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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 (2 $2^{\text {nd }}$ 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, $3^{\text {rd }}$ 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

A noninteracting many-particle quantum Hamiltonian may be written as

$$
\begin{equation*}
\hat{H}=\sum_{\alpha} \varepsilon_{\alpha} \hat{n}_{\alpha} \tag{5.1}
\end{equation*}
$$

where $\hat{n}_{\alpha}$ is the number of particles in the quantum state $\alpha$ with energy $\varepsilon_{\alpha}$. 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 $\hat{n}_{\alpha}$ number operators, and written as $\left|n_{1}, n_{2}, \ldots\right\rangle$. We then have

$$
\begin{equation*}
\hat{n}_{\alpha}|\vec{n}\rangle=n_{\alpha}|\vec{n}\rangle \tag{5.2}
\end{equation*}
$$

and

$$
\begin{equation*}
\hat{H}|\vec{n}\rangle=\sum_{\alpha} n_{\alpha} \varepsilon_{\alpha}|\vec{n}\rangle . \tag{5.3}
\end{equation*}
$$

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

$$
\begin{align*}
\text { bosons : } n_{\alpha} \in\{0,1,2,3, \ldots\}  \tag{5.4}\\
\text { fermions : } n_{\alpha} \in\{0,1\} .
\end{align*}
$$

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 $Z_{N}$ is then

$$
\begin{equation*}
Z_{N}=\sum_{\left\{n_{\alpha}\right\}} e^{-\beta \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha}} \delta_{N, \sum_{\alpha} n_{\alpha}} \tag{5.5}
\end{equation*}
$$

where the sum is over all allowed values of the set $\left\{n_{\alpha}\right\}$, which depends on the statistics of the particles. Bosons satisfy Bose-Einstein (BE) statistics, in which $n_{\alpha} \in\{0,1,2, \ldots\}$. 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

$$
\begin{equation*}
\Xi=\sum_{N} e^{\beta \mu N} Z_{N}=\sum_{\left\{n_{\alpha}\right\}} e^{-\beta \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha}} e^{\beta \mu \sum_{\alpha} n_{\alpha}}=\prod_{\alpha}\left(\sum_{n_{\alpha}} e^{-\beta\left(\varepsilon_{\alpha}-\mu\right) n_{\alpha}}\right) \tag{5.6}
\end{equation*}
$$

Note that the grand partition function $\Xi$ takes the form of a product over contributions from the individual single particle states.

We now perform the single particle sums:

$$
\begin{align*}
& \sum_{n=0}^{\infty} e^{-\beta(\varepsilon-\mu) n}=\frac{1}{1-e^{-\beta(\varepsilon-\mu)}} \quad \text { (bosons) }  \tag{5.7}\\
& \sum_{n=0}^{1} e^{-\beta(\varepsilon-\mu) n}=1+e^{-\beta(\varepsilon-\mu)} \quad \text { (fermions). } \tag{5.8}
\end{align*}
$$

Therefore we have

$$
\begin{align*}
& \Xi_{\mathrm{BE}}=\prod_{\alpha} \frac{1}{1-e^{-\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T}}  \tag{5.9}\\
& \Omega_{\mathrm{BE}}=k_{\mathrm{B}} T \sum_{\alpha} \ln \left(1-e^{-\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T}\right)
\end{align*}
$$

and

$$
\begin{align*}
& \Xi_{\mathrm{FD}}=\prod_{\alpha}\left(1+e^{-\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T}\right) \\
& \Omega_{\mathrm{FD}}=-k_{\mathrm{B}} T \sum_{\alpha} \ln \left(1+e^{-\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T}\right) . \tag{5.10}
\end{align*}
$$

We can combine these expressions into one, writing

$$
\begin{equation*}
\Omega(T, V, \mu)= \pm k_{\mathrm{B}} T \sum_{\alpha} \ln \left(1 \mp e^{-\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T}\right), \tag{5.11}
\end{equation*}
$$

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 $\alpha$ is

$$
\begin{equation*}
\left\langle\hat{n}_{\alpha}\right\rangle=\frac{\partial \Omega}{\partial \varepsilon_{\alpha}}=\frac{1}{e^{\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T} \mp 1} \tag{5.12}
\end{equation*}
$$

and the total particle number is then

$$
\begin{equation*}
N(T, V, \mu)=\sum_{\alpha} \frac{1}{e^{\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T} \mp 1} . \tag{5.13}
\end{equation*}
$$

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

### 5.2.2 Quantum statistics and the Maxwell-Boltzmann limit

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

$$
\begin{equation*}
\hat{H}=\sum_{j=1}^{N} \hat{h}_{j} \tag{5.14}
\end{equation*}
$$

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

$$
\begin{equation*}
Z \stackrel{?}{=} \sum_{\alpha_{1}} \cdots \sum_{\alpha_{N}} e^{-\beta\left(\varepsilon_{\alpha_{1}}+\varepsilon_{\alpha_{2}}+\ldots+\varepsilon_{\alpha_{N}}\right)}=\zeta^{N} \tag{5.15}
\end{equation*}
$$

where $\zeta$ is the single particle partition function, $\zeta=\sum_{\alpha} e^{-\beta \varepsilon_{\alpha}}$. 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 $n_{\alpha}$, which tell us how many particles are in the single-particle state $|\alpha\rangle$. The energy is $E=\sum_{\alpha} n_{\alpha} \varepsilon_{\alpha}$ and the total number of particles is $N=\sum_{\alpha} n_{\alpha}$. That is, each collection of occupation numbers $\left\{n_{\alpha}\right\}$ labels a unique many particle state $\left|\left\{n_{\alpha}\right\}\right\rangle$. In the product $\zeta^{N}$, the collection $\left\{n_{\alpha}\right\}$ 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 $\alpha_{j}$ to arrive at the same collection $\left\{n_{\alpha}\right\}$. This follows from the multinomial theorem,

$$
\begin{equation*}
\left(\sum_{\alpha=1}^{K} x_{\alpha}\right)^{N}=\sum_{n_{1}} \sum_{n_{2}} \cdots \sum_{n_{K}} \frac{N!}{n_{1}!n_{2}!\cdots n_{K}!} x_{1}^{n_{1}} x_{2}^{n_{2}} \cdots x_{K}^{n_{K}} \delta_{N, n_{1}+\ldots+n_{K}} . \tag{5.16}
\end{equation*}
$$

Thus, the correct expression for $Z_{N}$ is

$$
\begin{align*}
Z_{N} & =\sum_{\left\{n_{\alpha}\right\}} e^{-\beta \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha}} \delta_{N, \sum_{\alpha} n_{\alpha}} \\
& =\sum_{\alpha_{1}} \sum_{\alpha_{2}} \cdots \sum_{\alpha_{N}}\left(\frac{\prod_{\alpha} n_{\alpha}!}{N!}\right) e^{-\beta\left(\varepsilon_{\alpha_{1}}+\varepsilon_{\alpha_{2}}+\ldots+\varepsilon_{\alpha_{N}}\right)} . \tag{5.17}
\end{align*}
$$

In the high temperature limit, almost all the $n_{\alpha}$ 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 $\varepsilon_{\alpha}-\mu \gg k_{\mathrm{B}} T$, and consequently

$$
\begin{align*}
\Omega_{\mathrm{BE} / \mathrm{FD}} & = \pm k_{\mathrm{B}} T \sum_{\alpha} \ln \left(1 \mp e^{-\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T}\right) \\
& \approx-k_{\mathrm{B}} T \sum_{\alpha} e^{-\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T} \equiv \Omega_{\mathrm{MB}} \tag{5.18}
\end{align*}
$$

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

$$
\begin{equation*}
\left\langle\hat{n}_{\alpha}\right\rangle=e^{-\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T} . \tag{5.19}
\end{equation*}
$$

### 5.2.3 Single particle density of states

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

$$
\begin{equation*}
g(\varepsilon)=\frac{1}{V} \sum_{\alpha} \delta\left(\varepsilon-\varepsilon_{\alpha}\right) \tag{5.20}
\end{equation*}
$$

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

$$
\begin{equation*}
\Omega(T, V, \mu)= \pm V k_{\mathrm{B}} T \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \ln \left(1 \mp e^{-(\varepsilon-\mu) / k_{\mathrm{B}} T}\right) \tag{5.21}
\end{equation*}
$$

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

$$
\begin{equation*}
g(\varepsilon)=\mathrm{g} \int \frac{d^{d} k}{(2 \pi)^{d}} \delta(\varepsilon-\varepsilon(k)) \tag{5.22}
\end{equation*}
$$

where $\mathrm{g}=2 S+1$ is the spin degeneracy. When the dispersion is isotropic, i.e. $\varepsilon(\boldsymbol{k})=\varepsilon(k)$ with $k=|\boldsymbol{k}|$, we can write

$$
\begin{equation*}
g(\varepsilon) d \varepsilon=\mathrm{g} \frac{d^{d} k}{(2 \pi)^{d}}=\frac{\mathrm{g} \Omega_{d}}{(2 \pi)^{d}} k^{d-1} d k \quad \Rightarrow \quad g(\varepsilon)=\frac{\mathrm{g} \Omega_{d}}{(2 \pi)^{d}} \frac{k^{d-1}}{d \varepsilon / d k} . \tag{5.23}
\end{equation*}
$$

Examples:

$$
\begin{equation*}
g_{d=1}(\varepsilon)=\frac{\mathrm{g}}{\pi} \frac{d k}{d \varepsilon} \quad, \quad g_{d=2}(\varepsilon)=\frac{\mathrm{g}}{2 \pi} k \frac{d k}{d \varepsilon} \quad, \quad g_{d=3}(\varepsilon)=\frac{\mathrm{g}}{2 \pi^{2}} k^{2} \frac{d k}{d \varepsilon} \tag{5.24}
\end{equation*}
$$

For a spin- $S$ particle with ballistic dispersion $\varepsilon(\boldsymbol{k})=\hbar^{2} \boldsymbol{k}^{2} / 2 m$, we have $\mathrm{g}=2 S+1$ and

$$
\begin{equation*}
g(\varepsilon)=\frac{2 S+1}{\Gamma(d / 2)}\left(\frac{m}{2 \pi \hbar^{2}}\right)^{d / 2} \varepsilon^{(d-2) / 2} \Theta(\varepsilon) \tag{5.25}
\end{equation*}
$$

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 we are assuming a box of volume $V$ but we are ignoring the quantization of kinetic energy, and assuming that the difference between successive quantized single particle energy eigenvalues is negligible so that $g(\varepsilon)$ can be replaced by the average in the above expression. Note that

$$
\begin{equation*}
n(\varepsilon, T, \mu)=\frac{1}{e^{(\varepsilon-\mu) / k_{\mathrm{B}} T} \mp 1} . \tag{5.26}
\end{equation*}
$$

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

$$
\begin{equation*}
N(T, V, \mu)=V \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \frac{1}{e^{(\varepsilon-\mu) / k_{\mathrm{B}} T} \mp 1} \tag{5.27}
\end{equation*}
$$

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

### 5.3 Quantum Ideal Gases : Low Density Expansions

### 5.3.1 Expansion in powers of the fugacity

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

$$
\begin{equation*}
n(T, z)=\int_{-\infty}^{\infty} d \varepsilon \frac{g(\varepsilon)}{z^{-1} e^{\varepsilon / k_{\mathrm{B}} T} \mp 1}=\sum_{j=1}^{\infty} C_{j}(T) z^{j} \tag{5.28}
\end{equation*}
$$

where $z=\exp \left(\mu / k_{\mathrm{B}} T\right)$ is the fugacity. Taylor's theorem tells us that

$$
\begin{equation*}
\frac{1}{z^{-1} e^{\varepsilon / k_{\mathrm{B}} T} \mp 1}=\frac{z e^{-\varepsilon / k_{\mathrm{B}} T}}{1 \mp z e^{-\varepsilon / k_{\mathrm{B}} T}}=\sum_{j=1}^{\infty}( \pm 1)^{j-1} z^{j} e^{-j \varepsilon / k_{\mathrm{B}} T} \tag{5.29}
\end{equation*}
$$

and therefore

$$
\begin{equation*}
C_{j}(T)=( \pm 1)^{j-1} \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) e^{-j \varepsilon / k_{\mathrm{B}} T} \tag{5.30}
\end{equation*}
$$

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

$$
\begin{equation*}
p(T, z)=\mp k_{\mathrm{B}} T \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \ln \left(1 \mp z e^{-\varepsilon / k_{\mathrm{B}} T}\right)=k_{\mathrm{B}} T \sum_{j=1}^{\infty} j^{-1} C_{j}(T) z^{j} \tag{5.31}
\end{equation*}
$$

### 5.3.2 Virial expansion of the equation of state

Eqns. 5.28 and 5.31 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. 5.31 to obtain an equation of state $p=p(T, n)$ of the form

$$
\begin{equation*}
p(T, n)=n k_{\mathrm{B}} T\left(1+B_{2}(T) n+B_{3}(T) n^{2}+\ldots\right) \tag{5.32}
\end{equation*}
$$

where $B_{n}$ is the $n^{\text {th }}$ virial coefficient. 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 $n=C_{1} z+\mathcal{O}\left(z^{2}\right)$ and $p=k_{\mathrm{B}} T C_{1} z+\mathcal{O}\left(z^{2}\right)$. Dividing the second of these equations by the first yields $p=n k_{\mathrm{B}} T+\mathcal{O}\left(n^{2}\right)$, which is the ideal gas law. Note that $z=n / C_{1}+\mathcal{O}\left(n^{2}\right)$ can formally be written as a power series in $n$.

While it is easy to see that $B_{1}=1$, which we already showed above, there is no closed form expression for $B_{n}$ for general $n$. The first two nontrivial virial coefficients are not so difficult to derive, however:

$$
\begin{equation*}
B_{2}=-\frac{C_{2}}{2 C_{1}^{2}} \quad, \quad B_{3}=\frac{C_{2}^{2}}{C_{1}^{4}}-\frac{2 C_{3}}{C_{1}^{3}} \tag{5.33}
\end{equation*}
$$

It is easy to see that, in general, $B_{j}^{\mathrm{F}}=(-1)^{j-1} B_{j}^{\mathrm{B}}$, 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,

$$
\begin{equation*}
\left(p+\frac{a N^{2}}{V^{2}}\right)(V-N b)=N k_{\mathrm{B}} T . \tag{5.34}
\end{equation*}
$$

This may be recast as

$$
\begin{align*}
p & =\frac{n k_{\mathrm{B}} T}{1-b n}-a n^{2}  \tag{5.35}\\
& =n k_{\mathrm{B}} T+\left(b k_{\mathrm{B}} T-a\right) n^{2}+k_{\mathrm{B}} T b^{2} n^{3}+k_{\mathrm{B}} T b^{3} n^{4}+\ldots,
\end{align*}
$$

where $n=N / V$. Thus, for the van der Waals system, we have $B_{2}=\left(b k_{\mathrm{B}} T-a\right)$ and $B_{k}=k_{\mathrm{B}} T b^{k-1}$ for all $k \geq 3$.

### 5.3.3 Ballistic dispersion

For the ballistic dispersion $\varepsilon(k)=\hbar^{2} k^{2} / 2 m$ we computed the density of states in eqn. 5.25. Substituting the result for $g(\varepsilon)$ into eqn. 5.30 and defining $t \equiv \varepsilon / k_{\mathrm{B}} T$, we find

$$
\begin{equation*}
C_{j}(T)=\frac{\mathrm{g} \lambda_{T}^{-d}}{\Gamma(d / 2)} \int_{0}^{\infty} d t t^{\frac{d}{2}-1} e^{-j t}=\mathrm{g} \lambda_{T}^{-d} j^{-d / 2}, \tag{5.36}
\end{equation*}
$$

where $\lambda_{T}=\sqrt{2 \pi \hbar^{2} / m k_{\mathrm{B}} T}$ is the thermal wavelength. Thus, from eqn. 5.33, we have

$$
\begin{align*}
& B_{2}(T)=\mp 2^{-\left(\frac{d}{2}+1\right)} \cdot \mathrm{g}^{-1} \lambda_{T}^{d} \\
& B_{3}(T)=\left(2^{-(d+1)}-3^{-\left(\frac{d}{2}+1\right)}\right) \cdot 2 \mathrm{~g}^{-2} \lambda_{T}^{2 d} \tag{5.37}
\end{align*}
$$

Note that $B_{2}(T)$ is negative for bosons and positive for fermions. This is because bosons have a tendency to bunch and under certain circumstances may exhibit a phenomenon known as Bose-Einstein condensation (BEC). Fermions, on the other hand, obey the Pauli principle, which results in an extra positive correction to the pressure in the low density limit.

## Polylogarithms

We may also write

$$
\begin{equation*}
n(T, z)= \pm \mathrm{g} \lambda_{T}^{-d} \operatorname{Li}_{\frac{d}{2}}( \pm z) \tag{5.38}
\end{equation*}
$$

and

$$
\begin{equation*}
p(T, z)= \pm \mathrm{g} k_{\mathrm{B}} T \lambda_{T}^{-d} \operatorname{Li}_{\frac{d}{2}+1}( \pm z) \tag{5.39}
\end{equation*}
$$

where

$$
\begin{equation*}
\operatorname{Li}_{s}(z) \equiv \sum_{n=1}^{\infty} \frac{z^{n}}{n^{s}} \tag{5.40}
\end{equation*}
$$

is the polylogarithm function ${ }^{1}$. Note that $\mathrm{Li}_{s}(z)$ obeys a recursion relation in its index, viz.

$$
\begin{equation*}
z \frac{\partial}{\partial z} \operatorname{Li}_{s}(z)=\operatorname{Li}_{s-1}(z) \tag{5.41}
\end{equation*}
$$

and that

$$
\begin{equation*}
\operatorname{Li}_{s}(1)=\sum_{n=1}^{\infty} \frac{1}{n^{s}}=\zeta(s) \tag{5.42}
\end{equation*}
$$

To evaluate $\operatorname{Li}_{s}(z)$ for $|z| \ll 1$, we use the series expansion in eqn. 5.40. For $|z| \gg 1$, use $^{2}$

$$
\begin{equation*}
\mathrm{Li}_{s}(z)=\sum_{j=0}^{\infty}(-1)^{j}\left(1-2^{1-2 j}\right) \frac{(2 \pi)^{2 j} B_{2 j}}{(2 j)!} \frac{[\ln (-z)]^{s-2 j}}{\Gamma(1+s-2 j)} \tag{5.43}
\end{equation*}
$$

where $B_{2 j}$ is a Bernoulli number, with $B_{0}=1, B_{2}=\frac{1}{6}, B_{4}=-\frac{1}{30}, B_{6}=\frac{1}{42}$, etc. For intermediate values of $z$, where $|\ln z|<2 \pi$, one has ${ }^{3}$

$$
\begin{equation*}
\mathrm{Li}_{s}(z)=\Gamma(1-s)(-\ln z)^{s-1}+\sum_{k=0}^{\infty} \frac{\zeta(s-k)}{k!}(\ln z)^{k} \tag{5.44}
\end{equation*}
$$

where $s \notin\{1,2,3, \ldots\}$.

### 5.4 Entropy and Counting States

Suppose we are to partition $N$ particles among $J$ possible distinct single particle states. How many ways $\Omega$ are there of accomplishing this task? The answer depends on the statistics of the particles. If the particles are fermions, the answer is easy: $\Omega_{\mathrm{FD}}=\binom{J}{N}$. For bosons, the number of possible partitions can be evaluated via the following argument. Imagine that we line up all the $N$ particles in a row, and we place $J-1$ barriers among the particles, as shown below in fig. 5.1. The number of partitions is then the total number of ways of placing the $N$ particles among these $N+J-1$ objects (particles plus barriers), hence we have $\Omega_{\mathrm{BE}}=\left({ }_{N}^{N+J-1}\right)$. For Maxwell-Boltzmann statistics, we have $\Omega_{\mathrm{MB}}=J^{N} / N$ ! and for distinguishable particles, $\Omega_{\text {dist }}=J^{N}$. Note that $\Omega_{\mathrm{MB}}$ is not necessarily an integer, so MaxwellBoltzmann statistics does not represent any actual state counting. Rather, it manifests itself as a common limit of the Bose and Fermi distributions, as we have seen and shall see again shortly.

[^0]Figure 5.1: Partitioning $N$ bosons into $J$ possible states ( $N=14$ and $J=5$ shown). The $N$ black dots represent bosons, while the $J-1$ white dots represent markers separating the different single particle populations. Here $n_{1}=3, n_{2}=1, n_{3}=4, n_{4}=2$, and $n_{5}=4$.

The entropy in each case is simply $S=k_{\mathrm{B}} \ln \Omega$. We assume $N \gg 1$ and $J \gg 1$, with $n \equiv N / J$ finite. Then using Stirling's approximation, $\ln (K!)=K \ln K-K+\mathcal{O}(\ln K)$, we have

$$
\begin{align*}
& S_{\mathrm{MB}}=-J k_{\mathrm{B}} n \ln n \\
& S_{\mathrm{BE}}=-J k_{\mathrm{B}}[n \ln n-(1+n) \ln (1+n)]  \tag{5.45}\\
& S_{\mathrm{FD}}=-J k_{\mathrm{B}}[n \ln n+(1-n) \ln (1-n)] .
\end{align*}
$$

In the Maxwell-Boltzmann limit we gave $n \ll 1$, and all three expressions agree. Note that

$$
\begin{equation*}
\left(\frac{\partial S_{\mathrm{MB}}}{\partial N}\right)_{J}=-k_{\mathrm{B}}(1+\ln n) \quad, \quad\left(\frac{\partial S_{\mathrm{BE}}}{\partial N}\right)_{J}=k_{\mathrm{B}} \ln \left(n^{-1}+1\right) \quad, \quad\left(\frac{\partial S_{\mathrm{FD}}}{\partial N}\right)_{J}=k_{\mathrm{B}} \ln \left(n^{-1}-1\right) \tag{5.46}
\end{equation*}
$$

Now let's imagine grouping the single particle spectrum into intervals of $J$ consecutive energy states. If $J$ is finite and the spectrum is continuous and we are in the thermodynamic limit, then these states will all be degenerate. Therefore, using $\alpha$ as a label for the energies, we have that the grand potential $\Omega=E-T S-\mu N$ is given in each case by

$$
\begin{align*}
& \Omega_{\mathrm{MB}}=J \sum_{\alpha}\left[\left(\varepsilon_{\alpha}-\mu\right) n_{\alpha}+k_{\mathrm{B}} T n_{\alpha} \ln n_{\alpha}\right] \\
& \Omega_{\mathrm{BE}}=J \sum_{\alpha}\left[\left(\varepsilon_{\alpha}-\mu\right) n_{\alpha}+k_{\mathrm{B}} T n_{\alpha} \ln n_{\alpha}-k_{\mathrm{B}} T\left(1+n_{\alpha}\right) \ln \left(1+n_{\alpha}\right)\right]  \tag{5.47}\\
& \Omega_{\mathrm{FD}}=J \sum_{\alpha}\left[\left(\varepsilon_{\alpha}-\mu\right) n_{\alpha}+k_{\mathrm{B}} T n_{\alpha} \ln n_{\alpha}+k_{\mathrm{B}} T\left(1-n_{\alpha}\right) \ln \left(1-n_{\alpha}\right)\right] .
\end{align*}
$$

Now - lo and behold! - treating $\Omega$ as a function of the distribution $\left\{n_{\alpha}\right\}$ and extremizing in each case, subject to the constraint of total particle number $N=J \sum_{\alpha} n_{\alpha}$, one obtains the Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac distributions, respectively:

$$
\frac{\delta}{\delta n_{\alpha}}\left(\Omega-\lambda J \sum_{\alpha^{\prime}} n_{\alpha^{\prime}}\right)=0 \Rightarrow\left\{\begin{array}{l}
n_{\alpha}^{\mathrm{MB}}=e^{\left(\mu-\varepsilon_{\alpha}\right) / k_{\mathrm{B}} T}  \tag{5.48}\\
n_{\alpha}^{\mathrm{BE}}=\left[e^{\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T}-1\right]^{-1} \\
n_{\alpha}^{\mathrm{FD}}=\left[e^{\left(\varepsilon_{\alpha}-\mu\right) / k_{\mathrm{B}} T}+1\right]^{-1}
\end{array} .\right.
$$

As long as $J$ is finite, so the states in each block all remain at the same energy, the results are independent of $J$. In using Stirling's formula we have assumed $J \gg 1$, though. What is the average spacing between consecutive energy levels? For a single particle in a box, with periodic boundary conditions, we have $\varepsilon(\boldsymbol{k})=\hbar^{2} \boldsymbol{k}^{2} / 2 m$ and thus

$$
\begin{equation*}
\delta \varepsilon(\boldsymbol{k})=\frac{\hbar^{2}}{m}\left(k_{x} \delta k_{x}+k_{y} \delta k_{y}+k_{z} \delta k_{z}\right) \tag{5.49}
\end{equation*}
$$

where $\delta k_{\alpha}=2 \pi / L_{\alpha}(\alpha \in\{1, \ldots, d\}, d$ being the dimension of space). Thus, the level spacings are proportional to the inverse linear dimensions of the system, which is extremely small and we are justified in using Stirling's approximation.

### 5.5 Photon Statistics

### 5.5.1 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

$$
\begin{equation*}
\mu=\left(\frac{\partial F}{\partial N}\right)_{T . V}=0 \tag{5.50}
\end{equation*}
$$

The number distribution, from eqn. 5.12, is then

$$
\begin{equation*}
n(\varepsilon)=\frac{1}{e^{\beta \varepsilon}-1} \tag{5.51}
\end{equation*}
$$

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

$$
\begin{equation*}
\Omega(T, V)=V k_{\mathrm{B}} T \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \ln \left(1-e^{-\varepsilon / k_{\mathrm{B}} T}\right) \tag{5.52}
\end{equation*}
$$

where $g(\varepsilon)$ is the density of states per unit volume.
Suppose the particle dispersion is $\varepsilon(\boldsymbol{k})=A|\boldsymbol{k}|^{\sigma}$. We can compute the density of states $g(\varepsilon)$ :

$$
\begin{equation*}
g(\varepsilon)=\frac{\mathrm{g} \Omega_{d}}{(2 \pi)^{d}} \frac{k^{d-1}}{d \varepsilon / d k}=\frac{C_{d, \sigma}}{A^{d / \sigma}} \varepsilon^{\frac{d}{\sigma}-1} \Theta(\varepsilon) \tag{5.53}
\end{equation*}
$$

where

$$
\begin{equation*}
C_{d, \sigma}=\frac{\mathrm{g} \Omega_{d}}{(2 \pi)^{d} \sigma} . \tag{5.54}
\end{equation*}
$$

is a dimensionless constant and g is the internal degeneracy of the state at wavevector $\boldsymbol{k}$. Recall that $\Omega_{d}=2 \pi^{d / 2} / \Gamma(d / 2)$ for the solid angle in $d$ dimensions. The step function $\Theta(\varepsilon)$ reminds us that the energy spectrum is bounded from below by $\varepsilon=0$, i.e. there are no negative energy states.
For the photon, we have $\varepsilon(\boldsymbol{k})=\hbar c k$, so $\sigma=1$ and $A=\hbar c$, whence, with $C_{d} \equiv C_{d, \sigma=1}$,

$$
\begin{equation*}
g(\varepsilon)=\frac{C_{d}}{(h c)^{d}} \varepsilon^{d-1} \Theta(\varepsilon) \quad, \quad C_{d}=\frac{2 \mathrm{~g} \pi^{d / 2}}{\Gamma(d / 2)} \tag{5.55}
\end{equation*}
$$

In $d=3$ dimensions the degeneracy is $\mathrm{g}=2$, i.e. the number of independent polarization states. The
pressure $p(T)$ is then obtained using $\Omega=-p V$. We have

$$
\begin{align*}
p(T) & =-k_{\mathrm{B}} T \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \ln \left(1-e^{-\varepsilon / k_{\mathrm{B}} T}\right) \\
& =-\frac{C_{d}}{(h c)^{d}} k_{\mathrm{B}} T \int_{0}^{\infty} d \varepsilon \varepsilon^{d-1} \ln \left(1-e^{-\varepsilon / k_{\mathrm{B}} T}\right)  \tag{5.56}\\
& =-\frac{C_{d}}{(h c)^{d}}\left(k_{\mathrm{B}} T\right)^{d+1} \int_{0}^{\infty} d t t^{d-1} \ln \left(1-e^{-t}\right) .
\end{align*}
$$

We can make some progress with the dimensionless integral:

$$
\begin{equation*}
\mathcal{I}_{d} \equiv-\int_{0}^{\infty} d t t^{d-1} \ln \left(1-e^{-t}\right)=\sum_{n=1}^{\infty} \frac{1}{n} \int_{0}^{\infty} d t t^{d-1} e^{-n t}=\Gamma(d) \sum_{n=1}^{\infty} \frac{1}{n^{d+1}}=\Gamma(d) \zeta(d+1) \tag{5.57}
\end{equation*}
$$

We also may invoke a result from the mathematics of the gamma function known as the doubling formula,

$$
\begin{equation*}
\Gamma(z)=\frac{2^{z-1}}{\sqrt{\pi}} \Gamma\left(\frac{z}{2}\right) \Gamma\left(\frac{z+1}{2}\right) \tag{5.58}
\end{equation*}
$$

and define

$$
\begin{equation*}
B_{d} \equiv \Gamma(d) \cdot \frac{C_{d}}{(2 \pi)^{d}}=\mathrm{g} \pi^{-(d+1) / 2} \Gamma\left(\frac{d+1}{2}\right) . \tag{5.59}
\end{equation*}
$$

Putting it all together, we find

$$
\begin{equation*}
p(T)=\zeta(d+1) B_{d} \frac{\left(k_{\mathrm{B}} T\right)^{d+1}}{(\hbar c)^{d}} \tag{5.60}
\end{equation*}
$$

as well as

$$
\begin{equation*}
n(T)=\int_{-\infty}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{\varepsilon / k_{\mathrm{B}} T}-1}=\zeta(d) B_{d} \frac{\left(k_{\mathrm{B}} T\right)^{d}}{(\hbar c)^{d}} . \tag{5.61}
\end{equation*}
$$

Dividing these two equations, we obtain the equation of state

$$
\begin{equation*}
p=\frac{\zeta(d+1)}{\zeta(d)} n k_{\mathrm{B}} T . \tag{5.62}
\end{equation*}
$$

For photons in $d=3$ dimensions, we have $\mathrm{g}=2$ and $B_{d=3}=2 \pi^{-2}$, thus

$$
\begin{equation*}
n(T)=\frac{2 \zeta(3)}{\pi^{2}} \frac{\left(k_{\mathrm{B}} T\right)^{3}}{(\hbar c)^{3}} \quad, \quad p(T)=\frac{2 \zeta(4)}{\pi^{2}} \frac{\left(k_{\mathrm{B}} T\right)^{4}}{(\hbar c)^{3}} \tag{5.63}
\end{equation*}
$$

It turns out that $\zeta(4)=\frac{\pi^{4}}{90}$. Note that $\hbar c / k_{\mathrm{B}}=0.22855 \mathrm{~cm} \cdot \mathrm{~K}$, so

$$
\begin{equation*}
\frac{k_{\mathrm{B}} T}{\hbar c}=4.3755 T[\mathrm{~K}] \mathrm{cm}^{-1} \quad \Longrightarrow \quad n(T)=20.405 \times T^{3}\left[\mathrm{~K}^{3}\right] \mathrm{cm}^{-3} \tag{5.64}
\end{equation*}
$$

To find the entropy, we use Gibbs-Duhem:

$$
\begin{equation*}
d \mu=0=-s d T+v d p \quad \Longrightarrow \quad s=v \frac{d p}{d T} \tag{5.65}
\end{equation*}
$$

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

$$
\begin{equation*}
s(T)=(d+1) \frac{\zeta(d+1)}{\zeta(d)} k_{\mathrm{B}} . \tag{5.66}
\end{equation*}
$$

The entropy per particle is constant. The internal energy is

$$
\begin{equation*}
E=-\frac{\partial \ln \Xi}{\partial \beta}=-\frac{\partial}{\partial \beta}(\beta p V)=d p V \tag{5.67}
\end{equation*}
$$

and hence the energy per particle is

$$
\begin{equation*}
\varepsilon=\frac{E}{N}=d p v=\frac{d \zeta(d+1)}{\zeta(d)} k_{\mathrm{B}} T . \tag{5.68}
\end{equation*}
$$

### 5.5.2 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 $\lambda$. The cavity modes of the electromagnetic radiation have quantized wavevectors, even within classical electromagnetic theory, given by

$$
\begin{equation*}
\boldsymbol{k}=\left(\frac{2 \pi n_{x}}{L_{x}}, \frac{2 \pi n_{y}}{L_{y}}, \frac{2 \pi n_{z}}{L_{z}}\right) . \tag{5.69}
\end{equation*}
$$

Since the energy for a given mode is $\varepsilon(\boldsymbol{k})=\hbar c|\boldsymbol{k}|$, 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,

$$
\begin{equation*}
V\left(\frac{\partial E}{\partial V}\right)_{S}=\lambda\left(\frac{\partial E}{\partial \lambda}\right)_{S}=-\frac{1}{3} E \tag{5.70}
\end{equation*}
$$

Thus,

$$
\begin{equation*}
p=-\left(\frac{\partial E}{\partial V}\right)_{S}=\frac{E}{3 V} \tag{5.71}
\end{equation*}
$$

as we found in eqn. 5.67. Since $E=E(T, V)$ is extensive, we must have $p=p(T)$ alone.
2. Since $p=p(T)$ alone, we have

$$
\begin{equation*}
\left(\frac{\partial E}{\partial V}\right)_{T}=\left(\frac{\partial E}{\partial V}\right)_{p}=3 p=T\left(\frac{\partial p}{\partial T}\right)_{V}-p \tag{5.72}
\end{equation*}
$$

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 $d E=T d S-p d V$. Thus,

$$
\begin{equation*}
T \frac{d p}{d T}=4 p \quad \Longrightarrow \quad p(T)=A T^{4} \tag{5.73}
\end{equation*}
$$

where $A$ is a constant. Thus, we recover the temperature dependence found microscopically in eqn. 5.60.
3. Given an energy density $E / V$, the differential energy flux emitted in a direction $\theta$ relative to a surface normal is

$$
\begin{equation*}
d j_{\varepsilon}=c \cdot \frac{E}{V} \cdot \cos \theta \cdot \frac{d \Omega}{4 \pi} \tag{5.74}
\end{equation*}
$$

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

$$
\begin{equation*}
\frac{d P}{d A}=\frac{c E}{4 \pi V} \int_{0}^{\pi / 2} d \theta \int_{0}^{2 \pi} d \phi \sin \theta \cdot \cos \theta=\frac{c E}{4 V}=\frac{3}{4} c p(T) \equiv \sigma T^{4} \tag{5.75}
\end{equation*}
$$

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

$$
\begin{equation*}
\sigma=\frac{\pi^{2} k_{\mathrm{B}}^{4}}{60 c^{2} \hbar^{3}}=5.67 \times 10^{-8} \frac{\mathrm{~W}}{\mathrm{~m}^{2} \mathrm{~K}^{4}} \tag{5.76}
\end{equation*}
$$

is Stefan's constant.

### 5.5.3 Surface temperature of the earth

We derived the result $P=\sigma T^{4} \cdot A$ where $\sigma=5.67 \times 10^{-8} \mathrm{~W} / \mathrm{m}^{2} \mathrm{~K}^{4}$ 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 $R_{\odot}=6.96 \times 10^{8} \mathrm{~m}$, the radius of the earth $R_{\mathrm{e}}=6.38 \times 10^{6} \mathrm{~m}$, and the radius of the earth's orbit $a_{\mathrm{e}}=1.50 \times 10^{11} \mathrm{~m}$. Let's assume that the earth has achieved a steady state temperature of $T_{\mathrm{e}}$. We balance the total power incident upon the earth with the power radiated by the earth. The power incident upon the earth is

$$
\begin{equation*}
P_{\text {incident }}=\frac{\pi R_{\mathrm{e}}^{2}}{4 \pi a_{\mathrm{e}}^{2}} \cdot \sigma T_{\odot}^{4} \cdot 4 \pi R_{\odot}^{2}=\frac{R_{\mathrm{e}}^{2} R_{\odot}^{2}}{a_{\mathrm{e}}^{2}} \cdot \pi \sigma T_{\odot}^{4} . \tag{5.77}
\end{equation*}
$$

The power radiated by the earth is

$$
\begin{equation*}
P_{\text {radiated }}=\sigma T_{\mathrm{e}}^{4} \cdot 4 \pi R_{\mathrm{e}}^{2} \tag{5.78}
\end{equation*}
$$

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

$$
\begin{equation*}
T_{\mathrm{e}}=\left(\frac{R_{\odot}}{2 a_{\mathrm{e}}}\right)^{1 / 2} T_{\odot} \tag{5.79}
\end{equation*}
$$



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

Thus, we find $T_{\mathrm{e}}=0.04817 T_{\odot}$, and with $T_{\odot}=5780 \mathrm{~K}$, we obtain $T_{\mathrm{e}}=278.4 \mathrm{~K}$. The mean surface temperature of the earth is $\bar{T}_{\mathrm{e}}=287 \mathrm{~K}$, 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.

### 5.5.4 Distribution of blackbody radiation

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

$$
\begin{equation*}
\mathcal{N}(\nu, T) d \nu=\frac{2 V}{8 \pi^{3}} \cdot \frac{d^{3} k}{e^{\hbar c k / k_{\mathrm{B}} T}-1}=\frac{V}{\pi^{2}} \cdot \frac{k^{2} d k}{e^{\hbar c k / k_{\mathrm{B}} T}-1} . \tag{5.80}
\end{equation*}
$$

We therefore have

$$
\begin{equation*}
\mathcal{N}(\nu, T)=\frac{8 \pi V}{c^{3}} \cdot \frac{\nu^{2}}{e^{h \nu / k_{\mathrm{B}} T}-1} \tag{5.81}
\end{equation*}
$$

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

$$
\begin{equation*}
\mathcal{E}(\nu, T)=\frac{8 \pi h V}{c^{3}} \cdot \frac{\nu^{3}}{e^{h \nu / k_{\mathrm{B}} T}-1} . \tag{5.82}
\end{equation*}
$$

Note what happens if Planck's constant $h$ vanishes, as it does in the classical limit. The denominator can then be written

$$
\begin{equation*}
e^{h \nu / k_{\mathrm{B}} T}-1=\frac{h \nu}{k_{\mathrm{B}} T}+\mathcal{O}\left(h^{2}\right) \tag{5.83}
\end{equation*}
$$

and

$$
\begin{equation*}
\mathcal{E}_{\mathrm{CL}}(\nu, T)=\lim _{h \rightarrow 0} \mathcal{E}(\nu)=V \cdot \frac{8 \pi k_{\mathrm{B}} T}{c^{3}} \nu^{2} . \tag{5.84}
\end{equation*}
$$

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 $\nu$ part of the integral, which in the optical spectrum is the ultraviolet portion. With quantization, the Bose-Einstein factor imposes an effective ultraviolet cutoff $k_{\mathrm{B}} T / h$ on the frequency integral, and the total energy, as we found above, is finite:

$$
\begin{equation*}
E(T)=\int_{0}^{\infty} d \nu \mathcal{E}(\nu)=3 p V=V \cdot \frac{\pi^{2}}{15} \frac{\left(k_{\mathrm{B}} T\right)^{4}}{(\hbar c)^{3}} \tag{5.85}
\end{equation*}
$$

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

$$
\begin{equation*}
\rho_{\varepsilon}(\nu, T) \equiv \frac{\mathcal{E}(\nu, T)}{E(T)}=\frac{15}{\pi^{4}} \frac{h}{k_{\mathrm{B}} T} \frac{\left(h \nu / k_{\mathrm{B}} T\right)^{3}}{e^{h \nu / k_{\mathrm{B}} T}-1} \tag{5.86}
\end{equation*}
$$

so that $\rho_{\varepsilon}(\nu, T) d \nu$ is the fraction of the electromagnetic energy, under equilibrium conditions, between frequencies $\nu$ and $\nu+d \nu$, i.e. $\int_{0}^{\infty} d \nu \rho_{\varepsilon}(\nu, T)=1$. In fig. 5.2 we plot this in fig. 5.2 for three different temperatures. The maximum occurs when $s \equiv h \nu / k_{\mathrm{B}} T$ satisfies

$$
\begin{equation*}
\frac{d}{d s}\left(\frac{s^{3}}{e^{s}-1}\right)=0 \quad \Longrightarrow \quad \frac{s}{1-e^{-s}}=3 \quad \Longrightarrow \quad s=2.82144 \tag{5.87}
\end{equation*}
$$

### 5.5.5 What if the sun emitted ferromagnetic spin waves?

We saw in eqn. 5.74 that the power emitted per unit surface area by a blackbody is $\sigma T^{4}$. The power law here follows from the ultrarelativistic dispersion $\varepsilon=\hbar c k$ of the photons. Suppose that we replace this dispersion with the general form $\varepsilon=\varepsilon(\boldsymbol{k})$. Now consider a large box in equilibrium at temperature $T$. The energy current incident on a differential area $d A$ of surface normal to $\hat{z}$ is

$$
\begin{equation*}
d P=d A \cdot \int \frac{d^{3} k}{(2 \pi)^{3}} \Theta(\cos \theta) \cdot \varepsilon(\boldsymbol{k}) \cdot \frac{1}{\hbar} \frac{\partial \varepsilon(\boldsymbol{k})}{\partial k_{z}} \cdot \frac{1}{e^{\varepsilon(\boldsymbol{k}) / k_{\mathrm{B}} T}-1} . \tag{5.88}
\end{equation*}
$$

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

$$
\begin{equation*}
\frac{d P}{d A}=\widetilde{\sigma} T^{2+2 / \alpha} \tag{5.89}
\end{equation*}
$$

where

$$
\begin{equation*}
\widetilde{\sigma}=\zeta(2+2 / \alpha) \Gamma(2+2 / \alpha) \cdot \frac{\mathrm{g} k_{\mathrm{B}}^{2+2 / \alpha}}{8 \pi^{2} \hbar C^{2 / \alpha}} \tag{5.90}
\end{equation*}
$$

One can check that for $\mathrm{g}=2, C=\hbar c$, and $\alpha=1$ that this result reduces to that of eqn. 5.76. For the case of ferromagnetic spin waves, $\alpha=2$, in which case $\frac{d P}{d A}=\widetilde{\sigma} T^{3}$. What would be the surface temperature of the earth if the photon dispersion were $\varepsilon=C k^{\alpha}$ ? Generalizing the results from $\S 5.5 .3$, we find

$$
\begin{equation*}
T_{\mathrm{e}}=\left(\frac{R_{\odot}}{2 a_{\mathrm{e}}}\right)^{\frac{\alpha}{1+\alpha}} T_{\odot} \tag{5.91}
\end{equation*}
$$

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

### 5.6 Lattice Vibrations : Einstein and Debye Models

Crystalline solids support propagating waves called phonons, which are quantized vibrations of the lattice. Recall that the quantum mechanical Hamiltonian for a single harmonic oscillator, $\hat{H}=\frac{p^{2}}{2 m}+$ $\frac{1}{2} m \omega_{0}^{2} q^{2}$, may be written as $\hat{H}=\hbar \omega_{0}\left(a^{\dagger} a+\frac{1}{2}\right)$, where $a$ and $a^{\dagger}$ are 'ladder operators' satisfying commutation relations $\left[a, a^{\dagger}\right]=1$.

### 5.6.1 One-dimensional chain

Consider the linear chain of masses and springs depicted in fig. 5.3. We assume that our system consists of $N$ mass points on a large ring of circumference $L$. In equilibrium, the masses are spaced evenly by a distance $b=L / N$. That is, $x_{n}^{0}=n b$ is the equilibrium position of particle $n$. We define $u_{n}=x_{n}-x_{n}^{0}$ to be the difference between the position of mass $n$ and The Hamiltonian is then

$$
\begin{align*}
\hat{H} & =\sum_{n}\left[\frac{p_{n}^{2}}{2 m}+\frac{1}{2} \kappa\left(x_{n+1}-x_{n}-a\right)^{2}\right] \\
& =\sum_{n}\left[\frac{p_{n}^{2}}{2 m}+\frac{1}{2} \kappa\left(u_{n+1}-u_{n}\right)^{2}\right]+\frac{1}{2} N \kappa(b-a)^{2}, \tag{5.92}
\end{align*}
$$

where $a$ is the unstretched length of each spring, $m$ is the mass of each mass point, $\kappa$ is the force constant of each spring, and $N$ is the total number of mass points. If $b \neq a$ the springs are under tension in equilibrium, but as we see this only leads to an additive constant in the Hamiltonian, and hence does not enter the equations of motion.

The classical equations of motion are

$$
\begin{align*}
& \dot{u}_{n}=\frac{\partial \hat{H}}{\partial p_{n}}=\frac{p_{n}}{m} \\
& \dot{p}_{n}=-\frac{\partial \hat{H}}{\partial u_{n}}=\kappa\left(u_{n+1}+u_{n-1}-2 u_{n}\right) \tag{5.93}
\end{align*}
$$

Taking the time derivative of the first equation and substituting into the second yields

$$
\begin{equation*}
\ddot{u}_{n}=\frac{\kappa}{m}\left(u_{n+1}+u_{n-1}-2 u_{n}\right) . \tag{5.94}
\end{equation*}
$$

We now write

$$
\begin{equation*}
u_{n}=\frac{1}{\sqrt{N}} \sum_{k} \tilde{u}_{k} e^{i k n a} \tag{5.95}
\end{equation*}
$$



Figure 5.3: A linear chain of masses and springs. The black circles represent the equilibrium positions of the masses. The displacement of mass $n$ relative to its equilibrium value is $u_{n}$.
where periodicity $u_{N+n}=u_{n}$ requires that the $k$ values are quantized so that $e^{i k N a}=1$, i.e. $k=2 \pi j / N a$ where $j \in\{0,1, \ldots, N-1\}$. The inverse of this discrete Fourier transform is

$$
\begin{equation*}
\tilde{u}_{k}=\frac{1}{\sqrt{N}} \sum_{n} u_{n} e^{-i k n a} . \tag{5.96}
\end{equation*}
$$

Note that $\tilde{u}_{k}$ is in general complex, but that $\tilde{u}_{k}^{*}=\tilde{u}_{-k}$. In terms of the $\tilde{u}_{k}$, the equations of motion take the form

$$
\begin{equation*}
\ddot{\tilde{u}}_{k}=-\frac{2 \kappa}{m}(1-\cos (k a)) \tilde{u}_{k} \equiv-\omega_{k}^{2} \tilde{u}_{k} . \tag{5.97}
\end{equation*}
$$

Thus, each $\tilde{u}_{k}$ is a normal mode, and the normal mode frequencies are

$$
\begin{equation*}
\omega_{k}=2 \sqrt{\frac{\kappa}{m}}\left|\sin \left(\frac{1}{2} k a\right)\right| \tag{5.98}
\end{equation*}
$$

The density of states for this band of phonon excitations is

$$
\begin{equation*}
g(\varepsilon)=\int_{-\pi / a}^{\pi / a} \frac{d k}{2 \pi} \delta\left(\varepsilon-\hbar \omega_{k}\right)=\frac{2}{\pi a}\left(J^{2}-\varepsilon^{2}\right)^{-1 / 2} \Theta(\varepsilon) \Theta(J-\varepsilon) \tag{5.99}
\end{equation*}
$$

where $J=2 \hbar \sqrt{\kappa / m}$ is the phonon bandwidth. The step functions require $0 \leq \varepsilon \leq J$; outside this range there are no phonon energy levels and the density of states accordingly vanishes.
The entire theory can be quantized, taking $\left[p_{n}, u_{n^{\prime}}\right]=-i \hbar \delta_{n n^{\prime}}$. We then define

$$
\begin{equation*}
p_{n}=\frac{1}{\sqrt{N}} \sum_{k} \tilde{p}_{k} e^{i k n a} \quad, \quad \tilde{p}_{k}=\frac{1}{\sqrt{N}} \sum_{n} p_{n} e^{-i k n a} \tag{5.100}
\end{equation*}
$$

in which case $\left[\tilde{p}_{k}, \tilde{u}_{k^{\prime}}\right]=-i \hbar \delta_{k k^{\prime}}$. Note that $\tilde{u}_{k}^{\dagger}=\tilde{u}_{-k}$ and $\tilde{p}_{k}^{\dagger}=\tilde{p}_{-k}$. We then define the ladder operator

$$
\begin{equation*}
a_{k}=\left(\frac{1}{2 m \hbar \omega_{k}}\right)^{1 / 2} \tilde{p}_{k}-i\left(\frac{m \omega_{k}}{2 \hbar}\right)^{1 / 2} \tilde{u}_{k} \tag{5.101}
\end{equation*}
$$

and its Hermitean conjugate $a_{k^{\prime}}^{\dagger}$, in terms of which the Hamiltonian is

$$
\begin{equation*}
\hat{H}=\sum_{k} \hbar \omega_{k}\left(a_{k}^{\dagger} a_{k}+\frac{1}{2}\right) \tag{5.102}
\end{equation*}
$$

which is a sum over independent harmonic oscillator modes. Note that the sum over $k$ is restricted to an interval of width $2 \pi$, e.g. $k \in\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$, which is the first Brillouin zone for the one-dimensional chain structure. The state at wavevector $k+\frac{2 \pi}{a}$ is identical to that at $k$, as we see from eqn. 5.96.

### 5.6.2 General theory of lattice vibrations

The most general model of a harmonic solid is described by a Hamiltonian of the form

$$
\begin{equation*}
\hat{H}=\sum_{\boldsymbol{R}, i} \frac{\boldsymbol{p}_{i}^{2}(\boldsymbol{R})}{2 M_{i}}+\frac{1}{2} \sum_{i, j} \sum_{\alpha, \beta} \sum_{\boldsymbol{R}, \boldsymbol{R}^{\prime}} u_{i}^{\alpha}(\boldsymbol{R}) \Phi_{i j}^{\alpha \beta}\left(\boldsymbol{R}-\boldsymbol{R}^{\prime}\right) u_{j}^{\beta}\left(\boldsymbol{R}^{\prime}\right) \tag{5.103}
\end{equation*}
$$

where the dynamical matrix is

$$
\begin{equation*}
\Phi_{i j}^{\alpha \beta}\left(\boldsymbol{R}-\boldsymbol{R}^{\prime}\right)=\frac{\partial^{2} U}{\partial u_{i}^{\alpha}(\boldsymbol{R}) \partial u_{j}^{\beta}\left(\boldsymbol{R}^{\prime}\right)} \tag{5.104}
\end{equation*}
$$

where $U$ is the potential energy of interaction among all the atoms. Here we have simply expanded the potential to second order in the local displacements $u_{i}^{\alpha}(\boldsymbol{R})$. The lattice sites $\boldsymbol{R}$ are elements of a Bravais lattice. The indices $i$ and $j$ specify basis elements with respect to this lattice, and the indices $\alpha$ and $\beta$ range over $\{1, \ldots, d\}$, the number of possible directions in space. The subject of crystallography is beyond the scope of these notes, but, very briefly, a Bravais lattice in $d$ dimensions is specified by a set of $d$ linearly independent primitive direct lattice vectors $a_{l}$, such that any point in the Bravais lattice may be written as a sum over the primitive vectors with integer coefficients: $\boldsymbol{R}=\sum_{l=1}^{d} n_{l} \boldsymbol{a}_{l}$. The set of all such vectors $\{\boldsymbol{R}\}$ is called the direct lattice. The direct lattice is closed under the operation of vector addition: if $\boldsymbol{R}$ and $\boldsymbol{R}^{\prime}$ are points in a Bravais lattice, then so is $\boldsymbol{R}+\boldsymbol{R}^{\prime}$.

A crystal is a periodic arrangement of lattice sites. The fundamental repeating unit is called the unit cell. Not every crystal is a Bravais lattice, however. Indeed, Bravais lattices are special crystals in which there is only one atom per unit cell. Consider, for example, the structure in fig. 5.4. The blue dots form a square Bravais lattice with primitive direct lattice vectors $\boldsymbol{a}_{1}=a \hat{\boldsymbol{x}}$ and $\boldsymbol{a}_{2}=a \hat{\boldsymbol{y}}$, where $a$ is the lattice constant, which is the distance between any neighboring pair of blue dots. The red squares and green triangles, along with the blue dots, form a basis for the crystal structure which label each sublattice. Our crystal in fig. 5.4 is formally classified as a square Bravais lattice with a three element basis. To specify an arbitrary site in the crystal, we must specify both a direct lattice vector $\boldsymbol{R}$ as well as a basis index $j \in\{1, \ldots, r\}$, so that the location is $\boldsymbol{R}+\boldsymbol{\eta}_{j}$. The vectors $\left\{\boldsymbol{\eta}_{j}\right\}$ are the basis vectors for our crystal structure. We see that a general crystal structure consists of a repeating unit, known as a unit cell. The centers (or corners, if one prefers) of the unit cells form a Bravais lattice. Within a given unit cell, the individual sublattice sites are located at positions $\boldsymbol{\eta}_{j}$ with respect to the unit cell position $\boldsymbol{R}$.

Upon diagonalization, the Hamiltonian of eqn. 5.103 takes the form

$$
\begin{equation*}
\hat{H}=\sum_{\boldsymbol{k}, a} \hbar \omega_{a}(\boldsymbol{k})\left(A_{a}^{\dagger}(\boldsymbol{k}) A_{a}(\boldsymbol{k})+\frac{1}{2}\right) \tag{5.105}
\end{equation*}
$$

where

$$
\begin{equation*}
\left[A_{a}(\boldsymbol{k}), A_{b}^{\dagger}\left(\boldsymbol{k}^{\prime}\right)\right]=\delta_{a b} \delta_{k k^{\prime}} . \tag{5.106}
\end{equation*}
$$



Figure 5.4: A crystal structure with an underlying square Bravais lattice and a three element basis.

The eigenfrequencies are solutions to the eigenvalue equation

$$
\begin{equation*}
\sum_{j, \beta} \tilde{\Phi}_{i j}^{\alpha \beta}(\boldsymbol{k}) \mathrm{e}_{j \beta}^{(a)}(\boldsymbol{k})=M_{i} \omega_{a}^{2}(\boldsymbol{k}) \mathrm{e}_{i \alpha}^{(a)}(\boldsymbol{k}) \tag{5.107}
\end{equation*}
$$

where

$$
\begin{equation*}
\tilde{\Phi}_{i j}^{\alpha \beta}(\boldsymbol{k})=\sum_{\boldsymbol{R}} \Phi_{i j}^{\alpha \beta}(\boldsymbol{R}) e^{-i \boldsymbol{k} \cdot \boldsymbol{R}} \tag{5.108}
\end{equation*}
$$

Here, $\boldsymbol{k}$ lies within the first Brillouin zone, which is the unit cell of the reciprocal lattice of points $\boldsymbol{G}$ satisfying $e^{i \boldsymbol{G} \cdot \boldsymbol{R}}=1$ for all $\boldsymbol{G}$ and $\boldsymbol{R}$. The reciprocal lattice is also a Bravais lattice, with primitive reciprocal lattice vectors $\boldsymbol{b}_{l}$, such that any point on the reciprocal lattice may be written $\boldsymbol{G}=\sum_{l=1}^{d} m_{l} \boldsymbol{b}_{l}$. One also has that $\boldsymbol{a}_{l} \cdot \boldsymbol{b}_{l^{\prime}}=2 \pi \delta_{l l^{\prime}}$. The index $a$ ranges from 1 to $d \cdot r$ and labels the mode of oscillation at wavevector $\boldsymbol{k}$. The vector $\mathrm{e}_{i \alpha}^{(a)}(\boldsymbol{k})$ is the polarization vector for the $a^{\text {th }}$ phonon branch. In solids, along directions of high symmetry, phonon modes can be classified as longitudinal or transverse excitations.

For a crystalline lattice with an $r$-element basis, there are then $d \cdot r$ phonon modes for each wavevector $\boldsymbol{k}$ lying in the first Brillouin zone. If we impose periodic boundary conditions, then the $\boldsymbol{k}$ points within the first Brillouin zone are themselves quantized, as in the $d=1$ case where we found $k=2 \pi n / N$. There are $N$ distinct $\boldsymbol{k}$ points in the first Brillouin zone - one for every direct lattice site. The total number of modes is than $d \cdot r \cdot N$, which is the total number of translational degrees of freedom in our system: $r N$ total atoms ( $N$ unit cells each with an $r$ atom basis) each free to vibrate in $d$ dimensions. Of the $d \cdot r$ branches of phonon excitations, $d$ of them will be acoustic modes whose frequency vanishes as $\boldsymbol{k} \rightarrow 0$. The remaining $d(r-1)$ branches are optical modes and oscillate at finite frequencies. Basically, in an acoustic mode, for $\boldsymbol{k}$ close to the (Brillouin) zone center $\boldsymbol{k}=0$, all the atoms in each unit cell move together in the
same direction at any moment of time. In an optical mode, the different basis atoms move in different directions.

There is no number conservation law for phonons - they may be freely created or destroyed in anharmonic processes, where two photons with wavevectors $\boldsymbol{k}$ and $\boldsymbol{q}$ can combine into a single phonon with wavevector $\boldsymbol{k}+\boldsymbol{q}$, and vice versa. Therefore the chemical potential for phonons is $\mu=0$. We define the density of states $g_{a}(\omega)$ per unit cell for the $a^{\text {th }}$ phonon branch as

$$
\begin{equation*}
g_{a}(\omega)=\frac{1}{N} \sum_{k} \delta\left(\omega-\omega_{a}(\boldsymbol{k})\right)=\mathcal{V}_{0} \int_{\text {BZ }} \frac{d^{d} k}{(2 \pi)^{d}} \delta\left(\omega-\omega_{a}(\boldsymbol{k})\right), \tag{5.109}
\end{equation*}
$$

where $N$ is the number of unit cells, $\mathcal{V}_{0}$ is the unit cell volume of the direct lattice, and the $\boldsymbol{k}$ sum and integral are over the first Brillouin zone only. Note that $\omega$ here has dimensions of frequency. The functions $g_{a}(\omega)$ is normalized to unity: $\int_{0}^{\infty} d \omega g_{a}(\omega)=1$. The total phonon density of states per unit cell is given by ${ }^{4} g(\omega)=\sum_{a=1}^{d r} g_{a}(\omega)$.
The grand potential for the phonon gas is

$$
\begin{align*}
\Omega(T, V) & =-k_{\mathrm{B}} T \ln \prod_{\boldsymbol{k}, a} \sum_{n_{a}(\boldsymbol{k})=0}^{\infty} e^{-\beta \hbar \omega_{a}(\boldsymbol{k})\left(n_{a}(\boldsymbol{k})+\frac{1}{2}\right)} \\
& =k_{\mathrm{B}} T \sum_{k, a} \ln \left[2 \sinh \left(\frac{\hbar \omega_{a}(\boldsymbol{k})}{2 k_{\mathrm{B}} T}\right)\right]=N k_{\mathrm{B}} T \int_{0}^{\infty} d \omega g(\omega) \ln \left[2 \sinh \left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right)\right] \tag{5.110}
\end{align*}
$$

Note that $V=N \mathcal{V}_{0}$ since there are $N$ unit cells, each of volume $\mathcal{V}_{0}$. The entropy is given by $S=-\left(\frac{\partial \Omega}{\partial T}\right)_{V}$ and thus the heat capacity is

$$
\begin{equation*}
C_{V}=-T \frac{\partial^{2} \Omega}{\partial T^{2}}=N k_{\mathrm{B}} \int_{0}^{\infty} d \omega g(\omega)\left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right)^{2} \operatorname{csch}^{2}\left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right) \tag{5.111}
\end{equation*}
$$

Note that as $T \rightarrow \infty$ we have $\operatorname{csch}\left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right) \rightarrow \frac{2 k_{\mathrm{B}} T}{\hbar \omega}$, and therefore

$$
\begin{equation*}
\lim _{T \rightarrow \infty} C_{V}(T)=N k_{\mathrm{B}} \int_{0}^{\infty} d \omega g(\omega)=r d N k_{\mathrm{B}} \tag{5.112}
\end{equation*}
$$

This is the classical Dulong-Petit limit of $\frac{1}{2} k_{\mathrm{B}}$ per quadratic degree of freedom; there are $r N$ atoms moving in $d$ dimensions, hence $d \cdot r N$ positions and an equal number of momenta, resulting in a high temperature limit of $C_{V}=r d N k_{\mathrm{B}}$.

[^1]

Figure 5.5: Upper panel: phonon spectrum in elemental rhodium (Rh) at $T=297 \mathrm{~K}$ measured by high precision inelastic neutron scattering (INS) by A. Eichler et al., Phys. Rev. B 57, 324 (1998). Note the three acoustic branches and no optical branches, corresponding to $d=3$ and $r=1$. Lower panel: phonon spectrum in gallium arsenide (GaAs) at $T=12 \mathrm{~K}$, comparing theoretical lattice-dynamical calculations with INS results of D. Strauch and B. Dorner, J. Phys.: Condens. Matter 2, 1457 (1990). Note the three acoustic branches and three optical branches, corresponding to $d=3$ and $r=2$. The Greek letters along the $x$-axis indicate points of high symmetry in the Brillouin zone.

### 5.6.3 Einstein and Debye models

HIstorically, two models of lattice vibrations have received wide attention. First is the so-called Einstein model, in which there is no dispersion to the individual phonon modes. We approximate $g_{a}(\omega) \approx \delta(\omega-$ $\omega_{a}$ ), in which case

$$
\begin{equation*}
C_{V}(T)=N k_{\mathrm{B}} \sum_{a}\left(\frac{\hbar \omega_{a}}{2 k_{\mathrm{B}} T}\right)^{2} \operatorname{csch}^{2}\left(\frac{\hbar \omega_{a}}{2 k_{\mathrm{B}} T}\right) . \tag{5.113}
\end{equation*}
$$

At low temperatures, the contribution from each branch vanishes exponentially, $\operatorname{since} \operatorname{csch}^{2}\left(\frac{\hbar \omega_{a}}{2 k_{\mathrm{B}} T}\right) \simeq$ $4 e^{-\hbar \omega_{a} / k_{\mathrm{B}} T} \rightarrow 0$. Real solids don't behave this way.

A more realistic model. due to Debye, accounts for the low-lying acoustic phonon branches. Since the acoustic phonon dispersion vanishes linearly with $|\boldsymbol{k}|$ as $\boldsymbol{k} \rightarrow 0$, there is no temperature at which the acoustic phonons 'freeze out' exponentially, as in the case of Einstein phonons. Indeed, the Einstein model is appropriate in describing the $d(r-1)$ optical phonon branches, though it fails miserably for the acoustic branches.

In the vicinity of the zone center $\boldsymbol{k}=0$ (also called $\Gamma$ in crystallographic notation) the $d$ acoustic modes obey a linear dispersion, with $\omega_{a}(\boldsymbol{k})=c_{a}(\hat{\boldsymbol{k}}) k$. This results in an acoustic phonon density of states in $d=3$ dimensions of

$$
\begin{equation*}
\tilde{g}(\omega)=\frac{\mathcal{V}_{0} \omega^{2}}{2 \pi^{2}} \sum_{a} \int \frac{d \hat{\boldsymbol{k}}}{4 \pi} \frac{1}{c_{a}^{3}(\boldsymbol{k})} \Theta\left(\omega_{\mathrm{D}}-\omega\right)=\frac{3 \mathcal{V}_{0}}{2 \pi^{2} \bar{c}^{3}} \omega^{2} \Theta\left(\omega_{\mathrm{D}}-\omega\right) \tag{5.114}
\end{equation*}
$$

where $\bar{c}$ is an average acoustic phonon velocity (i.e. speed of sound) defined by

$$
\begin{equation*}
\frac{3}{\bar{c}^{3}}=\sum_{a} \int \frac{d \hat{\boldsymbol{k}}}{4 \pi} \frac{1}{c_{a}^{3}(\boldsymbol{k})} \tag{5.115}
\end{equation*}
$$

and $\omega_{\mathrm{D}}$ is a cutoff known as the Debye frequency. The cutoff is necessary because the phonon branch does not extend forever, but only to the boundaries of the Brillouin zone. Thus, $\omega_{\mathrm{D}}$ should roughly be equal to the energy of a zone boundary phonon. Alternatively, we can define $\omega_{\mathrm{D}}$ by the normalization condition

$$
\begin{equation*}
\int_{0}^{\infty} d \omega \tilde{g}(\omega)=3 \quad \Longrightarrow \quad \omega_{\mathrm{D}}=\left(6 \pi^{2} / \mathcal{V}_{0}\right)^{1 / 3} \bar{c} \tag{5.116}
\end{equation*}
$$

This allows us to write $\tilde{g}(\omega)=\left(9 \omega^{2} / \omega_{\mathrm{D}}^{3}\right) \Theta\left(\omega_{\mathrm{D}}-\omega\right)$.
The specific heat due to the acoustic phonons is then

$$
\begin{align*}
C_{V}(T) & =\frac{9 N k_{\mathrm{B}}}{\omega_{\mathrm{D}}^{3}} \int_{0}^{\omega_{\mathrm{D}}} d \omega \omega^{2}\left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right)^{2} \operatorname{csch}^{2}\left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right)  \tag{5.117}\\
& =9 N k_{\mathrm{B}}\left(\frac{2 T}{\Theta_{\mathrm{D}}}\right)^{3} \phi\left(\Theta_{\mathrm{D}} / 2 T\right),
\end{align*}
$$

where $\Theta_{\mathrm{D}}=\hbar \omega_{\mathrm{D}} / k_{\mathrm{B}}$ is the Debye temperature and

$$
\phi(x)=\int_{0}^{x} d t t^{4} \operatorname{csch}^{2} t=\left\{\begin{array}{ll}
x^{3} / 3 & x \rightarrow 0  \tag{5.118}\\
\pi^{4} / 30 & x \rightarrow \infty
\end{array} .\right.
$$

Therefore,

$$
C_{V}(T)=\left\{\begin{array}{ll}
\frac{12}{5} \pi^{4} N k_{\mathrm{B}}\left(T / \Theta_{\mathrm{D}}\right)^{3} & T \ll \Theta_{\mathrm{D}}  \tag{5.119}\\
3 N k_{\mathrm{B}} & T \gg \Theta_{\mathrm{D}}
\end{array} .\right.
$$

Thus, the heat capacity due to acoustic phonons obeys the Dulong-Petit rule in that $C_{V}(T \rightarrow \infty)=$ $3 N k_{\mathrm{B}}$, corresponding to the three acoustic degrees of freedom per unit cell. The remaining contribution of $3(r-1) N k_{\mathrm{B}}$ to the high temperature heat capacity comes from the optical modes not considered in the Debye model. The low temperature $T^{3}$ behavior of the heat capacity of crystalline solids is a generic feature, and its detailed description is a triumph of the Debye model.

| Element | Ag | Al | Au | C | Cd | Cr | Cu | Fe | Mn |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\Theta_{\mathrm{D}}(\mathrm{K})$ | 227 | 433 | 162 | 2250 | 210 | 606 | 347 | 477 | 409 |
| $T_{\text {melt }}(\mathrm{K})$ | 962 | 660 | 1064 | 3500 | 321 | 1857 | 1083 | 1535 | 1245 |
| Element | Ni | Pb | Pt | Si | Sn | Ta | Ti | W | Zn |
| $\Theta_{\mathrm{D}}(\mathrm{K})$ | 477 | 105 | 237 | 645 | 199 | 246 | 420 | 383 | 329 |
| $T_{\text {melt }}(\mathrm{K})$ | 1453 | 327 | 1772 | 1410 | 232 | 2996 | 1660 | 3410 | 420 |

Table 5.1: Debye temperatures (at $T=0$ ) and melting points for some common elements (carbon is assumed to be diamond and not graphite). (Source: the internet!)

### 5.6.4 Melting and the Lindemann criterion

## Atomic fluctuations in a crystal

For the one-dimensional chain, eqn. 5.101 gives

$$
\begin{equation*}
\tilde{u}_{k}=i\left(\frac{\hbar}{2 m \omega_{k}}\right)^{1 / 2}\left(a_{k}-a_{-k}^{\dagger}\right) . \tag{5.120}
\end{equation*}
$$

Therefore the RMS fluctuations at each site are given by

$$
\begin{equation*}
\left\langle u_{n}^{2}\right\rangle=\frac{1}{N} \sum_{k}\left\langle\tilde{u}_{k} \tilde{u}_{-k}\right\rangle=\frac{1}{N} \sum_{k} \frac{\hbar}{m \omega_{k}}\left(n(k)+\frac{1}{2}\right) \tag{5.121}
\end{equation*}
$$

where $n(k, T)=\left[\exp \left(\hbar \omega_{k} / k_{\mathrm{B}} T\right)-1\right]^{-1}$ is the Bose occupancy function.
Let us now generalize this expression to the case of a $d$-dimensional solid. The appropriate expression for the RMS position fluctuations of the $i^{\text {th }}$ basis atom in each unit cell is

$$
\begin{equation*}
\left\langle\boldsymbol{u}_{i}^{2}(\boldsymbol{R})\right\rangle=\frac{1}{N} \sum_{k} \sum_{a=1}^{d r} \frac{\hbar}{M_{i a}(\boldsymbol{k}) \omega_{a}(\boldsymbol{k})}\left(n_{a}(\boldsymbol{k})+\frac{1}{2}\right) \tag{5.122}
\end{equation*}
$$

Here we sum over all wavevectors $\boldsymbol{k}$ in the first Brilliouin zone, and over all normal modes $a$. There are $d r$ normal modes per unit cell i.e. $d$ branches of the phonon dispersion $\omega_{a}(\boldsymbol{k})$. (For the one-dimensional chain with $d=1$ and $r=1$ there was only one such branch to consider). Note also the quantity $M_{i a}(\boldsymbol{k})$, which has units of mass and is defined in terms of the polarization vectors $\mathrm{e}_{i \alpha}^{(a)}(\boldsymbol{k})$ as

$$
\begin{equation*}
\frac{1}{M_{i a}(\boldsymbol{k})}=\sum_{\mu=1}^{d}\left|\mathrm{e}_{i \mu}^{(a)}(\boldsymbol{k})\right|^{2} . \tag{5.123}
\end{equation*}
$$

The dimensions of the polarization vector are [mass] $]^{-1 / 2}$, since the generalized orthonormality condition on the normal modes is

$$
\begin{equation*}
\sum_{i, \mu} M_{i} \mathrm{e}_{i \mu}^{(a)^{*}}(\boldsymbol{k}) \mathrm{e}_{i \mu}^{(b)}(\boldsymbol{k})=\delta^{a b} \tag{5.124}
\end{equation*}
$$

where $M_{i}$ is the mass of the atom of species $i$ within the unit cell $(i \in\{1, \ldots, r\})$. For our purposes we can replace $M_{i a}(\boldsymbol{k})$ by an appropriately averaged quantity which we call $\mathrm{M}_{i}$; this 'effective mass' is then independent of the mode index $a$ as well as the wavevector $\boldsymbol{k}$. We may then write

$$
\begin{equation*}
\left\langle\boldsymbol{u}_{i}^{2}\right\rangle \approx \int_{0}^{\infty} d \omega g(\omega) \frac{\hbar}{\mathrm{M}_{i} \omega} \cdot\left\{\frac{1}{e^{\hbar \omega / k_{\mathrm{B}} T}-1}+\frac{1}{2}\right\} \tag{5.125}
\end{equation*}
$$

where we have dropped the site label $\boldsymbol{R}$ since translational invariance guarantees that the fluctuations are the same from one unit cell to the next. Note that the fluctuations $\left\langle\boldsymbol{u}_{i}^{2}\right\rangle$ can be divided into a temperature-dependent part $\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\text {th }}$ and a temperature-independent quantum contribution $\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\text {qu }}$, where

$$
\begin{equation*}
\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\mathrm{th}}=\frac{\hbar}{\mathrm{M}_{i}} \int_{0}^{\infty} d \omega \frac{g(\omega)}{\omega} \cdot \frac{1}{e^{\hbar \omega / k_{\mathrm{B}} T}-1} \quad, \quad\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\mathrm{qu}}=\frac{\hbar}{2 \mathrm{M}_{i}} \int_{0}^{\infty} d \omega \frac{g(\omega)}{\omega} . \tag{5.126}
\end{equation*}
$$

Let's evaluate these contributions within the Debye model, where we replace $g(\omega)$ by

$$
\begin{equation*}
\bar{g}(\omega)=\frac{d^{2} \omega^{d-1}}{\omega_{\mathrm{D}}^{d}} \Theta\left(\omega_{\mathrm{D}}-\omega\right) \tag{5.127}
\end{equation*}
$$

We then find

$$
\begin{equation*}
\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\mathrm{th}}=\frac{d^{2} \hbar}{\mathrm{M}_{i} \omega_{\mathrm{D}}}\left(\frac{k_{\mathrm{B}} T}{\hbar \omega_{\mathrm{D}}}\right)^{d-1} F_{d}\left(\hbar \omega_{\mathrm{D}} / k_{\mathrm{B}} T\right) \quad, \quad\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\mathrm{qu}}=\frac{d^{2}}{d-1} \cdot \frac{\hbar}{2 \mathrm{M}_{i} \omega_{\mathrm{D}}} \tag{5.128}
\end{equation*}
$$

where

$$
F_{d}(x)=\int_{0}^{x} d s \frac{s^{d-2}}{e^{s}-1}= \begin{cases}x^{d-2} /(d-2) & x \rightarrow 0  \tag{5.129}\\ \zeta(d-1) & x \rightarrow \infty\end{cases}
$$

We can now extract from these expressions several important conclusions:

1) The $T=0$ contribution to the the fluctuations, $\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\mathrm{qu}}$, diverges in $d=1$ dimensions. Therefore there are no one-dimensional quantum solids.
2) The thermal contribution to the fluctuations, $\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\mathrm{th}}$, diverges for any $T>0$ whenever $d \leq 2$. This is because the integrand of $F_{d}(x)$ goes as $s^{d-3}$ as $s \rightarrow 0$. Therefore, there are no two-dimensional classical solids.
3) Both the above conclusions are valid in the thermodynamic limit. Finite size imposes a cutoff on the frequency integrals, because there is a smallest wavevector $k_{\min } \sim 2 \pi / L$, where $L$ is the (finite) linear dimension of the system. This leads to a low frequency cutoff $\omega_{\min }=2 \pi \bar{c} / L$, where $\bar{c}$ is the appropriately averaged acoustic phonon velocity from eqn. 5.115 , which mitigates any divergences.

## Lindemann melting criterion

An old phenomenological theory of melting due to Lindemann says that a crystalline solid melts when the RMS fluctuations in the atomic positions exceeds a certain fraction $x^{*}$ of the lattice constant $a$. We therefore define the ratios

$$
\begin{align*}
& x_{i, \mathrm{th}}^{2} \equiv \frac{\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\mathrm{th}}}{a^{2}}=d^{2} \cdot\left(\frac{\hbar^{2}}{\mathrm{M}_{i} a^{2} k_{\mathrm{B}}}\right) \cdot \frac{T^{d-1}}{\Theta_{\mathrm{D}}^{d}} \cdot F\left(\Theta_{\mathrm{D}} / T\right) \\
& x_{i, \mathrm{qu}}^{2} \equiv \frac{\left\langle\boldsymbol{u}_{i}^{2}\right\rangle_{\mathrm{qu}}}{a^{2}}=\frac{d^{2}}{2(d-1)} \cdot\left(\frac{\hbar^{2}}{\mathrm{M}_{i} a^{2} k_{\mathrm{B}}}\right) \cdot \frac{1}{\Theta_{\mathrm{D}}} \tag{5.130}
\end{align*}
$$

with $x_{i}=\sqrt{x_{i, \text { th }}^{2}+x_{i, \mathrm{qu}}^{2}}=\sqrt{\left\langle\boldsymbol{u}_{i}^{2}\right\rangle} / a$.
Let's now work through an example of a three-dimensional solid. We'll assume a single element basis ( $r=1$ ). We have that

$$
\begin{equation*}
\frac{9 \hbar^{2} / 4 k_{\mathrm{B}}}{1 \mathrm{amu} \AA^{2}}=109 \mathrm{~K} \tag{5.131}
\end{equation*}
$$

According to table 5.1, the melting temperature always exceeds the Debye temperature, and often by a great amount. We therefore assume $T \gg \Theta_{\mathrm{D}}$, which puts us in the small $x$ limit of $F_{d}(x)$. We then find

$$
\begin{equation*}
x_{\mathrm{qu}}^{2}=\frac{\Theta^{\star}}{\Theta_{\mathrm{D}}} \quad, \quad x_{\mathrm{th}}^{2}=\frac{\Theta^{\star}}{\Theta_{\mathrm{D}}} \cdot \frac{4 T}{\Theta_{\mathrm{D}}} \quad, \quad x=\sqrt{\left(1+\frac{4 T}{\Theta_{\mathrm{D}}}\right) \frac{\Theta^{\star}}{\Theta_{\mathrm{D}}}} \tag{5.132}
\end{equation*}
$$

where

$$
\begin{equation*}
\Theta^{*}=\frac{109 \mathrm{~K}}{M[\mathrm{amu}] \cdot(a[\AA])^{2}} . \tag{5.133}
\end{equation*}
$$

The total position fluctuation is of course the sum $x^{2}=x_{i, \text { th }}^{2}+x_{i, \mathrm{qu}}^{2}$. Consider for example the case of copper, with $M=56$ amu and $a=2.87 \AA$. The Debye temperature is $\Theta_{\mathrm{D}}=347 \mathrm{~K}$. From this we find $x_{\mathrm{qu}}=0.026$, which says that at $T=0$ the RMS fluctuations of the atomic positions are not quite three percent of the lattice spacing (i.e. the distance between neighboring copper atoms). At room temperature, $T=293 \mathrm{~K}$, one finds $x_{\mathrm{th}}=0.048$, which is about twice as large as the quantum contribution. How big are the atomic position fluctuations at the melting point? According to our table, $T_{\text {melt }}=1083 \mathrm{~K}$ for copper, and from our formulae we obtain $x_{\text {melt }}=0.096$. The Lindemann criterion says that solids melt when $x(T) \approx 0.1$.

We were very lucky to hit the magic number $x_{\text {melt }}=0.1$ with copper. Let's try another example. Lead has $M=208$ amu and $a=4.95 \AA$. The Debye temperature is $\Theta_{\mathrm{D}}=105 \mathrm{~K}$ ('soft phonons'), and the melting point is $T_{\text {melt }}=327 \mathrm{~K}$. From these data we obtain $x(T=0)=0.014, x(293 \mathrm{~K})=0.050$ and $x(T=327 \mathrm{~K})=0.053$. Same ballpark.

We can turn the analysis around and predict a melting temperature based on the Lindemann criterion $x\left(T_{\text {melt }}\right)=x^{*}$, where $x^{*} \approx 0.1$. We obtain

$$
\begin{equation*}
T_{\mathrm{L}}=\left(\frac{\Theta_{\mathrm{D}}}{\Theta^{\star}} x^{* 2}-1\right) \cdot \frac{\Theta_{\mathrm{D}}}{4} . \tag{5.134}
\end{equation*}
$$

We call $T_{\mathrm{L}}$ the Lindemann temperature. Most treatments of the Lindemann criterion ignore the quantum correction, which gives the -1 contribution inside the above parentheses. But if we are more careful and include it, we see that it may be possible to have $T_{\mathrm{L}}<0$. This occurs for any crystal where $\Theta_{\mathrm{D}}<\Theta^{\star} / x^{* 2}$. In this case we might expect the crystalline solid to be unstable to a liquid phase even at $T=0$.

This is indeed the case for ${ }^{4} \mathrm{He}$, which at atmospheric pressure condenses into a liquid at $T_{\mathrm{c}}=4.2 \mathrm{~K}$ and remains in the liquid state down to absolute zero. At $p=1 \mathrm{~atm}$, it never solidifies! Why? The number density of liquid ${ }^{4} \mathrm{He}$ at $p=1 \mathrm{~atm}$ and $T=0 \mathrm{~K}$ is $2.2 \times 10^{22} \mathrm{~cm}^{-3}$. Let's say the helium atoms want to form a crystalline lattice. We don't know a priori what the lattice structure will be, so let's for the sake of simplicity assume a simple cubic lattice. From the number density we obtain a lattice spacing of $a=3.57 \AA$. OK now what do we take for the Debye temperature? Theoretically this should depend on the microscopic force constants which enter the small oscillations problem (i.e. the spring constants between pairs of helium atoms in equilibrium). We'll use the expression we derived for the Debye frequency, $\omega_{\mathrm{D}}=\left(6 \pi^{2} / \mathcal{V}_{0}\right)^{1 / 3} \bar{c}$, where $\mathcal{V}_{0}$ is the unit cell volume. We'll take $\bar{c}=238 \mathrm{~m} / \mathrm{s}$, which is the speed of sound in liquid helium at $T=0$. This gives $\Theta_{\mathrm{D}}=19.8 \mathrm{~K}$. We find $\Theta^{\star}=2.13 \mathrm{~K}$, and if we take $x^{*}=0.1$ this gives $\Theta^{\star} / x^{* 2}=213 \mathrm{~K}$, which significantly exceeds $\Theta_{\mathrm{D}}$. Thus, the solid should melt because the RMS fluctuations in the atomic positions at absolute zero are huge: $x_{\text {qu }}=\left(\Theta^{\star} / \Theta_{\mathrm{D}}\right)^{1 / 2}=0.33$. By applying pressure, one can get ${ }^{4} \mathrm{He}$ to crystallize above $p_{\mathrm{c}}=25 \mathrm{~atm}$ at $T=0$. Under pressure, the unit cell volume $\mathcal{V}_{0}$ decreases and the phonon velocity $\bar{c}$ increases, so the Debye temperature increases.

It is important to recognize that the Lindemann criterion does not provide us with a theory of melting per se. Rather it provides us with a heuristic allowing us to predict roughly when a solid should melt.

### 5.6.5 Goldstone bosons

The vanishing of the acoustic phonon dispersion at $\boldsymbol{k}=0$ is a consequence of Goldstone's theorem which says that associated with every broken generator of a continuous symmetry there is an associated bosonic gapless excitation (i.e. one whose frequency $\omega$ vanishes in the long wavelength limit). In the case of phonons, the 'broken generators' are the symmetries under spatial translation in the $x, y$, and $z$ directions. The crystal selects a particular location for its center-of-mass, which breaks this symmetry. There are, accordingly, three gapless acoustic phonons.

Magnetic materials support another branch of elementary excitations known as spin waves, or magnons. In isotropic magnets, there is a global symmetry associated with rotations in internal spin space, described by the group $\mathrm{SU}(2)$. If the system spontaneously magnetizes, meaning there is long-ranged ferromagnetic order $(\uparrow \uparrow \uparrow \cdots)$, or long-ranged antiferromagnetic order $(\uparrow \downarrow \uparrow \downarrow \cdots)$, then global spin rotation symmetry is broken. Typically a particular direction is chosen for the magnetic moment (or staggered moment, in the case of an antiferromagnet). Symmetry under rotations about this axis is then preserved, but rotations which do not preserve the selected axis are 'broken'. In the most straightforward case, that of the antiferromagnet, there are two such rotations for $\mathrm{SU}(2)$, and concomitantly two gapless magnon branches, with linearly vanishing dispersions $\omega_{a}(\boldsymbol{k})$. The situation is more subtle in the case of ferromagnets, because the total magnetization is conserved by the dynamics (unlike the total staggered magnetization in the case of antiferromagnets). Another wrinkle arises if there are long-ranged interactions present.
For our purposes, we can safely ignore the deep physical reasons underlying the gaplessness of Gold-
stone bosons and simply posit a gapless dispersion relation of the form $\omega(\boldsymbol{k})=A|\boldsymbol{k}|^{\sigma}$. The density of states for this excitation branch is then $g(\omega)=\mathcal{C} \omega^{\frac{d}{\sigma}-1} \Theta\left(\omega_{\mathrm{c}}-\omega\right)$, where $\mathcal{C}$ is a constant and $\omega_{\mathrm{c}}$ is the cutoff, which is the bandwidth for this excitation branch. ${ }^{5}$ Normalizing the density of states for this branch results in the identification $\omega_{\mathrm{c}}=(d / \sigma \mathcal{C})^{\sigma / d}$.

The heat capacity is then found to be

$$
\begin{equation*}
C_{V}=N k_{\mathrm{B}} \mathcal{C} \int_{0}^{\omega_{\mathrm{C}}} d \omega \omega^{\frac{d}{\sigma}-1}\left(\frac{\hbar \omega}{k_{\mathrm{B}} T}\right)^{2} \operatorname{csch}^{2}\left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T}\right)=\frac{d}{\sigma} N k_{\mathrm{B}}\left(\frac{2 T}{\Theta}\right)^{d / \sigma} \phi(\Theta / 2 T) \tag{5.135}
\end{equation*}
$$

where $\Theta=\hbar \omega_{\mathrm{c}} / k_{\mathrm{B}}$ and

$$
\phi(x)=\int_{0}^{x} d t t^{\frac{d}{\sigma}+1} \operatorname{csch}^{2} t= \begin{cases}\frac{\sigma}{d} x^{d / \sigma} & x \rightarrow 0  \tag{5.136}\\ 2^{-d / \sigma} \Gamma\left(2+\frac{d}{\sigma}\right) \zeta\left(2+\frac{d}{\sigma}\right) & x \rightarrow \infty,\end{cases}
$$

which is a generalization of our earlier results. Once again, we recover Dulong-Petit for $k_{\mathrm{B}} T \gg \hbar \omega_{\mathrm{c}}$, with $C_{V}\left(T \gg \hbar \omega_{\mathrm{c}} / k_{\mathrm{B}}\right)=N k_{\mathrm{B}}$.
In an isotropic ferromagnet, i.e.a ferromagnetic material where there is full $\operatorname{SU}(2)$ symmetry in internal 'spin' space, the magnons have a $k^{2}$ dispersion. Thus, a bulk three-dimensional isotropic ferromagnet will exhibit a heat capacity due to spin waves which behaves as $T^{3 / 2}$ at low temperatures. For sufficiently low temperatures this will overwhelm the phonon contribution, which behaves as $T^{3}$.

### 5.7 The Ideal Bose Gas

### 5.7.1 General formulation for noninteracting systems

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

$$
\begin{equation*}
\Xi=\prod_{\alpha}\left(\sum_{n_{\alpha}=0}^{\infty} e^{\beta\left(\mu-\varepsilon_{\alpha}\right) n_{\alpha}}\right)=\prod_{\alpha}\left(1-e^{\beta\left(\mu-\varepsilon_{\alpha}\right)}\right)^{-1} \tag{5.137}
\end{equation*}
$$

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

$$
\begin{equation*}
n(T, \mu)=-\frac{1}{V}\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}=\frac{1}{V} \sum_{\alpha} \frac{1}{e^{\beta\left(\varepsilon_{\alpha}-\mu\right)}-1}=\int_{\varepsilon_{0}}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}-1} \tag{5.138}
\end{equation*}
$$

where $g(\varepsilon)=\frac{1}{V} \sum_{\alpha} \delta\left(\varepsilon-\varepsilon_{\alpha}\right)$ is the density of single particle states per unit volume. We assume that $g(\varepsilon)=0$ for $\varepsilon<\varepsilon_{0}$; typically $\varepsilon_{0}=0$, as is the case for any dispersion of the form $\varepsilon(\boldsymbol{k})=A|\boldsymbol{k}|^{r}$, for

$$
{ }^{5} \text { If } \omega(\boldsymbol{k})=A k^{\sigma} \text {, then } \mathcal{C}=2^{1-d} \pi^{-\frac{d}{2}} \sigma^{-1} A^{-\frac{d}{\sigma}} \mathrm{~g} / \Gamma(d / 2)
$$

example. However, in the presence of a magnetic field, we could have $\varepsilon(\boldsymbol{k}, \sigma)=A|\boldsymbol{k}|^{r}-g \mu_{0} H \sigma$, in which case $\varepsilon_{0}=-g \mu_{0}|H|$.

Clearly $n(T, \mu)$ is an increasing function of both $T$ and $\mu$. At fixed $T$, the maximum possible value for $n(T, \mu)$, called the critical density $n_{\mathrm{c}}(T)$, is achieved for $\mu=\varepsilon_{0}$, i.e.

$$
\begin{equation*}
n_{\mathrm{c}}(T)=\int_{\varepsilon_{0}}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{\beta\left(\varepsilon-\varepsilon_{0}\right)}-1} \tag{5.139}
\end{equation*}
$$

The above integral converges provided $g\left(\varepsilon_{0}\right)=0$, assuming $g(\varepsilon)$ is continuous ${ }^{6}$. If $g\left(\varepsilon_{0}\right)>0$, the integral diverges, and $n_{\mathrm{c}}(T)=\infty$. In this latter case, one can always invert the equation for $n(T, \mu)$ to obtain the chemical potential $\mu(T, n)$. In the former case, where the $n_{\mathrm{c}}(T)$ is finite, we have a problem - what happens if $n>n_{\mathrm{c}}(T)$ ?

In the former case, where $n_{\mathrm{c}}(T)$ is finite, we can equivalently restate the problem in terms of a critical temperature $T_{\mathrm{c}}(n)$, defined by the equation $n_{\mathrm{c}}\left(T_{\mathrm{c}}\right)=n$. For $T<T_{\mathrm{c}}$, 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 $\varepsilon_{0}$. I.e. we write

$$
\begin{equation*}
n(T, \mu)=\overbrace{\frac{1}{V} \frac{\mathrm{~g}_{0}}{e^{\beta\left(\varepsilon_{0}-\mu\right)}-1}}^{n_{0}}+\overbrace{\int_{\varepsilon_{0}}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}-1}}^{n^{\prime}}, \tag{5.140}
\end{equation*}
$$

where $\mathrm{g}_{0}$ is the degeneracy of the single particle state with energy $\varepsilon_{0}$. We assume that $n_{0}$ is finite, which means that $N_{0}=V n_{0}$ is extensive. We say that the particles have condensed into the state with energy $\varepsilon_{0}$. The quantity $n_{0}$ is the condensate density. The remaining particles, with density $n^{\prime}$, are said to comprise the overcondensate. With the total density $n$ fixed, we have $n=n_{0}+n^{\prime}$. Note that $n_{0}$ finite means that $\mu$ is infinitesimally close to $\varepsilon_{0}$ :

$$
\begin{equation*}
\mu=\varepsilon_{0}-k_{\mathrm{B}} T \ln \left(1+\frac{\mathrm{g}_{0}}{V n_{0}}\right) \approx \varepsilon_{0}-\frac{\mathrm{g}_{0} k_{\mathrm{B}} T}{V n_{0}} . \tag{5.141}
\end{equation*}
$$

Note also that if $\varepsilon_{0}-\mu$ is finite, then $n_{0} \propto V^{-1}$ is infinitesimal.
Thus, for $T<T_{\mathrm{c}}(n)$, we have $\mu=\varepsilon_{0}$ with $n_{0}>0$, and

$$
\begin{equation*}
n\left(T, n_{0}\right)=n_{0}+\int_{\varepsilon_{0}}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{\left(\varepsilon-\varepsilon_{0}\right) / k_{\mathrm{B}} T}-1} \tag{5.142}
\end{equation*}
$$

For $T>T_{\mathrm{c}}(n)$, we have $n_{0}=0$ and

$$
\begin{equation*}
n(T, \mu)=\int_{\varepsilon_{0}}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{(\varepsilon-\mu) / k_{\mathrm{B}} T}-1} \tag{5.143}
\end{equation*}
$$

[^2]The equation for $T_{\mathrm{c}}(n)$ is

$$
\begin{equation*}
n=\int_{\varepsilon_{0}}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{\left(\varepsilon-\varepsilon_{0}\right) / k_{\mathrm{B}} T_{\mathrm{c}}}-1} \tag{5.144}
\end{equation*}
$$

For another take on ideal Bose gas condensation see the appendix in $\S 5.9$.

### 5.7.2 Ballistic dispersion

We already derived, in $\S 5.3 .3$, expressions for $n(T, z)$ and $p(T, z)$ for the ideal Bose gas (IBG) with ballistic dispersion $\varepsilon(\boldsymbol{p})=\boldsymbol{p}^{2} / 2 m$, We found

$$
\begin{align*}
& n(T, z)=\mathrm{g} \lambda_{T}^{-d} \operatorname{Li}_{\frac{d}{2}}(z)  \tag{5.145}\\
& p(T, z)=\mathrm{g} k_{\mathrm{B}} T \lambda_{T}^{-d} \operatorname{Li}_{\frac{d}{2}+1}(z)
\end{align*}
$$

where $\lambda_{T}=\sqrt{2 \pi \hbar^{2} / m k_{\mathrm{B}} T}$ is the thermal wavelength, and where g is the internal (e.g. spin) degeneracy of each single particle energy level. Here $z=e^{\mu / k_{\mathrm{B}} T}$ is the fugacity and

$$
\begin{equation*}
\mathrm{Li}_{s}(z)=\sum_{m=1}^{\infty} \frac{z^{m}}{m^{s}} \tag{5.146}
\end{equation*}
$$

is the polylogarithm function. For bosons with a spectrum bounded below by $\varepsilon_{0}=0$, the fugacity takes values on the interval $z \in[0,1]^{7}$. Note that $\operatorname{Li}_{s}(z=1)=\zeta(s)$, which is Riemann's zeta function; $\zeta(s)$ is finite for $s>1$.
Clearly $n(T, z)=\mathrm{g} \lambda_{T}^{-d} \operatorname{Li}_{\frac{d}{2}}(z)$ is an increasing function of $z$ for fixed $T$. In fig. 5.6 we plot the function $\operatorname{Li}_{s}(z)$ versus $z$ for three different values of $s$. We note that the maximum value $\operatorname{Li}_{s}(z=1)$ is finite if $s>1$. Thus, for $d>2$, there is a maximum density $n_{\max }(T)=\mathrm{g} \zeta(d / 2) \lambda_{T}^{-d}$ which is an increasing function of temperature $T$. Put another way, if we fix the density $n$, then there is a critical temperature $T_{\mathrm{c}}$ below which there is no solution to the equation $n=n(T, z)$. The critical temperature $T_{\mathrm{c}}(n)$ is then determined by the relation

$$
\begin{equation*}
n=\mathrm{g} \zeta\left(\frac{d}{2}\right)\left(\frac{m k_{\mathrm{B}} T_{\mathrm{c}}}{2 \pi \hbar^{2}}\right)^{d / 2} \quad \Longrightarrow \quad k_{\mathrm{B}} T_{\mathrm{c}}=\frac{2 \pi \hbar^{2}}{m}\left(\frac{n}{\mathrm{~g} \zeta\left(\frac{d}{2}\right)}\right)^{2 / d} \tag{5.147}
\end{equation*}
$$

What happens for $T<T_{\mathrm{c}}$ ?
As shown above in $\S 5.7$, we must separate out the contribution from the lowest energy single particle mode, which for ballistic dispersion lies at $\varepsilon_{0}=0$. Thus writing

$$
\begin{equation*}
n=\frac{1}{V} \frac{1}{z^{-1}-1}+\frac{1}{V} \sum_{\substack{\alpha \\\left(\varepsilon_{\alpha}>0\right)}} \frac{1}{z^{-1} e^{\varepsilon_{\alpha} / k_{\mathrm{B}} T}-1} \tag{5.148}
\end{equation*}
$$

[^3]

Figure 5.6: The polylogarithm function $\operatorname{Li}_{s}(z)$ versus $z$ for $s=\frac{1}{2}, s=\frac{3}{2}$, and $s=\frac{5}{2}$. Note that $\operatorname{Li}_{s}(1)=$ $\zeta(s)$ diverges for $s \leq 1$.
where we have taken $\mathrm{g}=1$. 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 $\boldsymbol{k}=0$ bosons $n_{0}$ is finite, then their total number $N_{0}$ satisfies

$$
\begin{equation*}
N_{0}=V n_{0}=\frac{1}{z^{-1}-1} \quad \Longrightarrow \quad z=\frac{1}{1+N_{0}^{-1}} \tag{5.149}
\end{equation*}
$$

The chemical potential is then

$$
\begin{equation*}
\mu=k_{\mathrm{B}} T \ln z=-k_{\mathrm{B}} T \ln \left(1+N_{0}^{-1}\right) \approx-\frac{k_{\mathrm{B}} T}{N_{0}} \rightarrow 0^{-} . \tag{5.150}
\end{equation*}
$$

In other words, the chemical potential is infinitesimally negative, because $N_{0}$ is assumed to be thermodynamically large.

According to eqn. 5.11, the contribution to the pressure from the $\boldsymbol{k}=0$ states is

$$
\begin{equation*}
p_{0}=-\frac{k_{\mathrm{B}} T}{V} \ln (1-z)=\frac{k_{\mathrm{B}} T}{V} \ln \left(1+N_{0}\right) \rightarrow 0^{+} . \tag{5.151}
\end{equation*}
$$

So the $\boldsymbol{k}=0$ bosons, which we identify as the condensate, contribute nothing to the pressure.
Having separated out the $\boldsymbol{k}=0$ mode, we can now replace the remaining sum over $\alpha$ by the usual integral over $\boldsymbol{k}$. We then have

$$
\begin{align*}
T<T_{\mathrm{c}} \quad: \quad n & =n_{0}+\mathrm{g} \zeta\left(\frac{d}{2}\right) \lambda_{T}^{-d}  \tag{5.152}\\
& p=\mathrm{g} \zeta\left(\frac{d}{2}+1\right) k_{\mathrm{B}} T \lambda_{T}^{-d}
\end{align*}
$$

and

$$
\begin{align*}
T>T_{\mathrm{c}} \quad: \quad n & =\operatorname{Li}_{\frac{d}{2}}(z) \lambda_{T}^{-d}  \tag{5.153}\\
& p=\operatorname{gLi}_{\frac{d}{2}+1}(z) k_{\mathrm{B}} T \lambda_{T}^{-d} .
\end{align*}
$$

The condensate fraction $n_{0} / n$ is unity at $T=0$, when all particles are in the condensate with $\boldsymbol{k}=0$, and decreases with increasing $T$ until $T=T_{\mathrm{c}}$, at which point it vanishes identically. Explicitly, we have

$$
\begin{equation*}
\frac{n_{0}(T)}{n}=1-\frac{\mathrm{g} \zeta\left(\frac{d}{2}\right)}{n \lambda_{T}^{d}}=1-\left(\frac{T}{T_{\mathrm{c}}(n)}\right)^{d / 2} \tag{5.154}
\end{equation*}
$$

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

$$
\begin{equation*}
\frac{\partial}{\partial \beta}(\beta \Omega)=\Omega+\beta \frac{\partial \Omega}{\partial \beta}=\Omega-T \frac{\partial \Omega}{\partial T}=\Omega+T S \tag{5.155}
\end{equation*}
$$

and therefore

$$
\begin{align*}
E=\Omega+T S+\mu N & =\mu N+\frac{\partial}{\partial \beta}(\beta \Omega) \\
& =V\left(\mu n-\frac{\partial}{\partial \beta}(\beta p)\right)=\frac{1}{2} d \mathrm{~g} V k_{\mathrm{B}} T \lambda_{T}^{-d} \operatorname{Li}_{\frac{d}{2}+1}(z) \tag{5.156}
\end{align*}
$$

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

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 $\mathrm{g}=1$.
The number of particles is

$$
N= \begin{cases}N_{0}+\zeta(3 / 2) V \lambda_{T}^{-3} & \left(T<T_{\mathrm{c}}\right)  \tag{5.157}\\ V \lambda_{T}^{-3} \mathrm{Li}_{3 / 2}(z) & \left(T>T_{\mathrm{c}}\right),\end{cases}
$$

and the energy is

$$
\begin{equation*}
E=\frac{3}{2} k_{\mathrm{B}} T \frac{V}{\lambda_{T}^{3}} \operatorname{Li}_{5 / 2}(z)=\frac{3}{2} p V \tag{5.158}
\end{equation*}
$$

For $T<T_{\mathrm{c}}$, we have $z=1$ and

$$
\begin{equation*}
C_{V, N}=\left(\frac{\partial E}{\partial T}\right)_{V, N}=\frac{15}{4} \zeta(5 / 2) k_{\mathrm{B}} \frac{V}{\lambda_{T}^{3}} . \tag{5.159}
\end{equation*}
$$

The molar heat capacity is therefore

$$
\begin{equation*}
c_{V, N}(T, n)=N_{\mathrm{A}} \cdot \frac{C_{V, N}}{N}=\frac{15}{4} \zeta(5 / 2) R \cdot\left(n \lambda_{T}^{3}\right)^{-1} . \tag{5.160}
\end{equation*}
$$

For $T>T_{\text {c }}$, we have

$$
\begin{equation*}
\left.d E\right|_{V}=\frac{15}{4} k_{\mathrm{B}} T \mathrm{Li}_{5 / 2}(z) \frac{V}{\lambda_{T}^{3}} \cdot \frac{d T}{T}+\frac{3}{2} k_{\mathrm{B}} T \mathrm{Li}_{3 / 2}(z) \frac{V}{\lambda_{T}^{3}} \cdot \frac{d z}{z}, \tag{5.161}
\end{equation*}
$$



Figure 5.7: Molar heat capacity of the ideal Bose gas (units of $R$ ). Note the cusp at $T=T_{\mathrm{c}}$.
where we have invoked eqn. 5.41. Taking the differential of $N$, we have

$$
\begin{equation*}
\left.d N\right|_{V}=\frac{3}{2} \operatorname{Li}_{3 / 2}(z) \frac{V}{\lambda_{T}^{3}} \cdot \frac{d T}{T}+\operatorname{Li}_{1 / 2}(z) \frac{V}{\lambda_{T}^{3}} \cdot \frac{d z}{z} . \tag{5.162}
\end{equation*}
$$

We set $d N=0$, which fixes $d z$ in terms of $d T$, resulting in

$$
\begin{equation*}
c_{V, N}(T, z)=\frac{3}{2} R \cdot\left[\frac{\frac{5}{2} \mathrm{Li}_{5 / 2}(z)}{\mathrm{Li}_{3 / 2}(z)}-\frac{\frac{3}{2} \mathrm{Li}_{3 / 2}(z)}{\mathrm{Li}_{1 / 2}(z)}\right] \tag{5.163}
\end{equation*}
$$

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

$$
\begin{equation*}
n(T, z)=\lambda_{T}^{-3} \mathrm{Li}_{3 / 2}(z) \tag{5.164}
\end{equation*}
$$

in order to obtain $z(T, n)$, and then insert this into eqn. 5.163. The results are shown in fig. 5.7. 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 $T / T_{\mathrm{c}}(n) \propto T n^{-2 / 3}$. Second, the high temperature limit is $\frac{3}{2} R$, which is the classical value. Finally, there is a cusp at $T=T_{\mathrm{c}}(n)$.
For another example, see $\S 5.10$.

### 5.7.3 Isotherms for the ideal Bose gas

Let $a$ be some length scale and define

$$
\begin{equation*}
v_{a}=a^{3} \quad, \quad p_{a}=\frac{2 \pi \hbar^{2}}{m a^{5}} \quad, \quad T_{a}=\frac{2 \pi \hbar^{2}}{m a^{2} k_{\mathrm{B}}} \tag{5.165}
\end{equation*}
$$



Figure 5.8: Phase diagrams for the ideal Bose gas. Left panel: $(p, v)$ plane. The solid blue curves are isotherms, and the green hatched region denotes $v<v_{\mathrm{c}}(T)$, where the system is partially condensed. Right panel: $(p, T)$ plane. The solid red curve is the coexistence curve $p_{\mathrm{c}}(T)$, along which Bose condensation occurs. No distinct thermodynamic phase exists in the yellow hatched region above $p=p_{\mathrm{c}}(T)$.

Then we have

$$
\begin{align*}
& \frac{v_{a}}{v}=\left(\frac{T}{T_{a}}\right)^{3 / 2} \mathrm{Li}_{3 / 2}(z)+v_{a} n_{0}  \tag{5.166}\\
& \frac{p}{p_{a}}=\left(\frac{T}{T_{a}}\right)^{5 / 2} \mathrm{Li}_{5 / 2}(z) \tag{5.167}
\end{align*}
$$

where $v=V / N$ is the volume per particle ${ }^{8}$ and $n_{0}$ is the condensate number density; $n_{0}$ vanishes for $T \geq T_{\mathrm{c}}$, where $z=1$. One identifies a critical volume $v_{\mathrm{c}}(T)$ by setting $z=1$ and $n_{0}=0$, leading to $v_{\mathrm{c}}(T)=v_{a}\left(T / T_{a}\right)^{3 / 2}$. For $v<v_{\mathrm{c}}(T)$, we set $z=1$ in eqn. 5.166 to find a relation between $v, T$, and $n_{0}$. For $v>v_{\mathrm{c}}(T)$, we set $n_{0}=0$ in eqn. 5.166 to relate $v, T$, and $z$. Note that the pressure is independent of volume for $T<T_{\mathrm{c}}$. The isotherms in the $(p, v)$ plane are then flat for $v<v_{\mathrm{c}}$. This resembles the coexistence region familiar from our study of the thermodynamics of the liquid-gas transition. The situation is depicted in fig. 5.8. In the $(T, p)$ plane, we identify $p_{\mathrm{c}}(T)=p_{a}\left(T / T_{a}\right)^{5 / 2}$ as the critical temperature at which condensation starts to occur.

Recall the Gibbs-Duhem equation, $d \mu=-s d T+v d p$. Along a coexistence curve, we have the ClausiusClapeyron relation,

$$
\begin{equation*}
\left(\frac{d p}{d T}\right)_{\text {coex }}=\frac{s_{2}-s_{1}}{v_{2}-v_{1}}=\frac{\ell}{T \Delta v}, \tag{5.168}
\end{equation*}
$$

where $\ell=T\left(s_{2}-s_{1}\right)$ 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. 5.8. There is no meaning to the

[^4]

Figure 5.9: Phase diagram of ${ }^{4} \mathrm{He}$. 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)
shaded region where $p>p_{\mathrm{c}}(T)$. Nevertheless, it is tempting to associate the curve $p=p_{\mathrm{c}}(T)$ with the coexistence of the $\boldsymbol{k}=0$ condensate and the remaining uncondensed $(\boldsymbol{k} \neq 0)$ bosons ${ }^{9}$.

The entropy in the coexistence region is given by

$$
\begin{equation*}
s=-\frac{1}{N}\left(\frac{\partial \Omega}{\partial T}\right)_{V}=\frac{5}{2} \zeta(5 / 2) k_{\mathrm{B}} v \lambda_{T}^{-3}=\frac{\frac{5}{2} \zeta(5 / 2)}{\zeta(3 / 2)} k_{\mathrm{B}}\left(1-\frac{n_{0}}{n}\right) . \tag{5.169}
\end{equation*}
$$

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 condensate, for which $s_{0}=v_{0}=0$, and the uncondensed bosons, for which $s^{\prime}=s(T)$ and $v^{\prime}=v_{\mathrm{c}}(T)$. 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 $p>$ $p_{\mathrm{c}}(T)$. Ideal Bose gas condensation is a second order transition, and not a first order transition.

### 5.7.4 The $\lambda$-transition in liquid ${ }^{4} \mathrm{He}$

Helium has two stable isotopes. ${ }^{4} \mathrm{He}$ is a boson, consisting of two protons, two neutrons, and two electrons (hence an even number of fermions). ${ }^{3} \mathrm{He}$ is a fermion, with one less neutron than ${ }^{4} \mathrm{He}$. Each ${ }^{4} \mathrm{He}$ atom can be regarded as a tiny hard sphere of mass $m=6.65 \times 10^{-24} \mathrm{~g}$ and diameter $a=2.65 \AA$. A sketch of the phase diagram is shown in fig. 5.9. At atmospheric pressure, helium liquefies at $T_{1}=4.2 \mathrm{~K}$. The gas-liquid transition is first order, as usual. However, as one continues to cool, a second transition sets in at $T=T_{\lambda}=2.17 \mathrm{~K}$ (at $p=1 \mathrm{~atm}$ ). The $\lambda$-transition, so named for the $\lambda$-shaped anomaly in the specific heat in the vicinity of the transition, as shown in fig. 5.10, is continuous (i.e. second order).

[^5]

Figure 5.10: Specific heat of liquid ${ }^{4} \mathrm{He}$ in the vicinity of the $\lambda$-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 $\Delta T=2 \mathrm{nK}$ of the transition.

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

$$
\begin{equation*}
C_{p}(T)=A\left|T-T_{\lambda}(p)\right|^{-\alpha} . \tag{5.170}
\end{equation*}
$$

$\alpha$ is an example of a critical exponent. We shall study the physics of critical phenomena later on in this course. While the cusp singularity of the type found in fig. 5.7 suggests $\alpha=-1$, this is true for $C_{V}(T)$, and for $C_{p}(T)$ one finds instead $\alpha=\frac{1}{2}$ (see the calculation in $\S 5.11$ ). The observed behavior of $C_{p}(T)$ in ${ }^{4} \mathrm{He}$ is very nearly logarithmic in $\left|T-T_{\lambda}\right|$. In fact, both theory (renormalization group on the $\mathrm{O}(2)$ model) and experiment concur that $\alpha$ is almost zero but in fact slightly negative, with $\alpha=-0.0127 \pm 0.0003$ in the best experiments (Lipa et al., 2003). The $\lambda$ transition is most definitely not an ideal Bose gas condensation. Theoretically, in the parlance of critical phenomena, IBG condensation and the $\lambda$-transition in ${ }^{4} \mathrm{He}$ lie in different universality classes ${ }^{10}$. Unlike the IBG, the condensed phase in ${ }^{4} \mathrm{He}$ is a distinct thermodynamic phase, known as a superfluid. Note that $C_{p}\left(T<T_{\mathrm{c}}\right)$ for the IBG is not even defined, since for $T<T_{\mathrm{c}}$ we

[^6]

Figure 5.11: 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.
have $p=p(T)$ and therefore $d p=0$ requires $d T=0$.

### 5.7.5 Fountain effect in superfluid ${ }^{4} \mathrm{He}$

At temperatures $T<T_{\lambda}$, liquid ${ }^{4} \mathrm{He}$ 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 $\rho_{\mathrm{s}}$. In ${ }^{4} \mathrm{He}$, for example, at $T=0$ the condensate fraction is only about $8 \%$, while the superfluid fraction $\rho_{\mathrm{s}} / \rho=1$. The distinction between $N_{0}$ and $\rho_{s}$ 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 maintained ${ }^{11}$.

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 $\omega(k)=c k$ where $c=238 \mathrm{~m} / \mathrm{s} .{ }^{12}$ The have no internal degrees of freedom, hence $\mathrm{g}=1$. 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. We can now compute the height difference $\Delta h$ in a U-tube experiment.

[^7]Clearly $\Delta h=\Delta p / \rho g$. so we must find $p(T)$ for the helium. In the grand canonical ensemble, we have

$$
\begin{align*}
p & =-\Omega / V=-k_{\mathrm{B}} T \int \frac{d^{3} k}{(2 \pi)^{3}} \ln \left(1-e^{-\hbar c k / k_{\mathrm{B}} T}\right) \\
& =-\frac{\left(k_{\mathrm{B}} T\right)^{4}}{(\hbar c)^{3}} \frac{4 \pi}{8 \pi^{3}} \int_{0}^{\infty} d u u^{2} \ln \left(1-e^{-u}\right)=\frac{\pi^{2}}{90} \frac{\left(k_{\mathrm{B}} T\right)^{4}}{(\hbar c)^{3}} . \tag{5.171}
\end{align*}
$$

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

$$
\begin{align*}
\frac{d h}{d T} & =\frac{2 \pi^{2}}{45}\left(\frac{k_{\mathrm{B}} T}{\hbar c}\right)^{3} \frac{k_{\mathrm{B}}}{\rho g}  \tag{5.172}\\
& =\frac{2 \pi^{2}}{45}\left(\frac{\left(1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}\right)(1 \mathrm{~K})}{\left(1.055 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s}\right)(238 \mathrm{~m} / \mathrm{s})}\right)^{3} \times \frac{\left(1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}\right)}{\left(148 \mathrm{~kg} / \mathrm{m}^{3}\right)\left(9.8 \mathrm{~m} / \mathrm{s}^{2}\right)} \simeq 32 \mathrm{~cm} / \mathrm{K}
\end{align*}
$$

a very noticeable effect!

### 5.8 The Ideal Fermi Gas

### 5.8.1 Grand potential and particle number

The grand potential of the ideal Fermi gas is, per eqn. 5.11,

$$
\begin{align*}
\Omega(T, V, \mu) & =-V k_{\mathrm{B}} T \sum_{\alpha} \ln \left(1+e^{\mu / k_{\mathrm{B}} T} e^{-\varepsilon_{\alpha} / k_{\mathrm{B}} T}\right) \\
& =-V k_{\mathrm{B}} T \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \ln \left(1+e^{(\mu-\varepsilon) / k_{\mathrm{B}} T}\right) . \tag{5.173}
\end{align*}
$$

The average number of particles in a state with energy $\varepsilon$ is

$$
\begin{equation*}
n(\varepsilon)=\frac{1}{e^{(\varepsilon-\mu) / k_{\mathrm{B}} T}+1} \tag{5.174}
\end{equation*}
$$

hence the total number of particles is

$$
\begin{equation*}
N=V \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \frac{1}{e^{(\varepsilon-\mu) / k_{\mathrm{B}} T}+1} \tag{5.175}
\end{equation*}
$$

### 5.8.2 The Fermi distribution

We define the function

$$
\begin{equation*}
f(\epsilon) \equiv \frac{1}{e^{\epsilon / k_{\mathbf{B}} T}+1} \tag{5.176}
\end{equation*}
$$



Figure 5.12: The Fermi distribution, $f(\epsilon)=\left[\exp \left(\epsilon / k_{\mathrm{B}} T\right)+1\right]^{-1}$. Here we have set $k_{\mathrm{B}}=1$ and taken $\mu=2$, with $T=\frac{1}{20}$ (blue), $T=\frac{3}{4}$ (green), and $T=2$ (red). In the $T \rightarrow 0$ limit, $f(\epsilon)$ approaches a step function $\Theta(-\epsilon)$.
known as the Fermi distribution. In the $T \rightarrow \infty$ limit, $f(\epsilon) \rightarrow \frac{1}{2}$ for all finite values of $\varepsilon$. As $T \rightarrow 0, f(\epsilon)$ approaches a step function $\Theta(-\epsilon)$. The average number of particles in a state of energy $\varepsilon$ in a system at temperature $T$ and chemical potential $\mu$ is $n(\varepsilon)=f(\varepsilon-\mu)$. In fig. 5.12 we plot $f(\varepsilon-\mu)$ versus $\varepsilon$ for three representative temperatures.

### 5.8.3 $T=0$ and the Fermi surface

At $T=0$, we therefore have $n(\varepsilon)=\Theta(\mu-\varepsilon)$, 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: $\varepsilon_{\mathrm{F}}=\mu(T=0)$. If the single particle dispersion $\varepsilon(\boldsymbol{k})$ depends only on the wavevector $\boldsymbol{k}$, then the locus of points in $\boldsymbol{k}$ space for which $\varepsilon(\boldsymbol{k})=\varepsilon_{\mathrm{F}}$ is called the Fermi surface. For isotropic systems, $\varepsilon(\boldsymbol{k})=\varepsilon(k)$ is a function only of the magnitude $k=|\boldsymbol{k}|$, 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, $k_{\mathrm{F}}$. 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 $k_{\mathrm{F}}$ and Fermi energy $\varepsilon_{\mathrm{F}}$ for the IFG with a ballistic dispersion $\varepsilon(\boldsymbol{k})=\hbar^{2} \boldsymbol{k}^{2} / 2 m$. The number density is

$$
\begin{equation*}
n=\mathrm{g} \int \frac{d^{d} k}{(2 \pi)^{d}} \Theta\left(k_{\mathrm{F}}-k\right)=\frac{\mathrm{g} \Omega_{d}}{(2 \pi)^{d}} \cdot \frac{k_{\mathrm{F}}^{d}}{d} \tag{5.177}
\end{equation*}
$$

and thus

$$
\begin{equation*}
n_{d=1}=\mathrm{g} k_{\mathrm{F}} / \pi \quad, \quad n_{d=2}=\mathrm{g} k_{\mathrm{F}}^{2} / 4 \pi \quad, \quad n_{d=3}=\mathrm{g} k_{\mathrm{F}}^{3} / 6 \pi^{2} \tag{5.178}
\end{equation*}
$$

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 $n\left(k_{\mathrm{F}}\right)$ is independent of the dispersion relation, so long as it remains isotropic. Inverting the above expressions, we obtain $k_{\mathrm{F}}(n)=2 \pi\left(d n / \mathrm{g} \Omega_{d}\right)^{1 / d}$ :

$$
\begin{equation*}
k_{\mathrm{F}, d=1}=\pi n / \mathrm{g} \quad, \quad k_{\mathrm{F}, d=2}=(4 \pi n / \mathrm{g})^{1 / 2} \quad, \quad k_{\mathrm{F}, d=3}=\left(6 \pi^{2} n / \mathrm{g}\right)^{1 / 3} \tag{5.179}
\end{equation*}
$$

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

$$
\begin{equation*}
\varepsilon_{\mathrm{F}}=\frac{\hbar^{2} k_{\mathrm{F}}^{2}}{2 m}=\frac{2 \pi^{2} \hbar^{2}}{m}\left(\frac{d n}{\mathrm{~g} \Omega_{d}}\right)^{2 / d}, \tag{5.180}
\end{equation*}
$$

and so

$$
\begin{equation*}
\varepsilon_{\mathrm{F}, d=1}=\frac{\pi^{2} \hbar^{2} n^{2}}{2 \mathrm{~g}^{2} m} \quad, \quad \varepsilon_{\mathrm{F}, d=2}=\frac{2 \pi \hbar^{2} n}{\mathrm{~g} m} \quad, \quad \varepsilon_{\mathrm{F}, d=3}=\frac{\hbar^{2}}{2 m}\left(\frac{6 \pi^{2} n}{\mathrm{~g}}\right)^{2 / 3} \tag{5.181}
\end{equation*}
$$

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

$$
\begin{equation*}
g\left(\varepsilon_{\mathrm{F}}\right)=\frac{\mathrm{g} \Omega_{d}}{(2 \pi)^{d}} \cdot \frac{m k_{\mathrm{F}}^{d-2}}{\hbar^{2}}=\frac{d}{2} \cdot \frac{n}{\varepsilon_{\mathrm{F}}} \tag{5.182}
\end{equation*}
$$

That $g\left(\varepsilon_{\mathrm{F}}\right)$ must be a numerical factor multiplied by $n / \varepsilon_{\mathrm{F}}$ is obvious on dimensional grounds.
For the electron gas, we have $\mathrm{g}=2$. In a metal, one typically has $k_{\mathrm{F}} \sim 0.5 \AA^{-1}$ to $2 \AA^{-1}$, and $\varepsilon_{\mathrm{F}} \sim$ $1 \mathrm{eV}-10 \mathrm{eV}$. Due to the effects of the crystalline lattice, electrons in a solid behave as if they had 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.

Nonisotropic dispersions $\varepsilon(\boldsymbol{k})$ 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

$$
\begin{equation*}
\varepsilon\left(k_{x}, k_{y}\right)=-2 t \cos \left(k_{x} a\right)-2 t \cos \left(k_{y} a\right) \tag{5.183}
\end{equation*}
$$

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

$$
\begin{equation*}
\varepsilon\left(k_{x}, k_{y}\right)=-4 t+t a^{2}\left(k_{x}^{2}+k_{y}^{2}\right)-\frac{1}{12} t a^{4}\left(k_{x}^{4}+k_{y}^{4}\right)+\ldots . \tag{5.184}
\end{equation*}
$$

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 $k_{\mathrm{F}}^{2}=\left(\varepsilon_{\mathrm{F}}+4 t\right) / t a^{2}$. As the energy increases further, the continuous $\mathrm{O}(2)$ rotational invariance is broken down to the discrete group of rotations of the square, $C_{4 v}$. The Fermi surfaces distort and eventually, at $\varepsilon_{\mathrm{F}}=0$, the Fermi surface is itself a square. As $\varepsilon_{\mathrm{F}}$ increases further, the square turns back into a circle, but centered about the point $\left(\frac{\pi}{a}, \frac{\pi}{a}\right)$. 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. 5.13.
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. 5.13. The electronic configuration of cesium (Cs) is $[\mathrm{Xe}] 6 s^{1}$. The $6 s$ 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 $\boldsymbol{k}$ space, known as the first Brillouin zone, turns out to be a dodecahedron. In yttrium, the electronic structure is $[\mathrm{Kr}] 5 s^{2} 4 d^{1}$, 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.


Figure 5.13: Fermi surfaces for two and three-dimensional structures. 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 $6 s$ orbital shell. Lower right: the Fermi surface of yttrium has two parts. One part (yellow) is predominantly due to $5 s$ electrons, while the other (pink) is due to $4 d$ electrons. (Source: www.phys.ufl.edu/fermisurface/)

## Spin-split Fermi surfaces

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

$$
\begin{equation*}
\hat{H}=\frac{\boldsymbol{p}^{2}}{2 m}+\mu_{\mathrm{B}} H \sigma \tag{5.185}
\end{equation*}
$$

where $\mu_{\mathrm{B}}$ is the Bohr magneton, $\mu_{\mathrm{B}}=e \hbar / 2 m c=5.788 \times 10^{-9} \mathrm{eV} / \mathrm{G}$. It is convenient to keep in mind the ratio $\mu_{\mathrm{B}} / k_{\mathrm{B}}=6.717 \times 10^{-5} \mathrm{~K} / \mathrm{G}$. 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 $k_{\mathrm{F} \uparrow}$, and a down spin Fermi surface, with Fermi wavevector $k_{\mathrm{F} \downarrow}$. The individual Fermi energies, on the other hand, must be equal, hence

$$
\begin{equation*}
\frac{\hbar^{2} k_{\mathrm{F} \uparrow}^{2}}{2 m}+\mu_{\mathrm{B}} H=\frac{\hbar^{2} k_{\mathrm{F} \downarrow}^{2}}{2 m}-\mu_{\mathrm{B}} H, \tag{5.186}
\end{equation*}
$$

which says

$$
\begin{equation*}
k_{\mathrm{F} \downarrow}^{2}-k_{\mathrm{F} \uparrow}^{2}=\frac{2 e H}{\hbar c} . \tag{5.187}
\end{equation*}
$$

The total density is

$$
\begin{equation*}
n=\frac{k_{\mathrm{F} \uparrow}^{3}}{6 \pi^{2}}+\frac{k_{\mathrm{F} \downarrow}^{3}}{6 \pi^{2}} \quad \Longrightarrow \quad k_{\mathrm{F} \uparrow}^{3}+k_{\mathrm{F} \downarrow}^{3}=6 \pi^{2} n \tag{5.188}
\end{equation*}
$$

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 $k_{\mathrm{F} \uparrow}=0$. Solving for the critical field, we obtain

$$
\begin{equation*}
H_{\mathrm{c}}=\frac{\hbar c}{2 e} \cdot\left(6 \pi^{2} n\right)^{2 / 3} . \tag{5.189}
\end{equation*}
$$

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. 5.13.

### 5.8.4 The Sommerfeld expansion

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

$$
\begin{equation*}
\mathcal{I}(T, \mu) \equiv \int_{-\infty}^{\infty} d \varepsilon f(\varepsilon-\mu) \phi(\varepsilon) \tag{5.190}
\end{equation*}
$$

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

$$
\begin{equation*}
\Phi(\varepsilon) \equiv \int_{-\infty}^{\varepsilon} d \varepsilon^{\prime} \phi\left(\varepsilon^{\prime}\right) \tag{5.191}
\end{equation*}
$$

so that $\phi(\varepsilon)=\Phi^{\prime}(\varepsilon)$. We then have

$$
\begin{equation*}
\mathcal{I}(T, \mu)=\int_{-\infty}^{\infty} d \varepsilon f(\varepsilon-\mu) \frac{d \Phi}{d \varepsilon}=-\int_{-\infty}^{\infty} d \varepsilon f^{\prime}(\varepsilon) \Phi(\mu+\varepsilon) \tag{5.192}
\end{equation*}
$$

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

$$
\begin{equation*}
\Phi(\mu+\varepsilon)=\sum_{n=0}^{\infty} \frac{\varepsilon^{n}}{n!} \frac{d^{n} \Phi}{d \mu^{n}}=\exp \left(\varepsilon \frac{d}{d \mu}\right) \Phi(\mu) . \tag{5.193}
\end{equation*}
$$

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

$$
\begin{equation*}
f^{\prime}(\varepsilon)=-\frac{1}{k_{\mathrm{B}} T} \frac{e^{\varepsilon / k_{\mathrm{B}} T}}{\left(e^{\varepsilon / k_{\mathrm{B}} T}+1\right)^{2}} \tag{5.194}
\end{equation*}
$$



Figure 5.14: Deformation of the complex integration contour in eqn. 5.196.
we define

$$
\begin{equation*}
\widetilde{\mathcal{I}}(T, \mu)=\int_{-\infty}^{\infty} d v \frac{e^{v D}}{\left(e^{v}+1\right)\left(e^{-v}+1\right)} \Phi(\mu) \tag{5.195}
\end{equation*}
$$

with $v=\varepsilon / k_{\mathrm{B}} T$, where $D=k_{\mathrm{B}} T \frac{d}{d \mu}$ is a dimensionless differential operator. The integral can now be done using the methods of complex integration: ${ }^{13}$

$$
\begin{align*}
\int_{-\infty}^{\infty} d v \frac{e^{v D}}{\left(e^{v}+1\right)\left(e^{-v}+1\right)} & =2 \pi i \sum_{n=1}^{\infty} \operatorname{Res}\left[\frac{e^{v D}}{\left(e^{v}+1\right)\left(e^{-v}+1\right)}\right]_{v=(2 n+1) i \pi}  \tag{5.196}\\
& =-2 \pi i \sum_{n=0}^{\infty} D e^{(2 n+1) i \pi D}=-\frac{2 \pi i D e^{i \pi D}}{1-e^{2 \pi i D}}=\pi D \csc \pi D
\end{align*}
$$

Thus,

$$
\begin{equation*}
\tilde{\mathcal{I}}(T, \mu)=\pi D \csc (\pi D) \Phi(\mu) \tag{5.197}
\end{equation*}
$$

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

$$
\begin{equation*}
\pi D \csc (\pi D)=1+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} \frac{d^{2}}{d \mu^{2}}+\frac{7 \pi^{4}}{360}\left(k_{\mathrm{B}} T\right)^{4} \frac{d^{4}}{d \mu^{4}}+\ldots . \tag{5.198}
\end{equation*}
$$

Thus,

$$
\begin{equation*}
\widetilde{\mathcal{I}}(T, \mu)=\int_{-\infty}^{\infty} d \varepsilon f(\varepsilon-\mu) \phi(\varepsilon)=\int_{-\infty}^{\mu} d \varepsilon \phi(\varepsilon)+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} \phi^{\prime}(\mu)+\frac{7 \pi^{4}}{360}\left(k_{\mathrm{B}} T\right)^{4} \phi^{\prime \prime \prime}(\mu)+\ldots \tag{5.199}
\end{equation*}
$$

[^8]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 $\left(k_{\mathrm{B}} T / \mu\right)^{2}$. This procedure is known as the Sommerfeld expansion. The reason we introduce the notation $\widetilde{I}(T, \mu)$ is that the function $I(T, \mu)$ may contain nonanalytic terms which are invisible in the Taylor series expansion, 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

$$
\begin{equation*}
n=\int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) f(\varepsilon-\mu)=\int_{-\infty}^{\mu} d \varepsilon g(\varepsilon)+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} g^{\prime}(\mu)+\ldots \tag{5.200}
\end{equation*}
$$

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

$$
\begin{align*}
n & =\int_{-\infty}^{\varepsilon_{\mathrm{F}}+\delta \mu} d \varepsilon g(\varepsilon)+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} g^{\prime}\left(\varepsilon_{\mathrm{F}}+\delta \mu\right)+\ldots  \tag{5.201}\\
& =\int_{-\infty}^{\varepsilon_{\mathrm{F}}} d \varepsilon g(\varepsilon)+g\left(\varepsilon_{\mathrm{F}}\right) \delta \mu+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} g^{\prime}\left(\varepsilon_{\mathrm{F}}\right)+\ldots,
\end{align*}
$$

from which we derive

$$
\begin{equation*}
\delta \mu=-\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} \frac{g^{\prime}\left(\varepsilon_{\mathrm{F}}\right)}{g\left(\varepsilon_{\mathrm{F}}\right)}+\mathcal{O}\left(T^{4}\right) . \tag{5.202}
\end{equation*}
$$

Note that $g^{\prime} / g=(\ln g)^{\prime}$. For a ballistic dispersion, assuming $g=2$,

$$
\begin{equation*}
g(\varepsilon)=2 \int \frac{d^{3} k}{(2 \pi)^{3}} \delta\left(\varepsilon-\frac{\hbar^{2} k^{2}}{2 m}\right)=\left.\frac{m k(\varepsilon)}{\pi^{2} \hbar^{2}}\right|_{k(\varepsilon)=\frac{1}{\hbar} \sqrt{2 m \varepsilon}} \tag{5.203}
\end{equation*}
$$

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

$$
\begin{equation*}
\mu(n, T)=\varepsilon_{\mathrm{F}}-\frac{\pi^{2}}{12} \frac{\left(k_{\mathrm{B}} T\right)^{2}}{\varepsilon_{\mathrm{F}}}+\ldots \tag{5.204}
\end{equation*}
$$

where $\varepsilon_{\mathrm{F}}(n)=\frac{\hbar^{2}}{2 m}\left(3 \pi^{2} n\right)^{2 / 3}$.

## Specific heat

The energy of the electron gas is

$$
\begin{align*}
\frac{E}{V} & =\int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \varepsilon f(\varepsilon-\mu) \\
& =\int_{-\infty}^{\mu} d \varepsilon g(\varepsilon) \varepsilon+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} \frac{d}{d \mu}(\mu g(\mu))+\ldots  \tag{5.205}\\
& =\int_{-\infty}^{\varepsilon_{\mathrm{F}}} d \varepsilon g(\varepsilon) \varepsilon+g\left(\varepsilon_{\mathrm{F}}\right) \varepsilon_{\mathrm{F}} \delta \mu+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} \varepsilon_{\mathrm{F}} g^{\prime}\left(\varepsilon_{\mathrm{F}}\right)+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} g\left(\varepsilon_{\mathrm{F}}\right)+\ldots \\
& =\varepsilon_{0}+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} g\left(\varepsilon_{\mathrm{F}}\right)+\ldots
\end{align*}
$$

where $\varepsilon_{0}=\int_{-\infty}^{\varepsilon_{\mathrm{F}}} d \varepsilon g(\varepsilon) \varepsilon$. is the ground state energy density (i.e. ground state energy per unit volume). Thus, to order $T^{2}$,

$$
\begin{equation*}
C_{V, N}=\left(\frac{\partial E}{\partial T}\right)_{V, N}=\frac{\pi^{2}}{3} V k_{\mathrm{B}}^{2} T g\left(\varepsilon_{\mathrm{F}}\right) \equiv V \gamma T \tag{5.206}
\end{equation*}
$$

where $\gamma(n)=\frac{\pi^{2}}{3} k_{\mathrm{B}}^{2} g\left(\varepsilon_{\mathrm{F}}(n)\right)$. Note that the molar heat capacity is

$$
\begin{equation*}
c_{V}=\frac{N_{\mathrm{A}}}{N} \cdot C_{V}=\frac{\pi^{2}}{3} R \cdot \frac{k_{\mathrm{B}} T g\left(\varepsilon_{\mathrm{F}}\right)}{n}=\frac{\pi^{2}}{2}\left(\frac{k_{\mathrm{B}} T}{\varepsilon_{\mathrm{F}}}\right) R \tag{5.207}
\end{equation*}
$$

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

$$
\begin{equation*}
\frac{g\left(\varepsilon_{\mathrm{F}}\right)}{n}=\frac{\mathrm{g} m k_{\mathrm{F}}}{2 \pi^{2} \hbar^{2}} \cdot \frac{6 \pi^{2}}{\mathrm{~g} k_{\mathrm{F}}^{3}}=\frac{3}{2 \varepsilon_{\mathrm{F}}} \tag{5.208}
\end{equation*}
$$

The molar heat capacity in eqn. 5.207 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 $\left(\pi^{2} / 3\right) \times\left(k_{\mathrm{B}} T / \varepsilon_{\mathrm{F}}\right)$, 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 capacity ${ }^{14}$ : Starting with eqn. 5.202 for $\mu(T)-\varepsilon_{\mathrm{F}} \equiv \delta \mu(T)$, note that $g\left(\varepsilon_{\mathrm{F}}\right)=d n / d \varepsilon_{\mathrm{F}}$, so we may write $\delta \mu=-\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2}(d g / d n)+\mathcal{O}\left(T^{4}\right)$. Next, use the Maxwell relation $(\partial S / \partial N)_{T, V}=-(\partial \mu / \partial T)_{N, V}$ to arrive at

$$
\begin{equation*}
\left(\frac{\partial s}{\partial n}\right)_{T}=\frac{\pi^{2}}{3} k_{\mathrm{B}}^{2} T \frac{\partial g\left(\varepsilon_{\mathrm{F}}\right)}{\partial n}+\mathcal{O}\left(T^{3}\right) \tag{5.209}
\end{equation*}
$$

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.

[^9]
## 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

$$
\begin{equation*}
\mathcal{I}(T, \mu)=\int_{0}^{\infty} d \varepsilon f(\varepsilon-\mu)=\mu+k_{\mathrm{B}} T \ln \left(1+e^{-\mu / k_{\mathrm{B}} T}\right) \tag{5.210}
\end{equation*}
$$

By contrast, the Sommerfeld expansion, assuming $\mu \neq 0$, yields $\widetilde{I}(T, \mu)=\mu$, and is missing the second term above. This is because $\exp \left(-\mu / k_{\mathrm{B}} T\right)$ 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

$$
\begin{equation*}
\widetilde{\mathcal{I}}(T, \mu)=\frac{1}{2} \mu^{2}+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} \tag{5.211}
\end{equation*}
$$

while the exact result is

$$
\begin{equation*}
\mathcal{I}(T, \mu)=\frac{1}{2} \mu^{2}+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2}+\left(k_{\mathrm{B}} T\right)^{2} \sum_{j=1}^{\infty} \frac{(-1)^{j}}{j^{2}} e^{-j \mu / k_{\mathrm{B}} T} \tag{5.212}
\end{equation*}
$$

which follows from the polylogarithm identity

$$
\begin{equation*}
\mathrm{Li}_{2}(z)+\mathrm{Li}_{2}(1 / z)=-\frac{1}{2}[\ln (-z)]^{2}-\frac{\pi^{2}}{6} \tag{5.213}
\end{equation*}
$$

Again we see that the Sommerfeld expansion terminates at a finite order in $T$, and is missing nonanalytic terms in the $T \rightarrow 0$ limit $^{15}$. This is a generic state of affairs for the case where $\phi(\varepsilon)$ is a finite order polynomial in $\varepsilon$.

### 5.8.5 Magnetic susceptibility

## Pauli paramagnetism

Magnetism has two origins: (i) orbital currents of charged particles, and (ii) intrinsic magnetic moment. The intrinsic magnetic moment $m$ of a particle is related to its quantum mechanical spin according to $\boldsymbol{m}=g \mu_{0} \boldsymbol{S} / \hbar$, where $\mu_{0}=q \hbar /$ over $2 m c$ is the magneton. Here $g$ is the particle's $g$-factor, $\mu_{0}$ its magnetic moment, and $S$ is the vector of quantum mechanical spin operators satisfying $\left[S^{\alpha}, S^{\beta}\right]=i \hbar \epsilon_{\alpha \beta \gamma} S^{\gamma}$, i.e. $\mathrm{SU}(2)$ commutation relations. The Hamiltonian for a single particle is then

$$
\begin{equation*}
\hat{H}=\frac{1}{2 m^{*}}\left(\boldsymbol{p}-\frac{q}{c} \boldsymbol{A}\right)^{2}-\boldsymbol{H} \cdot \boldsymbol{m}=\frac{1}{2 m^{*}}\left(\boldsymbol{p}+\frac{e}{c} \boldsymbol{A}\right)^{2}+\frac{g}{2} \mu_{\mathrm{B}} H \sigma \tag{5.214}
\end{equation*}
$$

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

[^10]can always absorb the small difference into the definition of $\mu_{\mathrm{B}}$, writing $\mu_{\mathrm{B}} \rightarrow \tilde{\mu}_{\mathrm{B}}=g e \hbar / 4 m c$. 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 $\boldsymbol{p}^{2} / 2 m^{*}$, but it is the electron mass $m$ itself ( $m=511 \mathrm{keV}$ ) 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
\[

$$
\begin{equation*}
\varepsilon_{\sigma}(\boldsymbol{k})=\frac{\hbar^{2} \boldsymbol{k}^{2}}{2 m^{*}}+\tilde{\mu}_{\mathrm{B}} H \sigma . \tag{5.215}
\end{equation*}
$$

\]

At $T=0$, we have the results of $\S 5.8 .3$. At finite $T$, we once again use the Sommerfeld expansion. We then have

$$
\begin{align*}
n & =\int_{-\infty}^{\infty} d \varepsilon g_{\uparrow}(\varepsilon) f(\varepsilon-\mu)+\int_{-\infty}^{\infty} d \varepsilon g_{\downarrow}(\varepsilon) f(\varepsilon-\mu) \\
& =\frac{1}{2} \int_{-\infty}^{\infty} d \varepsilon\left\{g\left(\varepsilon-\tilde{\mu}_{\mathrm{B}} H\right)+g\left(\varepsilon+\tilde{\mu}_{\mathrm{B}} H\right)\right\} f(\varepsilon-\mu)  \tag{5.216}\\
& =\int_{-\infty}^{\infty} d \varepsilon\left\{g(\varepsilon)+\left(\tilde{\mu}_{\mathrm{B}} H\right)^{2} g^{\prime \prime}(\varepsilon)+\ldots\right\} f(\varepsilon-\mu) .
\end{align*}
$$

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

$$
\begin{align*}
n & =\int_{-\infty}^{\mu} d \varepsilon g(\varepsilon)+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} g^{\prime}(\mu)+\left(\tilde{\mu}_{\mathrm{B}} H\right)^{2} g^{\prime}(\mu)+\ldots \\
& =\int_{-\infty}^{\varepsilon_{\mathrm{F}}} d \varepsilon g(\varepsilon)+g\left(\varepsilon_{\mathrm{F}}\right) \delta \mu+\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2} g^{\prime}\left(\varepsilon_{\mathrm{F}}\right)+\left(\tilde{\mu}_{\mathrm{B}} H\right)^{2} g^{\prime}\left(\varepsilon_{\mathrm{F}}\right)+\ldots \tag{5.217}
\end{align*}
$$

Note that the density of states for spin species $\sigma$ is $g_{\sigma}(\varepsilon)=\frac{1}{2} g\left(\varepsilon-\tilde{\mu}_{\mathrm{B}} H \sigma\right)$, 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

$$
\begin{equation*}
\delta \mu(T, n, H)=-\left\{\frac{\pi^{2}}{6}\left(k_{\mathrm{B}} T\right)^{2}+\left(\tilde{\mu}_{\mathrm{B}} H\right)^{2}\right\} \frac{g^{\prime}\left(\varepsilon_{\mathrm{F}}\right)}{g\left(\varepsilon_{\mathrm{F}}\right)}+\ldots . \tag{5.218}
\end{equation*}
$$

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

$$
\begin{align*}
n_{\uparrow}-n_{\downarrow} & =\int_{-\infty}^{\infty} d \varepsilon\left\{g_{\uparrow}(\varepsilon)-g_{\downarrow}(\varepsilon)\right\} f(\varepsilon-\mu) \\
& =\frac{1}{2} \int_{-\infty}^{\infty} d \varepsilon\left\{g\left(\varepsilon-\tilde{\mu}_{\mathrm{B}} H\right)-g\left(\varepsilon+\tilde{\mu}_{\mathrm{B}} H\right)\right\} f(\varepsilon-\mu)  \tag{5.219}\\
& =-\tilde{\mu}_{\mathrm{B}} H \cdot \pi D \csc (\pi D) g(\mu)+\mathcal{O}\left(H^{3}\right)
\end{align*}
$$



Figure 5.15: Fermi distributions in the presence of an external Zeeman-coupled magnetic field.

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

$$
\begin{equation*}
M=-\tilde{\mu}_{\mathrm{B}}\left(n_{\uparrow}-n_{\downarrow}\right)=\tilde{\mu}_{\mathrm{B}}^{2} g\left(\varepsilon_{\mathrm{F}}\right) H \tag{5.220}
\end{equation*}
$$

in which the magnetic susceptibility is

$$
\begin{equation*}
\chi=\left(\frac{\partial M}{\partial H}\right)_{T, N}=\tilde{\mu}_{\mathrm{B}}^{2} g\left(\varepsilon_{\mathrm{F}}\right) \tag{5.221}
\end{equation*}
$$

This is called the Pauli paramagnetic susceptibility.

## Landau diamagnetism

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

$$
\begin{equation*}
\varepsilon\left(n, k_{z}, \sigma\right)=\left(n+\frac{1}{2}\right) \hbar \omega_{\mathrm{c}}+\frac{\hbar^{2} k_{z}^{2}}{2 m^{*}}+\tilde{\mu}_{\mathrm{B}} H \sigma \tag{5.222}
\end{equation*}
$$

Here $n$ is a Landau level index, and $\omega_{\mathrm{c}}=e H / m^{*} c$ is the cyclotron frequency. Note that

$$
\begin{equation*}
\frac{\tilde{\mu}_{\mathrm{B}} H}{\hbar \omega_{\mathrm{c}}}=\frac{g e \hbar H}{4 m c} \cdot \frac{m^{*} c}{\hbar e H}=\frac{g}{4} \cdot \frac{m^{*}}{m} . \tag{5.223}
\end{equation*}
$$

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

$$
\begin{equation*}
\varepsilon\left(n, k_{z}, \sigma\right)=\left(n+\frac{1}{2}+\frac{1}{2} r \sigma\right) \hbar \omega_{\mathrm{c}}+\frac{\hbar^{2} k_{z}^{2}}{2 m^{*}} \tag{5.224}
\end{equation*}
$$

The grand potential is then given by

$$
\begin{equation*}
\Omega=-\frac{H A}{\phi_{0}} \cdot L_{z} \cdot k_{\mathrm{B}} T \int_{-\infty}^{\infty} \frac{d k_{z}}{2 \pi} \sum_{n=0}^{\infty} \sum_{\sigma= \pm 1} \ln \left[1+e^{\mu / k_{\mathrm{B}} T} e^{-\left(n+\frac{1}{2}+\frac{1}{2} r \sigma\right) \hbar \omega_{\mathrm{c}} / k_{\mathrm{B}} T} e^{-\hbar^{2} k_{z}^{2} / 2 m^{*} k_{\mathrm{B}} T}\right] . \tag{5.225}
\end{equation*}
$$

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: $N_{\phi}=H A / \phi_{0}$, where $\phi_{0}=h c / e$ is the Dirac flux quantum. Note that

$$
\begin{equation*}
\frac{H A}{\phi_{0}} \cdot L_{z} \cdot k_{\mathrm{B}} T=\hbar \omega_{\mathrm{c}} \cdot \frac{V}{\lambda_{T}^{3}} \tag{5.226}
\end{equation*}
$$

hence we can write

$$
\begin{equation*}
\Omega(T, V, \mu, H)=\hbar \omega_{\mathrm{c}} \sum_{n=0}^{\infty} \sum_{\sigma= \pm 1} Q\left(\left(n+\frac{1}{2}+\frac{1}{2} r \sigma\right) \hbar \omega_{\mathrm{c}}-\mu\right) \tag{5.227}
\end{equation*}
$$

where

$$
\begin{equation*}
Q(\varepsilon)=-\frac{V}{\lambda_{T}^{2}} \int_{-\infty}^{\infty} \frac{d k_{z}}{2 \pi} \ln \left[1+e^{-\varepsilon / k_{\mathrm{B}} T} e^{-\hbar^{2} k_{z}^{2} / 2 m^{*} k_{\mathrm{B}} T}\right] \tag{5.228}
\end{equation*}
$$

We now invoke the Euler-MacLaurin formula,

$$
\begin{equation*}
\sum_{n=0}^{\infty} F(n)=\int_{0}^{\infty} d x F(x)+\frac{1}{2} F(0)-\frac{1}{12} F^{\prime}(0)+\ldots \tag{5.229}
\end{equation*}
$$

resulting in

$$
\begin{align*}
& \Omega=\sum_{\sigma} \int_{-\infty}^{\infty} d \varepsilon Q(\varepsilon-\mu) \Theta\left(\varepsilon-\frac{1}{2}(1+\sigma r) \hbar \omega_{\mathrm{c}}\right)  \tag{5.230}\\
&+\sum_{\sigma}\left[\frac{1}{2} \hbar \omega_{\mathrm{c}} Q\left(\frac{1}{2}(1+\sigma r) \hbar \omega_{\mathrm{c}}-\mu\right)-\frac{1}{12}\left(\hbar \omega_{\mathrm{c}}\right)^{2} Q^{\prime}\left(\frac{1}{2}(1+\sigma r) \hbar \omega_{\mathrm{c}}-\mu\right)+\ldots\right]
\end{align*}
$$

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

$$
\begin{equation*}
\Omega(T, V, \mu, H)=2 \int_{0}^{\infty} d \varepsilon Q(\varepsilon-\mu)+\left(\frac{1}{4} r^{2}-\frac{1}{12}\right)\left(\hbar \omega_{\mathrm{c}}\right)^{2} Q^{\prime}(-\mu)+\ldots \tag{5.231}
\end{equation*}
$$

Thus, the magnetic susceptibility is

$$
\begin{align*}
\chi & =-\frac{1}{V} \frac{\partial^{2} \Omega}{\partial H^{2}}=\left(r^{2}-\frac{1}{3}\right) \cdot \tilde{\mu}_{\mathrm{B}}^{2} \cdot\left(m / m^{*}\right)^{2} \cdot\left\{-\frac{2}{V} Q^{\prime}(-\mu)\right\} \\
& =\left(\frac{g^{2}}{4}-\frac{m^{2}}{3 m^{* 2}}\right) \cdot \tilde{\mu}_{\mathrm{B}}^{2} \cdot n^{2} \kappa_{T}, \tag{5.232}
\end{align*}
$$

where $\kappa_{T}$ is the isothermal compressibility ${ }^{16}$. 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

[^11]$m^{*}=0.067 m$. Thus, semiconductors can have a diamagnetic response. If we take $g=2$ and $m^{*}=m$, we 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 $-\frac{2}{V} Q^{\prime}(-\mu)=n^{2} \kappa_{T}$.

### 5.8.6 White dwarf stars

We follow the nice discussion of this material in R. K. Pathria, Statistical Mechanics. As a model, consider a mass $M \sim 10^{33} \mathrm{~g}$ of helium at nuclear densities of $\rho \sim 10^{7} \mathrm{~g} / \mathrm{cm}^{3}$ and temperature $T \sim 10^{7} \mathrm{~K}$. This temperature is much larger than the ionization energy of ${ }^{4} \mathrm{He}$, hence we may safely assume that all helium atoms are ionized. If there are $N$ electrons, then the number of $\alpha$ particles (i.e. ${ }^{4} \mathrm{He}$ nuclei) must be $\frac{1}{2} N$. The mass of the $\alpha$ particle is $m_{\alpha} \approx 4 m_{\mathrm{p}}$. The total stellar mass $M$ is almost completely due to $\alpha$ particle cores.

The electron density is then

$$
\begin{equation*}
n=\frac{N}{V}=\frac{2 \cdot M / 4 m_{\mathrm{p}}}{V}=\frac{\rho}{2 m_{\mathrm{p}}} \approx 10^{30} \mathrm{~cm}^{-3}, \tag{5.233}
\end{equation*}
$$

since $M=N \cdot m_{\mathrm{e}}+\frac{1}{2} N \cdot 4 m_{\mathrm{p}}$. From the number density $n$ we find for the electrons

$$
\begin{align*}
k_{\mathrm{F}}=\left(3 \pi^{2} n\right)^{1 / 3} & =2.14 \times 10^{10} \mathrm{~cm}^{-1} \\
p_{\mathrm{F}}=\hbar k_{\mathrm{F}} & =2.26 \times 10^{-17} \mathrm{~g} \mathrm{~cm} / \mathrm{s}  \tag{5.234}\\
m c & =\left(9.1 \times 10^{-28} \mathrm{~g}\right)\left(3 \times 10^{10} \mathrm{~m} / \mathrm{s}\right)=2.7 \times 10^{-17} \mathrm{~g} \mathrm{~cm} / \mathrm{s}
\end{align*}
$$

Since $p_{\mathrm{F}} \sim m c$, we conclude that the electrons are relativistic. The Fermi temperature will then be $T_{\mathrm{F}} \sim m c^{2} \sim 10^{6} \mathrm{eV} \sim 10^{12} \mathrm{~K}$. Thus, $T \ll T_{\mathrm{f}}$ 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

$$
\begin{equation*}
\varepsilon(\boldsymbol{p})=\sqrt{\boldsymbol{p}^{2} c^{2}+m^{2} c^{4}}-m c^{2} . \tag{5.235}
\end{equation*}
$$

The velocity is

$$
\begin{equation*}
\boldsymbol{v}=\frac{\partial \varepsilon}{\partial \boldsymbol{p}}=\frac{\boldsymbol{p} c^{2}}{\sqrt{p^{2} c^{2}+m^{2} c^{4}}} \tag{5.236}
\end{equation*}
$$

The pressure in the ground state is

$$
\begin{align*}
p_{0} & =\frac{1}{3} n\langle\boldsymbol{p} \cdot \boldsymbol{v}\rangle=\frac{1}{3 \pi^{2} \hbar^{3}} \int_{0}^{p_{\mathrm{F}}} d p p^{2} \cdot \frac{p^{2} c^{2}}{\sqrt{p^{2} c^{2}+m^{2} c^{4}}} \\
& =\frac{m^{4} c^{5}}{3 \pi^{2} \hbar^{3}} \int_{0}^{\theta_{\mathrm{F}}} d \theta \sinh ^{4} \theta=\frac{m^{4} c^{5}}{96 \pi^{2} \hbar^{3}}\left(\sinh \left(4 \theta_{\mathrm{F}}\right)-8 \sinh \left(2 \theta_{\mathrm{F}}\right)+12 \theta_{\mathrm{F}}\right) \tag{5.237}
\end{align*}
$$



Figure 5.16: Mass-radius relationship for white dwarf stars. (Source: Wikipedia).
where we use the substitution

$$
\begin{equation*}
p=m c \sinh \theta \quad, \quad v=c \tanh \theta \quad \Longrightarrow \quad \theta=\frac{1}{2} \ln \left(\frac{c+v}{c-v}\right) . \tag{5.238}
\end{equation*}
$$

Note that $p_{\mathrm{F}}=\hbar k_{\mathrm{F}}=\hbar\left(3 \pi^{2} n\right)^{1 / 3}$, and that

$$
\begin{equation*}
n=\frac{M}{2 m_{\mathrm{p}} V} \quad \Longrightarrow \quad 3 \pi^{2} n=\frac{9 \pi}{8} \frac{M}{R^{3} m_{\mathrm{p}}} . \tag{5.239}
\end{equation*}
$$

Now in equilibrium the pressure $p$ is balanced by gravitational pressure. We have

$$
\begin{equation*}
d E_{0}=-p_{0} d V=-p_{0}(R) \cdot 4 \pi R^{2} d R . \tag{5.240}
\end{equation*}
$$

This must be balanced by gravity:

$$
\begin{equation*}
d E_{\mathrm{g}}=\gamma \cdot \frac{G M^{2}}{R^{2}} d R \tag{5.241}
\end{equation*}
$$

where $\gamma$ depends on the radial mass distribution. Equilibrium then implies

$$
\begin{equation*}
p_{0}(R)=\frac{\gamma}{4 \pi} \frac{G M^{2}}{R^{4}} . \tag{5.242}
\end{equation*}
$$

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

$$
\begin{equation*}
\frac{\gamma}{4 \pi} \frac{g M^{2}}{R^{4}}=\frac{m^{4} c^{5}}{96 \pi^{2} \hbar^{3}}\left(\sinh \left(4 \theta_{\mathrm{F}}\right)-8 \sinh \left(2 \theta_{\mathrm{F}}\right)+12 \theta_{\mathrm{F}}\right) . \tag{5.243}
\end{equation*}
$$

Note that

$$
\sinh \left(4 \theta_{\mathrm{F}}\right)-8 \sinh \left(2 \theta_{\mathrm{F}}\right)+12 \theta_{\mathrm{F}}= \begin{cases}\frac{96}{15} \theta_{\mathrm{F}}^{5} & \theta_{\mathrm{F}} \rightarrow 0  \tag{5.244}\\ \frac{1}{2} e^{4 \theta_{\mathrm{F}}} & \theta_{\mathrm{F}} \rightarrow \infty\end{cases}
$$

Thus, we may write

$$
p_{0}(R)=\frac{\gamma}{4 \pi} \frac{g M^{2}}{R^{4}}= \begin{cases}\frac{\hbar^{2}}{15 \pi^{2} m}\left(\frac{9 \pi}{8} \frac{M}{R^{3} m_{\mathrm{p}}}\right)^{5 / 3} & \theta_{\mathrm{F}} \rightarrow 0  \tag{5.245}\\ \frac{\hbar c}{12 \pi^{2}}\left(\frac{9 \pi}{8} \frac{M}{R^{3} m_{\mathrm{p}}}\right)^{4 / 3} & \theta_{\mathrm{F}} \rightarrow \infty\end{cases}
$$

In the limit $\theta_{\mathrm{F}} \rightarrow 0$, we solve for $R(M)$ and find

$$
\begin{equation*}
R=\frac{3}{40 \gamma}(9 \pi)^{2 / 3} \frac{\hbar^{2}}{G m_{\mathrm{p}}^{5 / 3} m M^{1 / 3}} \propto M^{-1 / 3} . \tag{5.246}
\end{equation*}
$$

In the opposite limit $\theta_{\mathrm{F}} \rightarrow \infty$, the $R$ factors divide out and we obtain

$$
\begin{equation*}
M=M_{0}=\frac{9}{64}\left(\frac{3 \pi}{\gamma^{3}}\right)^{1 / 2}\left(\frac{\hbar c}{G}\right)^{3 / 2} \frac{1}{m_{\mathrm{p}}^{2}} \tag{5.247}
\end{equation*}
$$

To find the $R$ dependence, we must go beyond the lowest order expansion of eqn. 5.244, in which case we find

$$
\begin{equation*}
R=\left(\frac{9 \pi}{8}\right)^{1 / 3}\left(\frac{\hbar}{m c}\right)\left(\frac{M}{m_{\mathrm{p}}}\right)^{1 / 3}\left[1-\left(\frac{M}{M_{0}}\right)^{2 / 3}\right]^{1 / 2} \tag{5.248}
\end{equation*}
$$

The value $M_{0}$ is the limiting size for a white dwarf. It is called the Chandrasekhar limit.

### 5.9 Appendix I : Ideal Bose Gas Condensation

We begin with the grand canonical Hamiltonian $K=H-\mu N$ for the ideal Bose gas,

$$
\begin{equation*}
K=\sum_{k}\left(\varepsilon_{k}-\mu\right) b_{k}^{\dagger} b_{k}-\sqrt{N} \sum_{k}\left(\nu_{k} b_{k}^{\dagger}+\bar{\nu}_{k} b_{k}\right) . \tag{5.249}
\end{equation*}
$$

Here $b_{k}^{\dagger}$ is the creation operator for a boson in a state of wavevector $\boldsymbol{k}$, hence $\left[b_{k}, b_{k^{\prime}}^{\dagger}\right]=\delta_{\boldsymbol{k} \boldsymbol{k}^{\prime}}$. The dispersion relation is given by the function $\varepsilon_{k}$, which is the energy of a particle with wavevector $\boldsymbol{k}$. We must have $\varepsilon_{k}-\mu \geq 0$ for all $\boldsymbol{k}$, lest the spectrum of $K$ be unbounded from below. The fields $\left\{\nu_{\boldsymbol{k}}, \bar{\nu}_{\boldsymbol{k}}\right\}$ break a global $\mathrm{O}(2)$ symmetry.

Students who have not taken a course in solid state physics can skip the following paragraph, and be aware that $N=V / v_{0}$ is the total volume of the system in units of a fundamental "unit cell" volume. The thermodynamic limit is then $N \rightarrow \infty$. Note that $N$ is not the boson particle number, which we'll call $N_{b}$.
Solid state physics boilerplate : We presume a setting in which the real space Hamiltonian is defined by some boson hopping model on a Bravais lattice. The wavevectors $\boldsymbol{k}$ are then restricted to the first

Brillouin zone, $\hat{\Omega}$, and assuming periodic boundary conditions are quantized according to the condition $\exp \left(i N_{l} \boldsymbol{k} \cdot \boldsymbol{a}_{l}\right)=1$ for all $l \in\{1, \ldots, d\}$, where $\boldsymbol{a}_{l}$ is the $l^{\text {th }}$ fundamental direct lattice vector and $N_{l}$ is the size of the system in the $\boldsymbol{a}_{l}$ direction; $d$ is the dimension of space. The total number of unit cells is $N \equiv \prod_{l} N_{l}$. Thus, quantization entails $\boldsymbol{k}=\sum_{l}\left(2 \pi n_{l} / N_{l}\right) \boldsymbol{b}_{l}$, where $\boldsymbol{b}_{l}$ is the $l^{\text {th }}$ elementary reciprocal lattice vector ( $\boldsymbol{a}_{l} \cdot \boldsymbol{b}_{l^{\prime}}=2 \pi \delta_{l^{\prime}}$ ) and $n_{l}$ ranges over $N_{l}$ distinct integers such that the allowed $\boldsymbol{k}$ points form a discrete approximation to $\hat{\Omega}$.

To solve, we first shift the boson creation and annihilation operators, writing

$$
\begin{equation*}
K=\sum_{k}\left(\varepsilon_{k}-\mu\right) \beta_{k}^{\dagger} \beta_{k}-N \sum_{k} \frac{\left|\nu_{k}\right|^{2}}{\varepsilon_{k}-\mu} \tag{5.250}
\end{equation*}
$$

where

$$
\begin{equation*}
\beta_{k}=b_{k}-\frac{\sqrt{N} \nu_{k}}{\varepsilon_{k}-\mu} \quad, \quad \beta_{k}^{\dagger}=b_{k}^{\dagger}-\frac{\sqrt{N} \bar{\nu}_{k}}{\varepsilon_{k}-\mu} \tag{5.251}
\end{equation*}
$$

Note that $\left[\beta_{k}, \beta_{k^{\prime}}^{\dagger}\right]=\delta_{k k^{\prime}}$ so the above transformation is canonical. The Landau free energy $\Omega=$ $-k_{\mathrm{B}} T \ln \Xi$, where $\Xi=\operatorname{Tr} e^{-K / k_{\mathrm{B}} T}$, is given by

$$
\begin{equation*}
\Omega=N k_{\mathrm{B}} T \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \ln \left(1-e^{(\mu-\varepsilon) / k_{\mathrm{b}} T}\right)-N \sum_{k} \frac{\left|\nu_{\boldsymbol{k}}\right|^{2}}{\varepsilon_{\boldsymbol{k}}-\mu} \tag{5.252}
\end{equation*}
$$

where $g(\varepsilon)$ is the density of energy states per unit cell,

$$
\begin{equation*}
g(\varepsilon)=\frac{1}{N} \sum_{k} \delta\left(\varepsilon-\varepsilon_{k}\right) \xrightarrow[N \rightarrow \infty]{ } \int_{\hat{\Omega}} \frac{d^{d} k}{(2 \pi)^{d}} \delta\left(\varepsilon-\varepsilon_{k}\right) \tag{5.253}
\end{equation*}
$$

Note that

$$
\begin{equation*}
\psi_{k} \equiv \frac{1}{\sqrt{N}}\left\langle b_{k}\right\rangle=-\frac{1}{N} \frac{\partial \Omega}{\partial \bar{\nu}_{k}}=\frac{\nu_{k}}{\varepsilon_{k}-\mu} . \tag{5.254}
\end{equation*}
$$

In the condensed phase, $\psi_{k}$ is nonzero.
The Landau free energy (grand potential) is a function $\Omega(T, N, \mu, \nu, \bar{\nu})$. We now make a Legendre transformation,

$$
\begin{equation*}
Y(T, N, \mu, \psi, \bar{\psi})=\Omega(T, N, \mu, \nu, \bar{\nu})+N \sum_{k}\left(\nu_{\boldsymbol{k}} \bar{\psi}_{\boldsymbol{k}}+\bar{\nu}_{\boldsymbol{k}} \psi_{\boldsymbol{k}}\right) \tag{5.255}
\end{equation*}
$$

Note that

$$
\begin{equation*}
\frac{\partial Y}{\partial \bar{\nu}_{k}}=\frac{\partial \Omega}{\partial \bar{\nu}_{k}}+N \psi_{k}=0 \tag{5.256}
\end{equation*}
$$

by the definition of $\psi_{\boldsymbol{k}}$. Similarly, $\partial Y / \partial \nu_{\boldsymbol{k}}=0$. We now have

$$
\begin{equation*}
Y(T, N, \mu, \psi, \bar{\psi})=N k_{\mathrm{B}} T \int_{-\infty}^{\infty} d \varepsilon g(\varepsilon) \ln \left(1-e^{(\mu-\varepsilon) / k_{\mathrm{b}} T}\right)+N \sum_{k}\left(\varepsilon_{\boldsymbol{k}}-\mu\right)\left|\psi_{\boldsymbol{k}}\right|^{2} \tag{5.257}
\end{equation*}
$$

Therefore, the boson particle number per unit cell is given by the dimensionless density,

$$
\begin{equation*}
n=\frac{N_{b}}{N}=-\frac{1}{N} \frac{\partial Y}{\partial \mu}=\sum_{k}\left|\psi_{\boldsymbol{k}}\right|^{2}+\int_{-\infty}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{(\varepsilon-\mu) / k_{\mathrm{B}} T}-1} \tag{5.258}
\end{equation*}
$$

and the condensate amplitude at wavevector $\boldsymbol{k}$ is

$$
\begin{equation*}
\nu_{k}=\frac{1}{N} \frac{\partial Y}{\partial \bar{\psi}_{k}}=\left(\varepsilon_{k}-\mu\right) \psi_{k} \tag{5.259}
\end{equation*}
$$

Recall that $\nu_{k}$ acts as an external field. Let the dispersion $\varepsilon_{\boldsymbol{k}}$ be minimized at $\boldsymbol{k}=\boldsymbol{K}$. Without loss of generality, we may assume this minimum value is $\varepsilon_{\boldsymbol{K}}=0$. We see that if $\nu_{\boldsymbol{k}}=0$ then one of two must be true:
(i) $\psi_{\boldsymbol{k}}=0$ for all $\boldsymbol{k}$
(ii) $\mu=\varepsilon_{\boldsymbol{K}}$, in which case $\psi_{\boldsymbol{K}}$ can be nonzero.

Thus, for $\nu=\bar{\nu}=0$ and $\mu>0$, we have the usual equation of state,

$$
\begin{equation*}
n(T, \mu)=\int_{-\infty}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{(\varepsilon-\mu) / k_{\mathrm{B}} T}-1} \tag{5.260}
\end{equation*}
$$

which relates the intensive variables $n, T$, and $\mu$. When $\mu=0$, the equation of state becomes

$$
\begin{equation*}
n(T, \mu=0)=\overbrace{\sum_{\boldsymbol{K}}\left|\psi_{\boldsymbol{K}}\right|^{2}}^{n_{0}}+\overbrace{\int_{-\infty}^{\infty} d \varepsilon \frac{g(\varepsilon)}{e^{\varepsilon / k_{\mathrm{B}} T}-1}}^{n_{>}(T)}, \tag{5.261}
\end{equation*}
$$

where now the sum is over only those $\boldsymbol{K}$ for which $\varepsilon_{\boldsymbol{K}}=0$. Typically this set has only one member, $\boldsymbol{K}=0$, but it is quite possible, due to symmetry reasons, that there are more such $\boldsymbol{K}$ values. This last equation of state is one which relates the intensive variables $n, T$, and $n_{0}$, where $n_{0}=\sum_{\boldsymbol{K}}\left|\psi_{\boldsymbol{K}}\right|^{2}$ is the dimensionless condensate density. If the integral $n_{>}(T)$ in eqn. 5.261 is finite, then for $n>n_{0}(T)$ we must have $n_{0}>0$. Note that, for any $T, n_{>}(T)$ diverges logarithmically whenever $g(0)$ is finite. This means that eqn. 5.260 can always be inverted to yield a finite $\mu(n, T)$, no matter how large the value of $n$, in which case there is no condensation and $n_{0}=0$. If $g(\varepsilon) \propto \varepsilon^{\alpha}$ with $\alpha>0$, the integral converges and $n_{>}(T)$ is finite and monotonically increasing for all $T$. Thus, for fixed dimensionless number $n$, there will be a critical temperature $T_{\mathrm{c}}$ for which $n=n_{>}\left(T_{\mathrm{c}}\right)$. For $T<T_{\mathrm{c}}$, eqn. 5.260 has no solution for any $\mu$ and we must appeal to eqn. 5.261. The condensate density, given by $n_{0}(n, T)=n-n_{>}(T)$, is then finite for $T<T_{\mathrm{c}}$, and vanishes for $T \geq T_{\mathrm{c}}$.

In the condensed phase, the phase of the order parameter $\psi$ inherits its phase from the external field $\nu$, which is taken to zero, in the same way the magnetization in the symmetry-broken phase of an Ising ferromagnet inherits its direction from an applied field $h$ which is taken to zero. The important feature is that in both cases the applied field is taken to zero after the approach to the thermodynamic limit.

### 5.10 Appendix II : Example Bose Condensation Problem

PROBLEM: A three-dimensional gas of noninteracting bosonic particles obeys the dispersion relation $\varepsilon(\boldsymbol{k})=A|\boldsymbol{k}|^{1 / 2}$.
(a) Obtain an expression for the density $n(T, z)$ where $z=\exp \left(\mu / k_{\mathrm{B}} T\right)$ is the fugacity. Simplify your expression as best you can, adimensionalizing any integral or infinite sum which may appear. You may find it convenient to define

$$
\begin{equation*}
\operatorname{Li}_{\nu}(z) \equiv \frac{1}{\Gamma(\nu)} \int_{0}^{\infty} d t \frac{t^{\nu-1}}{z^{-1} e^{t}-1}=\sum_{k=1}^{\infty} \frac{z^{k}}{k^{\nu}} \tag{5.262}
\end{equation*}
$$

Note $\operatorname{Li}_{\nu}(z)(1)=\zeta(\nu)$, the Riemann zeta function.
(b) Find the critical temperature for Bose condensation, $T_{\mathrm{c}}(n)$. Your expression should only include the density $n$, the constant $A$, physical constants, and numerical factors (which may be expressed in terms of integrals or infinite sums).
(c) What is the condensate density $n_{0}$ when $T=\frac{1}{2} T_{\mathrm{c}}$ ?
(d) Do you expect the second virial coefficient to be positive or negative? Explain your reasoning. (You don't have to do any calculation.)

SOLUTION: We work in the grand canonical ensemble, using Bose-Einstein statistics.
(a) The density for Bose-Einstein particles are given by

$$
\begin{align*}
n(T, z) & =\int \frac{d^{3} k}{(2 \pi)^{3}} \frac{1}{z^{-1} \exp \left(A k^{1 / 2} / k_{\mathrm{B}} T\right)-1} \\
& =\frac{1}{\pi^{2}}\left(\frac{k_{\mathrm{B}} T}{A}\right)^{6} \int_{0}^{\infty} d s \frac{s^{5}}{z^{-1} e^{s}-1}=\frac{120}{\pi^{2}}\left(\frac{k_{\mathrm{B}} T}{A}\right)^{6} \operatorname{Li}_{6}(z) \tag{5.263}
\end{align*}
$$

where we have changed integration variables from $k$ to $s=A k^{1 / 2} / k_{\mathrm{B}} T$, and we have defined the functions $\operatorname{Li}_{\nu}(z)$ as above, in eqn. 5.262. Note $\operatorname{Li}_{\nu}(1)=\zeta(\nu)$, the Riemann zeta function.
(b) Bose condensation sets in for $z=1$, i.e. $\mu=0$. Thus, the critical temperature $T_{\mathrm{c}}$ and the density $n$ are related by

$$
\begin{equation*}
n=\frac{120 \zeta(6)}{\pi^{2}}\left(\frac{k_{\mathrm{B}} T_{\mathrm{c}}}{A}\right)^{6} \tag{5.264}
\end{equation*}
$$

or

$$
\begin{equation*}
T_{\mathrm{c}}(n)=\frac{A}{k_{\mathrm{B}}}\left(\frac{\pi^{2} n}{120 \zeta(6)}\right)^{1 / 6} . \tag{5.265}
\end{equation*}
$$

(c) For $T<T_{\mathrm{c}}$, we have

$$
\begin{equation*}
n=n_{0}+\frac{120 \zeta(6)}{\pi^{2}}\left(\frac{k_{\mathrm{B}} T}{A}\right)^{6}=n_{0}+\left(\frac{T}{T_{\mathrm{c}}}\right)^{6} n \tag{5.266}
\end{equation*}
$$

where $n_{0}$ is the condensate density. Thus, at $T=\frac{1}{2} T_{\mathrm{c}}$,

$$
\begin{equation*}
n_{0}\left(T=\frac{1}{2} T_{\mathrm{c}}\right)=\frac{63}{64} n . \tag{5.267}
\end{equation*}
$$

(d) The virial expansion of the equation of state is

$$
\begin{equation*}
p=n k_{\mathrm{B}} T\left(1+B_{2}(T) n+B_{3}(T) n^{2}+\ldots\right) \tag{5.268}
\end{equation*}
$$

We expect $B_{2}(T)<0$ for noninteracting bosons, reflecting the tendency of the bosons to condense. (Correspondingly, for noninteracting fermions we expect $B_{2}(T)>0$.)
For the curious, we compute $B_{2}(T)$ by eliminating the fugacity $z$ from the equations for $n(T, z)$ and $p(T, z)$. First, we find $p(T, z)$ :

$$
\begin{align*}
p(T, z) & =-k_{\mathrm{B}} T \int \frac{d^{3} k}{(2 \pi)^{3}} \ln \left(1-z \exp \left(-A k^{1 / 2} / k_{\mathrm{B}} T\right)\right) \\
& =-\frac{k_{\mathrm{B}} T}{\pi^{2}}\left(\frac{k_{\mathrm{B}} T}{A}\right)^{6} \int_{0}^{\infty} d s s^{5} \ln \left(1-z e^{-s}\right)=\frac{120 k_{\mathrm{B}} T}{\pi^{2}}\left(\frac{k_{\mathrm{B}} T}{A}\right)^{6} \operatorname{Li}_{7}(z) . \tag{5.269}
\end{align*}
$$

Expanding in powers of the fugacity, we have

$$
\begin{align*}
n & =\frac{120}{\pi^{2}}\left(\frac{k_{\mathrm{B}} T}{A}\right)^{6}\left\{z+\frac{z^{2}}{2^{6}}+\frac{z^{3}}{3^{6}}+\ldots\right\}  \tag{5.270}\\
\frac{p}{k_{\mathrm{B}} T} & =\frac{120}{\pi^{2}}\left(\frac{k_{\mathrm{B}} T}{A}\right)^{6}\left\{z+\frac{z^{2}}{2^{7}}+\frac{z^{3}}{3^{7}}+\ldots\right\} .
\end{align*}
$$

Solving for $z(n)$ using the first equation, we obtain, to order $n^{2}$,

$$
\begin{equation*}
z=\left(\frac{\pi^{2} A^{6} n}{120\left(k_{\mathrm{B}} T\right)^{6}}\right)-\frac{1}{2^{6}}\left(\frac{\pi^{2} A^{6} n}{120\left(k_{\mathrm{B}} T\right)^{6}}\right)^{2}+\mathcal{O}\left(n^{3}\right) . \tag{5.271}
\end{equation*}
$$

Plugging this into the equation for $p(T, z)$, we obtain the first nontrivial term in the virial expansion, with

$$
\begin{equation*}
B_{2}(T)=-\frac{\pi^{2}}{15360}\left(\frac{A}{k_{\mathrm{B}} T}\right)^{6} \tag{5.272}
\end{equation*}
$$

which is negative, as expected. Note that the ideal gas law is recovered for $T \rightarrow \infty$, for fixed $n$.

### 5.11 Appendix III : $C_{p, N}$ for the Ideal Bose Gas

The phase diagram for the ideal Bose gas in the ( $T, p$ ) plane was considered in $\S 5.7 .3$ and in fig. 5.8. Let's compute the behavior of $C_{p, N}(T, p, N)$ and explore how it behaves as one approaches the critical curve
$p=p_{\mathrm{c}}(T)=\zeta(5 / 2) k_{\mathrm{B}} T / \lambda_{T}^{3}$. We found that when the fugacity $z=\exp \left(\mu / k_{\mathrm{B}} T\right)$ is larger than one, then the density and pressure are given by

$$
\begin{equation*}
n(z, T)=\mathrm{Li}_{3 / 2}(z) \lambda_{T}^{-3} \quad, \quad p(z, T)=\mathrm{Li}_{5 / 2}(z) k_{\mathrm{B}} T \lambda_{T}^{-3} \tag{5.273}
\end{equation*}
$$

The energy is $E=\frac{3}{2} p V$, as we obtained in eqn. 5.158.
To obtain $C_{p, N}$, we first set $d p=0$, which is of course equivalent to setting $d \ln p=0$ :

$$
\begin{equation*}
d \ln p=0=\frac{\mathrm{Li}_{3 / 2}(z)}{\mathrm{Li}_{5 / 2}(z)} d \ln z+\frac{5}{2} d \ln T \quad \Rightarrow \quad\left(\frac{\partial \ln z}{\partial \ln T}\right)_{p}=-\frac{5 \mathrm{Li}_{5 / 2}(z)}{3 \mathrm{Li}_{3 / 2}(z)} \tag{5.274}
\end{equation*}
$$

We wish to evaluate

$$
\begin{equation*}
C_{p, N}=\left(\frac{\partial E}{\partial T}\right)_{p, N}+p\left(\frac{\partial V}{\partial T}\right)_{p, N}=\frac{5}{2} p\left(\frac{\partial V}{\partial T}\right)_{p, N} \tag{5.275}
\end{equation*}
$$

Thus, we need

$$
\begin{align*}
\left(\frac{\partial V}{\partial T}\right)_{p, N} & =\left(\frac{\partial N / n}{\partial T}\right)_{p, N}=-\frac{N}{n}\left(\frac{\partial \ln n}{\partial T}\right)_{p, N} \\
& =-\frac{N}{n T}\left\{\frac{\operatorname{Li}_{1 / 2}(z)}{\mathrm{Li}_{3 / 2}(z)}\left(\frac{\partial \ln z}{\partial \ln T}\right)_{p}+\frac{3}{2}\right\}=\frac{N}{n T}\left\{\frac{5 \mathrm{Li}_{5 / 2}(z) \mathrm{Li}_{1 / 2}(z)}{2 \mathrm{Li}_{3 / 2}^{2}(z)}-\frac{3}{2}\right\} \tag{5.276}
\end{align*}
$$

Thus, we have

$$
\begin{equation*}
c_{p, N} \equiv \frac{N_{\mathrm{A}} C_{p, N}}{N}=\frac{25 R}{4} \frac{\mathrm{Li}_{5 / 2}(z)}{\mathrm{Li}_{3 / 2}(z)}\left\{\frac{\mathrm{Li}_{5 / 2}(z) \mathrm{Li}_{1 / 2}(z)}{\mathrm{Li}_{3 / 2}^{2}(z)}-\frac{3}{5}\right\}, \tag{5.277}
\end{equation*}
$$

where $R=N_{\mathrm{A}} k_{\mathrm{B}}$ is the gas constant.
As we approach the critical line $p=p_{\mathrm{c}}(T)$, the fugacity approaches unity: $z \rightarrow 1$. In this limit we have $\mathrm{Li}_{3 / 2}(z \rightarrow 1)=\zeta(3 / 2)$ and $\mathrm{Li}_{5 / 2}(z \rightarrow 1)=\zeta(5 / 2)$, but $\mathrm{Li}_{1 / 2}(z \rightarrow 1)$ is divergent. We write $z \equiv \exp (-\epsilon)$, with

$$
\begin{equation*}
\frac{p}{p_{\mathrm{c}}(T)}=\frac{\mathrm{Li}_{5 / 2}(z)}{\zeta(5 / 2)}=1-\zeta(3 / 2) \epsilon+\ldots \tag{5.278}
\end{equation*}
$$

allows us to write

$$
\begin{equation*}
\epsilon=\frac{1}{\zeta(3 / 2)}\left(1-\frac{p}{p_{\mathrm{c}}(T)}\right) \tag{5.279}
\end{equation*}
$$

Here we have appealed to the expansion in eqn. 5.44 , which also gives

$$
\begin{equation*}
\mathrm{Li}_{1 / 2}\left(e^{-\epsilon}\right)=\sqrt{\pi}\left[\frac{p_{\mathrm{c}}(T)-p}{\zeta(3 / 2) p_{\mathrm{c}}(T)}\right]+\ldots \tag{5.280}
\end{equation*}
$$

Thus, from eqn. 5.276, we have that $c_{p, N}$ diverges as we approach $p=p_{\mathrm{c}}(T)$ from below as

$$
\begin{equation*}
c_{p, N}(T, p)=\frac{25 \sqrt{\pi}}{4} \frac{\zeta^{2}(5 / 2)}{\zeta^{5 / 2}(3 / 2)}\left(\frac{p_{\mathrm{c}}(T)-p}{p_{\mathrm{c}}(T)}\right)^{-1 / 2}+\ldots . \tag{5.281}
\end{equation*}
$$

Equivalently, we can consider approaching the curve $T=T_{\mathrm{c}}(p)$ from the right. In both cases we have

$$
\begin{equation*}
c_{p, N}(T, p) \propto\left|p-p_{\mathrm{c}}(T)\right|^{-1 / 2} \quad, \quad c_{p, N}(T, p) \propto\left|T-T_{\mathrm{c}}(p)\right|^{-1 / 2} \tag{5.282}
\end{equation*}
$$

In other words, the critical exponent is $\alpha=\frac{1}{2}$. and unlike $c_{V, N}(T, n)$ which has a cusp at $T=T_{\mathrm{c}}(n)$ yet remains finite, the specific heat at constant pressure diverges ${ }^{17}$.

[^12]
[^0]:    ${ }^{1}$ Several texts, such as Pathria and Reichl, write $g_{s}(z)$ for $\mathrm{Li}_{s}(z)$. I adopt the latter notation since we are already using the symbol $g$ for the density of states function $g(\varepsilon)$ and for the internal degeneracy $g$.
    ${ }^{2}$ See the Wikipedia entry on "Polylogarithm."
    ${ }^{3}$ See Digital Library of Mathematical Functions §25.12.12.

[^1]:    ${ }^{4}$ Note the dimensions of $g(\omega)$ are (frequency) ${ }^{-1}$. By contrast, the dimensions of $g(\varepsilon)$ in eqn. 5.25 are (energy) ${ }^{-1} \cdot(\text { volume })^{-1}$. The difference lies in the a factor of $\mathcal{V}_{0} \cdot \hbar$, where $\mathcal{V}_{0}$ is the unit cell volume.

[^2]:    ${ }^{6} \mathrm{OK}$, that isn't quite true. For example, if $g(\varepsilon) \sim 1 / \ln \varepsilon$, then the integral has a very weak $\ln \ln (1 / \eta)$ divergence, where $\eta$ is the lower cutoff. But for any power law density of states $g(\varepsilon) \propto \varepsilon^{r}$ with $r>0$, the integral converges.

[^3]:    ${ }^{7}$ It is easy to see that the chemical potential for noninteracting bosons can never exceed the minimum value $\varepsilon_{0}$ of the single particle dispersion.

[^4]:    ${ }^{8}$ Note that in the thermodynamics chapter we used $v$ to denote the molar volume, $N_{\mathrm{A}} V / N$.

[^5]:    ${ }^{9}$ The $\boldsymbol{k} \neq 0$ particles are sometimes called the overcondensate.

[^6]:    ${ }^{10}$ IBG condensation is in the universality class of the spherical model. The $\lambda$-transition is in the universality class of the $X Y$ model.

[^7]:    ${ }^{11}$ Recall that two bodies in thermal equilibrium will have identical temperatures if they are free to exchange energy.
    ${ }^{12}$ The phonon velocity $c$ is slightly temperature dependent.

[^8]:    ${ }^{13}$ Note that writing $v=(2 n+1) i \pi+\epsilon$ we have $e^{ \pm v}=-1 \mp \epsilon-\frac{1}{2} \epsilon^{2}+\ldots$, so $\left(e^{v}+1\right)\left(e^{-v}+1\right)=-\epsilon^{2}+\ldots$ We then expand $e^{v D}=e^{(2 n+1) i \pi D}(1+\epsilon D+\ldots)$ to find the residue: Res $=-D e^{(2 n+1) i \pi D}$.

[^9]:    ${ }^{14}$ I thank my colleague Tarun Grover for this observation.

[^10]:    ${ }^{15}$ Once again I thank my colleague Tarun Grover for pointing this out to me.

[^11]:    ${ }^{16} \mathrm{We}^{\prime}$ ve used $-\frac{2}{V} Q^{\prime}(\mu)=-\frac{1}{V} \frac{\partial^{2} \Omega}{\partial \mu^{2}}=n^{2} \kappa_{T}$.

[^12]:    ${ }^{17}$ I thank Andre Vieira for prompting me to clarify the differences between $c_{V, N}(T, n)$ and $c_{p, N}(T, p)$ in this context.

