ to find the residue: $\text{Res} = -D e^{(2n+1)i\pi D}$.

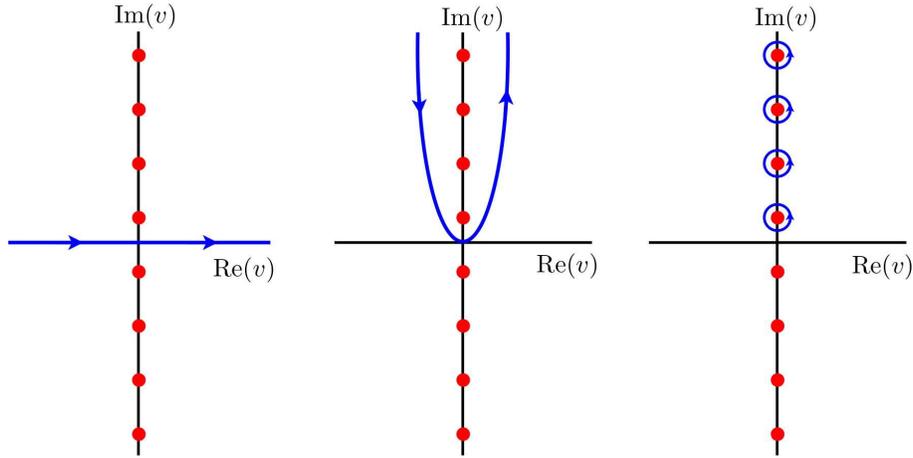


Figure 5.11: Deformation of the complex integration contour in eqn. 5.145.

Thus,

$$\tilde{\mathcal{I}}(T, \mu) = \pi D \csc(\pi D) \Phi(\mu) \quad , \quad (5.146)$$

which is to be understood as the differential operator $\pi D \csc(\pi D)$ acting on the function $\Phi(\mu)$. Appealing once more to Taylor's theorem, we have

$$\pi D \csc(\pi D) = 1 + \frac{\pi^2}{6} (k_B T)^2 \frac{d^2}{d\mu^2} + \frac{7\pi^4}{360} (k_B T)^4 \frac{d^4}{d\mu^4} + \dots \quad . \quad (5.147)$$

Thus,

$$\tilde{\mathcal{I}}(T, \mu) = \int_{-\infty}^{\infty} d\varepsilon f(\varepsilon - \mu) \phi(\varepsilon) = \int_{-\infty}^{\mu} d\varepsilon \phi(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 \phi'(\mu) + \frac{7\pi^4}{360} (k_B T)^4 \phi'''(\mu) + \dots \quad . \quad (5.148)$$

If $\phi(\varepsilon)$ is a polynomial function of its argument, then each derivative effectively reduces the order of the polynomial by one degree, and the dimensionless parameter of the expansion is $(k_B T/\mu)^2$. This procedure is known as the *Sommerfeld expansion*. We introduce the notation $\tilde{\mathcal{I}}(T, \mu)$ because the function $\mathcal{I}(T, \mu)$ may contain nonanalytic terms which are invisible in the Taylor series expansion $\tilde{\mathcal{I}}(T, \mu)$, as we will see below.

Chemical potential shift

As our first application of the Sommerfeld expansion formalism, let us compute $\mu(n, T)$ for the ideal Fermi gas. The number density $n(T, \mu)$ is

$$n = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon - \mu) = \int_{-\infty}^{\mu} d\varepsilon g(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + \dots \quad . \quad (5.149)$$

Let us write $\mu = \varepsilon_F + \delta\mu$, where $\varepsilon_F = \mu(T = 0, n)$ is the Fermi energy, which is the chemical potential at $T = 0$. We then have

$$\begin{aligned} n &= \int_{-\infty}^{\varepsilon_F + \delta\mu} d\varepsilon g(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F + \delta\mu) + \dots \\ &= \int_{-\infty}^{\varepsilon_F} d\varepsilon g(\varepsilon) + g(\varepsilon_F) \delta\mu + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) + \dots \quad , \end{aligned} \quad (5.150)$$

from which we derive

$$\delta\mu = -\frac{\pi^2}{6} (k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} + \mathcal{O}(T^4) \quad . \quad (5.151)$$

Note that $g'/g = (\log g)'$. For a ballistic dispersion, assuming $g = 2$,

$$g(\varepsilon) = 2 \int \frac{d^3k}{(2\pi)^3} \delta\left(\varepsilon - \frac{\hbar^2 k^2}{2m}\right) = \frac{m k(\varepsilon)}{\pi^2 \hbar^2} \Big|_{k(\varepsilon) = \frac{1}{\hbar} \sqrt{2m\varepsilon}} \quad (5.152)$$

Thus, $g(\varepsilon) \propto \varepsilon^{1/2}$ and $(\log g)' = \frac{1}{2} \varepsilon^{-1}$, so

$$\mu(n, T) = \varepsilon_F - \frac{\pi^2}{12} \frac{(k_B T)^2}{\varepsilon_F} + \dots \quad , \quad (5.153)$$

where $\varepsilon_F(n) = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$.

Specific heat

The energy of the electron gas is

$$\begin{aligned} \frac{E}{V} &= \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \varepsilon f(\varepsilon - \mu) = \int_{-\infty}^{\mu} d\varepsilon g(\varepsilon) \varepsilon + \frac{\pi^2}{6} (k_B T)^2 \frac{d}{d\mu} (\mu g(\mu)) + \dots \\ &= \int_{-\infty}^{\varepsilon_F} d\varepsilon g(\varepsilon) \varepsilon + g(\varepsilon_F) \varepsilon_F \delta\mu + \frac{\pi^2}{6} (k_B T)^2 \varepsilon_F g'(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) + \dots \\ &= \varepsilon_0 + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) + \dots \quad , \end{aligned} \quad (5.154)$$

where $\varepsilon_0 = \int_{-\infty}^{\varepsilon_F} d\varepsilon g(\varepsilon) \varepsilon$ is the ground state energy density (*i.e.* ground state energy per unit volume).

Thus, to order T^2 ,

$$C_{V,N} = \left(\frac{\partial E}{\partial T} \right)_{V,N} = \frac{\pi^2}{3} V k_B^2 T g(\varepsilon_F) \equiv V \gamma T \quad , \quad (5.155)$$

where $\gamma(n) = \frac{\pi^2}{3} k_B^2 g(\varepsilon_F(n))$. Note that the molar heat capacity is

$$c_V = \frac{N_A}{N} \cdot C_V = \frac{\pi^2}{3} R \cdot \frac{k_B T g(\varepsilon_F)}{n} = \frac{\pi^2}{2} \left(\frac{k_B T}{\varepsilon_F} \right) R, \quad (5.156)$$

where in the last expression on the RHS we have assumed a ballistic dispersion, for which

$$\frac{g(\varepsilon_F)}{n} = \frac{g m k_F}{2\pi^2 \hbar^2} \cdot \frac{6\pi^2}{g k_F^3} = \frac{3}{2\varepsilon_F}. \quad (5.157)$$

The molar heat capacity in eqn. 5.156 is to be compared with the classical ideal gas value of $\frac{3}{2}R$. Relative to the classical ideal gas, the IFG value is reduced by a fraction of $(\pi^2/3) \times (k_B T/\varepsilon_F)$, which in most metals is very small and even at room temperature is only on the order of 10^{-2} . Most of the heat capacity of metals at room temperature is due to the energy stored in lattice vibrations.

A niftier way to derive the heat capacity¹³: Starting with eqn. 5.151 for $\mu(T) - \varepsilon_F \equiv \delta\mu(T)$, note that $g(\varepsilon_F) = dn/d\varepsilon_F$, so we may write $\delta\mu = -\frac{\pi^2}{6} (k_B T)^2 (dg/dn) + \mathcal{O}(T^4)$. Next, use the Maxwell relation $(\partial S/\partial N)_{T,V} = -(\partial\mu/\partial T)_{N,V}$ to arrive at

$$\left(\frac{\partial s}{\partial n} \right)_T = \frac{\pi^2}{3} k_B^2 T \frac{\partial g(\varepsilon_F)}{\partial n} + \mathcal{O}(T^3), \quad (5.158)$$

where $s = S/V$ is the entropy per unit volume. Now use $S(T=0) = 0$ and integrate with respect to the density n to arrive at $S(T, V, N) = V\gamma T$, where $\gamma(n)$ is defined above.

Nonanalytic terms

As we've seen, the Sommerfeld expansion is an expansion in powers of T . Consider the case where $\phi(\varepsilon) = \Theta(\varepsilon)$. We then have

$$\mathcal{I}(T, \mu) = \int_0^\infty d\varepsilon f(\varepsilon - \mu) = \mu + k_B T \log(1 + e^{-\mu/k_B T}). \quad (5.159)$$

By contrast, the Sommerfeld expansion, assuming $\mu \neq 0$, yields $\tilde{\mathcal{I}}(T, \mu) = \mu$, and is missing the second term above. This is because $\exp(-\mu/k_B T)$ is nonanalytic in T and cannot appear in any order of a Taylor expansion about $T = 0$. As a second example, consider the case $\phi(\varepsilon) = \varepsilon \Theta(\varepsilon)$. The Sommerfeld expansion yields

$$\tilde{\mathcal{I}}(T, \mu) = \frac{1}{2}\mu^2 + \frac{\pi^2}{6} (k_B T)^2, \quad (5.160)$$

while the exact result is

$$\mathcal{I}(T, \mu) = \frac{1}{2}\mu^2 + \frac{\pi^2}{6} (k_B T)^2 + (k_B T)^2 \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} e^{-j\mu/k_B T}, \quad (5.161)$$

¹³I thank my colleague Tarun Grover for this observation.

which follows from the polylogarithm identity

$$\text{Li}_2(z) + \text{Li}_2(1/z) = -\frac{1}{2} [\log(-z)]^2 - \frac{\pi^2}{6} . \quad (5.162)$$

Again we see that the Sommerfeld expansion terminates at a finite order in T , and is missing nonanalytic terms in the $T \rightarrow 0$ limit¹⁴. This is a generic state of affairs for the case where $\phi(\varepsilon)$ is a finite order polynomial in ε .

5.6.5 Magnetic susceptibility

Pauli paramagnetism

Magnetism has two origins: (i) orbital currents of charged particles, and (ii) intrinsic magnetic moment. The intrinsic magnetic moment \mathbf{m} of a particle is related to its quantum mechanical *spin* according to $\mathbf{m} = g\mu_0\mathbf{S}/\hbar$, where $\mu_0 = q\hbar/2mc$ is the magneton. Here g is the particle's g -factor, μ_0 its magnetic moment, and \mathbf{S} is the vector of quantum mechanical spin operators satisfying $[S^\alpha, S^\beta] = i\hbar\epsilon_{\alpha\beta\gamma}S^\gamma$, i.e. SU(2) commutation relations. The Hamiltonian for a single particle is then

$$\hat{H} = \frac{1}{2m^*} \left(\mathbf{p} - \frac{q}{c} \mathbf{A} \right)^2 - \mathbf{H} \cdot \mathbf{m} = \frac{1}{2m^*} \left(\mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 + \frac{g}{2} \mu_B H \sigma , \quad (5.163)$$

where in the last line we've restricted our attention to the electron, for which $q = -e$. The g -factor for an electron is $g = 2$ at tree level, and when radiative corrections are accounted for using quantum electrodynamics (QED) one finds $g = 2.0023193043617(15)$. For our purposes we can take $g = 2$, although we can always absorb the small difference into the definition of μ_B , writing $\mu_B \rightarrow \tilde{\mu}_B = ge\hbar/4mc$. We've chosen the \hat{z} -axis in spin space to point in the direction of the magnetic field, and we wrote the eigenvalues of S^z as $\frac{1}{2}\hbar\sigma$, where $\sigma = \pm 1$. The quantity m^* is the *effective mass* of the electron, which we mentioned earlier. An important distinction is that it is m^* which enters into the kinetic energy term $\mathbf{p}^2/2m^*$, but it is the electron mass m itself ($m = 511$ keV) which enters into the definition of the Bohr magneton. We shall discuss the consequences of this further below.

In the absence of orbital magnetic coupling, the single particle dispersion is

$$\varepsilon_\sigma(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m^*} + \tilde{\mu}_B H \sigma . \quad (5.164)$$

At $T = 0$, we have the results of §5.6.3. At finite T , we once again use the Sommerfeld expansion. We

¹⁴Once again I thank my colleague Tarun Grover for pointing this out to me.

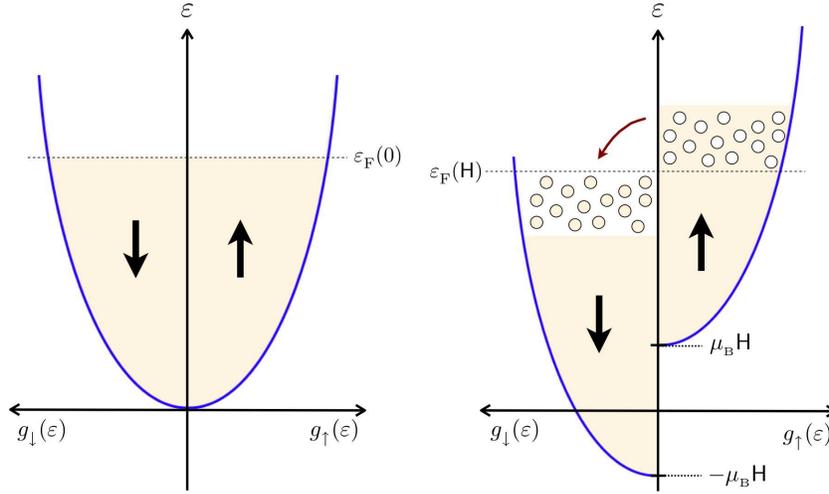


Figure 5.12: Fermi distributions in the presence of an external Zeeman-coupled magnetic field.

then have

$$\begin{aligned}
 n &= \int_{-\infty}^{\infty} d\varepsilon g_{\uparrow}(\varepsilon) f(\varepsilon - \mu) + \int_{-\infty}^{\infty} d\varepsilon g_{\downarrow}(\varepsilon) f(\varepsilon - \mu) \\
 &= \frac{1}{2} \int_{-\infty}^{\infty} d\varepsilon \left\{ g(\varepsilon - \tilde{\mu}_B H) + g(\varepsilon + \tilde{\mu}_B H) \right\} f(\varepsilon - \mu) \\
 &= \int_{-\infty}^{\infty} d\varepsilon \left\{ g(\varepsilon) + (\tilde{\mu}_B H)^2 g''(\varepsilon) + \dots \right\} f(\varepsilon - \mu) \quad .
 \end{aligned} \tag{5.165}$$

We now invoke the Sommerfeld expansion to find the temperature dependence:

$$\begin{aligned}
 n &= \int_{-\infty}^{\mu} d\varepsilon g(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + (\tilde{\mu}_B H)^2 g'(\mu) + \dots \\
 &= \int_{-\infty}^{\varepsilon_F} d\varepsilon g(\varepsilon) + g(\varepsilon_F) \delta\mu + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) + (\tilde{\mu}_B H)^2 g'(\varepsilon_F) + \dots \quad ,
 \end{aligned} \tag{5.166}$$

where $\varepsilon_F = \mu(T = 0, n, H = 0)$. The density of states for spin species σ is $g_{\sigma}(\varepsilon) = \frac{1}{2} g(\varepsilon - \tilde{\mu}_B H \sigma)$, where $g(\varepsilon)$ is the total density of states per unit volume, for both spin species, in the absence of a magnetic field. We conclude that the chemical potential shift in an external field is

$$\delta\mu(T, n, H) = - \left\{ \frac{\pi^2}{6} (k_B T)^2 + (\tilde{\mu}_B H)^2 \right\} \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} + \dots \quad . \tag{5.167}$$

We next compute the difference $n_\uparrow - n_\downarrow$ in the densities of up and down spin electrons:

$$\begin{aligned}
n_\uparrow - n_\downarrow &= \int_{-\infty}^{\infty} d\varepsilon \left\{ g_\uparrow(\varepsilon) - g_\downarrow(\varepsilon) \right\} f(\varepsilon - \mu) \\
&= \frac{1}{2} \int_{-\infty}^{\infty} d\varepsilon \left\{ g(\varepsilon - \tilde{\mu}_B H) - g(\varepsilon + \tilde{\mu}_B H) \right\} f(\varepsilon - \mu) \\
&= -\tilde{\mu}_B H \cdot \pi D \operatorname{csc}(\pi D) g(\mu) + \mathcal{O}(H^3) \quad .
\end{aligned} \tag{5.168}$$

We needn't go beyond the trivial lowest order term in the Sommerfeld expansion, because H is already assumed to be small. Thus, the magnetization density is

$$M = -\tilde{\mu}_B (n_\uparrow - n_\downarrow) = \tilde{\mu}_B^2 g(\varepsilon_F) H \quad . \tag{5.169}$$

in which the magnetic susceptibility is

$$\chi = \left(\frac{\partial M}{\partial H} \right)_{T,N} = \tilde{\mu}_B^2 g(\varepsilon_F) \quad . \tag{5.170}$$

This is called the *Pauli paramagnetic susceptibility*.

Landau diamagnetism

When orbital effects are included, the single particle energy levels are given by

$$\varepsilon(n, k_z, \sigma) = \left(n + \frac{1}{2}\right) \hbar \omega_c + \frac{\hbar^2 k_z^2}{2m^*} + \sigma \tilde{\mu}_B H \quad . \tag{5.171}$$

Here n is a Landau level index, and $\omega_c = eH/m^*c$ is the *cyclotron frequency*. Note that

$$\frac{\tilde{\mu}_B H}{\hbar \omega_c} = \frac{ge\hbar H}{4mc} \cdot \frac{m^*c}{\hbar eH} = \frac{g}{4} \cdot \frac{m^*}{m} \quad . \tag{5.172}$$

Accordingly, we define the ratio $r \equiv (g/2) \times (m^*/m)$. We can then write

$$\varepsilon(n, k_z, \sigma) = \left(n + \frac{1}{2} + \frac{1}{2}r\sigma\right) \hbar \omega_c + \frac{\hbar^2 k_z^2}{2m^*} \quad . \tag{5.173}$$

The grand potential is then given by

$$\Omega = -\frac{HA}{\phi_0} \cdot L_z \cdot k_B T \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} \log \left[1 + e^{\mu/k_B T} e^{-(n+\frac{1}{2}+\frac{1}{2}r\sigma)\hbar\omega_c/k_B T} e^{-\hbar^2 k_z^2/2m^* k_B T} \right] \quad . \tag{5.174}$$

A few words are in order here regarding the prefactor. In the presence of a uniform magnetic field, the energy levels of a two-dimensional ballistic charged particle collapse into Landau levels. The number

of states per Landau level scales with the area of the system, and is equal to the number of flux quanta through the system: $N_\phi = HA/\phi_0$, where $\phi_0 = hc/e$ is the Dirac flux quantum. Note that

$$\frac{HA}{\phi_0} \cdot L_z \cdot k_B T = \hbar\omega_c \cdot \frac{V}{\lambda_T^2} \quad , \quad (5.175)$$

hence we can write

$$\Omega(T, V, \mu, H) = \hbar\omega_c \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} Q\left(\left(n + \frac{1}{2} + \frac{1}{2}r\sigma\right)\hbar\omega_c - \mu\right) \quad , \quad (5.176)$$

where

$$Q(\varepsilon) = -\frac{V}{\lambda_T^2} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \log\left[1 + e^{-\varepsilon/k_B T} e^{-\hbar^2 k_z^2 / 2m^* k_B T}\right] = \frac{V}{\lambda_T^3} \text{Li}_{3/2}(e^{-\varepsilon/k_B T}) \quad . \quad (5.177)$$

We now invoke the Euler-MacLaurin formula,

$$\sum_{n=0}^{\infty} F(n) = \int_0^{\infty} dx F(x) + \frac{1}{2} F(0) - \frac{1}{12} F'(0) + \dots \quad , \quad (5.178)$$

resulting in

$$\begin{aligned} \Omega = \sum_{\sigma} \int_{-\infty}^{\infty} d\varepsilon Q(\varepsilon - \mu) \Theta\left(\varepsilon - \frac{1}{2}(1 + \sigma r)\hbar\omega_c\right) \\ + \sum_{\sigma} \left[\frac{1}{2} \hbar\omega_c Q\left(\frac{1}{2}(1 + \sigma r)\hbar\omega_c - \mu\right) - \frac{1}{12} (\hbar\omega_c)^2 Q'\left(\frac{1}{2}(1 + \sigma r)\hbar\omega_c - \mu\right) + \dots \right] \quad . \end{aligned} \quad (5.179)$$

We next expand in powers of the magnetic field H to obtain

$$\Omega(T, V, \mu, H) = 2 \int_0^{\infty} d\varepsilon Q(\varepsilon - \mu) + \left(\frac{1}{4}r^2 - \frac{1}{12}\right) (\hbar\omega_c)^2 Q'(-\mu) + \dots \quad . \quad (5.180)$$

Thus, the magnetic susceptibility is

$$\begin{aligned} \chi &= -\frac{1}{V} \frac{\partial^2 \Omega}{\partial H^2} = \left(r^2 - \frac{1}{3}\right) \cdot \tilde{\mu}_B^2 \cdot (m/m^*)^2 \cdot \left\{ -\frac{2}{V} Q'(-\mu) \right\} \\ &= \left(\frac{g^2}{4} - \frac{m^2}{3m^{*2}}\right) \cdot \tilde{\mu}_B^2 \cdot n^2 \kappa_T \quad , \end{aligned} \quad (5.181)$$

where κ_T is the isothermal compressibility¹⁵. In most metals we have $m^* \approx m$ and the term in brackets is positive (recall $g \approx 2$). In semiconductors, however, we can have $m^* \ll m$; for example in GaAs we have $m^* = 0.067 m$. Thus, semiconductors can have a *diamagnetic* response. If we take $g = 2$ and $m^* = m$, we

¹⁵We've used $-\frac{2}{V} Q'(\mu) = -\frac{1}{V} \frac{\partial^2 \Omega}{\partial \mu^2} = n^2 \kappa_T$.

see that the orbital currents give rise to a diamagnetic contribution to the magnetic susceptibility which is exactly $-\frac{1}{3}$ times as large as the contribution arising from Zeeman coupling. The net result is then paramagnetic ($\chi > 0$) and $\frac{2}{3}$ as large as the Pauli susceptibility. The orbital currents can be understood within the context of *Lenz's law*.

Exercise : Show that $-\frac{2}{V} Q'(-\mu) = n^2 \kappa_T$.

5.6.6 White dwarf stars

The term *white dwarf*, coined by W. J. Luyten in 1922, refers to an end stage of stellar evolution in cases where the star's mass is too small to transition to a neutron star or collapse into a black hole. White dwarfs are typically earth-sized objects which have masses $M \sim M_\odot$ on the order of that of the sun, hence they are extremely compact. They are also very faint, and occupy a region in the lower left of the Hertzsprung-Russell diagram¹⁶ In so-called main sequence stars, heat and radiation is generated by hydrogen-to-helium fusion, which roughly occurs in three steps: (i) $p + p \rightarrow d + e^+ + \nu_e$, (ii) $d + p \rightarrow {}^3\text{He}$, and (iii) ${}^3\text{He} + {}^3\text{He} \rightarrow {}^4\text{He} + 2p$, where ${}^4\text{He}$ is a helium-4 nucleus, *i.e.* an α -particle. For low mass stars ($M < M_\odot$), the radius typically scales as $R(M) \propto M^{0.8}$. In the white dwarf stage, however, all the hydrogen has burned and fusion has ceased. There is longer a heat source to support the star against gravitational collapse. Rather, its gravitational stability is due to electron degeneracy pressure; this mechanism is responsible for their ultra-high density. Ultimately the α -particles themselves burn in a two-stage *triple-alpha* process in which, effectively, $3\alpha \rightarrow {}^{12}\text{C} + 2\gamma$ – this is a key process in stellar nucleosynthesis, and the chain continues with ${}^{12}\text{C} + \alpha \rightarrow {}^{16}\text{O}$. Typically, the cores of white dwarfs consist of carbon and oxygen, but depending on the initial mass of the star, its core may contain Ne. Helium fusion itself is suppressed in very low mass stars, which can end up as helium white dwarfs.

Here we follow the nice discussion of this material in R. K. Pathria, *Statistical Mechanics*. As a model, consider a mass $M \sim 10^{33}$ g of helium at nuclear densities of $\rho \sim 10^7$ g/cm³ and temperature $T \sim 10^7$ K. (We neglect the effects of helium burning.) This temperature is much larger than the ionization energy of ${}^4\text{He}$, hence we may safely assume that all helium atoms are ionized. If there are N electrons, then the number of α particles (*i.e.* ${}^4\text{He}$ nuclei) must be $\frac{1}{2}N$. The mass of the α particle is $m_\alpha \approx 4m_p$. The total stellar mass M is almost completely due to α particle cores.

The electron density is then

$$n = \frac{N}{V} = \frac{2 \cdot M/4m_p}{V} = \frac{\rho}{2m_p} \approx 10^{30} \text{ cm}^{-3} \quad , \quad (5.182)$$

since $M = N \cdot m_e + \frac{1}{2}N \cdot 4m_p$. From the number density n , including both spin polarizations, we find for the electrons

$$\begin{aligned} k_F &= (3\pi^2 n)^{1/3} = 2.14 \times 10^{10} \text{ cm}^{-1} \\ p_F &= \hbar k_F = 2.26 \times 10^{-17} \text{ g cm/s} \\ mc &= (9.1 \times 10^{-28} \text{ g})(3 \times 10^{10} \text{ m/s}) = 2.7 \times 10^{-17} \text{ g cm/s} \quad . \end{aligned} \quad (5.183)$$

¹⁶The H-R diagram plots luminosity *versus* surface temperature (*i.e.* color or spectral class).

Since $p_F \sim mc$, we conclude that the electrons are relativistic. The Fermi temperature will then be $T_F \sim mc^2 \sim 10^6 \text{ eV} \sim 10^{12} \text{ K}$. Thus, $T \ll T_F$ which says that the electron gas is degenerate and may be considered to be at $T \sim 0$. So we need to understand the ground state properties of the relativistic electron gas.

The kinetic energy is given by

$$\varepsilon(\mathbf{p}) = \sqrt{\mathbf{p}^2 c^2 + m^2 c^4} - mc^2 \quad . \quad (5.184)$$

The velocity is

$$\mathbf{v} = \frac{\partial \varepsilon}{\partial \mathbf{p}} = \frac{\mathbf{p} c^2}{\sqrt{\mathbf{p}^2 c^2 + m^2 c^4}} \quad . \quad (5.185)$$

The pressure in the ground state is

$$\begin{aligned} p_0 &= \frac{1}{3} n \langle \mathbf{p} \cdot \mathbf{v} \rangle = \frac{1}{3\pi^2 \hbar^3} \int_0^{p_F} dp p^2 \cdot \frac{p^2 c^2}{\sqrt{p^2 c^2 + m^2 c^4}} \\ &= \frac{m^4 c^5}{3\pi^2 \hbar^3} \int_0^{\theta_F} d\theta \sinh^4 \theta = \frac{m^4 c^5}{96\pi^2 \hbar^3} (\sinh(4\theta_F) - 8 \sinh(2\theta_F) + 12 \theta_F) \quad , \end{aligned} \quad (5.186)$$

where we use the substitution

$$p = mc \sinh \theta \quad , \quad v = c \tanh \theta \quad \implies \quad \theta = \frac{1}{2} \log \left(\frac{c+v}{c-v} \right) \quad . \quad (5.187)$$

Note that $p_F = \hbar k_F = \hbar(3\pi^2 n)^{1/3}$, and that

$$n = \frac{M}{2m_p V} \quad \implies \quad 3\pi^2 n = \frac{9\pi}{8} \frac{M}{R^3 m_p} \quad . \quad (5.188)$$

Now in equilibrium the pressure p is balanced by gravitational pressure. Let R be the radius of the star. Then we have

$$dE_0 = -p_0 dV = -p_0(R) \cdot 4\pi R^2 dR \quad . \quad (5.189)$$

This must be balanced by gravity:

$$dE_g = \alpha \cdot \frac{GM^2}{R^2} dR \quad , \quad (5.190)$$

where the phenomenological constant α depends on the radial mass distribution. Equilibrium then implies

$$p_0(R) = \frac{\alpha}{4\pi} \frac{GM^2}{R^4} \quad . \quad (5.191)$$

To find the relation $R = R(M)$, we must solve

$$\frac{\alpha}{4\pi} \frac{gM^2}{R^4} = \frac{m^4 c^5}{96\pi^2 \hbar^3} (\sinh(4\theta_F) - 8 \sinh(2\theta_F) + 12 \theta_F) \quad . \quad (5.192)$$

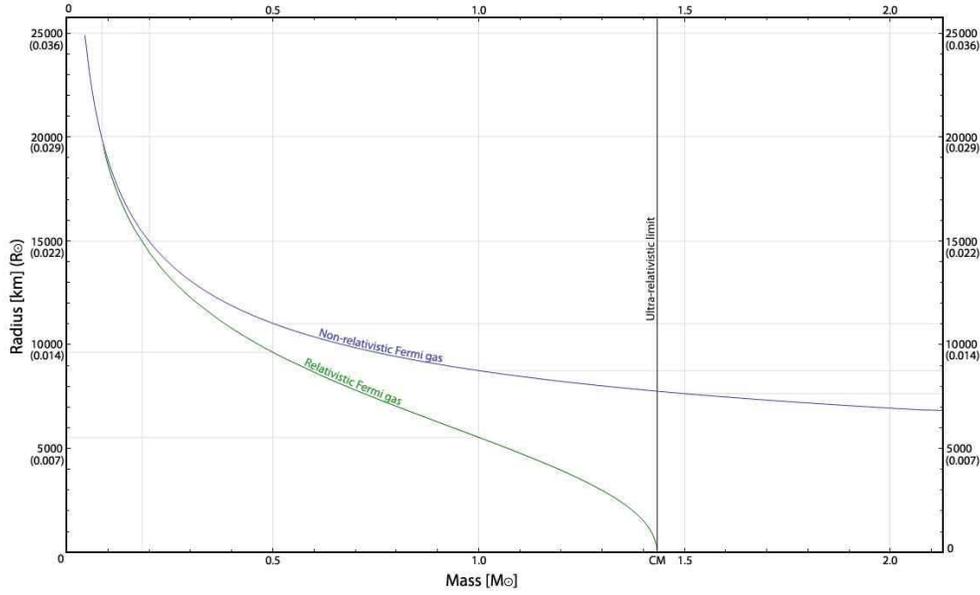


Figure 5.13: Mass-radius relationship for white dwarf stars. (Source: Wikipedia).

Note that

$$\sinh(4\theta_F) - 8 \sinh(2\theta_F) + 12\theta_F = \begin{cases} \frac{96}{15} \theta_F^5 & \theta_F \rightarrow 0 \\ \frac{1}{2} e^{4\theta_F} & \theta_F \rightarrow \infty \end{cases} . \quad (5.193)$$

Thus, we may write

$$p_0(R) = \frac{\alpha}{4\pi} \frac{gM^2}{R^4} = \begin{cases} \frac{\hbar^2}{15\pi^2 m} \left(\frac{9\pi}{8} \frac{M}{R^3 m_p} \right)^{5/3} & \theta_F \rightarrow 0 \\ \frac{\hbar c}{12\pi^2} \left(\frac{9\pi}{8} \frac{M}{R^3 m_p} \right)^{4/3} & \theta_F \rightarrow \infty \end{cases} . \quad (5.194)$$

In the limit $\theta_F \rightarrow 0$, we solve for $R(M)$ and find

$$R(M) = \frac{3(9\pi)^{2/3}}{40\alpha} \frac{\hbar^2}{G m_p^{5/3} m M^{1/3}} \propto M^{-1/3} . \quad (5.195)$$

In the opposite limit $\theta_F \rightarrow \infty$, the R factors on either side of the equality in eqn. 5.194 cancel, and we obtain $M = M_0$ with

$$M_0 = \frac{9}{64} \left(\frac{3\pi}{\alpha^3} \right)^{1/2} \left(\frac{\hbar c}{G} \right)^{3/2} \frac{1}{m_p^2} \approx 0.8 \alpha^{-3/2} M_\odot . \quad (5.196)$$

To find the R dependence in this limit, we must go beyond the lowest order expansion of eqn. 5.193, in which case we find

$$R(M) = \left(\frac{9\pi}{8} \right)^{1/3} \left(\frac{\hbar}{mc} \right) \left(\frac{M}{m_p} \right)^{1/3} \left[1 - \left(\frac{M}{M_0} \right)^{2/3} \right]^{1/2} . \quad (5.197)$$

Since we must have $R(M) > 0$, we conclude that the value M_0 is the maximum mass for a white dwarf. Beyond this mass, the degeneracy pressure cannot resist the force of gravity. More correctly stated, there is no possibility for a stable equilibrium between pressure and gravitational forces. This is called the *Chandrasekhar limit*. The actual value is $M_0 \simeq 1.44 M_\odot$, which requires a fudge factor $\alpha = 0.677$. Remarkably, the mass-radius relation is *inverted* for white dwarfs, *i.e.* radius *decreases* with increasing stellar mass.

The Lane-Emden equation

We've assumed a mass uniform density ρ in our derivation, but this is a significant simplification of the physics. If we assume hydrostatic equilibrium throughout, then for all $r \in [0, R]$ we must have

$$\frac{dp(r)}{dr} = -\frac{GM(r)\rho(r)}{r^2} \quad , \quad \frac{dM(r)}{dr} = 4\pi r^2 \rho(r) \quad . \quad (5.198)$$

Here $M(r)$ is the total mass up to a radius r . To close this system we need the adiabatic equation of state relating pressure to density, which takes the form $p = K\rho^\gamma$ where $\gamma = C_p/C_V$ for ideal gases. This leads to the dimensionless *Lane-Emden equation*,

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left(\xi^2 \frac{d\theta}{d\xi} \right) = -\theta^{1/(\gamma-1)} \quad (5.199)$$

where

$$\theta = \left(\frac{\rho}{\rho_c} \right)^{\gamma-1} \quad , \quad \xi = \frac{r}{b} \quad , \quad b = \sqrt{\frac{\gamma K \rho_c^{\gamma-2}}{4\pi(\gamma-1)G}} \quad , \quad (5.200)$$

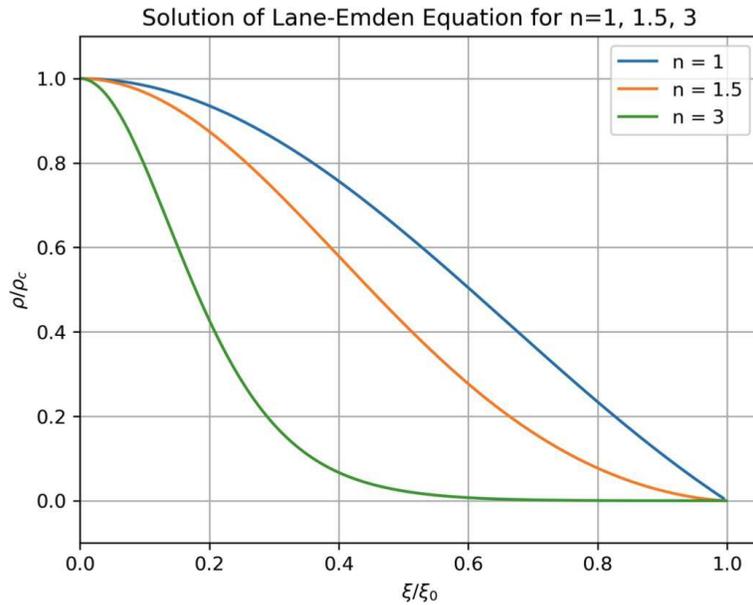


Figure 5.14: Solutions to the Lane-Emden equation for $n = 1$, $n = \frac{3}{2}$, and $n = 3$.

and $\rho_c = \rho(r = 0)$ the central (maximum) density. One conventionally defines $n \equiv 1/(\gamma - 1)$ as the *polytropic index*. For nonrelativistic particles $\gamma = \frac{5}{3}$ ($n = \frac{3}{2}$) while for ultrarelativistic $\gamma = \frac{4}{3}$ ($n = 3$). The radius of the star is then given by $R = b\xi_0$, where $\theta(\xi_0) = 0$. By adjusting the constant α in the simplified derivation one can better approximate the exact results.