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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^{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* (3^{rd} 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^{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[1]

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

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

$$\hat{n}_\alpha \, \big| \, \vec{n} \, \big\rangle = n_\alpha \, \big| \, \vec{n} \, \big\rangle \tag{5.2}$$

and

$$\hat{H} \, \big| \, \vec{n} \, \big\rangle = \sum_\alpha n_\alpha \, \varepsilon_\alpha \, \big| \, \vec{n} \, \big\rangle \quad . \tag{5.3}$$

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

$$\begin{aligned} \text{bosons} : n_\alpha &\in \big\{ 0 \, , \, 1 \, , \, 2 \, , \, 3 \, , \, \ldots \big\} \\ \text{fermions} : n_\alpha &\in \big\{ 0 \, , \, 1 \big\} \quad . \end{aligned} \tag{5.4}$$

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

The N-particle partition function Z_N is then

$$Z_N = \sum_{\{n_\alpha\}} e^{-\beta \sum_\alpha n_\alpha \varepsilon_\alpha} \, \delta_{N \, , \sum_\alpha n_\alpha} \quad , \tag{5.5}$$

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

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

---

[1] For a review of the formalism of second quantization, see the appendix in §5.9.

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

We now perform the single particle sums:

$$\sum_{n=0}^{\infty} e^{-\beta(\varepsilon-\mu)\,n} = \frac{1}{1-e^{-\beta(\varepsilon-\mu)}} \qquad \text{(bosons)} \tag{5.7}$$

$$\sum_{n=0}^{1} e^{-\beta(\varepsilon-\mu)\,n} = 1+e^{-\beta(\varepsilon-\mu)} \qquad \text{(fermions)} \quad . \tag{5.8}$$

Therefore we have

$$\begin{aligned} \Xi_{\rm BE} &= \prod_\alpha \frac{1}{1-e^{-(\varepsilon_\alpha-\mu)/k_{\rm B}T}} \\ \varOmega_{\rm BE} &= k_{\rm B}T \sum_\alpha \ln\Big(1-e^{-(\varepsilon_\alpha-\mu)/k_{\rm B}T}\Big) \end{aligned} \tag{5.9}$$

and

$$\begin{aligned} \Xi_{\rm FD} &= \prod_\alpha \Big(1+e^{-(\varepsilon_\alpha-\mu)/k_{\rm B}T}\Big) \\ \varOmega_{\rm FD} &= -k_{\rm B}T \sum_\alpha \ln\Big(1+e^{-(\varepsilon_\alpha-\mu)/k_{\rm B}T}\Big) \quad . \end{aligned} \tag{5.10}$$

We can combine these expressions into one, writing

$$\varOmega(T,V,\mu) = \pm k_{\rm B}T \sum_\alpha \ln\Big(1\mp e^{-(\varepsilon_\alpha-\mu)/k_{\rm B}T}\Big) \quad , \tag{5.11}$$

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

$$\langle \hat{n}_\alpha \rangle = \frac{\partial\varOmega}{\partial\varepsilon_\alpha} = \frac{1}{e^{(\varepsilon_\alpha-\mu)/k_{\rm B}T}\mp 1} \quad , \tag{5.12}$$

and the total particle number is then

$$N(T,V,\mu) = \sum_\alpha \frac{1}{e^{(\varepsilon_\alpha-\mu)/k_{\rm B}T}\mp 1} \quad . \tag{5.13}$$

We will henceforth write $n_\alpha(\mu,T) = \langle \hat{n}_\alpha \rangle$ 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

$$\hat{H} = \sum_{j=1}^{N} \hat{h}_j \quad . \tag{5.14}$$

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

$$Z \overset{?}{=} \sum_{\alpha_1} \cdots \sum_{\alpha_N} e^{-\beta\big(\varepsilon_{\alpha_1} + \varepsilon_{\alpha_2} + \ldots + \varepsilon_{\alpha_N}\big)} = \zeta^N \quad , \tag{5.15}$$

where ζ 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_α, 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 $\{n_\alpha\}$ labels a unique many particle state $\big|\,\{n_\alpha\}\,\big\rangle$. In the product ζ^N, the collection $\{n_\alpha\}$ occurs many times. We have therefore *overcounted* the contribution to Z_N due to this state. By what factor have we overcounted? It is easy to see that the overcounting factor is

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

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

$$\left(\sum_{\alpha=1}^{K} x_\alpha\right)^{N} = \sum_{n_1}\sum_{n_2}\cdots\sum_{n_K} \frac{N!}{n_1!\,n_2!\cdots n_K!}\; x_1^{n_1}\, x_2^{n_2}\cdots x_K^{n_K}\;\delta_{N,n_1+\ldots+n_K} \quad . \tag{5.16}$$

Thus, the correct expression for Z_N is

$$\begin{aligned} Z_N &= \sum_{\{n_\alpha\}} e^{-\beta\sum_\alpha n_\alpha \varepsilon_\alpha}\, \delta_{N,\sum_\alpha n_\alpha} \\ &= \sum_{\alpha_1}\sum_{\alpha_2}\cdots\sum_{\alpha_N} \left(\frac{\prod_\alpha n_\alpha!}{N!}\right) e^{-\beta(\varepsilon_{\alpha_1} + \varepsilon_{\alpha_2} + \ldots + \varepsilon_{\alpha_N})} \quad . \end{aligned} \tag{5.17}$$

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

Finally, starting with the expressions for the grand partition function for Bose-Einstein or Fermi-Dirac particles, and working in the low density limit where $n_\alpha(\mu, T) \ll 1$, we have $\varepsilon_\alpha - \mu \gg k_\mathrm{B}T$, and consequently

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

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

$$\langle \hat{n}_\alpha \rangle = e^{-(\varepsilon_\alpha-\mu)/k_\mathrm{B}T} \quad . \tag{5.19}$$

5.2.3 Single particle density of states

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

$$g(\varepsilon) = \frac{1}{V}\sum_\alpha \delta(\varepsilon - \varepsilon_\alpha) \quad . \tag{5.20}$$

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 $\big[g(\varepsilon)\big] = E^{-1}L^{-d}$, where E stands for energy and L for length. We may now write

$$\Omega(T,V,\mu) = \pm V k_\mathrm{B} T \int\limits_{-\infty}^{\infty} \! d\varepsilon\; g(\varepsilon)\, \ln\!\Big(1 \mp e^{-(\varepsilon-\mu)/k_\mathrm{B}T}\Big) \quad . \tag{5.21}$$

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

$$g(\varepsilon) = \mathsf{g}\int\!\frac{d^d\!k}{(2\pi)^d}\,\delta\big(\varepsilon - \varepsilon(\boldsymbol{k})\big) = \frac{\mathsf{g}\,\Omega_d}{(2\pi)^d}\,\frac{k^{d-1}}{d\varepsilon/dk} \quad . \tag{5.22}$$

where $\mathsf{g} = 2S{+}1$ is the spin degeneracy, and where we assume that $\varepsilon(\boldsymbol{k})$ is both isotropic and a monotonically increasing function of k. Thus, we have

$$g_{d=1}(\varepsilon) = \frac{\mathsf{g}}{\pi}\,\frac{dk}{d\varepsilon} \quad , \quad g_{d=2}(\varepsilon) = \frac{\mathsf{g}}{2\pi}\,k\,\frac{dk}{d\varepsilon} \quad , \quad g_{d=3}(\varepsilon) = \frac{\mathsf{g}}{2\pi^2}\,k^2\,\frac{dk}{d\varepsilon} \quad . \tag{5.23}$$

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

$$g(\varepsilon)\,d\varepsilon = \mathsf{g}\,\frac{d^d\!k}{(2\pi)^d} = \frac{\mathsf{g}\,\Omega_d}{(2\pi)^d}\,k^{d-1}\,dk \quad . \tag{5.24}$$

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

$$g(\varepsilon) = \frac{2S{+}1}{\Gamma(d/2)}\left(\frac{m}{2\pi\hbar^2}\right)^{\!d/2} \varepsilon^{(d-2)/2}\,\Theta(\varepsilon) \quad , \tag{5.25}$$

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

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

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

$$N(T,V,\mu) = V\!\int\limits_{-\infty}^{\infty}\! d\varepsilon\; g(\varepsilon)\,\frac{1}{e^{(\varepsilon-\mu)/k_\mathrm{B}T} \mp 1} \quad , \tag{5.27}$$

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

$$n(T,z) = \int\limits_{-\infty}^{\infty} d\varepsilon \, \frac{g(\varepsilon)}{z^{-1} \, e^{\varepsilon/k_\mathrm{B}T} \mp 1} = \sum_{j=1}^{\infty} C_j(T) \, z^j \quad , \tag{5.28}$$

where $z = \exp(\mu/k_\mathrm{B}T)$ is the fugacity and

$$C_j(T) = (\pm 1)^{j-1} \int\limits_{-\infty}^{\infty} d\varepsilon \; g(\varepsilon) \, e^{-j\varepsilon/k_\mathrm{B}T} \quad . \tag{5.29}$$

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

$$p(T,z) = \mp \, k_\mathrm{B}T \int\limits_{-\infty}^{\infty} d\varepsilon \; g(\varepsilon) \; \ln\!\Big(1 \mp z \, e^{-\varepsilon/k_\mathrm{B}T}\Big) = k_\mathrm{B}T \sum_{j=1}^{\infty} j^{-1} C_j(T) \, z^j \quad . \tag{5.30}$$

5.3.2 Virial expansion of the equation of state

Eqns. 5.28 and 5.30 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. 5.30 to obtain an equation of state $p = p(T,n)$ of the form

$$p(T,n) = n \, k_\mathrm{B}T \, \Big(1 + B_2(T) \, n + B_3(T) \, n^2 + \ldots\Big) \quad . \tag{5.31}$$

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

Unfortunately, there is no general analytic expression for the virial coefficients $B_j(T)$ in terms of the expansion coefficients $n_j(T)$. However our work is made somewhat easier by appealing to a method of Lagrange. We regard the series

$$\pi(T,n) \equiv \frac{p(T,n)}{k_\mathrm{B}T} = \sum_{l=1}^{\infty} B_k \, n^k \tag{5.32}$$

as a power series in a *complex* variable n. We then have

$$B_k = \oint \frac{dn}{2\pi i} \, \frac{\pi(n)}{n^{k+1}} = \oint \frac{dz}{2\pi i} \, \frac{n'(z) \, \pi(z)}{\big[n(z)\big]^{k+1}} = -\frac{1}{k} \oint \frac{dz}{2\pi i} \, \pi(z) \, \frac{d}{dz} \big[n(z)\big]^{-k} \quad , \tag{5.33}$$

where the contour encloses the origin in the complex plane. Integrating by parts, and using the relation $z\,\pi'(z) = n(z)$, we obtain[2]

$$B_k = \frac{1}{k}\oint\frac{dz}{2\pi i}\,\pi'(z)\,\big[n(z)\big]^{-k} = \frac{1}{k}\oint\frac{dz}{2\pi i}\,\frac{1}{z}\,\big[n(z)\big]^{-(k-1)} \quad . \tag{5.34}$$

Defining the dimensionless ratios $\gamma_j \equiv C_j/C_1$, we have the result

$$B_k = \frac{1}{k\,C_1^{k-1}}\oint\frac{dz}{2\pi i}\,\frac{f_k(z)}{z^k} \quad , \tag{5.35}$$

where

$$f_k(z) \equiv \big(1 + \gamma_2\,z + \gamma_3\,z^2 + \ldots\big)^{-(k-1)} \quad . \tag{5.36}$$

Note that $[B_k] = V^{k-1}$. Expanding by hand to order z^2 isn't so difficult, and we obtain

$$f_k(z) = 1 - (k-1)\gamma_2 z + (k-1)\Big(\tfrac{1}{2}\,k\gamma_2^2 - \gamma_3\Big)z^2 + \mathcal{O}(z^3) \quad . \tag{5.37}$$

From this, we may now read off $B_1 = 1$, which we already showed above, and

$$B_2 = -\frac{\gamma_2}{2C_1} = -\frac{C_2}{2C_1^2} \qquad , \qquad B_3 = \frac{\gamma_2^2 - \frac{2}{3}\gamma_3}{C_1^2} = \frac{C_2^2}{C_1^4} - \frac{2C_3}{C_1^3} \quad . \tag{5.38}$$

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

$$\bigg(p + \frac{aN^2}{V^2}\bigg)(V - Nb) = Nk_{\rm B}T \quad . \tag{5.39}$$

This may be recast as

$$\begin{aligned} p &= \frac{nk_{\rm B}T}{1-bn} - an^2 \\ &= nk_{\rm B}T + \big(b\,k_{\rm B}T - a\big)\,n^2 + k_{\rm B}T\,b^2n^3 + k_{\rm B}T\,b^3n^4 + \ldots \quad , \end{aligned} \tag{5.40}$$

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

5.3.3 Ballistic dispersion

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

$$C_j(T) = \frac{\mathsf{g}_S\,\lambda_T^{-d}}{\Gamma(d/2)}\int\limits_0^\infty dt\,t^{\frac{d}{2}-1}\,e^{-jt} = \mathsf{g}_S\,\lambda_T^{-d}\,j^{-d/2} \quad , \tag{5.41}$$

---

[2] Since there is no term proportional to $\ln z$ in the Laurent expansion of $\pi(z)\big[n(z)\big]^{-k}$, there is no residue arising from integrating its derivative around the unit circle.

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_{\rm B}T}$ is the thermal wavelength. We then have

$$\begin{aligned} B_2(T) &= \mp\, 2^{-(\frac{d}{2}+1)} \cdot {\rm g}_S^{-1}\, \lambda_T^d \\ B_3(T) &= \Big(2^{-(d+1)} - 3^{-(\frac{d}{2}+1)}\Big) \cdot 2\, {\rm g}_S^{-2}\, \lambda_T^{2d} \quad . \end{aligned} \tag{5.42}$$

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.

We may also write

$$n(T,z) = \pm {\rm g}_S\, \lambda_T^{-d}\ {\rm Li}_{\frac{d}{2}}(\pm z) \tag{5.43}$$

and

$$p(T,z) = \pm {\rm g}_S\, k_{\rm B}T\, \lambda_T^{-d}\ {\rm Li}_{\frac{d}{2}+1}(\pm z) \quad , \tag{5.44}$$

where

$${\rm Li}_s(z) \equiv \sum_{n=1}^\infty \frac{z^n}{n^s} \tag{5.45}$$

is the *polylogarithm function*[3]. Note that ${\rm Li}_s(z)$ obeys a recursion relation in its index, *viz.*

$$z\,\frac{\partial}{\partial z}\,{\rm Li}_s(z) = {\rm Li}_{s-1}(z) \quad , \tag{5.46}$$

and that

$${\rm Li}_s(1) = \sum_{n=1}^\infty \frac{1}{n^s} = \zeta(s) \quad . \tag{5.47}$$

To evaluate ${\rm Li}_s(z)$ for $|z| \ll 1$, we use the series expansion in eqn. 5.45. For $|z| \gg 1$, use[4]

$${\rm Li}_s(z) = \sum_{j=0}^\infty (-1)^j \big(1 - 2^{1-2j}\big)\, \frac{(2\pi)^{2j} B_{2j}}{(2j)!}\, \frac{\big[\ln(-z)\big]^{s-2j}}{\Gamma(1+s-2j)} \quad , \tag{5.48}$$

where B_{2j} 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[5]

$${\rm Li}_s(z) = \Gamma(1-s)\,(-\ln z)^{s-1} + \sum_{k=0}^\infty \frac{\zeta(s-k)}{k!}\,(\ln z)^k \quad . \tag{5.49}$$

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

---

[3] Several texts, such as Pathria and Reichl, write $g_s(z)$ for ${\rm Li}_s(z)$. 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.

[4] See the Wikipedia entry on "Polylogarithm."

[5] See *Digital Library of Mathematical Functions* §25.12.12.

5.4 Entropy and Counting States

Suppose we are to partition N particles among J possible distinct single particle states. How many ways Ω are there of accomplishing this task? The answer depends on the statistics of the particles. If the particles are fermions, the answer is easy: $\Omega_{\text{FD}} = \binom{J}{N}$. 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 $\Omega_{\text{BE}} = \binom{N+J-1}{N}$. For Maxwell-Boltzmann statistics, we take $\Omega_{\text{MB}} = J^N/N!$ Note that Ω_{MB} is not necessarily an integer, so Maxwell-Boltzmann 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.

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 $S = k_{\text{B}} \ln \Omega$. 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

$$\begin{aligned} S_{\text{MB}} &= -J k_{\text{B}}\, n \ln n \\ S_{\text{BE}} &= -J k_{\text{B}} \big[n \ln n - (1+n) \ln(1+n) \big] \\ S_{\text{FD}} &= -J k_{\text{B}} \big[n \ln n + (1-n) \ln(1-n) \big] \quad . \end{aligned} \tag{5.50}$$

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

$$\bigg(\frac{\partial S_{\text{MB}}}{\partial N} \bigg)_{\!J} = -k_{\text{B}} \left(1 + \ln n\right) \quad , \quad \bigg(\frac{\partial S_{\text{BE}}}{\partial N} \bigg)_{\!J} = k_{\text{B}} \ln\!\big(n^{-1} + 1\big) \quad , \quad \bigg(\frac{\partial S_{\text{FD}}}{\partial N} \bigg)_{\!J} = k_{\text{B}} \ln\!\big(n^{-1} - 1\big) \quad . \tag{5.51}$$

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 α as a label for the energies, we have that the grand potential $\mathit{\Omega} = E - TS - \mu N$ is given in each case by

$$\begin{aligned} \mathit{\Omega}_{\text{MB}} &= J \sum_\alpha \Big[(\varepsilon_\alpha - \mu)\, n_\alpha + k_{\text{B}} T\, n_\alpha \ln n_\alpha \Big] \\ \mathit{\Omega}_{\text{BE}} &= J \sum_\alpha \Big[(\varepsilon_\alpha - \mu)\, n_\alpha + k_{\text{B}} T\, n_\alpha \ln n_\alpha - k_{\text{B}} T\, (1 + n_\alpha) \ln(1 + n_\alpha) \Big] \\ \mathit{\Omega}_{\text{FD}} &= J \sum_\alpha \Big[(\varepsilon_\alpha - \mu)\, n_\alpha + k_{\text{B}} T\, n_\alpha \ln n_\alpha + k_{\text{B}} T\, (1 - n_\alpha) \ln(1 - n_\alpha) \Big] \quad . \end{aligned} \tag{5.52}$$

Now - *lo and behold!* - treating $\mathit{\Omega}$ as a function of the distribution $\{n_\alpha\}$ 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:

$$\frac{\delta}{\delta n_\alpha}\Big(\varOmega - \lambda\, J \sum_{\alpha'} n_{\alpha'}\Big) = 0 \quad \Rightarrow \quad \begin{cases} n^{\rm MB}_\alpha = e^{(\mu-\varepsilon_\alpha)/k_{\rm B}T} \\ n^{\rm BE}_\alpha = \big[e^{(\varepsilon_\alpha-\mu)/k_{\rm B}T}-1\big]^{-1} \\ n^{\rm FD}_\alpha = \big[e^{(\varepsilon_\alpha-\mu)/k_{\rm B}T}+1\big]^{-1} \quad . \end{cases} \tag{5.53}$$

As long as J is finite, so the states in each block all remain at the same energy, the results are independent of J.

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

$$\mu = \bigg(\frac{\partial F}{\partial N}\bigg)_{T.V} = 0 \quad . \tag{5.54}$$

The number distribution, from eqn. 5.12, is then

$$n(\varepsilon) = \frac{1}{e^{\beta\varepsilon}-1} \quad . \tag{5.55}$$

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

$$\varOmega(T,V) = V k_{\rm B}T \int\limits_{-\infty}^{\infty} \! d\varepsilon\; g(\varepsilon)\;\ln\big(1-e^{-\varepsilon/k_{\rm B}T}\big) \quad , \tag{5.56}$$

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 $g(\varepsilon)$:

$$g(\varepsilon) = \frac{{\sf g}\varOmega_d}{(2\pi)^d}\,\frac{k^{d-1}}{d\varepsilon/dk} = \frac{C_{d,\sigma}}{A^{d/\sigma}}\,\varepsilon^{\frac{d}{\sigma}-1}\,\Theta(\varepsilon) \tag{5.57}$$

where

$$C_{d,\sigma} = \frac{{\sf g}\varOmega_d}{(2\pi)^d\,\sigma} \quad . \tag{5.58}$$

is a dimensionless constant and ${\sf g}$ is the internal degeneracy of the state at wavevector $\boldsymbol{k}$. Recall that $\varOmega_d = 2\pi^{d/2}/\Gamma(d/2)$ 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 $\varepsilon(\boldsymbol{k}) = \hbar ck$, so $\sigma = 1$ and $A = \hbar c$, whence, with $C_d \equiv C_{d,\sigma=1}$,

$$g(\varepsilon) = \frac{C_d}{(\hbar c)^d}\, \varepsilon^{d-1}\, \Theta(\varepsilon) \qquad , \qquad C_d = \frac{2\,\mathsf{g}\,\pi^{d/2}}{\Gamma(d/2)} \quad . \tag{5.59}$$

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

$$\begin{aligned} p(T) &= -k_{\mathrm{B}}T \int\limits_{-\infty}^{\infty} \! d\varepsilon\, g(\varepsilon)\, \ln\big(1 - e^{-\varepsilon/k_{\mathrm{B}}T}\big) \\ &= -\frac{C_d}{(\hbar c)^d}\, k_{\mathrm{B}}T \int\limits_0^{\infty} \! d\varepsilon\, \varepsilon^{d-1}\, \ln\big(1 - e^{-\varepsilon/k_{\mathrm{B}}T}\big) \\ &= -\frac{C_d}{(\hbar c)^d}\, (k_{\mathrm{B}}T)^{d+1} \int\limits_0^{\infty} \! dt\, t^{d-1} \ln\big(1 - e^{-t}\big) \quad . \end{aligned} \tag{5.60}$$

We can make some progress with the dimensionless integral:

$$\mathcal{I}_d \equiv -\int\limits_0^{\infty} \! dt\, t^{d-1} \ln\big(1 - e^{-t}\big) = \sum_{n=1}^{\infty} \frac{1}{n} \int\limits_0^{\infty} \! dt\, t^{d-1}\, e^{-nt} = \Gamma(d) \sum_{n=1}^{\infty} \frac{1}{n^{d+1}} = \Gamma(d)\, \zeta(d+1) \quad . \tag{5.61}$$

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

$$\Gamma(z) = \frac{2^{z-1}}{\sqrt{\pi}}\, \Gamma\big(\tfrac{z}{2}\big)\, \Gamma\big(\tfrac{z+1}{2}\big) \quad , \tag{5.62}$$

and define

$$B_d \equiv \Gamma(d) \cdot \frac{C_d}{(2\pi)^d} = \mathsf{g}\, \pi^{-(d+1)/2}\, \Gamma\big(\tfrac{d+1}{2}\big) \quad . \tag{5.63}$$

Putting it all together, we find

$$p(T) = \zeta(d+1)\, B_d\, \frac{(k_{\mathrm{B}}T)^{d+1}}{(\hbar c)^d} \tag{5.64}$$

as well as

$$n(T) = \int\limits_{-\infty}^{\infty} \! d\varepsilon\, \frac{g(\varepsilon)}{e^{\varepsilon/k_{\mathrm{B}}T} - 1} = \zeta(d)\, B_d\, \frac{(k_{\mathrm{B}}T)^d}{(\hbar c)^d} \quad . \tag{5.65}$$

Dividing these two equations, we obtain the equation of state

$$p = \frac{\zeta(d+1)}{\zeta(d)}\, n k_{\mathrm{B}}T \quad . \tag{5.66}$$

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

$$n(T) = \frac{2\,\zeta(3)}{\pi^2}\, \frac{(k_{\mathrm{B}}T)^3}{(\hbar c)^3} \qquad , \qquad p(T) = \frac{2\,\zeta(4)}{\pi^2}\, \frac{(k_{\mathrm{B}}T)^4}{(\hbar c)^3} \quad . \tag{5.67}$$

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

$$\frac{k_{\rm B}T}{\hbar c}=4.3755\,T[{\rm K}]\,{\rm cm}^{-1}\qquad\Longrightarrow\qquad n(T)=20.405\times T^3[{\rm K}^3]\,{\rm cm}^{-3}\quad . \tag{5.68}$$

To find the entropy, we use Gibbs-Duhem:

$$d\mu=0=-s\,dT+v\,dp\qquad\Longrightarrow\qquad s=v\,\frac{dp}{dT}\quad , \tag{5.69}$$

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

$$s(T)=(d{+}1)\,\frac{\zeta(d{+}1)}{\zeta(d)}\,k_{\rm B}\quad . \tag{5.70}$$

The entropy per particle is constant. The internal energy is

$$E=-\frac{\partial\ln\Xi}{\partial\beta}=-\frac{\partial}{\partial\beta}(\beta pV)=d\,p\,V\quad , \tag{5.71}$$

and hence the energy per particle is

$$\varepsilon=\frac{E}{N}=d\,pv=\frac{d\,\zeta(d{+}1)}{\zeta(d)}\,k_{\rm B}T\quad . \tag{5.72}$$

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 λ. The cavity modes of the electromagnetic radiation have quantized wavevectors, even within classical electromagnetic theory, given by

$$\boldsymbol{k}=\bigg(\frac{2\pi n_x}{L_x}\,,\,\frac{2\pi n_y}{L_y}\,,\,\frac{2\pi n_z}{L_z}\bigg)\quad . \tag{5.73}$$

   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 $V\to\lambda V$, where the distribution of different electromagnetic mode occupancies remains fixed. Thus,

$$V\bigg(\frac{\partial E}{\partial V}\bigg)_{\!S}=\lambda\bigg(\frac{\partial E}{\partial\lambda}\bigg)_{\!S}=-\tfrac{1}{3}E\quad . \tag{5.74}$$

   Thus,

$$p=-\bigg(\frac{\partial E}{\partial V}\bigg)_{\!S}=\frac{E}{3V}\quad , \tag{5.75}$$

   as we found in eqn. 5.71. Since $E=E(T,V)$ is extensive, we must have $p=p(T)$ alone.

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

$$\begin{aligned}\left(\frac{\partial E}{\partial V}\right)_{\!T} = \left(\frac{\partial E}{\partial V}\right)_{\!p} &= 3p \\ &= T\left(\frac{\partial p}{\partial T}\right)_{\!V} - p \quad ,\end{aligned} \tag{5.76}$$

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

$$T\,\frac{dp}{dT} = 4p \quad \Longrightarrow \quad p(T) = A\,T^4 \quad , \tag{5.77}$$

where A is a constant. Thus, we recover the temperature dependence found microscopically in eqn. 5.64.

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

$$dj_\varepsilon = c \cdot \frac{E}{V} \cdot \cos\theta \cdot \frac{d\Omega}{4\pi} \quad , \tag{5.78}$$

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

$$\frac{dP}{dA} = \frac{cE}{4\pi V}\int\limits_0^{\pi/2}\!d\theta\int\limits_0^{2\pi}\!d\phi\,\sin\theta\cdot\cos\theta = \frac{cE}{4V} = \tfrac{3}{4}\,c\,p(T) \equiv \sigma\,T^4 \quad , \tag{5.79}$$

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

$$\sigma = \frac{\pi^2 k_{\rm B}^4}{60\,c^2\,\hbar^3} = 5.67 \times 10^{-8}\,\frac{\rm W}{\rm m^2\,K^4} \tag{5.80}$$

is *Stefan's constant*.

5.5.3 Surface temperature of the earth

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

$$P_{\rm incident} = \frac{\pi R_{\rm e}^2}{4\pi a_{\rm e}^2} \cdot \sigma T_\odot^4 \cdot 4\pi R_\odot^2 = \frac{R_{\rm e}^2\,R_\odot^2}{a_{\rm e}^2} \cdot \pi\sigma T_\odot^4 \quad . \tag{5.81}$$

The power radiated by the earth is

$$P_{\rm radiated} = \sigma T_{\rm e}^4 \cdot 4\pi R_{\rm e}^2 \quad . \tag{5.82}$$

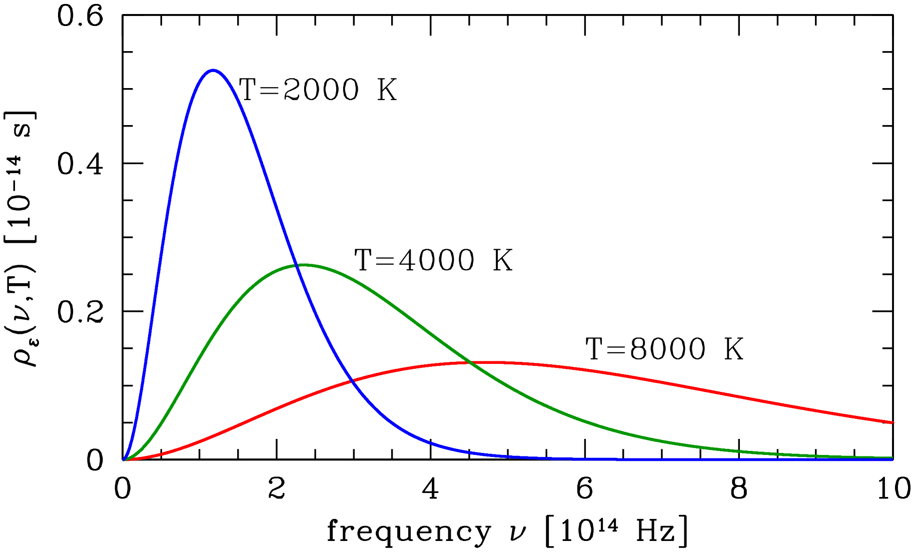

Figure 5.2: Spectral density $\rho_\varepsilon(\nu,T)$ for blackbody radiation at three temperatures.

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

$$T_{\text{e}} = \left(\frac{R_\odot}{2\,a_{\text{e}}}\right)^{1/2} T_\odot \quad . \tag{5.83}$$

Thus, we find $T_{\text{e}} = 0.04817\,T_\odot$, and with $T_\odot = 5780\,\text{K}$, we obtain $T_{\text{e}} = 278.4\,\text{K}$. The mean surface temperature of the earth is $\bar{T}_{\text{e}} = 287\,\text{K}$, which is only about $10\,\text{K}$ 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 $\nu = c/\lambda = ck/2\pi$. Therefore the number of photons $\mathcal{N}_T(\nu,T)$ per unit frequency in thermodynamic equilibrium is (recall there are two polarization states)

$$\mathcal{N}(\nu,T)\,d\nu = \frac{2\,V}{8\pi^3}\cdot\frac{d^3\!k}{e^{\hbar ck/k_{\text{B}}T}-1} = \frac{V}{\pi^2}\cdot\frac{k^2\,dk}{e^{\hbar ck/k_{\text{B}}T}-1} \quad . \tag{5.84}$$

We therefore have

$$\mathcal{N}(\nu,T) = \frac{8\pi V}{c^3}\cdot\frac{\nu^2}{e^{h\nu/k_{\text{B}}T}-1} \quad . \tag{5.85}$$

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

$$\mathcal{E}(\nu,T) = \frac{8\pi hV}{c^3}\cdot\frac{\nu^3}{e^{h\nu/k_{\text{B}}T}-1} \quad . \tag{5.86}$$

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

$$e^{h\nu/k_{\mathrm{B}}T}-1=\frac{h\nu}{k_{\mathrm{B}}T}+\mathcal{O}(h^2) \tag{5.87}$$

and

$$\mathcal{E}_{\mathrm{CL}}(\nu,T)=\lim_{h\to 0}\mathcal{E}(\nu)=V\cdot\frac{8\pi k_{\mathrm{B}}T}{c^3}\,\nu^2 \quad . \tag{5.88}$$

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

$$E(T)=\int\limits_0^\infty d\nu\,\mathcal{E}(\nu)=3pV=V\cdot\frac{\pi^2}{15}\,\frac{(k_{\mathrm{B}}T)^4}{(\hbar c)^3} \quad . \tag{5.89}$$

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

$$\rho_\varepsilon(\nu,T)\equiv\frac{\mathcal{E}(\nu,T)}{E(T)}=\frac{15}{\pi^4}\,\frac{h}{k_{\mathrm{B}}T}\,\frac{(h\nu/k_{\mathrm{B}}T)^3}{e^{h\nu/k_{\mathrm{B}}T}-1} \tag{5.90}$$

so that $\rho_\varepsilon(\nu,T)\,d\nu$ is the fraction of the electromagnetic energy, under equilibrium conditions, between frequencies ν and $\nu+d\nu$, *i.e.* $\int\limits_0^\infty d\nu\,\rho_\varepsilon(\nu,T)=1$. 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

$$\frac{d}{ds}\left(\frac{s^3}{e^s-1}\right)=0 \qquad\Longrightarrow\qquad \frac{s}{1-e^{-s}}=3 \qquad\Longrightarrow\qquad s=2.82144 \quad . \tag{5.91}$$

5.5.5 What if the sun emitted ferromagnetic spin waves?

We saw in eqn. 5.78 that the power emitted per unit surface area by a blackbody is σT^4. The power law here follows from the ultrarelativistic dispersion $\varepsilon=\hbar ck$ of the photons. Suppose that we replace this dispersion with the general form $\varepsilon=\varepsilon(\boldsymbol{k})$. Now consider a large box in equilibrium at temperature T. The *energy current* incident on a differential area dA of surface normal to $\hat{\boldsymbol{z}}$ is

$$dP=dA\cdot\int\!\frac{d^3\!k}{(2\pi)^3}\,\Theta(\cos\theta)\cdot\varepsilon(\boldsymbol{k})\cdot\frac{1}{\hbar}\frac{\partial\varepsilon(\boldsymbol{k})}{\partial k_z}\cdot\frac{1}{e^{\varepsilon(\boldsymbol{k})/k_{\mathrm{B}}T}-1} \quad . \tag{5.92}$$

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

$$\frac{dP}{dA}=\widetilde{\sigma}\,T^{2+2/\alpha} \quad , \tag{5.93}$$

where

$$\widetilde{\sigma}=\zeta(2+2/\alpha)\,\Gamma(2+2/\alpha)\cdot\frac{\mathsf{g}\,k_{\mathrm{B}}^{2+2/\alpha}}{8\pi^2\hbar\,C^{2/\alpha}} \quad . \tag{5.94}$$

One can check that for $\mathrm{g}=2$, $C=\hbar c$, and $\alpha=1$ that this result reduces to that of eqn. 5.80. For the case of ferromagnetic spin waves, $\alpha=2$, in which case $\frac{dP}{dA}=\widetilde{\sigma}T^3$. What would be the surface temperature of the earth if the photon dispersion were $\varepsilon=Ck^\alpha$? Generalizing the results from §5.5.3, we find

$$T_{\mathrm{e}}=\left(\frac{R_\odot}{2\,a_{\mathrm{e}}}\right)^{\frac{\alpha}{1+\alpha}}T_\odot \quad . \tag{5.95}$$

With $R_\odot/2\,a_{\mathrm{e}}=2.32\times10^{-3}$, 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, $\hat{H}=\frac{p^2}{2m}+\frac{1}{2}m\omega_0^2q^2$, may be written as $\hat{H}=\hbar\omega_0(a^\dagger a+\frac{1}{2})$, where a and $a^\dagger$ are 'ladder operators' satisfying commutation relations $\big[a\,,a^\dagger\big]=1$.

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, $x_n^0=nb$ 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

$$\begin{aligned}\hat{H}&=\sum_n\left[\frac{p_n^2}{2m}+\tfrac{1}{2}\kappa\,(x_{n+1}-x_n-a)^2\right]\\&=\sum_n\left[\frac{p_n^2}{2m}+\tfrac{1}{2}\kappa\,(u_{n+1}-u_n)^2\right]+\tfrac{1}{2}N\kappa(b-a)^2 \quad ,\end{aligned}\tag{5.96}$$

where a is the unstretched length of each spring, m is the mass of each mass point, κ 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

$$\begin{aligned}\dot{u}_n&=\frac{\partial\hat{H}}{\partial p_n}=\frac{p_n}{m}\\\dot{p}_n&=-\frac{\partial\hat{H}}{\partial u_n}=\kappa\,\big(u_{n+1}+u_{n-1}-2u_n\big) \quad .\end{aligned}\tag{5.97}$$

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

$$\ddot{u}_n=\frac{\kappa}{m}\,\big(u_{n+1}+u_{n-1}-2u_n\big) \quad . \tag{5.98}$$

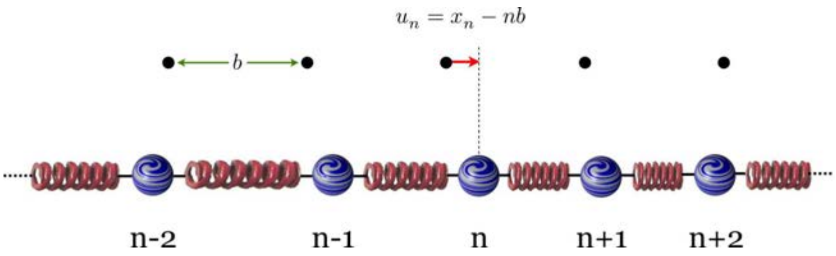

Figure 5.3: A linear chain of masses and springs. The black circles represent the equilibrium positions of the masses. The displacement of mass n relative to its equilibrium value is u_n.

We now write

$$u_n = \frac{1}{\sqrt{N}} \sum_k \tilde{u}_k \, e^{ikna} \quad , \tag{5.99}$$

where periodicity $u_{N+n} = u_n$ requires that the k values are quantized so that $e^{ikNa} = 1$, *i.e.* $k = 2\pi j/Na$ where $j \in \{0, 1, \ldots, N-1\}$. The inverse of this discrete Fourier transform is

$$\tilde{u}_k = \frac{1}{\sqrt{N}} \sum_n u_n \, e^{-ikna} \quad . \tag{5.100}$$

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

$$\ddot{\tilde{u}}_k = -\frac{2\kappa}{m} \big(1 - \cos(ka)\big) \, \tilde{u}_k \equiv -\omega^2_k \, \tilde{u}_k \quad . \tag{5.101}$$

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

$$\omega_k = 2 \sqrt{\frac{\kappa}{m}} \, \big|\sin\big(\tfrac{1}{2}ka\big)\big| \quad . \tag{5.102}$$

The density of states for this band of phonon excitations is

$$g(\varepsilon) = \int\limits_{-\pi/a}^{\pi/a} \frac{dk}{2\pi} \, \delta(\varepsilon - \hbar\omega_k) = \frac{2}{\pi a} \big(J^2 - \varepsilon^2\big)^{-1/2} \, \Theta(\varepsilon) \, \Theta(J - \varepsilon) \quad , \tag{5.103}$$

where $J = 2\hbar\sqrt{\kappa/m}$ is the phonon bandwidth. The step functions require $0 \le \varepsilon \le J$; outside this range there are no phonon energy levels and the density of states accordingly vanishes.

The entire theory can be quantized, taking $\big[p_n \, , u_{n'}\big] = -i\hbar\delta_{nn'}$. We then define

$$p_n = \frac{1}{\sqrt{N}} \sum_k \tilde{p}_k \, e^{ikna} \quad , \quad \tilde{p}_k = \frac{1}{\sqrt{N}} \sum_n p_n \, e^{-ikna} \quad , \tag{5.104}$$

in which case $\big[\tilde{p}_k \, , \tilde{u}_{k'}\big] = -i\hbar\delta_{kk'}$. Note that $\tilde{u}^\dagger_k = \tilde{u}_{-k}$ and $\tilde{p}^\dagger_k = \tilde{p}_{-k}$. We then define the ladder operator

$$a_k = \bigg(\frac{1}{2m\hbar\omega_k}\bigg)^{1/2} \tilde{p}_k - i\bigg(\frac{m\omega_k}{2\hbar}\bigg)^{1/2} \tilde{u}_k \tag{5.105}$$

and its Hermitean conjugate $a_k^\dagger$, in terms of which the Hamiltonian is

$$\hat{H} = \sum_k \hbar\omega_k \left(a_k^\dagger a_k + \tfrac{1}{2}\right) \quad , \tag{5.106}$$

which is a sum over independent harmonic oscillator modes. Note that the sum over k is restricted to an interval of width 2π, *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. 5.100.

5.6.2 General theory of lattice vibrations

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

$$\hat{H} = \sum_{\boldsymbol{R},i} \frac{\boldsymbol{p}_i^2(\boldsymbol{R})}{2M_i} + \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \sum_{\boldsymbol{R},\boldsymbol{R}'} u_i^\alpha(\boldsymbol{R})\, \Phi_{ij}^{\alpha\beta}(\boldsymbol{R}-\boldsymbol{R}')\, u_j^\beta(\boldsymbol{R}') \quad , \tag{5.107}$$

where the *dynamical matrix* is

$$\Phi_{ij}^{\alpha\beta}(\boldsymbol{R}-\boldsymbol{R}') = \frac{\partial^2 U}{\partial u_i^\alpha(\boldsymbol{R})\, \partial u_j^\beta(\boldsymbol{R}')} \quad , \tag{5.108}$$

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 α and β 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* $\boldsymbol{a}_l$, 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 $\boldsymbol{R}'$ are points in a Bravais lattice, then so is $\boldsymbol{R}+\boldsymbol{R}'$.

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 $\{\boldsymbol{\eta}_j\}$ 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. 5.107 takes the form

$$\hat{H} = \sum_{\boldsymbol{k},a} \hbar\omega_a(\boldsymbol{k}) \left(A_a^\dagger(\boldsymbol{k})\, A_a(\boldsymbol{k}) + \tfrac{1}{2}\right) \quad , \tag{5.109}$$

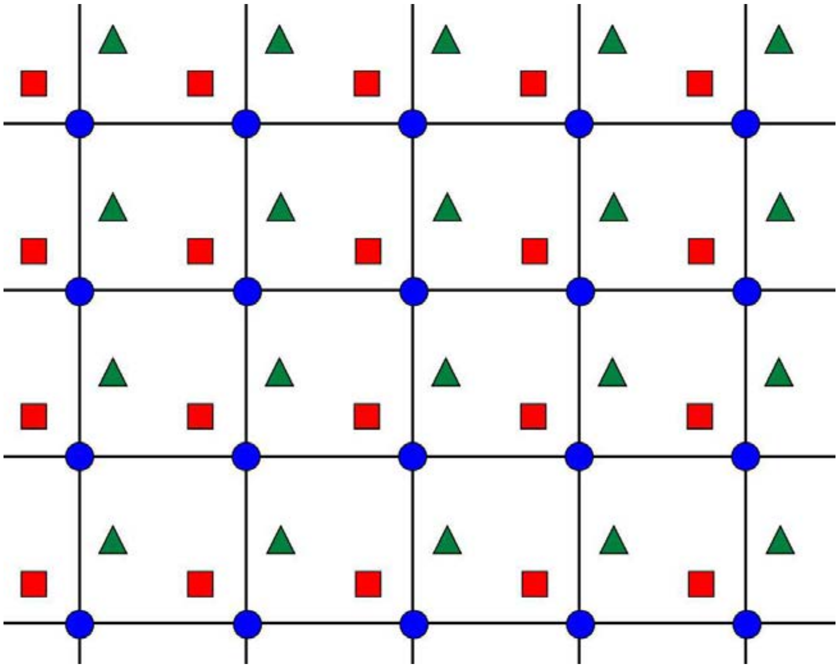

Figure 5.4: A crystal structure with an underlying square Bravais lattice and a three element basis.

where

$$\big[A_a(\boldsymbol{k})\,,\,A^\dagger_b(\boldsymbol{k}')\big] = \delta_{ab}\,\delta_{\boldsymbol{k}\boldsymbol{k}'} \quad . \tag{5.110}$$

The eigenfrequencies are solutions to the eigenvalue equation

$$\sum_{j,\beta} \tilde\Phi^{\alpha\beta}_{ij}(\boldsymbol{k})\,\mathsf{e}^{(a)}_{j\beta}(\boldsymbol{k}) = M_i\,\omega_a^2(\boldsymbol{k})\,\mathsf{e}^{(a)}_{i\alpha}(\boldsymbol{k}) \quad , \tag{5.111}$$

where

$$\tilde\Phi^{\alpha\beta}_{ij}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} \Phi^{\alpha\beta}_{ij}(\boldsymbol{R})\,e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \quad . \tag{5.112}$$

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 $\boldsymbol{a}_l\cdot\boldsymbol{b}_{l'} = 2\pi\delta_{ll'}$. The index a ranges from 1 to $d\cdot r$ and labels the *mode* of oscillation at wavevector $\boldsymbol{k}$. The vector $\mathsf{e}^{(a)}_{i\alpha}(\boldsymbol{k})$ is the *polarization vector* for the $a^{\rm th}$ phonon branch. In solids, along directions of 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: rN 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 $\boldsymbol{k}\to 0$. 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^{th} phonon mode to be

$$g_a(\omega)=\frac{1}{N}\sum_{\boldsymbol{k}}\delta\big(\omega-\omega_a(\boldsymbol{k})\big)=\mathcal{V}_0\int\limits_{\text{BZ}}\frac{d^d\!k}{(2\pi)^d}\,\delta\big(\omega-\omega_a(\boldsymbol{k})\big)\quad, \tag{5.113}$$

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 ω here has dimensions of frequency. The functions $g_a(\omega)$ is normalized to unity: $\int\limits_0^\infty d\omega\, g_a(\omega)=1$. The total phonon density of states per unit cell is given by[6] $g(\omega)=\sum_{a=1}^{dr} g_a(\omega)$.

The grand potential for the phonon gas is

$$\begin{aligned}\Omega(T,V)&=-k_{\text{B}}T\ln\prod_{\boldsymbol{k},a}\sum_{n_a(\boldsymbol{k})=0}^{\infty}e^{-\beta\hbar\omega_a(\boldsymbol{k})\left(n_a(\boldsymbol{k})+\frac{1}{2}\right)}\\&=k_{\text{B}}T\sum_{\boldsymbol{k},a}\ln\left[2\sinh\left(\frac{\hbar\omega_a(\boldsymbol{k})}{2k_{\text{B}}T}\right)\right]=Nk_{\text{B}}T\int\limits_0^\infty d\omega\, g(\omega)\,\ln\left[2\sinh\left(\frac{\hbar\omega}{2k_{\text{B}}T}\right)\right]\quad.\end{aligned} \tag{5.114}$$

Note that $V=N\mathcal{V}_0$ since there are N unit cells, each of volume $\mathcal{V}_0$. The entropy is given by $S=-\big(\frac{\partial\Omega}{\partial T}\big)_V$ and thus the heat capacity is

$$C_V=-T\frac{\partial^2\Omega}{\partial T^2}=Nk_{\text{B}}\int\limits_0^\infty d\omega\, g(\omega)\left(\frac{\hbar\omega}{2k_{\text{B}}T}\right)^2\text{csch}^2\left(\frac{\hbar\omega}{2k_{\text{B}}T}\right) \tag{5.115}$$

Note that as $T\to\infty$ we have $\text{csch}\big(\frac{\hbar\omega}{2k_{\text{B}}T}\big)\to\frac{2k_{\text{B}}T}{\hbar\omega}$, and therefore

$$\lim_{T\to\infty}C_V(T)=Nk_{\text{B}}\int\limits_0^\infty d\omega\, g(\omega)=rdNk_{\text{B}}\quad. \tag{5.116}$$

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

---

[6] Note the dimensions of $g(\omega)$ are $(\text{frequency})^{-1}$. By contrast, the dimensions of $g(\varepsilon)$ in eqn. 5.25 are $(\text{energy})^{-1}\cdot(\text{volume})^{-1}$. The difference lies in the a factor of $\mathcal{V}_0\cdot\hbar$, where $\mathcal{V}_0$ is the unit cell volume.

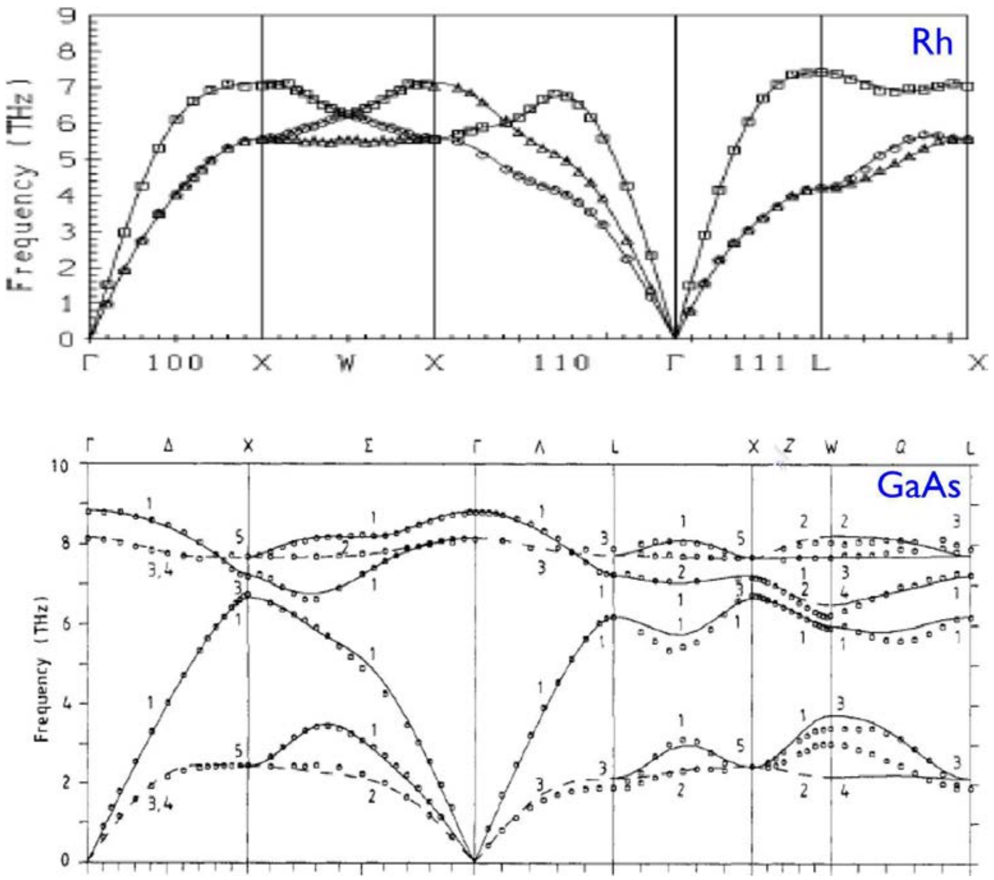

Figure 5.5: Upper panel: phonon spectrum in elemental rhodium (Rh) at $T = 297\,\text{K}$ measured by high precision inelastic neutron scattering (INS) by A. Eichler *et al.*, *Phys. Rev. B* **57**, 324 (1998). Note the three acoustic branches and no optical branches, corresponding to $d = 3$ and $r = 1$. Lower panel: phonon spectrum in gallium arsenide (GaAs) at $T = 12\,\text{K}$, 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

$$C_V(T) = N k_\text{B} \sum_a \left(\frac{\hbar\omega_a}{2k_\text{B}T}\right)^2 \text{csch}^2\left(\frac{\hbar\omega_a}{2k_\text{B}T}\right) \quad . \tag{5.117}$$

At low temperatures, the contribution from each branch vanishes exponentially, since $\text{csch}^2\big(\frac{\hbar\omega_a}{2k_\text{B}T}\big) \simeq 4\,e^{-\hbar\omega_a/k_\text{B}T} \to 0$. 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 $\boldsymbol{k} \to 0$, 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 $\varGamma$ 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

$$\tilde{g}(\omega) = \frac{\mathcal{V}_0\,\omega^2}{2\pi^2}\sum_a \int \frac{d\hat{\boldsymbol{k}}}{4\pi}\,\frac{1}{c_a^3(\boldsymbol{k})}\,\Theta(\omega_{\mathrm{D}} - \omega) = \frac{3\mathcal{V}_0}{2\pi^2\bar{c}^3}\,\omega^2\,\Theta(\omega_{\mathrm{D}} - \omega) \quad , \tag{5.118}$$

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

$$\frac{3}{\bar{c}^3} = \sum_a \int \frac{d\hat{\boldsymbol{k}}}{4\pi}\,\frac{1}{c_a^3(\boldsymbol{k})} \tag{5.119}$$

and ω_{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, ω_{D} should roughly be equal to the energy of a zone boundary phonon. Alternatively, we can define ω_{D} by the normalization condition

$$\int\limits_0^\infty d\omega\;\tilde{g}(\omega) = 3 \quad \Longrightarrow \quad \omega_{\mathrm{D}} = (6\pi^2/\mathcal{V}_0)^{1/3}\,\bar{c} \quad . \tag{5.120}$$

This allows us to write $\tilde{g}(\omega) = \big(9\omega^2/\omega_{\mathrm{D}}^3\big)\,\Theta(\omega_{\mathrm{D}} - \omega)$.

The specific heat due to the acoustic phonons is then

$$\begin{aligned} C_V(T) &= \frac{9Nk_{\mathrm{B}}}{\omega_{\mathrm{D}}^3}\int\limits_0^{\omega_{\mathrm{D}}} d\omega\,\omega^2 \left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)^2 \mathrm{csch}^2\!\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right) \\ &= 9Nk_{\mathrm{B}}\left(\frac{2T}{\varTheta_{\mathrm{D}}}\right)^3 \phi(\varTheta_{\mathrm{D}}/2T) \quad , \end{aligned} \tag{5.121}$$

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

$$\phi(x) = \int\limits_0^x dt\;t^4\;\mathrm{csch}^2 t = \begin{cases} x^3/3 & x \to 0 \\ \pi^4/30 & x \to \infty \quad . \end{cases} \tag{5.122}$$

Therefore,

$$C_V(T) = \begin{cases} \frac{12}{5}\pi^4 Nk_{\mathrm{B}}\,(T/\varTheta_{\mathrm{D}})^3 & T \ll \varTheta_{\mathrm{D}} \\ 3Nk_{\mathrm{B}} & T \gg \varTheta_{\mathrm{D}} \quad . \end{cases} \tag{5.123}$$

Thus, the heat capacity due to acoustic phonons obeys the Dulong-Petit rule in that $C_V(T \to \infty) = 3Nk_{\mathrm{B}}$, corresponding to the three acoustic degrees of freedom per unit cell. The remaining contribution of $3(r-1)Nk_{\mathrm{B}}$ 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	Ni	Pb	Pt	Si	Sn	Ta	Ti	W	Zn
$\Theta_{\rm D}$ (K)	227	433	162	2250	210	606	347	477	409	477	105	237	645	199	246	420	383	329
$T_{\rm melt}$ (K)	962	660	1064	3500	321	1857	1083	1535	1245	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. 5.105 gives

$$\tilde{u}_k = i\left(\frac{\hbar}{2m\omega_k}\right)^{1/2}\big(a_k - a^\dagger_{-k}\big) \quad . \tag{5.124}$$

Therefore the RMS fluctuations at each site are given by

$$\langle u_n^2\rangle = \frac{1}{N}\sum_k \langle \tilde{u}_k\,\tilde{u}_{-k}\rangle = \frac{1}{N}\sum_k \frac{\hbar}{m\omega_k}\,\big(n(k) + \tfrac{1}{2}\big) \quad , \tag{5.125}$$

where $n(k,T) = \big[\exp(\hbar\omega_k/k_{\rm B}T) - 1\big]^{-1}$ 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 $i^{\rm th}$ basis atom in each unit cell is

$$\langle \boldsymbol{u}_i^2(\boldsymbol{R})\rangle = \frac{1}{N}\sum_{\boldsymbol{k}}\sum_{a=1}^{dr} \frac{\hbar}{M_{ia}(\boldsymbol{k})\,\omega_a(\boldsymbol{k})}\,\big(n_a(\boldsymbol{k}) + \tfrac{1}{2}\big) \quad . \tag{5.126}$$

Here we sum over all wavevectors $\boldsymbol{k}$ in the first Brilliouin zone, and over all normal modes a. There are dr 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 $M_{ia}(\boldsymbol{k})$, which has units of mass and is defined in terms of the polarization vectors $\mathsf{e}^{(a)}_{i\alpha}(\boldsymbol{k})$ as

$$\frac{1}{M_{ia}(\boldsymbol{k})} = \sum_{\mu=1}^{d} \big|\mathsf{e}^{(a)}_{i\mu}(\boldsymbol{k})\big|^2 \quad . \tag{5.127}$$

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

$$\sum_{i,\mu} M_i\,\mathsf{e}^{(a)\,*}_{i\mu}(\boldsymbol{k})\,\mathsf{e}^{(b)}_{i\mu}(\boldsymbol{k}) = \delta^{ab} \quad , \tag{5.128}$$

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 $M_{ia}(\boldsymbol{k})$ by an appropriately averaged quantity which we call M_i ; this 'effective mass' is then independent of the mode index a as well as the wavevector $\boldsymbol{k}$. We may then write

$$\langle\, \boldsymbol{u}_i^2 \,\rangle \approx \int\limits_0^\infty \! d\omega \; g(\omega)\, \frac{\hbar}{\mathsf{M}_i\, \omega} \cdot \left\{ \frac{1}{e^{\hbar\omega/k_\mathrm{B}T} - 1} + \frac{1}{2} \right\} \quad , \tag{5.129}$$

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 $\langle\, \boldsymbol{u}_i^2 \,\rangle$ can be divided into a temperature-dependent part $\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{th}$ and a temperature-independent quantum contribution $\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{qu}$, where

$$\begin{aligned} \langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{th} &= \frac{\hbar}{\mathsf{M}_i} \int\limits_0^\infty \! d\omega \; \frac{g(\omega)}{\omega} \cdot \frac{1}{e^{\hbar\omega/k_\mathrm{B}T} - 1} \\ \langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{qu} &= \frac{\hbar}{2\mathsf{M}_i} \int\limits_0^\infty \! d\omega \; \frac{g(\omega)}{\omega} \quad . \end{aligned} \tag{5.130}$$

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

$$\bar{g}(\omega) = \frac{d^2\, \omega^{d-1}}{\omega_\mathrm{D}^d}\, \Theta(\omega_\mathrm{D} - \omega) \quad . \tag{5.131}$$

We then find

$$\begin{aligned} \langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{th} &= \frac{d^2 \hbar}{\mathsf{M}_i\, \omega_\mathrm{D}} \left(\frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{D}} \right)^{d-1} F_d(\hbar\omega_\mathrm{D}/k_\mathrm{B}T) \\ \langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{qu} &= \frac{d^2}{d-1} \cdot \frac{\hbar}{2\mathsf{M}_i\, \omega_\mathrm{D}} \quad , \end{aligned} \tag{5.132}$$

where

$$F_d(x) = \int\limits_0^x \! ds \; \frac{s^{d-2}}{e^s - 1} = \begin{cases} x^{d-2}/(d-2) & x \to 0 \\ \zeta(d-1) & x \to \infty \end{cases} \quad . \tag{5.133}$$

We can now extract from these expressions several important conclusions:

1) The $T = 0$ contribution to the the fluctuations, $\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{qu}$, diverges in $d = 1$ dimensions. *Therefore there are no one-dimensional quantum solids.*

2) The thermal contribution to the fluctuations, $\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{th}$, diverges for any $T > 0$ whenever $d \leq 2$. This is because the integrand of $F_d(x)$ goes as s^{d-3} as $s \to 0$. *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 $k_\mathrm{min} \sim 2\pi/L$, where L is the (finite) linear dimension of the system. This leads to a low frequency cutoff $\omega_\mathrm{min} = 2\pi\bar{c}/L$, where $\bar{c}$ is the appropriately averaged acoustic phonon velocity from eqn. 5.119, 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

$$\begin{aligned} x^2_{i,\text{th} } &\equiv \frac{\langle\, \boldsymbol{u}_i^2 \,\rangle_\text{th} }{a^2} = d^2 \cdot \left(\frac{\hbar^2}{\mathsf{M}_i \, a^2 \, k_\text{B} } \right) \cdot \frac{T^{d-1} }{\Theta^d_\text{D} } \cdot F(\Theta_\text{D}/T) \\ x^2_{i,\text{qu} } &\equiv \frac{\langle\, \boldsymbol{u}_i^2 \,\rangle_\text{qu} }{a^2} = \frac{d^2}{2(d-1)} \cdot \left(\frac{\hbar^2}{\mathsf{M}_i \, a^2 \, k_\text{B} } \right) \cdot \frac{1}{\Theta_\text{D} } \quad , \end{aligned} \tag{5.134}$$

with $x_i = \sqrt{x^2_{i,\text{th} } + x^2_{i,\text{qu} } } = \sqrt{\langle\, \boldsymbol{u}_i^2 \,\rangle} \Big/ a$.

Let's now work through an example of a three-dimensional solid. We'll assume a single element basis $(r = 1)$. We have that

$$\frac{9\hbar^2/4k_\text{B} }{1\,\texttt{amu}\,\text{Å}^2} = 109\,\text{K} \quad . \tag{5.135}$$

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

$$x^2_\text{qu} = \frac{\Theta^\star}{\Theta_\text{D} } \quad , \quad x^2_\text{th} = \frac{\Theta^\star}{\Theta_\text{D} } \cdot \frac{4T}{\Theta_\text{D} } \quad , \quad x = \sqrt{\left(1 + \frac{4T}{\Theta_\text{D} }\right) \frac{\Theta^\star}{\Theta_\text{D} } } \quad . \tag{5.136}$$

where

$$\Theta^* = \frac{109\,\text{K} }{M[\texttt{amu}] \cdot \big(a[\text{Å}]\big)^2} \quad . \tag{5.137}$$

The total position fluctuation is of course the sum $x^2 = x^2_{i,\text{th} } + x^2_{i,\text{qu} }$. Consider for example the case of copper, with $M = 56\,\texttt{amu}$ and $a = 2.87\,\text{Å}$. The Debye temperature is $\Theta_\text{D} = 347\,\text{K}$. From this we find $x_\text{qu} = 0.026$, 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, $T = 293\,\text{K}$, one finds $x_\text{th} = 0.048$, 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, $T_\text{melt} = 1083\,\text{K}$ 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 $M = 208\,\texttt{amu}$ and $a = 4.95\,\text{Å}$. The Debye temperature is $\Theta_\text{D} = 105\,\text{K}$ ('soft phonons'), and the melting point is $T_\text{melt} = 327\,\text{K}$. From these data we obtain $x(T = 0) = 0.014$, $x(293\,\text{K}) = 0.050$ and $x(T = 327\,\text{K}) = 0.053$. Same ballpark.

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

$$T_\text{L} = \left(\frac{\Theta_\text{D} }{\Theta^\star} \, x^{*2} - 1 \right) \cdot \frac{\Theta_\text{D} }{4} \quad . \tag{5.138}$$

We call $T_{\rm L}$ 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 $T_{\rm L} < 0$. This occurs for any crystal where $\Theta_{\rm D} < \Theta^\star/x^{*2}$. 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}He, which at atmospheric pressure condenses into a liquid at $T_{\rm c} = 4.2\,{\rm K}$ and remains in the liquid state down to absolute zero. At $p = 1\,{\rm atm}$, it never solidifies! Why? The number density of liquid ^{4}He at $p = 1\,{\rm atm}$ and $T = 0\,{\rm K}$ is $2.2 \times 10^{22}\,{\rm cm}^{-3}$. 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 $a = 3.57\,$Å. 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, $\omega_{\rm D} = (6\pi^2/\mathcal{V}_0)^{1/3}\bar{c}$, where $\mathcal{V}_0$ is the unit cell volume. We'll take $\bar{c} = 238\,{\rm m/s}$, which is the speed of sound in liquid helium at $T = 0$. This gives $\Theta_{\rm D} = 19.8\,{\rm K}$. We find $\Theta^\star = 2.13\,{\rm K}$, and if we take $x^* = 0.1$ this gives $\Theta^\star/x^{*2} = 213\,{\rm K}$, which significantly exceeds $\Theta_{\rm D}$. Thus, the solid should melt because the RMS fluctuations in the atomic positions at absolute zero are huge: $x_{\rm qu} = (\Theta^\star/\Theta_{\rm D})^{1/2} = 0.33$. By applying pressure, one can get ^{4}He to crystallize above $p_{\rm c} = 25\,{\rm atm}$ 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 ω 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 ${\rm SU}(2)$. 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 ${\rm SU}(2)$, 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 Goldstone 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 $g(\omega) = \mathcal{C}\,\omega^{\frac{d}{\sigma}-1}\,\Theta(\omega_{\rm c} - \omega)$, where $\mathcal{C}$ is a constant and $\omega_{\rm c}$ is the cutoff, which is the bandwidth for this excitation branch.[7] Normalizing the density of states for this branch results in the identification $\omega_{\rm c} = (d/\sigma\mathcal{C})^{\sigma/d}$.

The heat capacity is then found to be

$$C_V = N k_{\rm B}\,\mathcal{C}\int\limits_0^{\omega_{\rm c}} d\omega\,\omega^{\frac{d}{\sigma}-1}\left(\frac{\hbar\omega}{k_{\rm B}T}\right)^2 \text{csch}^2\!\left(\frac{\hbar\omega}{2k_{\rm B}T}\right) = \frac{d}{\sigma}\,N k_{\rm B}\left(\frac{2T}{\Theta}\right)^{d/\sigma}\phi(\Theta/2T) \quad , \tag{5.139}$$

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

$$\phi(x) = \int\limits_0^x dt\,t^{\frac{d}{\sigma}+1}\;\text{csch}^2 t = \begin{cases} \frac{\sigma}{d}\,x^{d/\sigma} & x \to 0 \\ 2^{-d/\sigma}\,\Gamma\big(2+\frac{d}{\sigma}\big)\,\zeta\big(2+\frac{d}{\sigma}\big) & x \to \infty \end{cases} \quad , \tag{5.140}$$

which is a generalization of our earlier results. Once again, we recover Dulong-Petit for $k_{\rm B}T \gg \hbar\omega_{\rm c}$, with $C_V(T \gg \hbar\omega_{\rm c}/k_{\rm B}) = N k_{\rm B}$.

In an isotropic ferromagnet, *i.e.*a ferromagnetic material where there is full 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

$$\Xi = \prod_\alpha \left(\sum_{n_\alpha=0}^\infty e^{\beta(\mu-\varepsilon_\alpha)n_\alpha}\right) = \prod_\alpha \Big(1 - e^{\beta(\mu-\varepsilon_\alpha)}\Big)^{-1} \quad , \tag{5.141}$$

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

$$n(T,\mu) = -\frac{1}{V}\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \frac{1}{V}\sum_\alpha \frac{1}{e^{\beta(\varepsilon_\alpha-\mu)} - 1} = \int\limits_{\varepsilon_0}^\infty d\varepsilon\,\frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1} \quad , \tag{5.142}$$

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

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[7] If $\omega(\boldsymbol{k}) = Ak^\sigma$, then $\mathcal{C} = 2^{1-d}\,\pi^{-\frac{d}{2}}\,\sigma^{-1}\,A^{-\frac{d}{\sigma}}\,\mathsf{g}\,/\,\Gamma(d/2)$.

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 μ. At fixed T, the maximum possible value for $n(T,\mu)$, called the *critical density* $n_c(T)$, is achieved for $\mu = \varepsilon_0$, *i.e.*

$$n_c(T) = \int\limits_{\varepsilon_0}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\varepsilon_0)} - 1} \quad . \tag{5.143}$$

The above integral converges provided $g(\varepsilon_0) = 0$, assuming $g(\varepsilon)$ is continuous[8]. If $g(\varepsilon_0) > 0$, the integral diverges, and $n_c(T) = \infty$. 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 $n_c(T)$ is finite, we have a problem – what happens if $n > n_c(T)$?

In the former case, where $n_c(T)$ is finite, we can equivalently restate the problem in terms of a *critical temperature* $T_c(n)$, defined by the equation $n_c(T_c) = n$. For $T < T_c$, we apparently can no longer invert to obtain $\mu(T,n)$, so clearly something has gone wrong. The remedy is to recognize that the single particle energy levels are discrete, and separate out the contribution from the lowest energy state ε_0. *I.e.* we write

$$n(T,\mu) = \overbrace{\frac{1}{V}\,\frac{\mathrm{g}_0}{e^{\beta(\varepsilon_0-\mu)} - 1}}^{n_0} + \overbrace{\int\limits_{\varepsilon_0}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1}}^{n'} \quad , \tag{5.144}$$

where g_0 is the degeneracy of the single particle state with energy ε_0. We assume that n_0 is finite, which means that $N_0 = Vn_0$ is extensive. We say that the particles have *condensed* into the state with energy ε_0. The quantity n_0 is the *condensate density*. The remaining particles, with density n', are said to comprise the *overcondensate*. With the total density n fixed, we have $n = n_0 + n'$. Note that n_0 finite means that μ is infinitesimally close to ε_0:

$$\mu = \varepsilon_0 - k_B T \ln\!\left(1 + \frac{\mathrm{g}_0}{Vn_0}\right) \approx \varepsilon_0 - \frac{\mathrm{g}_0 k_B T}{Vn_0} \quad . \tag{5.145}$$

Note also that if $\varepsilon_0 - \mu$ is finite, then $n_0 \propto V^{-1}$ is infinitesimal.

Thus, for $T < T_c(n)$, we have $\mu = \varepsilon_0$ with $n_0 > 0$, and

$$n(T,n_0) = n_0 + \int\limits_{\varepsilon_0}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{(\varepsilon-\varepsilon_0)/k_B T} - 1} \quad . \tag{5.146}$$

For $T > T_c(n)$, we have $n_0 = 0$ and

$$n(T,\mu) = \int\limits_{\varepsilon_0}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/k_B T} - 1} \quad . \tag{5.147}$$

---

[8] 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 η is the lower cutoff. But for any power law density of states $g(\varepsilon) \propto \varepsilon^r$ with $r > 0$, the integral converges.

The equation for $T_c(n)$ is

$$n = \int\limits_{\varepsilon_0}^{\infty} d\varepsilon \, \frac{g(\varepsilon)}{e^{(\varepsilon-\varepsilon_0)/k_B T_c} - 1} \quad . \tag{5.148}$$

For another take on ideal Bose gas condensation see the appendix in §5.10.

5.7.2 Ballistic dispersion

We already derived, in §5.3.3, expressions for $n(T,z)$ and $p(T,z)$ for the ideal Bose gas (IBG) with ballistic dispersion $\varepsilon(\boldsymbol{p}) = \boldsymbol{p}^2/2m$, We found

$$\begin{aligned} n(T,z) &= \mathsf{g}\, \lambda_T^{-d} \ \mathrm{Li}_{\frac{d}{2}}(z) \\ p(T,z) &= \mathsf{g}\, k_B T\, \lambda_T^{-d} \ \mathrm{Li}_{\frac{d}{2}+1}(z), \end{aligned} \tag{5.149}$$

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

$$\mathrm{Li}_s(z) = \sum_{m=1}^{\infty} \frac{z^m}{m^s} \tag{5.150}$$

is the polylogarithm function. For bosons with a spectrum bounded below by $\varepsilon_0 = 0$, the fugacity takes values on the interval $z \in [0,1]$[9]. Note that $\mathrm{Li}_s(z=1) = \zeta(s)$, which is Riemann's zeta function; $\zeta(s)$ is finite for $s > 1$.

Clearly $n(T,z) = \mathsf{g}\, \lambda_T^{-d} \ \mathrm{Li}_{\frac{d}{2}}(z)$ is an increasing function of z for fixed T. In fig. 5.6 we plot the function $\mathrm{Li}_s(z)$ *versus* z for three different values of s. We note that the maximum value $\mathrm{Li}_s(z=1)$ is *finite* if $s > 1$. Thus, for $d > 2$, there is a *maximum density* $n_{\mathrm{max}}(T) = \mathsf{g}\, \zeta(d/2)\, \lambda_T^{-d}$ which is an increasing function of temperature T. Put another way, if we fix the density n, then there is a *critical temperature* T_c below which there is no solution to the equation $n = n(T,z)$. The critical temperature $T_c(n)$ is then determined by the relation

$$n = \mathsf{g}\, \zeta\big(\tfrac{d}{2}\big) \left(\frac{mk_B T_c}{2\pi\hbar^2}\right)^{d/2} \qquad \Longrightarrow \qquad k_B T_c = \frac{2\pi\hbar^2}{m} \left(\frac{n}{\mathsf{g}\, \zeta\big(\tfrac{d}{2}\big)}\right)^{2/d} \quad . \tag{5.151}$$

What happens for $T < T_c$?

As shown above in §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

$$n = \frac{1}{V}\, \frac{1}{z^{-1} - 1} + \frac{1}{V} \sum_{\substack{\alpha \\ (\varepsilon_\alpha > 0)}} \frac{1}{z^{-1}\, e^{\varepsilon_\alpha/k_B T} - 1} \quad , \tag{5.152}$$

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

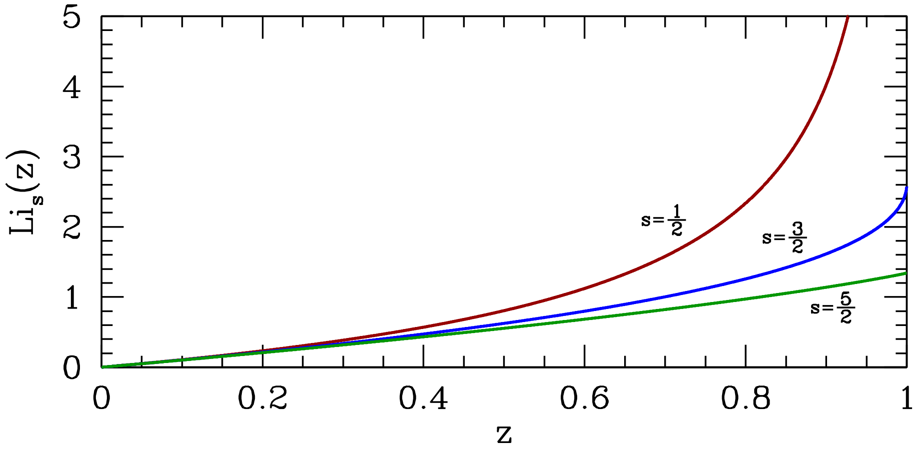

Figure 5.6: The polylogarithm function $\mathrm{Li}_s(z)$ *versus* z for $s=\frac{1}{2}$, $s=\frac{3}{2}$, and $s=\frac{5}{2}$. Note that $\mathrm{Li}_s(1)=\zeta(s)$ diverges for $s\le 1$.

where we have taken $\mathsf{g}=1$. Now V^{-1} is of course very small, since V is thermodynamically large, but if $\mu\to 0$ 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

$$N_0 = V n_0 = \frac{1}{z^{-1}-1} \qquad \Longrightarrow \qquad z=\frac{1}{1+N_0^{-1}} \quad . \tag{5.153}$$

The chemical potential is then

$$\mu = k_{\mathrm{B}}T\ln z = -k_{\mathrm{B}}T\ln\left(1+N_0^{-1}\right) \approx -\frac{k_{\mathrm{B}}T}{N_0} \to 0^- \quad . \tag{5.154}$$

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

$$p_0 = -\frac{k_{\mathrm{B}}T}{V}\ln(1-z) = \frac{k_{\mathrm{B}}T}{V}\ln(1+N_0) \to 0^+ \quad . \tag{5.155}$$

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 α by the usual integral over $\boldsymbol{k}$. We then have

$$\begin{aligned} T<T_{\mathrm{c}} \qquad : \qquad & n = n_0 + \mathsf{g}\,\zeta\big(\tfrac{d}{2}\big)\,\lambda_T^{-d} \\ & p = \mathsf{g}\,\zeta\big(\tfrac{d}{2}{+}1\big)\,k_{\mathrm{B}}T\,\lambda_T^{-d} \end{aligned} \tag{5.156}$$

and

$$\begin{aligned} T>T_{\mathrm{c}} \qquad : \qquad & n = \mathsf{g}\,\mathrm{Li}_{\frac{d}{2}}(z)\,\lambda_T^{-d} \\ & p = \mathsf{g}\,\mathrm{Li}_{\frac{d}{2}+1}(z)\,k_{\mathrm{B}}T\,\lambda_T^{-d} \quad . \end{aligned} \tag{5.157}$$

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 $T=T_c$, at which point it vanishes identically. Explicitly, we have

$$\frac{n_0(T)}{n} = 1 - \frac{\mathsf{g}\,\zeta\big(\frac{d}{2}\big)}{n\,\lambda_T^d} = 1 - \left(\frac{T}{T_c(n)}\right)^{d/2} \quad . \tag{5.158}$$

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

$$\frac{\partial}{\partial\beta}\,(\beta\Omega) = \Omega + \beta\,\frac{\partial\Omega}{\partial\beta} = \Omega - T\,\frac{\partial\Omega}{\partial T} = \Omega + TS \tag{5.159}$$

and therefore

$$\begin{aligned} E = \Omega + TS + \mu N &= \mu N + \frac{\partial}{\partial\beta}\,(\beta\Omega) \\ &= V\Big(\mu\,n - \frac{\partial}{\partial\beta}\,(\beta p)\Big) = \tfrac{1}{2} d\,\mathsf{g} V k_B T\,\lambda_T^{-d}\,\mathrm{Li}_{\frac{d}{2}+1}(z) \quad . \end{aligned} \tag{5.160}$$

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

We now investigate the heat capacity $C_{V,N} = \big(\frac{\partial E}{\partial T}\big)_{V,N}$. 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 $d \le 2$ and $d>3$ is unphysical. While we're at it, we'll also set $\mathsf{g}=1$.

The number of particles is

$$N = \begin{cases} N_0 + \zeta(3/2)\,V\,\lambda_T^{-3} & (T<T_c) \\ V\,\lambda_T^{-3}\,\mathrm{Li}_{3/2}(z) & (T>T_c) \end{cases} \quad , \tag{5.161}$$

and the energy is

$$E = \tfrac{3}{2}\,k_B T\,\frac{V}{\lambda_T^3}\,\mathrm{Li}_{5/2}(z) = \tfrac{3}{2}\,pV \quad . \tag{5.162}$$

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

$$C_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \tfrac{15}{4}\,\zeta(5/2)\,k_B\,\frac{V}{\lambda_T^3} \quad . \tag{5.163}$$

The molar heat capacity is therefore

$$c_{V,N}(T,n) = N_A \cdot \frac{C_{V,N}}{N} = \tfrac{15}{4}\,\zeta(5/2)\,R \cdot \big(n\,\lambda_T^3\big)^{-1} \quad . \tag{5.164}$$

For $T>T_c$, we have

$$dE\big|_V = \tfrac{15}{4}\,k_B T\,\mathrm{Li}_{5/2}(z)\,\frac{V}{\lambda_T^3}\cdot\frac{dT}{T} + \tfrac{3}{2}\,k_B T\,\mathrm{Li}_{3/2}(z)\,\frac{V}{\lambda_T^3}\cdot\frac{dz}{z} \quad , \tag{5.165}$$

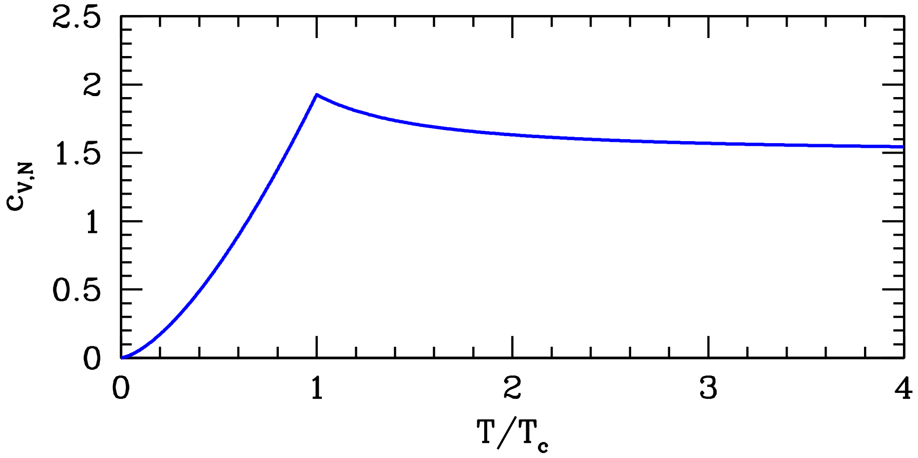

Figure 5.7: Molar heat capacity of the ideal Bose gas (units of R). Note the cusp at $T = T_c$.

where we have invoked eqn. 5.46. Taking the differential of N, we have

$$dN\big|_V = \tfrac{3}{2}\,\mathrm{Li}_{3/2}(z)\,\frac{V}{\lambda_T^3}\cdot\frac{dT}{T} + \mathrm{Li}_{1/2}(z)\,\frac{V}{\lambda_T^3}\cdot\frac{dz}{z} \quad . \tag{5.166}$$

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

$$c_{V,N}(T,z) = \tfrac{3}{2}R\cdot\left[\frac{\frac{5}{2}\,\mathrm{Li}_{5/2}(z)}{\mathrm{Li}_{3/2}(z)} - \frac{\frac{3}{2}\,\mathrm{Li}_{3/2}(z)}{\mathrm{Li}_{1/2}(z)}\right] \quad . \tag{5.167}$$

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

$$n(T,z) = \lambda_T^{-3}\,\mathrm{Li}_{3/2}(z) \tag{5.168}$$

in order to obtain $z(T,n)$, and then insert this into eqn. 5.167. 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 $T/T_c(n) \propto T\,n^{-2/3}$. Second, the high temperature limit is $\frac{3}{2}R$, which is the classical value. Finally, there is a *cusp* at $T = T_c(n)$.

For another example, see §5.11.

5.7.3 Isotherms for the ideal Bose gas

Let a be some length scale and define

$$v_a = a^3 \quad , \quad p_a = \frac{2\pi\hbar^2}{ma^5} \quad , \quad T_a = \frac{2\pi\hbar^2}{ma^2 k_B} \tag{5.169}$$

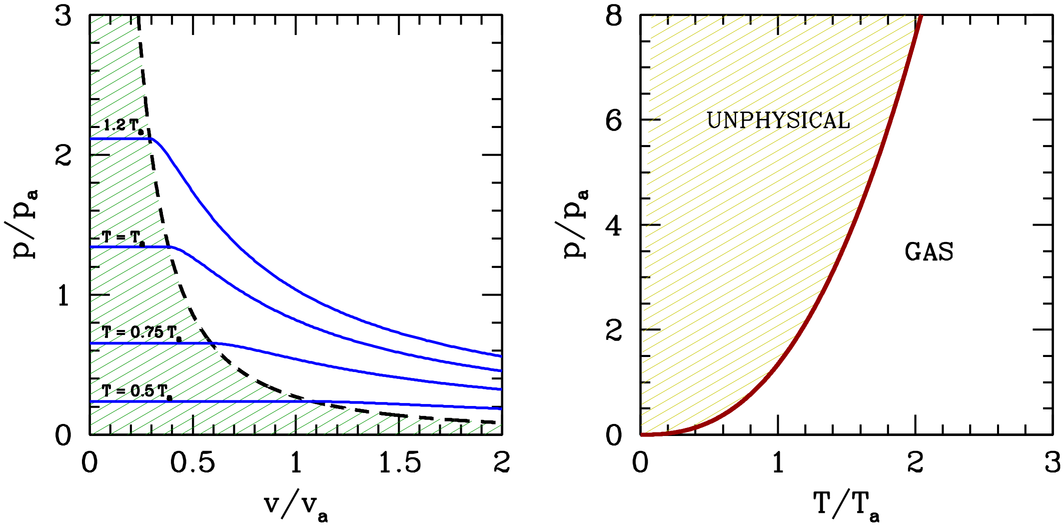

Figure 5.8: Phase diagrams for the ideal Bose gas. Left panel: (p,v) plane. The solid blue curves are isotherms, and the green hatched region denotes $v < v_{\rm c}(T)$, where the system is partially condensed. Right panel: (p,T) plane. The solid red curve is the coexistence curve $p_{\rm c}(T)$, along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

Then we have

$$\frac{v_a}{v} = \left(\frac{T}{T_a}\right)^{3/2} {\rm Li}_{3/2}(z) + v_a\, n_0 \tag{5.170}$$

$$\frac{p}{p_a} = \left(\frac{T}{T_a}\right)^{5/2} {\rm Li}_{5/2}(z) \quad , \tag{5.171}$$

where $v = V/N$ is the volume per particle[10] and n_0 is the condensate number density; n_0 vanishes for $T \ge T_{\rm c}$, where $z = 1$. One identifies a critical volume $v_{\rm c}(T)$ by setting $z = 1$ and $n_0 = 0$, leading to $v_{\rm c}(T) = v_a\,(T/T_a)^{3/2}$. For $v < v_{\rm c}(T)$, we set $z = 1$ in eqn. 5.170 to find a relation between v, T, and n_0. For $v > v_{\rm c}(T)$, we set $n_0 = 0$ in eqn. 5.170 to relate v, T, and z. Note that the pressure is independent of volume for $T < T_{\rm c}$. The isotherms in the (p,v) plane are then flat for $v < v_{\rm c}$. 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 $p_{\rm c}(T) = p_a (T/T_a)^{5/2}$ as the critical temperature at which condensation starts to occur.

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

$$\left(\frac{dp}{dT}\right)_{\rm coex} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T\,\Delta v} \quad , \tag{5.172}$$

where $\ell = T\,(s_2 - s_1)$ is the latent heat per mole, and $\Delta v = v_2 - v_1$. For ideal gas Bose condensation, the coexistence curve resembles the red curve in the right hand panel of fig. 5.8. There is no meaning to the

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[10] Note that in the thermodynamics chapter we used v to denote the molar volume, $N_{\rm A}\, V/N$.

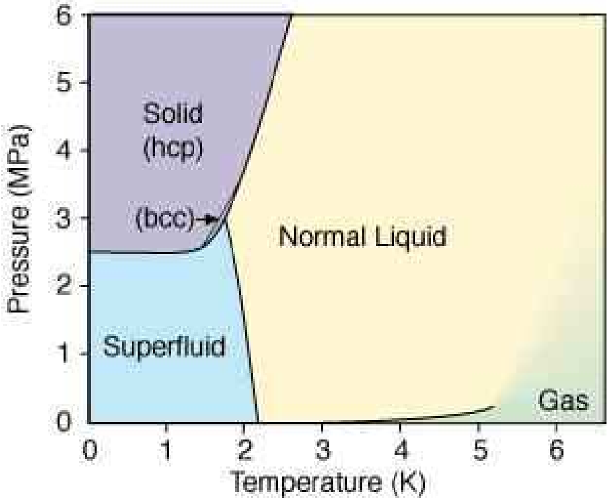

Figure 5.9: Phase diagram of ^{4}He. All phase boundaries are first order transition lines, with the exception of the normal liquid-superfluid transition, which is second order. (*Source: University of Helsinki*)

shaded region where $p > p_c(T)$. Nevertheless, it is tempting to associate the curve $p = p_c(T)$ with the coexistence of the $\boldsymbol{k} = 0$ condensate and the remaining uncondensed ($\boldsymbol{k} \neq 0$) bosons[11].

The entropy in the coexistence region is given by

$$s = -\frac{1}{N}\left(\frac{\partial\Omega}{\partial T}\right)_V = \tfrac{5}{2}\,\zeta(5/2)\,k_B\,v\,\lambda_T^{-3} = \frac{\tfrac{5}{2}\,\zeta(5/2)}{\zeta(3/2)}\,k_B\left(1 - \frac{n_0}{n}\right) \quad . \tag{5.173}$$

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

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

5.7.4 The λ-transition in liquid ^{4}He

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

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[11] The $\boldsymbol{k} \neq 0$ particles are sometimes called the *overcondensate*.

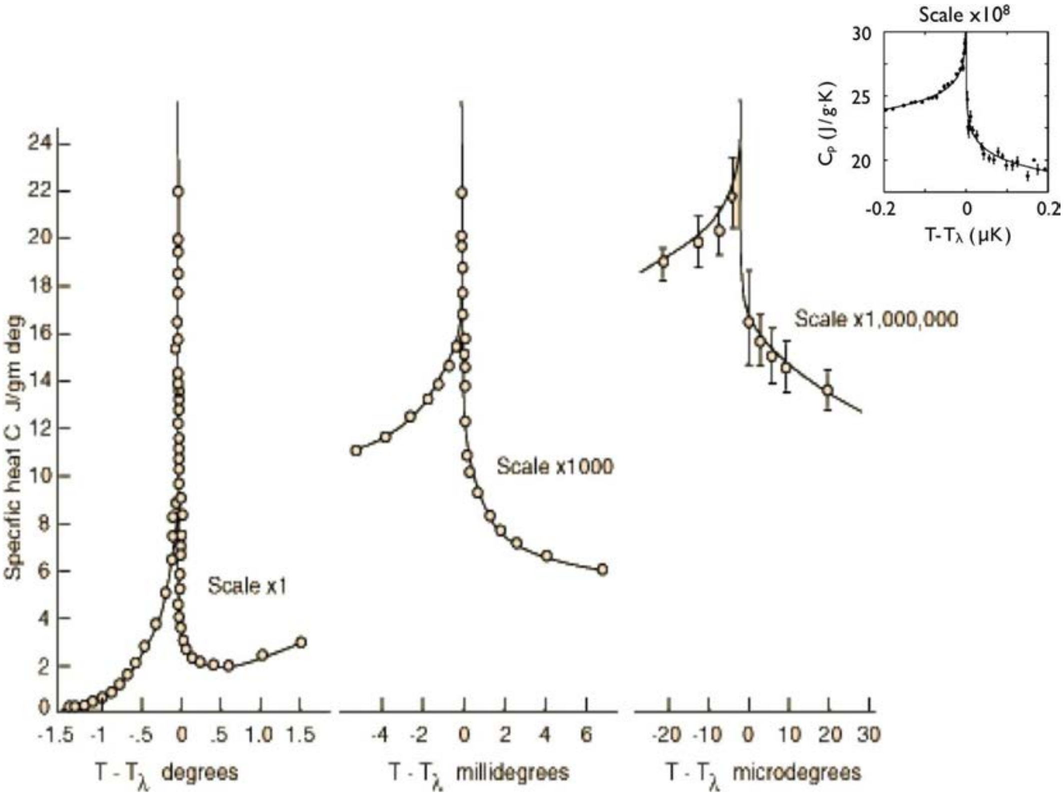

Figure 5.10: Specific heat of liquid ^{4}He in the vicinity of the λ-transition. Data from M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, C. J. Gortner, ed. (North-Holland, 1961). Inset at upper right: more recent data of J. A. Lipa *et al.*, *Phys. Rev. B* **68**, 174518 (2003) performed in zero gravity earth orbit, to within $\Delta T = 2\,\text{nK}$ of the transition.

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

$$C_p(T) = A\,\big|T - T_\lambda(p)\big|^{-\alpha} \quad . \tag{5.174}$$

α 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 §5.12). The observed behavior of $C_p(T)$ in ^{4}He is very nearly logarithmic in $|T - T_\lambda|$. In fact, both theory (renormalization group on the $\text{O}(2)$ model) and experiment concur that α is almost zero but in fact slightly negative, with $\alpha = -0.0127 \pm 0.0003$ in the best experiments (Lipa *et al.*, 2003). The λ transition is most definitely *not* an ideal Bose gas condensation. Theoretically, in the parlance of critical phenomena, IBG condensation and the λ-transition in ^{4}He lie in different *universality classes*[12]. Unlike the IBG, the condensed phase in ^{4}He is a distinct thermodynamic phase, known as a *superfluid*. Note that $C_p(T < T_\text{c})$ for the IBG is not even defined, since for $T < T_\text{c}$ we

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

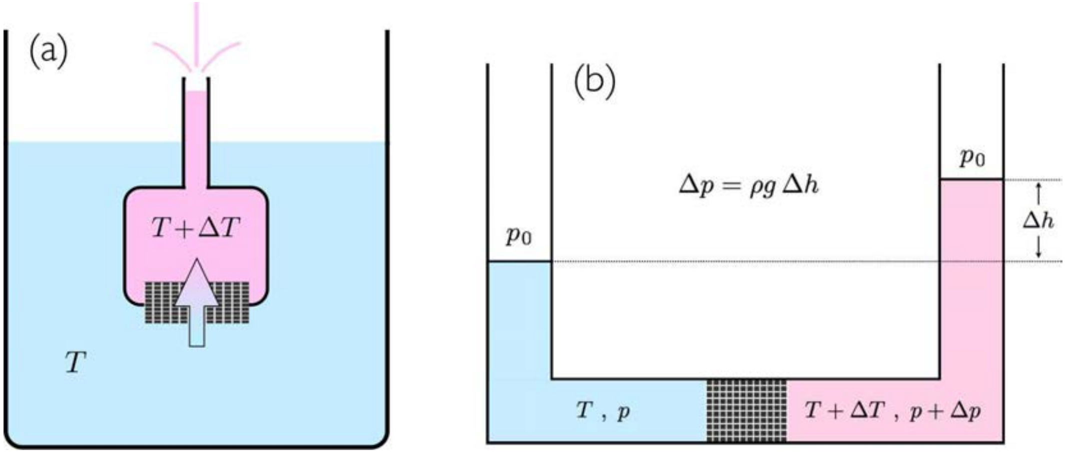

Figure 5.11: The fountain effect. In each case, a temperature gradient is maintained across a porous plug through which only superfluid can flow. This results in a pressure gradient which can result in a fountain or an elevated column in a U-tube.

have $p = p(T)$ and therefore $dp = 0$ requires $dT = 0$.

5.7.5 Fountain effect in superfluid ^{4}He

At temperatures $T < T_\lambda$, liquid ^{4}He has a superfluid component which is a type of Bose condensate. In fact, there is an important difference between condensate fraction $N_{\boldsymbol{k}=0}/N$ and superfluid density, which is denoted by the symbol ρ_s. In ^{4}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 ρ_s is very interesting but lies beyond the scope of this course.

One aspect of the superfluid state is its complete absence of viscosity. For this reason, superfluids can flow through tiny cracks called *microleaks* that will not pass normal fluid. Consider then a porous plug which permits the passage of superfluid but not of normal fluid. The key feature of the superfluid component is that it has zero energy density. Therefore even though there is a transfer of particles across the plug, there is no energy exchange, and therefore a temperature gradient across the plug can be maintained[13].

The elementary excitations in the superfluid state are sound waves called *phonons*. They are compressional waves, just like longitudinal phonons in a solid, but here in a liquid. Their dispersion is acoustic, given by $\omega(k) = ck$ where $c = 238\,\mathrm{m/s}$.[14] The have no internal degrees of freedom, hence g $= 1$. Like phonons in a solid, the phonons in liquid helium are not conserved. Hence their chemical potential vanishes and these excitations are described by photon statistics. We can now compute the height difference Δh in a U-tube experiment.

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[13] Recall that two bodies in thermal equilibrium will have identical temperatures *if they are free to exchange energy*.

[14] The phonon velocity c is slightly temperature dependent.

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

$$\begin{aligned} p = -\Omega/V &= -k_{\rm B}T \int \frac{d^3\!k}{(2\pi)^3}\, \ln\big(1 - e^{-\hbar c k/k_{\rm B}T}\big) \\ &= -\frac{(k_{\rm B}T)^4}{(\hbar c)^3}\, \frac{4\pi}{8\pi^3} \int\limits_0^\infty \! du\, u^2\, \ln(1-e^{-u}) = \frac{\pi^2}{90}\, \frac{(k_{\rm B}T)^4}{(\hbar c)^3} \quad . \end{aligned} \tag{5.175}$$

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

$$\begin{aligned} \frac{dh}{dT} &= \frac{2\pi^2}{45} \left(\frac{k_{\rm B}T}{\hbar c}\right)^3 \frac{k_{\rm B}}{\rho g} \\ &= \frac{2\pi^2}{45} \left(\frac{(1.38\times 10^{-23}\,{\rm J/K})(1\,{\rm K})}{(1.055\times 10^{-34}\,{\rm J\cdot s})(238\,{\rm m/s})}\right)^3 \times \frac{(1.38\times 10^{-23}\,{\rm J/K})}{(148\,{\rm kg/m^3})(9.8\,{\rm m/s^2})} \simeq 32\,{\rm cm/K} \quad , \end{aligned} \tag{5.176}$$

a very noticeable effect!

5.7.6 Bose condensation in optical traps

The 2001 Nobel Prize in Physics was awarded to Weiman, Cornell, and Ketterle for the experimental observation of Bose condensation in dilute atomic gases. The experimental techniques required to trap and cool such systems are a true *tour de force*, and we shall not enter into a discussion of the details here[15].

The optical trapping of neutral bosonic atoms, such as ^{87}Rb, results in a confining potential $V(\boldsymbol{r})$ which is quadratic in the atomic positions. Thus, the single particle Hamiltonian for a given atom is written

$$\hat H = -\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}^2 + \tfrac{1}{2} m \big(\omega_1^2\, x^2 + \omega_2^2\, y^2 + \omega_3^2\, z^2\big) \quad , \tag{5.177}$$

where $\omega_{1,2,3}$ are the angular frequencies of the trap. This is an anisotropic three-dimensional harmonic oscillator, the solution of which is separable into a product of one-dimensional harmonic oscillator wavefunctions. The eigenspectrum is then given by a sum of one-dimensional spectra, *viz.*

$$E_{n_1,n_2,n_3} = \big(n_1 + \tfrac{1}{2}\big)\,\hbar\omega_1 + \big(n_2 + \tfrac{1}{2}\big)\,\hbar\omega_2 + \big(n_3 + \tfrac{1}{2}\big)\,\hbar\omega_3 \quad . \tag{5.178}$$

According to eqn. 5.13, the number of particles in the system is

$$\begin{aligned} N &= \sum_{n_1=0}^\infty \sum_{n_2=0}^\infty \sum_{n_3=0}^\infty \Big[y^{-1}\, e^{n_1\hbar\omega_1/k_{\rm B}T}\, e^{n_2\hbar\omega_2/k_{\rm B}T}\, e^{n_3\hbar\omega_3/k_{\rm B}T} - 1\Big]^{-1} \\ &= \sum_{k=1}^\infty y^k \left(\frac{1}{1-e^{-k\hbar\omega_1/k_{\rm B}T}}\right) \left(\frac{1}{1-e^{-k\hbar\omega_2/k_{\rm B}T}}\right) \left(\frac{1}{1-e^{-k\hbar\omega_3/k_{\rm B}T}}\right) \quad , \end{aligned} \tag{5.179}$$

where we've defined $y \equiv e^{\mu/k_{\rm B}T}\, e^{-\hbar\omega_1/2k_{\rm B}T}\, e^{-\hbar\omega_2/2k_{\rm B}T}\, e^{-\hbar\omega_3/2k_{\rm B}T} \in [0,1]$.

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[15] Many reliable descriptions may be found on the web. Check Wikipedia, for example.

Let's assume that the trap is approximately anisotropic, which entails that the frequency ratios ω_1/ω_2 *etc.* are all numbers on the order of one. Let us further assume that $k_{\rm B}T \gg \hbar\omega_{1,2,3}$. Then

$$\frac{1}{1-e^{-k\hbar\omega_j/k_{\rm B}T}} \approx \begin{cases} k_{\rm B}T/k\hbar\omega_j & k \lesssim k^*(T) \\ 1 & k > k^*(T) \end{cases} \tag{5.180}$$

where $k^*(T) = k_{\rm B}T/\hbar\bar{\omega} \gg 1$, with $\bar{\omega} = \big(\omega_1\,\omega_2\,\omega_3\big)^{1/3}$. We then have

$$N(T,y) \approx \frac{y^{k^*+1}}{1-y} + \bigg(\frac{k_{\rm B}T}{\hbar\bar{\omega}}\bigg)^3 \sum_{k=1}^{k^*} \frac{y^k}{k^3} \quad , \tag{5.181}$$

where the first term on the RHS is due to $k > k^*$ and the second term from $k \le k^*$ in the previous sum. Since $k^* \gg 1$ and since the sum of inverse cubes is convergent, we may safely extend the limit on the above sum to infinity. To help make more sense of the first term, write $N_0 = \big(y^{-1}-1\big)^{-1}$ for the number of particles in the $(n_1,n_2,n_3) = (0,0,0)$ state. Then $y = N_0/(N_0+1)$, which is true always. The issue *vis-a-vis* Bose-Einstein condensation is whether $N_0 \gg 1$. At any rate, we now see that we can write

$$N \approx N_0\,\big(1+N_0^{-1}\big)^{-k^*} + \bigg(\frac{k_{\rm B}T}{\hbar\bar{\omega}}\bigg)^3 {\rm Li}_3(y) \quad . \tag{5.182}$$

As for the first term, we have

$$N_0\,\big(1+N_0^{-1}\big)^{-k^*} = \begin{cases} 0 & N_0 \ll k^* \\ N_0 & N_0 \gg k^* \end{cases} \tag{5.183}$$

Thus, as in the case of IBG condensation of ballistic particles, we identify the critical temperature by the condition $y = N_0/(N_0+1) \approx 1$, and we have

$$T_{\rm c} = \frac{\hbar\bar{\omega}}{k_{\rm B}}\bigg(\frac{N}{\zeta(3)}\bigg)^{1/3} = 4.5\,\bigg(\frac{\bar{\nu}}{100\,{\rm Hz}}\bigg)\,N^{1/3}\,[\,{\rm nK}\,] \quad , \tag{5.184}$$

where $\bar{\nu} = \bar{\omega}/2\pi$. We see that $k_{\rm B}T_{\rm c} \gg \hbar\bar{\omega}$ if the number of particles in the trap is large: $N \gg 1$. In this regime, we have

$$\begin{aligned} T < T_{\rm c} \ : \qquad & N = N_0 + \zeta(3)\bigg(\frac{k_{\rm B}T}{\hbar\bar{\omega}}\bigg)^3 \\ T > T_{\rm c} \ : \qquad & N = \bigg(\frac{k_{\rm B}T}{\hbar\bar{\omega}}\bigg)^3 {\rm Li}_3(y) \quad . \end{aligned} \tag{5.185}$$

It is interesting to note that BEC can also occur in two-dimensional traps, which is to say traps which are very anisotropic, with oblate equipotential surfaces $V(\boldsymbol{r}) = V_0$. This happens when $\hbar\omega_3 \gg k_{\rm B}T \gg \omega_{1,2}$. We then have

$$T_{\rm c}^{(d=2)} = \frac{\hbar\bar{\omega}}{k_{\rm B}} \cdot \bigg(\frac{6N}{\pi^2}\bigg)^{1/2} \tag{5.186}$$

with $\bar{\omega} = \big(\omega_1\,\omega_2\big)^{1/2}$. The particle number then obeys a set of equations like those in eqns. 5.185, *mutatis mutandis*[16].

For extremely prolate traps, with $\omega_3 \ll \omega_{1,2}$, the situation is different because $\mathrm{Li}_1(y)$ diverges for $y = 1$. We then have

$$N = N_0 + \frac{k_\mathrm{B}T}{\hbar\omega_3}\,\ln\big(1+N_0\big) \quad . \tag{5.187}$$

Here we have simply replaced y by the equivalent expression $N_0/(N_0+1)$. If our criterion for condensation is that $N_0 = \alpha N$, where α is some fractional value, then we have

$$T_\mathrm{c}(\alpha) = (1-\alpha)\,\frac{\hbar\omega_3}{k_\mathrm{B}}\cdot\frac{N}{\ln N} \quad . \tag{5.188}$$

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,

$$\begin{aligned}\Omega(T,V,\mu) &= -Vk_\mathrm{B}T\sum_\alpha \ln\Big(1+e^{\mu/k_\mathrm{B}T}\,e^{-\varepsilon_\alpha/k_\mathrm{B}T}\Big)\\ &= -Vk_\mathrm{B}T\int\limits_{-\infty}^{\infty}\!d\varepsilon\;g(\varepsilon)\,\ln\Big(1+e^{(\mu-\varepsilon)/k_\mathrm{B}T}\Big) \quad .\end{aligned} \tag{5.189}$$

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

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_\mathrm{B}T}+1} \quad , \tag{5.190}$$

hence the total number of particles is

$$N = V\!\int\limits_{-\infty}^{\infty}\!d\varepsilon\;g(\varepsilon)\,\frac{1}{e^{(\varepsilon-\mu)/k_\mathrm{B}T}+1} \quad . \tag{5.191}$$

5.8.2 The Fermi distribution

We define the function

$$f(\epsilon) \equiv \frac{1}{e^{\epsilon/k_\mathrm{B}T}+1} \quad , \tag{5.192}$$

known as the *Fermi distribution*. In the $T\to\infty$ limit, $f(\epsilon)\to\frac{1}{2}$ for all finite values of ε. As $T\to 0$, $f(\epsilon)$ approaches a step function $\Theta(-\epsilon)$. The average number of particles in a state of energy ε in a system at temperature T and chemical potential μ is $n(\varepsilon) = f(\varepsilon-\mu)$. In fig. 5.12 we plot $f(\varepsilon-\mu)$ *versus* ε for three representative temperatures.

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[16] Explicitly, one replaces $\zeta(3)$ with $\zeta(2)=\frac{\pi^2}{6}$, $\mathrm{Li}_3(y)$ with $\mathrm{Li}_2(y)$, and $\big(k_\mathrm{B}T/\hbar\bar{\omega}\big)^3$ with $\big(k_\mathrm{B}T/\hbar\bar{\omega}\big)^2$.

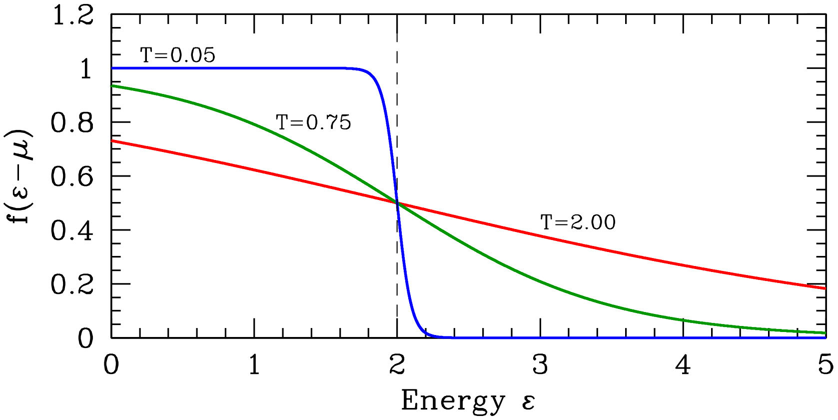

Figure 5.12: The Fermi distribution, $f(\epsilon) = \big[\exp(\epsilon/k_{\rm B}T) + 1\big]^{-1}$. Here we have set $k_{\rm B} = 1$ and taken $\mu = 2$, with $T = \frac{1}{20}$ (blue), $T = \frac{3}{4}$ (green), and $T = 2$ (red). In the $T \to 0$ limit, $f(\epsilon)$ approaches a step function $\Theta(-\epsilon)$.

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*: $\varepsilon_{\rm F} = \mu(T = 0)$. 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 $\varepsilon(\boldsymbol{k}) = \varepsilon_{\rm F}$ 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*, $k_{\rm F}$. 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 $k_{\rm F}$ and Fermi energy $\varepsilon_{\rm F}$ for the IFG with a ballistic dispersion $\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$. The number density is

$$n = {\sf g}\!\int\!\frac{d^d\!k}{(2\pi)^d}\,\Theta(k_{\rm F} - k) = \frac{{\sf g}\,\Omega_d}{(2\pi)^d}\cdot\frac{k_{\rm F}^d}{d} \tag{5.193}$$

and thus

$$n_{d=1} = {\sf g}\,k_{\rm F}/\pi \qquad , \qquad n_{d=2} = {\sf g}\,k_{\rm F}^2/4\pi \qquad , \qquad n_{d=3} = {\sf g}\,k_{\rm F}^3/6\pi^2 \quad , \tag{5.194}$$

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

$$k_{{\rm F},d=1} = \pi n/{\sf g} \qquad , \qquad k_{{\rm F},d=2} = (4\pi n/{\sf g})^{1/2} \qquad , \qquad k_{{\rm F},d=3} = (6\pi^2 n/{\sf g})^{1/3} \quad . \tag{5.195}$$

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

$$\varepsilon_{\rm F} = \frac{\hbar^2 k_{\rm F}^2}{2m} = \frac{2\pi^2\hbar^2}{m}\left(\frac{d\,n}{{\sf g}\,\Omega_d}\right)^{2/d} \quad , \tag{5.196}$$

and so

$$\varepsilon_{\mathrm{F},d=1} = \frac{\pi^2\hbar^2 n^2}{2\mathrm{g}^2 m} \quad , \quad \varepsilon_{\mathrm{F},d=2} = \frac{2\pi\hbar^2\, n}{\mathrm{g}\, m} \quad , \quad \varepsilon_{\mathrm{F},d=3} = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{\mathrm{g}}\right)^{2/3} \quad . \tag{5.197}$$

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

$$g(\varepsilon_{\mathrm{F}}) = \frac{\mathrm{g}\,\Omega_d}{(2\pi)^d} \cdot \frac{m k_{\mathrm{F}}^{d-2}}{\hbar^2} = \frac{d}{2} \cdot \frac{n}{\varepsilon_{\mathrm{F}}} \quad . \tag{5.198}$$

That $g(\varepsilon_{\mathrm{F}})$ 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 $k_{\mathrm{F}} \sim 0.5\,\text{Å}^{-1}$ to $2\,\text{Å}^{-1}$, 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

$$\varepsilon(k_x, k_y) = -2t\,\cos(k_x a) - 2t\,\cos(k_y a) \quad , \tag{5.199}$$

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 (k_x, k_y) which satisfies $\varepsilon(k_x, k_y) = \varepsilon_{\mathrm{F}}$. When ε_{F} achieves its minimum value of $\varepsilon_{\mathrm{F}}^{\mathrm{min}} = -4t$, the Fermi surface collapses to a point at $(k_x, k_y) = (0, 0)$. For energies just above this minimum value, we can expand the dispersion in a power series, writing

$$\varepsilon(k_x, k_y) = -4t + ta^2\left(k_x^2 + k_y^2\right) - \tfrac{1}{12}\,ta^4\left(k_x^4 + k_y^4\right) + \ldots \quad . \tag{5.200}$$

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 $k_{\mathrm{F}}^2 = (\varepsilon_{\mathrm{F}} + 4t)/ta^2$. 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_{4v}. The Fermi surfaces distort and eventually, at $\varepsilon_{\mathrm{F}} = 0$, the Fermi surface is itself a square. As ε_{F} increases further, the square turns back into a circle, but centered about the point $\left(\frac{\pi}{a}, \frac{\pi}{a}\right)$. 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 $[\mathrm{Xe}]\,6s^1$. The $6s$ electrons 'hop' from site to site on a body centered cubic (BCC) lattice, a generalization of the simple two-dimensional square lattice hopping model discussed above. The elementary unit cell in $\boldsymbol{k}$ space, known as the *first Brillouin zone*, turns out to be a dodecahedron. In yttrium, the electronic structure is $[\mathrm{Kr}]\,5s^2\,4d^1$, and there are two electronic energy bands at the Fermi level, meaning two Fermi surfaces. Yttrium forms a hexagonal close packed (HCP) crystal structure, and its first Brillouin zone is shaped like a hexagonal pillbox.

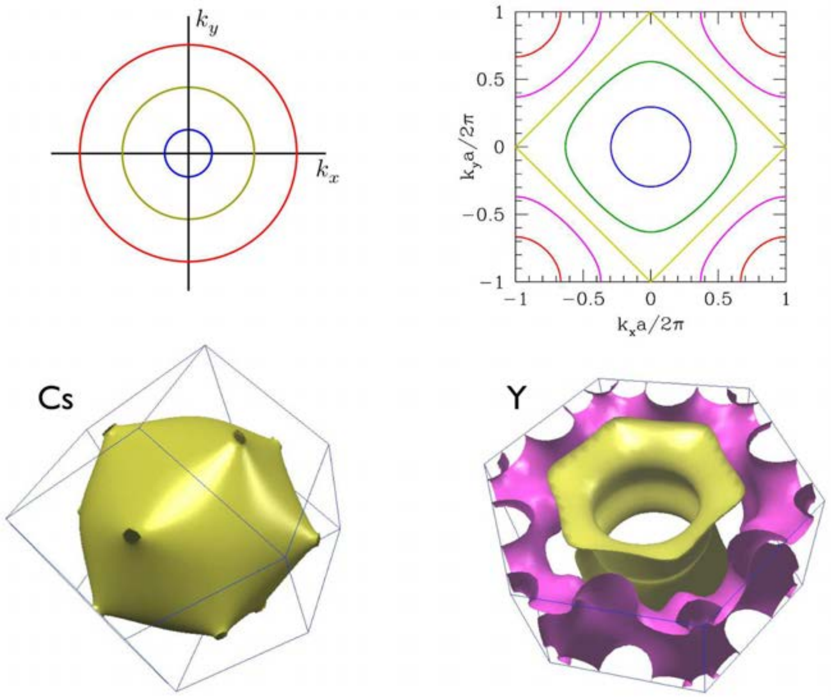

Figure 5.13: Fermi surfaces for two and three-dimensional structures. Upper left: free particles in two dimensions. Upper right: 'tight binding' electrons on a square lattice. Lower left: Fermi surface for cesium, which is predominantly composed of electrons in the $6s$ orbital shell. Lower right: the Fermi surface of yttrium has two parts. One part (yellow) is predominantly due to $5s$ electrons, while the other (pink) is due to $4d$ electrons. (*Source: www.phys.ufl.edu/fermisurface/*)

Spin-split Fermi surfaces

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

$$\hat{H} = \frac{\boldsymbol{p}^2}{2m} + \mu_{\rm B} H \, \sigma \quad , \tag{5.201}$$

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

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

$$\frac{\hbar^2 k^2_{{\rm F}\uparrow}}{2m} + \mu_{\rm B} H = \frac{\hbar^2 k^2_{{\rm F}\downarrow}}{2m} - \mu_{\rm B} H \quad , \tag{5.202}$$

which says

$$k^2_{{\rm F}\downarrow} - k^2_{{\rm F}\uparrow} = \frac{2eH}{\hbar c} \quad . \tag{5.203}$$

The total density is

$$n = \frac{k^3_{\text{F}\uparrow}}{6\pi^2} + \frac{k^3_{\text{F}\downarrow}}{6\pi^2} \qquad \Longrightarrow \qquad k^3_{\text{F}\uparrow} + k^3_{\text{F}\downarrow} = 6\pi^2 n \quad . \tag{5.204}$$

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

$$H_\text{c} = \frac{\hbar c}{2e} \cdot \big(6\pi^2 n\big)^{1/3} \quad . \tag{5.205}$$

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

$$\mathcal{I}(T,\mu) \equiv \int\limits_{-\infty}^{\infty} d\varepsilon \, f(\varepsilon - \mu)\, \phi(\varepsilon) \quad . \tag{5.206}$$

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

$$\varPhi(\varepsilon) \equiv \int\limits_{-\infty}^{\varepsilon} d\varepsilon' \, \phi(\varepsilon') \tag{5.207}$$

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

$$\mathcal{I}(T,\mu) = \int\limits_{-\infty}^{\infty} d\varepsilon \, f(\varepsilon - \mu)\, \frac{d\varPhi}{d\varepsilon} = -\int\limits_{-\infty}^{\infty} d\varepsilon \, f'(\varepsilon)\, \varPhi(\mu + \varepsilon) \quad , \tag{5.208}$$

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

$$\varPhi(\mu + \varepsilon) = \sum_{n=0}^{\infty} \frac{\varepsilon^n}{n\,!}\, \frac{d^n\varPhi}{d\mu^n} = \exp\!\left(\varepsilon \, \frac{d}{d\mu}\right) \varPhi(\mu) \quad . \tag{5.209}$$

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

$$f'(\varepsilon) = -\frac{1}{k_\text{B} T}\, \frac{e^{\varepsilon/k_\text{B}T}}{\big(e^{\varepsilon/k_\text{B}T} + 1\big)^2} \quad , \tag{5.210}$$

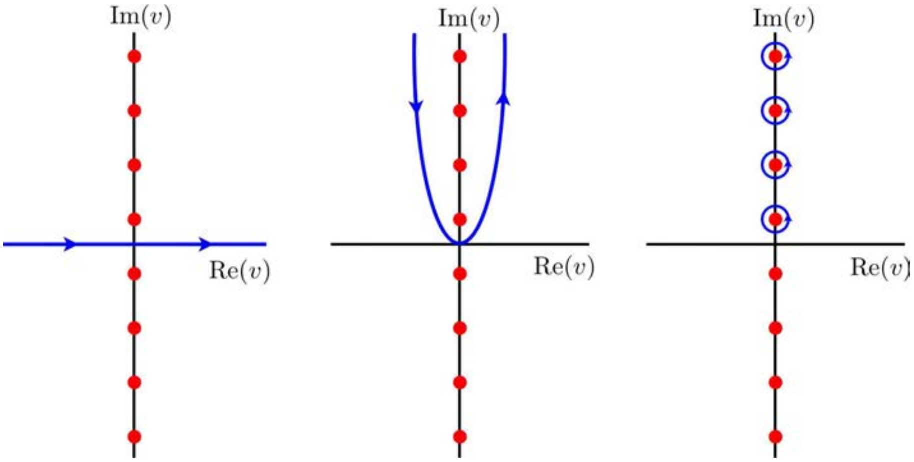

Figure 5.14: Deformation of the complex integration contour in eqn. 5.212.

we define

$$\widetilde{\mathcal{I}}(T,\mu)=\int\limits_{-\infty}^{\infty}\!dv\,\frac{e^{vD}}{(e^{v}+1)(e^{-v}+1)}\,\Phi(\mu)\quad, \tag{5.211}$$

with $v=\varepsilon/k_{\rm B}T$, where $D=k_{\rm B}T\,\frac{d}{d\mu}$ is a dimensionless differential operator. The integral can now be done using the methods of complex integration:[17]

$$\begin{aligned}\int\limits_{-\infty}^{\infty}\!dv\,\frac{e^{vD}}{(e^{v}+1)(e^{-v}+1)}&=2\pi i\sum_{n=1}^{\infty}\text{Res}\left[\frac{e^{vD}}{(e^{v}+1)(e^{-v}+1)}\right]_{v=(2n+1)i\pi}\\&=-2\pi i\sum_{n=0}^{\infty}D\,e^{(2n+1)i\pi D}=-\frac{2\pi i D\,e^{i\pi D}}{1-e^{2\pi i D}}=\pi D\,\csc\pi D\quad.\end{aligned}\tag{5.212}$$

Thus,

$$\widetilde{\mathcal{I}}(T,\mu)=\pi D\csc(\pi D)\,\Phi(\mu)\quad, \tag{5.213}$$

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

$$\pi D\csc(\pi D)=1+\frac{\pi^2}{6}\,(k_{\rm B}T)^2\,\frac{d^2}{d\mu^2}+\frac{7\pi^4}{360}\,(k_{\rm B}T)^4\,\frac{d^4}{d\mu^4}+\ldots\quad. \tag{5.214}$$

Thus,

$$\widetilde{\mathcal{I}}(T,\mu)=\int\limits_{-\infty}^{\infty}\!d\varepsilon\;f(\varepsilon-\mu)\,\phi(\varepsilon)=\int\limits_{-\infty}^{\mu}\!d\varepsilon\;\phi(\varepsilon)+\frac{\pi^2}{6}\,(k_{\rm B}T)^2\,\phi'(\mu)+\frac{7\pi^4}{360}\,(k_{\rm B}T)^4\,\phi'''(\mu)+\ldots\quad. \tag{5.215}$$

---

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

If $\phi(\varepsilon)$ is a polynomial function of its argument, then each derivative effectively reduces the order of the polynomial by one degree, and the dimensionless parameter of the expansion is $(k_{\rm B}T/\mu)^2$. 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

$$n = \int\limits_{-\infty}^{\infty} \!d\varepsilon\; g(\varepsilon)\; f(\varepsilon-\mu) = \int\limits_{-\infty}^{\mu} \!d\varepsilon\; g(\varepsilon) + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g'(\mu) + \ldots \quad . \tag{5.216}$$

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

$$\begin{aligned} n &= \int\limits_{-\infty}^{\varepsilon_{\rm F}+\delta\mu} \!d\varepsilon\; g(\varepsilon) + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g'(\varepsilon_{\rm F}+\delta\mu) + \ldots \\ &= \int\limits_{-\infty}^{\varepsilon_{\rm F}} \!d\varepsilon\; g(\varepsilon) + g(\varepsilon_{\rm F})\,\delta\mu + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g'(\varepsilon_{\rm F}) + \ldots \quad , \end{aligned} \tag{5.217}$$

from which we derive

$$\delta\mu = -\frac{\pi^2}{6}\,(k_{\rm B}T)^2\,\frac{g'(\varepsilon_{\rm F})}{g(\varepsilon_{\rm F})} + \mathcal{O}(T^4) \quad . \tag{5.218}$$

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

$$g(\varepsilon) = 2\int\!\frac{d^3\!k}{(2\pi)^3}\;\delta\bigg(\varepsilon - \frac{\hbar^2k^2}{2m}\bigg) = \frac{m\,k(\varepsilon)}{\pi^2\hbar^2}\bigg|_{k(\varepsilon)=\frac{1}{\hbar}\sqrt{2m\varepsilon}} \tag{5.219}$$

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

$$\mu(n,T) = \varepsilon_{\rm F} - \frac{\pi^2}{12}\,\frac{(k_{\rm B}T)^2}{\varepsilon_{\rm F}} + \ldots \quad , \tag{5.220}$$

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

Specific heat

The energy of the electron gas is

$$\begin{aligned}
\frac{E}{V} &= \int\limits_{-\infty}^{\infty} d\varepsilon \; g(\varepsilon)\, \varepsilon\, f(\varepsilon-\mu) \\
&= \int\limits_{-\infty}^{\mu} d\varepsilon \; g(\varepsilon)\, \varepsilon + \frac{\pi^2}{6}\, (k_{\rm B}T)^2\, \frac{d}{d\mu}\Big(\mu\, g(\mu)\Big) + \ldots \\
&= \int\limits_{-\infty}^{\varepsilon_{\rm F}} d\varepsilon \; g(\varepsilon)\, \varepsilon + g(\varepsilon_{\rm F})\, \varepsilon_{\rm F}\, \delta\mu + \frac{\pi^2}{6}\, (k_{\rm B}T)^2\, \varepsilon_{\rm F}\, g'(\varepsilon_{\rm F}) + \frac{\pi^2}{6}\, (k_{\rm B}T)^2\, g(\varepsilon_{\rm F}) + \ldots \\
&= \varepsilon_0 + \frac{\pi^2}{6}\, (k_{\rm B}T)^2\, g(\varepsilon_{\rm F}) + \ldots \quad ,
\end{aligned} \tag{5.221}$$

where $\varepsilon_0 = \int\limits_{-\infty}^{\varepsilon_{\rm F}} d\varepsilon \; g(\varepsilon)\, \varepsilon$. is the ground state energy density (*i.e.* ground state energy per unit volume). Thus, to order T^2,

$$C_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{\pi^2}{3}\, V k_{\rm B}^2\, T\, g(\varepsilon_{\rm F}) \equiv V \gamma\, T \quad , \tag{5.222}$$

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

$$c_V = \frac{N_{\rm A}}{N} \cdot C_V = \frac{\pi^2}{3} R \cdot \frac{k_{\rm B}T\, g(\varepsilon_{\rm F})}{n} = \frac{\pi^2}{2} \left(\frac{k_{\rm B}T}{\varepsilon_{\rm F}}\right) R \quad , \tag{5.223}$$

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

$$\frac{g(\varepsilon_{\rm F})}{n} = \frac{{\sf g}\, m k_{\rm F}}{2\pi^2\hbar^2} \cdot \frac{6\pi^2}{{\sf g}\, k_{\rm F}^3} = \frac{3}{2\, \varepsilon_{\rm F}} \quad . \tag{5.224}$$

The molar heat capacity in eqn. 5.223 is to be compared with the classical ideal gas value of $\frac{3}{2}R$. Relative to the classical ideal gas, the IFG value is reduced by a fraction of $(\pi^2/3) \times (k_{\rm B}T/\varepsilon_{\rm F})$, which in most metals is very small and even at room temperature is only on the order of 10^{-2}. Most of the heat capacity of metals at room temperature is due to the energy stored in lattice vibrations.

A niftier way to derive the heat capacity[18]: Starting with eqn. 5.218 for $\mu(T) - \varepsilon_{\rm F} \equiv \delta\mu(T)$, note that $g(\varepsilon_{\rm F}) = dn/d\varepsilon_{\rm F}$, so we may write $\delta\mu = -\frac{\pi^2}{6}(k_{\rm B}T)^2 (dg/dn) + \mathcal{O}(T^4)$. Next, use the Maxwell relation $(\partial S/\partial N)_{T,V} = -(\partial\mu/\partial T)_{N,V}$ to arrive at

$$\left(\frac{\partial s}{\partial n}\right)_T = \frac{\pi^2}{3}\, k_{\rm B}^2 T\, \frac{\partial g(\varepsilon_{\rm F})}{\partial n} + \mathcal{O}(T^3) \quad , \tag{5.225}$$

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.

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[18] I thank my colleague Tarun Grover for this observation.

Nonanalytic terms

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

$$\mathcal{I}(T,\mu) = \int\limits_0^\infty \! d\varepsilon \; f(\varepsilon - \mu) = \mu + k_{\rm B}T \ln\!\big(1 + e^{-\mu/k_{\rm B}T}\big) \quad . \tag{5.226}$$

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 $\exp(-\mu/k_{\rm B}T)$ is nonanalytic in T and cannot appear in any order of a Taylor expansion about $T = 0$. As a second example, consider the case $\phi(\varepsilon) = \varepsilon\,\Theta(\varepsilon)$. The Sommerfeld expansion yields

$$\widetilde{\mathcal{I}}(T,\mu) = \tfrac{1}{2}\mu^2 + \frac{\pi^2}{6}(k_{\rm B}T)^2 \quad , \tag{5.227}$$

while the exact result is

$$\mathcal{I}(T,\mu) = \tfrac{1}{2}\mu^2 + \frac{\pi^2}{6}(k_{\rm B}T)^2 + (k_{\rm B}T)^2 \sum_{j=1}^\infty \frac{(-1)^j}{j^2}\, e^{-j\mu/k_{\rm B}T} \quad , \tag{5.228}$$

which follows from the polylogarithm identity

$$\text{Li}_2(z) + \text{Li}_2(1/z) = -\tfrac{1}{2}\big[\ln(-z)\big]^2 - \frac{\pi^2}{6} \quad . \tag{5.229}$$

Again we see that the Sommerfeld expansion terminates at a finite order in T, and is missing nonanalytic terms in the $T \to 0$ limit[19]. This is a generic state of affairs for the case where $\phi(\varepsilon)$ is a finite order polynomial in ε.

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 $\boldsymbol{m}$ of a particle is related to its quantum mechanical *spin* according to $\boldsymbol{m} = g\mu_0 \boldsymbol{S}/\hbar$, where $\mu_0 = q\hbar/over2mc$ is the magneton. Here g is the particle's g-factor, μ_0 its magnetic moment, and $\boldsymbol{S}$ is the vector of quantum mechanical spin operators satisfying $\big[S^\alpha\,,\,S^\beta\big] = i\hbar\epsilon_{\alpha\beta\gamma}\,S^\gamma$, *i.e.* SU(2) commutation relations. The Hamiltonian for a single particle is then

$$\hat{H} = \frac{1}{2m^*}\Big(\boldsymbol{p} - \frac{q}{c}\boldsymbol{A}\Big)^2 - \boldsymbol{H}\!\cdot\!\boldsymbol{m} = \frac{1}{2m^*}\Big(\boldsymbol{p} + \frac{e}{c}\boldsymbol{A}\Big)^2 + \frac{g}{2}\,\mu_{\rm B} H\,\sigma \quad , \tag{5.230}$$

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

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[19] Once again I thank my colleague Tarun Grover for pointing this out to me.

can always absorb the small difference into the definition of $\mu_{\rm B}$, writing $\mu_{\rm B} \to \tilde{\mu}_{\rm B} = ge\hbar/4mc$. We've chosen the $\hat{\boldsymbol{z}}$-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 $\boldsymbol{p}^2/2m^*$, but it is the electron mass m itself ($m = 511\,{\rm keV}$) which enters into the definition of the Bohr magneton. We shall discuss the consequences of this further below.

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

$$\varepsilon_\sigma(\boldsymbol{k}) = \frac{\hbar^2\boldsymbol{k}^2}{2m^*} + \tilde{\mu}_{\rm B} H\,\sigma \quad . \tag{5.231}$$

At $T = 0$, we have the results of §5.8.3. At finite T, we once again use the Sommerfeld expansion. We then have

$$\begin{aligned} n &= \int\limits_{-\infty}^{\infty} \! d\varepsilon\; g_\uparrow(\varepsilon)\, f(\varepsilon-\mu) \;+ \int\limits_{-\infty}^{\infty} \! d\varepsilon\; g_\downarrow(\varepsilon)\, f(\varepsilon-\mu) \\ &= \tfrac{1}{2} \int\limits_{-\infty}^{\infty} \! d\varepsilon\, \Big\{ g(\varepsilon - \tilde{\mu}_{\rm B} H) + g(\varepsilon + \tilde{\mu}_{\rm B} H) \Big\}\, f(\varepsilon-\mu) \\ &= \int\limits_{-\infty}^{\infty} \! d\varepsilon\, \Big\{ g(\varepsilon) + (\tilde{\mu}_{\rm B} H)^2\, g''(\varepsilon) + \ldots \Big\}\, f(\varepsilon-\mu) \quad . \end{aligned} \tag{5.232}$$

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

$$\begin{aligned} n &= \int\limits_{-\infty}^{\mu} \! d\varepsilon\; g(\varepsilon) + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g'(\mu) + (\tilde{\mu}_{\rm B} H)^2\, g'(\mu) + \ldots \\ &= \int\limits_{-\infty}^{\varepsilon_{\rm F}} \! d\varepsilon\; g(\varepsilon) + g(\varepsilon_{\rm F})\,\delta\mu + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g'(\varepsilon_{\rm F}) + (\tilde{\mu}_{\rm B} H)^2\, g'(\varepsilon_{\rm F}) + \ldots \quad . \end{aligned} \tag{5.233}$$

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

$$\delta\mu(T,n,H) = -\bigg\{ \frac{\pi^2}{6}\,(k_{\rm B}T)^2 + (\tilde{\mu}_{\rm B} H)^2 \bigg\}\, \frac{g'(\varepsilon_{\rm F})}{g(\varepsilon_{\rm F})} + \ldots \quad . \tag{5.234}$$

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

$$\begin{aligned} n_\uparrow - n_\downarrow &= \int\limits_{-\infty}^{\infty} \! d\varepsilon\, \Big\{ g_\uparrow(\varepsilon) - g_\downarrow(\varepsilon) \Big\}\, f(\varepsilon-\mu) \\ &= \tfrac{1}{2} \int\limits_{-\infty}^{\infty} \! d\varepsilon\, \Big\{ g(\varepsilon - \tilde{\mu}_{\rm B} H) - g(\varepsilon + \tilde{\mu}_{\rm B} H) \Big\}\, f(\varepsilon-\mu) \\ &= -\tilde{\mu}_{\rm B} H \cdot \pi D\, \csc(\pi D)\, g(\mu) + \mathcal{O}(H^3) \quad . \end{aligned} \tag{5.235}$$

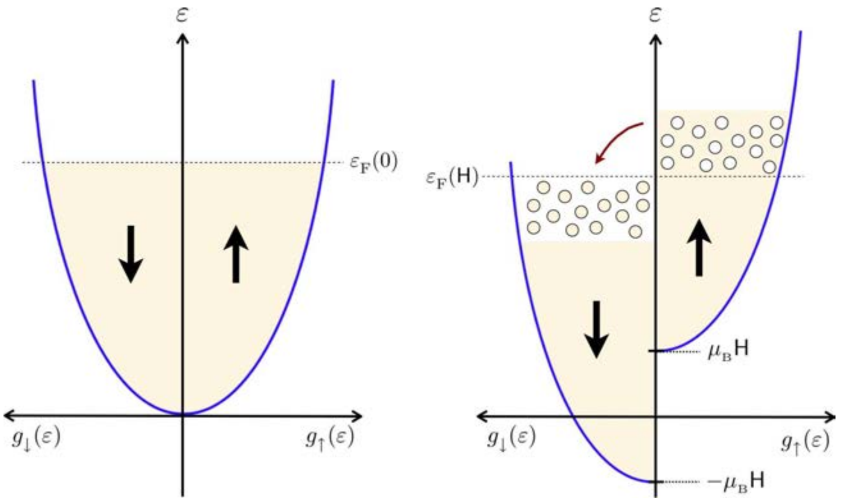

Figure 5.15: Fermi distributions in the presence of an external Zeeman-coupled magnetic field.

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

$$M = -\tilde{\mu}_{\rm B}(n_\uparrow - n_\downarrow) = \tilde{\mu}_{\rm B}^2\, g(\varepsilon_{\rm F})\, H \quad . \tag{5.236}$$

in which the magnetic susceptibility is

$$\chi = \left(\frac{\partial M}{\partial H}\right)_{T,N} = \tilde{\mu}_{\rm B}^2\, g(\varepsilon_{\rm F}) \quad . \tag{5.237}$$

This is called the *Pauli paramagnetic susceptibility*.

Landau diamagnetism

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

$$\varepsilon(n,k_z,\sigma) = (n+\tfrac{1}{2})\hbar\omega_{\rm c} + \frac{\hbar^2 k_z^2}{2m^*} + \tilde{\mu}_{\rm B} H\,\sigma \quad . \tag{5.238}$$

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

$$\frac{\tilde{\mu}_{\rm B} H}{\hbar\omega_{\rm c}} = \frac{ge\hbar H}{4mc}\cdot\frac{m^* c}{\hbar e H} = \frac{g}{4}\cdot\frac{m^*}{m} \quad . \tag{5.239}$$

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

$$\varepsilon(n,k_z,\sigma) = \big(n+\tfrac{1}{2}+\tfrac{1}{2}r\sigma\big)\hbar\omega_{\rm c} + \frac{\hbar^2 k_z^2}{2m^*} \quad . \tag{5.240}$$

The grand potential is then given by

$$\varOmega = -\frac{HA}{\phi_0}\cdot L_z\cdot k_{\rm B}T\int\limits_{-\infty}^{\infty}\frac{dk_z}{2\pi}\sum_{n=0}^{\infty}\sum_{\sigma=\pm 1}\ln\Big[1 + e^{\mu/k_{\rm B}T}\, e^{-(n+\frac{1}{2}+\frac{1}{2}r\sigma)\hbar\omega_{\rm c}/k_{\rm B}T}\, e^{-\hbar^2 k_z^2/2m^* k_{\rm B}T}\Big] \quad . \tag{5.241}$$

A few words are in order here regarding the prefactor. In the presence of a uniform magnetic field, the energy levels of a two-dimensional ballistic charged particle collapse into Landau levels. The number of states per Landau level scales with the area of the system, and is equal to the number of flux quanta through the system: $N_\phi = HA/\phi_0$, where $\phi_0 = hc/e$ is the Dirac flux quantum. Note that

$$\frac{HA}{\phi_0} \cdot L_z \cdot k_{\rm B}T = \hbar\omega_{\rm c} \cdot \frac{V}{\lambda_T^3} \quad , \tag{5.242}$$

hence we can write

$$\varOmega(T,V,\mu,H) = \hbar\omega_{\rm c} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} Q\big((n + \tfrac{1}{2} + \tfrac{1}{2}r\sigma)\hbar\omega_{\rm c} - \mu\big) \quad , \tag{5.243}$$

where

$$Q(\varepsilon) = -\frac{V}{\lambda_T^2} \int\limits_{-\infty}^{\infty} \frac{dk_z}{2\pi} \, \ln\Big[1 + e^{-\varepsilon/k_{\rm B}T} e^{-\hbar^2 k_z^2/2m^* k_{\rm B}T}\Big] \quad . \tag{5.244}$$

We now invoke the Euler-MacLaurin formula,

$$\sum_{n=0}^{\infty} F(n) = \int\limits_0^{\infty} dx\, F(x) + \tfrac{1}{2}\, F(0) - \tfrac{1}{12}\, F'(0) + \ldots \quad , \tag{5.245}$$

resulting in

$$\begin{aligned} \varOmega = \sum_\sigma \int\limits_{-\infty}^{\infty} & d\varepsilon\, Q(\varepsilon - \mu)\, \Theta\big(\varepsilon - \tfrac{1}{2}(1+\sigma r)\hbar\omega_{\rm c}\big) \\ & + \sum_\sigma \Big[\tfrac{1}{2}\,\hbar\omega_{\rm c}\, Q\big(\tfrac{1}{2}(1+\sigma r)\hbar\omega_{\rm c} - \mu\big) - \tfrac{1}{12}\,(\hbar\omega_{\rm c})^2\, Q'\big(\tfrac{1}{2}(1+\sigma r)\hbar\omega_{\rm c} - \mu\big) + \ldots\Big] \quad . \end{aligned} \tag{5.246}$$

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

$$\varOmega(T,V,\mu,H) = 2\int\limits_0^{\infty} d\varepsilon\, Q(\varepsilon - \mu) + \big(\tfrac{1}{4}r^2 - \tfrac{1}{12}\big)\,(\hbar\omega_{\rm c})^2\, Q'(-\mu) + \ldots \quad . \tag{5.247}$$

Thus, the magnetic susceptibility is

$$\begin{aligned} \chi = -\frac{1}{V}\frac{\partial^2\varOmega}{\partial H^2} &= \big(r^2 - \tfrac{1}{3}\big) \cdot \tilde{\mu}_{\rm B}^2 \cdot \big(m/m^*\big)^2 \cdot \Big\{-\frac{2}{V}\, Q'(-\mu)\Big\} \\ &= \bigg(\frac{g^2}{4} - \frac{m^2}{3m^{*2}}\bigg) \cdot \tilde{\mu}_{\rm B}^2 \cdot n^2 \kappa_T \quad , \end{aligned} \tag{5.248}$$

where κ_T is the isothermal compressibility[20]. 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

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[20] We've used $-\frac{2}{V}Q'(\mu) = -\frac{1}{V}\frac{\partial^2\varOmega}{\partial\mu^2} = n^2\kappa_T$.

$m^* = 0.067\, m$. 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 $-\frac{2}{V}\, Q'(-\mu) = n^2 \kappa_T$.

5.8.6 Moment formation in interacting itinerant electron systems

The Hubbard model

A noninteracting electron gas exhibits paramagnetism or diamagnetism, depending on the sign of χ, but never develops a spontaneous magnetic moment: $\boldsymbol{M}(\boldsymbol{H} = 0) = 0$. What gives rise to magnetism in solids? Overwhelmingly, the answer is that Coulomb repulsion between electrons is responsible for magnetism, in those instances in which magnetism arises. At first thought this might seem odd, since the Coulomb interaction is spin-independent. How then can it lead to a spontaneous magnetic moment?

To understand how Coulomb repulsion leads to magnetism, it is useful to consider a model interacting system, described by the Hamiltonian

$$\hat{H} = -t \sum_{ij,\sigma} \Big(c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma} \Big) + U \sum_i n_{i\uparrow}\, n_{i\downarrow} + \mu_{\rm B} \boldsymbol{H} \cdot \sum_{i,\alpha,\beta} c^\dagger_{i\alpha}\, \boldsymbol{\sigma}_{\alpha\beta}\, c_{i\beta} \quad . \tag{5.249}$$

This is none other than the famous *Hubbard model*, which has served as a kind of Rosetta stone for interacting electron systems. The first term describes hopping of electrons along the links of some regular lattice (the symbol ij denotes a link between sites i and j). The second term describes the local (on-site) repulsion of electrons. This is a single orbital model, so the repulsion exists when one tries to put two electrons in the orbital, with opposite spin polarization. Typically the Hubbard U parameter is on the order of electron volts. The last term is the Zeeman interaction of the electron spins with an external magnetic field. Orbital effects can be modeled by associating a phase $\exp(iA_{ij})$ to the hopping matrix element t between sites i and j, where the directed sum of A_{ij} around a plaquette yields the total magnetic flux through the plaquette in units of $\phi_0 = hc/e$. We will ignore orbital effects here. Note that the interaction term is short-ranged, whereas the Coulomb interaction falls off as $1/|\boldsymbol{R}_i - \boldsymbol{R}_j|$. The Hubbard model is thus unrealistic, although screening effects in metals do effectively render the interaction to be short-ranged.

Within the Hubbard model, the interaction term is local and written as $Un_\uparrow n_\downarrow$ on any given site. This term favors a local moment. This is because the chemical potential will fix the mean value of the total occupancy $n_\uparrow + n_\downarrow$, in which case it always pays to maximize the difference $|n_\uparrow - n_\downarrow|$.

Stoner mean field theory

There are no general methods available to solve for even the ground state of an interacting many-body Hamiltonian. We'll solve this problem using a *mean field* theory due to Stoner. The idea is to write the occupancy $n_{i\sigma}$ as a sum of average and fluctuating terms:

$$n_{i\sigma} = \langle n_{i\sigma} \rangle + \delta n_{i\sigma} \quad . \tag{5.250}$$

Here, $\langle n_{i\sigma} \rangle$ is the thermodynamic average; the above equation may then be taken as a definition of the fluctuating piece, $\delta n_{i\sigma}$. We assume that the average is site-independent. This is a significant assumption, for while we understand why each site should favor developing a moment, it is not clear that all these local moments should want to line up parallel to each other. Indeed, on a bipartite lattice, it is possible that the individual local moments on neighboring sites will be antiparallel, corresponding to an *antiferromagnetic* order of the pins. Our mean field theory will be one for *ferromagnetic* states.

We now write the interaction term as

$$\begin{aligned} n_{i\uparrow} n_{i\downarrow} &= \langle n_\uparrow \rangle \langle n_\downarrow \rangle + \langle n_\uparrow \rangle \, \delta n_{i\downarrow} + \langle n_\downarrow \rangle \, \delta n_{i\uparrow} + \overbrace{\delta n_{i\uparrow} \, \delta n_{i\downarrow}}^{(\text{fluct}^{\text{s}})^2} \\ &= -\langle n_\uparrow \rangle \langle n_\downarrow \rangle + \langle n_\uparrow \rangle \, n_{i\downarrow} + \langle n_\downarrow \rangle \, n_{i\uparrow} + \mathcal{O}\big((\delta n)^2\big) \\ &= \tfrac{1}{4}(m^2 - n^2) + \tfrac{1}{2} n \, (n_{i\uparrow} + n_{i\downarrow}) + \tfrac{1}{2} m \, (n_{i\uparrow} - n_{i\downarrow}) + \mathcal{O}\big((\delta n)^2\big) \quad , \end{aligned} \tag{5.251}$$

where n and m are the average occupancy per spin and average spin polarization, each per unit cell:

$$\begin{aligned} n &= \langle n_\downarrow \rangle + \langle n_\uparrow \rangle \\ m &= \langle n_\downarrow \rangle - \langle n_\uparrow \rangle \quad , \end{aligned} \tag{5.252}$$

i.e. $\langle n_\sigma \rangle = \frac{1}{2}(n - \sigma m)$. The mean field grand canonical Hamiltonian $\mathcal{K} = \hat{H} - \mu \mathcal{N}$, may then be written as

$$\begin{aligned} \mathcal{K}^{\text{MF}} &= -\tfrac{1}{2} \sum_{i,j,\sigma} t_{ij} \Big(c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma} \Big) - \big(\mu - \tfrac{1}{2} U n\big) \sum_{i\sigma} c^\dagger_{i\sigma} c_{i\sigma} \\ &\qquad + \big(\mu_{\text{B}} H + \tfrac{1}{2} U m\big) \sum_{i\sigma} \sigma \, c^\dagger_{i\sigma} c_{i\sigma} + \tfrac{1}{4} N_{\text{sites}} \, U (m^2 - n^2) \quad , \end{aligned} \tag{5.253}$$

where we've quantized spins along the direction of $\boldsymbol{H}$, defined as $\hat{\boldsymbol{z}}$. You should take note of two things here. First, the chemical potential is shifted *downward* (or the electron energies shifted *upward*) by an amount $\frac{1}{2} U n$, corresponding to the average energy of repulsion with the background. Second, the effective magnetic field has been shifted by an amount $\frac{1}{2} U m / \mu_{\text{B}}$, so the effective field is

$$H_{\text{eff}} = H + \frac{U m}{2 \mu_{\text{B}}} \quad . \tag{5.254}$$

The *bare* single particle dispersions are given by $\varepsilon_\sigma(\boldsymbol{k}) = -\hat{t}(\boldsymbol{k}) + \sigma \mu_{\text{B}} H$, where

$$\hat{t}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} t(\boldsymbol{R}) \, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \quad , \tag{5.255}$$

and $t_{ij} = t(\boldsymbol{R}_i - \boldsymbol{R}_j)$. For nearest neighbor hopping on a d-dimensional cubic lattice, $\hat{t}(\boldsymbol{k}) = -t \sum_{\mu=1}^{d} \cos(k_\mu a)$, where a is the lattice constant. Including the mean field effects, the *effective* single particle dispersions become

$$\widetilde{\varepsilon}_\sigma(\boldsymbol{k}) = -\hat{t}(\boldsymbol{k}) - \tfrac{1}{2} U n + \big(\mu_{\text{B}} H + \tfrac{1}{2} U m\big) \, \sigma \quad . \tag{5.256}$$

We now solve the mean field theory, by obtaining the free energy per site, $\varphi(n,T,H)$. First, note that $\varphi = \omega + \mu n$, where $\omega = \varOmega/N_{\rm sites}$ is the Landau, or grand canonical, free energy per site. This follows from the general relation $\varOmega = F - \mu N$; note that the total electron number is $N = nN_{\rm sites}$, since n is the electron number per unit cell (including both spin species). If $g(\varepsilon)$ is the density of states per unit cell (rather than per unit volume), then we have[21]

$$\varphi = \tfrac{1}{4}U(m^2+n^2) + \bar\mu n - \tfrac{1}{2}k_{\rm B}T\int\limits_{-\infty}^{\infty}\!d\varepsilon\, g(\varepsilon)\,\bigg\{\ln\Big(1+e^{(\bar\mu-\varepsilon-\varDelta)/k_{\rm B}T}\Big) + \ln\Big(1+e^{(\bar\mu-\varepsilon+\varDelta)/k_{\rm B}T}\Big)\bigg\} \qquad (5.257)$$

where $\bar\mu \equiv \mu - \frac{1}{2}Un$ and $\varDelta \equiv \mu_{\rm B}H + \frac{1}{2}Um$. From this free energy we derive two self-consistent equations for μ and m. The first comes from demanding that φ be a function of n and not of μ, *i.e.* $\partial\varphi/\partial\mu = 0$, which leads to

$$n = \tfrac{1}{2}\int\limits_{-\infty}^{\infty}\!d\varepsilon\, g(\varepsilon)\,\Big\{f(\varepsilon-\varDelta-\bar\mu) + f(\varepsilon+\varDelta-\bar\mu)\Big\} \quad , \qquad (5.258)$$

where $f(y) = \big[\exp(y/k_{\rm B}T)+1\big]^{-1}$ is the Fermi function. The second equation comes from minimizing f with respect to average moment m:

$$m = \tfrac{1}{2}\int\limits_{-\infty}^{\infty}\!d\varepsilon\, g(\varepsilon)\,\Big\{f(\varepsilon-\varDelta-\bar\mu) - f(\varepsilon+\varDelta-\bar\mu)\Big\} \quad . \qquad (5.259)$$

Here, we will solve the first equation, eq. 5.258, and use the results to generate a Landau expansion of the free energy φ in powers of m^2. We assume that $\varDelta$ is small, in which case we may write

$$n = \int\limits_{-\infty}^{\infty}\!d\varepsilon\, g(\varepsilon)\,\Big\{f(\varepsilon-\bar\mu) + \tfrac{1}{2}\varDelta^2 f''(\varepsilon-\bar\mu) + \tfrac{1}{24}\,\varDelta^4 f''''(\varepsilon-\bar\mu) + \ldots\Big\} \quad . \qquad (5.260)$$

We write $\bar\mu(\varDelta) = \bar\mu_0 + \delta\bar\mu$ and expand in $\delta\bar\mu$. Since n is fixed in our (canonical) ensemble, we have

$$n = \int\limits_{-\infty}^{\infty}\!d\varepsilon\, g(\varepsilon)\, f\big(\varepsilon-\bar\mu_0\big) \quad , \qquad (5.261)$$

which defines $\bar\mu_0(n,T)$.[22] The remaining terms in the $\delta\bar\mu$ expansion of eqn. 5.260 must sum to zero. This yields

$$D(\bar\mu_0)\,\delta\bar\mu + \tfrac{1}{2}\varDelta^2\, D'(\bar\mu_0) + \tfrac{1}{2}(\delta\bar\mu)^2\, D'(\bar\mu_0) + \tfrac{1}{2}D''(\bar\mu_0)\,\varDelta^2\,\delta\bar\mu + \tfrac{1}{24}\,D'''(\bar\mu_0)\,\varDelta^4 + \mathcal{O}(\varDelta^6) = 0 \quad , \qquad (5.262)$$

where

$$D(\mu) = -\int\limits_{-\infty}^{\infty}\!d\varepsilon\, g(\varepsilon)\, f'(\varepsilon-\mu) \qquad (5.263)$$

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[21] Note that we have written $\mu n = \bar\mu n + \frac{1}{2}Un^2$, which explains the sign of the coefficient of n^2.

[22] The Gibbs-Duhem relation guarantees that such an equation of state exists, relating any three intensive thermodynamic quantities.

is the thermally averaged *bare* density of states at energy μ. Note that the $k^{\rm th}$ derivative is

$$D^{(k)}(\mu) = -\int\limits_{-\infty}^{\infty} \! d\varepsilon \; g^{(k)}(\varepsilon)\, f'(\varepsilon - \mu) \quad . \tag{5.264}$$

Solving for $\delta\bar{\mu}$, we obtain

$$\delta\bar{\mu} = -\tfrac{1}{2} a_1 \varDelta^2 - \tfrac{1}{24}\big(3a_1^3 - 6a_1 a_2 + a_3\big)\,\varDelta^4 + \mathcal{O}(\varDelta^6) \quad , \tag{5.265}$$

where $a_k \equiv D^{(k)}(\bar{\mu}_0)/D(\bar{\mu}_0)$.

After integrating by parts and inserting this result for $\delta\bar{\mu}$ into our expression for the free energy f, we obtain the expansion

$$\varphi(n,T,m) = \varphi_0(n,T) + \tfrac{1}{4} U m^2 - \tfrac{1}{2} D(\bar{\mu}_0)\,\varDelta^2 + \tfrac{1}{8}\left(\frac{\big[D'(\bar{\mu}_0)\big]^2}{D(\bar{\mu}_0)} - \tfrac{1}{3}\,D''(\bar{\mu}_0)\right)\varDelta^4 + \ldots \quad , \tag{5.266}$$

where prime denotes differentiation with respect to argument, at $m=0$, and

$$\varphi_0(n,T) = \tfrac{1}{4} U n^2 + n\bar{\mu}_0 - \int\limits_{-\infty}^{\infty} \! d\varepsilon\, \mathcal{N}(\varepsilon)\, f\big(\varepsilon - \bar{\mu}_0\big) \quad , \tag{5.267}$$

where $g(\varepsilon) = \mathcal{N}'(\varepsilon)$, so $\mathcal{N}(\varepsilon)$ is the integrated bare density of states per unit cell in the absence of any magnetic field (including both spin species).

We assume that H and m are small, in which case

$$\varphi = \varphi_0 + \tfrac{1}{2} a m^2 + \tfrac{1}{4} b m^4 - \tfrac{1}{2}\chi_0\, H^2 - \frac{U\chi_0}{2\mu_{\rm B}}\, H m + \ldots \quad , \tag{5.268}$$

where $\chi_0 = \mu_{\rm B}^2\, D(\bar{\mu}_0)$ is the Pauli susceptibility, and

$$a = \tfrac{1}{2} U\big(1 - \tfrac{1}{2} U D\big) \quad , \quad b = \tfrac{1}{32}\left(\frac{(D')^2}{D} - \tfrac{1}{3}\,D''\right) U^4 \quad , \tag{5.269}$$

where the argument of each $D^{(k)}$ above is $\bar{\mu}_0(n,T)$. The magnetization density (per unit cell, rather than per unit volume) is given by

$$M = -\frac{\partial\varphi}{\partial H} = \chi_0 H + \frac{U\chi_0}{2\mu_{\rm B}}\, m \quad . \tag{5.270}$$

Minimizing with respect to m yields

$$a m + b m^3 - \frac{U\chi_0}{2\mu_{\rm B}}\, H = 0 \quad , \tag{5.271}$$

which gives, for small m,

$$m = \frac{\chi_0}{\mu_{\rm B}}\,\frac{H}{1 - \tfrac{1}{2} U D} \quad . \tag{5.272}$$

Figure 5.16: A graduate student experiences the Stoner enhancement

We therefore obtain $M = \chi\, H$ with

$$\chi = \frac{\chi_0}{1 - \frac{U}{U_c}} \quad , \tag{5.273}$$

where $U_c = 2/D(\bar{\mu}_0)$ is the critical value of U. The denominator of χ increases the susceptibility above the bare Pauli value χ_0, and is referred to as – I kid you not – the *Stoner enhancement* (see fig. 5.16).

It is worth emphasizing that the magnetization per unit cell is given by

$$M = -\frac{1}{N_{\text{sites}}} \frac{\delta \hat{H}}{\delta H} = \mu_B m \quad . \tag{5.274}$$

This is an operator identity and is valid for any value of m, and not only small m.

When $H = 0$ we can still get a magnetic moment, provided $U > U_c$. This is a consequence of the simple Landau theory we have derived. Solving for m when $H = 0$ gives $m = 0$ when $U < U_c$ and

$$m(U) = \pm \left(\frac{U}{2b\, U_c}\right)^{1/2} \sqrt{U - U_c} \quad , \tag{5.275}$$

when $U > U_c$, and assuming $b > 0$. Thus we have the usual mean field order parameter exponent of $\beta = \frac{1}{2}$.

Antiferromagnetic solution

In addition to ferromagnetism, there may be other ordered states which solve the mean field theory. One such example is antiferromagnetism. On a bipartite lattice, the antiferromagnetic mean field theory is obtained from

$$\langle n_{i\sigma} \rangle = \tfrac{1}{2} n + \tfrac{1}{2} \sigma\, e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_i}\, m \quad , \tag{5.276}$$

where $\boldsymbol{Q} = (\pi/a, \pi/a, \ldots, \pi/a)$ is the antiferromagnetic ordering wavevector. The grand canonical Hamiltonian is then

$$\begin{aligned}\mathcal{K}^{\rm MF} &= -\tfrac{1}{2}\sum_{i,j,\sigma} t_{ij}\Big(c^\dagger_{i\sigma}c_{j\sigma} + c^\dagger_{j\sigma}c_{i\sigma}\Big) - \big(\mu - \tfrac{1}{2}Un\big)\sum_{i\sigma} c^\dagger_{i\sigma}c_{i\sigma} \\ &\qquad\qquad + \tfrac{1}{2}Um\sum_{i\sigma} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_i}\,\sigma\, c^\dagger_{i\sigma}c_{i\sigma} + \tfrac{1}{4}N_{\rm sites}\,U(m^2 - n^2) \qquad (5.277) \\ &= \tfrac{1}{2}\sum_{\boldsymbol{k}\sigma}\Big(c^\dagger_{\boldsymbol{k},\sigma} \quad c^\dagger_{\boldsymbol{k}+\boldsymbol{Q},\sigma}\Big)\begin{pmatrix} \varepsilon(\boldsymbol{k}) - \mu + \frac{1}{2}Un & \frac{1}{2}\sigma\, Um \\ \frac{1}{2}\sigma\, Um & \varepsilon(\boldsymbol{k}+\boldsymbol{Q}) - \mu + \frac{1}{2}Un\end{pmatrix}\begin{pmatrix} c_{\boldsymbol{k},\sigma} \\ c_{\boldsymbol{k}+\boldsymbol{Q},\sigma}\end{pmatrix} + \tfrac{1}{4}N_{\rm sites}\,U(m^2 - n^2) \quad ,\end{aligned}$$

(5.278)

where $\varepsilon(\boldsymbol{k}) = -\hat{t}(\boldsymbol{k})$, as before. On a bipartite lattice, with nearest neighbor hopping only, we have $\varepsilon(\boldsymbol{k}+\boldsymbol{Q}) = -\varepsilon(\boldsymbol{k})$. The above matrix is diagonalized by a unitary transformation, yielding the eigenvalues

$$\lambda_\pm = \pm\sqrt{\varepsilon^2(\boldsymbol{k}) + \Delta^2} - \bar{\mu} \qquad (5.279)$$

with $\Delta = \frac{1}{2}Um$ and $\bar{\mu} = \mu - \frac{1}{2}Un$ as before. The free energy per unit cell is then

$$\varphi = \tfrac{1}{4}U(m^2+n^2) + \bar{\mu}n - \tfrac{1}{2}k_{\rm B}T\int\limits_{-\infty}^{\infty}\! d\varepsilon\; g(\varepsilon)\left\{\ln\Big(1+e^{(\bar{\mu}-\sqrt{\varepsilon^2+\Delta^2})/k_{\rm B}T}\Big) + \ln\Big(1+e^{(\bar{\mu}+\sqrt{\varepsilon^2+\Delta^2})/k_{\rm B}T}\Big)\right\} \quad . \qquad (5.280)$$

The mean field equations are then

$$n = \tfrac{1}{2}\int\limits_{-\infty}^{\infty}\! d\varepsilon\; g(\varepsilon)\left\{f\Big(-\sqrt{\varepsilon^2+\Delta^2} - \bar{\mu}\Big) + f\Big(\sqrt{\varepsilon^2+\Delta^2} - \bar{\mu}\Big)\right\} \qquad (5.281)$$

$$\frac{1}{U} = \tfrac{1}{2}\int\limits_{-\infty}^{\infty}\! d\varepsilon\; \frac{g(\varepsilon)}{\sqrt{\varepsilon^2+\Delta^2}}\left\{f\Big(-\sqrt{\varepsilon^2+\Delta^2} - \bar{\mu}\Big) - f\Big(\sqrt{\varepsilon^2+\Delta^2} - \bar{\mu}\Big)\right\}. \qquad (5.282)$$

As in the case of the ferromagnet, a paramagnetic solution with $m = 0$ always exists, in which case the second of the above equations is no longer valid.

Mean field phase diagram of the Hubbard model

Let us compare the mean field theories for the ferromagnetic and antiferromagnetic states at $T = 0$ and $H = 0$. Due to particle-hole symmetry, we may assume $0 \le n \le 1$ without loss of generality. (The solutions repeat themselves under $n \to 2 - n$.) For the paramagnet, we have

$$n = \int\limits_{-\infty}^{\bar{\mu}}\! d\varepsilon\; g(\varepsilon) \qquad (5.283)$$

$$\varphi = \tfrac{1}{4}Un^2 + \int\limits_{-\infty}^{\bar{\mu}}\! d\varepsilon\; g(\varepsilon)\,\varepsilon \quad , \qquad (5.284)$$

with $\bar{\mu} = \mu - \frac{1}{2}Un$ is the 'renormalized' Fermi energy and $g(\varepsilon)$ is the density of states per unit cell in the absence of any explicit (H) or implicit (m) symmetry breaking, including both spin polarizations.

For the ferromagnet,

$$n = \tfrac{1}{2}\int\limits_{-\infty}^{\bar{\mu}-\Delta} d\varepsilon\, g(\varepsilon) + \tfrac{1}{2}\int\limits_{-\infty}^{\bar{\mu}+\Delta} d\varepsilon\, g(\varepsilon) \tag{5.285}$$

$$\frac{4\Delta}{U} = \int\limits_{\bar{\mu}-\Delta}^{\bar{\mu}+\Delta} d\varepsilon\, g(\varepsilon) \tag{5.286}$$

$$\varphi = \tfrac{1}{4}Un^2 - \frac{\Delta^2}{U} + \int\limits_{-\infty}^{\bar{\mu}-\Delta} d\varepsilon\, g(\varepsilon)\,\varepsilon + \int\limits_{-\infty}^{\bar{\mu}+\Delta} d\varepsilon\, g(\varepsilon)\,\varepsilon \quad . \tag{5.287}$$

Here, $\Delta = \frac{1}{2}Um$ is nonzero in the ordered phase.

Finally, the antiferromagnetic mean field equations are

$$n_{\bar{\mu}<0} = \int\limits_{\varepsilon_0}^{\infty} d\varepsilon\, g(\varepsilon) \qquad ; \qquad n_{\bar{\mu}>0} = 2 - \int\limits_{\varepsilon_0}^{\infty} d\varepsilon\, g(\varepsilon) \tag{5.288}$$

$$\frac{2}{U} = \int\limits_{\varepsilon_0}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{\sqrt{\varepsilon^2 + \Delta^2}} \tag{5.289}$$

$$\varphi = \tfrac{1}{4}Un^2 + \frac{\Delta^2}{U} - \int\limits_{\varepsilon_0}^{\infty} d\varepsilon\, g(\varepsilon)\,\sqrt{\varepsilon^2 + \Delta^2} \quad , \tag{5.290}$$

where $\varepsilon_0 = \sqrt{\bar{\mu}^2 - \Delta^2}$ and $\Delta = \frac{1}{2}Um$ as before. Note that $|\bar{\mu}| \geq \Delta$ for these solutions. Exactly at half-filling, we have $n = 1$ and $\bar{\mu} = 0$. We then set $\varepsilon_0 = 0$.

The paramagnet to ferromagnet transition may be first or second order, depending on the details of $g(\varepsilon)$. If second order, it occurs at $U_{\rm c}^{\rm F} = 1/g(\bar{\mu}_{\rm P})$, where $\bar{\mu}_{\rm P}(n)$ is the paramagnetic solution for $\bar{\mu}$. The paramagnet to antiferromagnet transition is always second order in this mean field theory, since the RHS of eqn. (5.289) is a monotonic function of Δ. This transition occurs at $U_{\rm c}^{\rm A} = 2\Big/\int\limits_{\bar{\mu}_{\rm P}}^{\infty} d\varepsilon\, g(\varepsilon)\,\varepsilon^{-1}$. Note that $U_{\rm c}^{\rm A} \to 0$ logarithmically for $n \to 1$, since $\bar{\mu}_{\rm P} = 0$ at half-filling.

For large U, the ferromagnetic solution always has the lowest energy, and therefore if $U_{\rm c}^{\rm A} < U_{\rm c}^{\rm F}$, there will be a first-order antiferromagnet to ferromagnet transition at some value $U^* > U_{\rm c}^{\rm F}$. In fig. 5.17, I plot the phase diagram obtained by solving the mean field equations assuming a semicircular density of states $g(\varepsilon) = \frac{2}{\pi}\, W^{-2}\sqrt{W^2 - \varepsilon^2}$. Also shown is the phase diagram for the $d = 2$ square lattice Hubbard model obtained by J. Hirsch (1985).

How well does Stoner theory describe the physics of the Hubbard model? Quantum Monte Carlo calculations by J. Hirsch (1985) found that the actual phase diagram of the $d = 2$ square lattice Hubbard

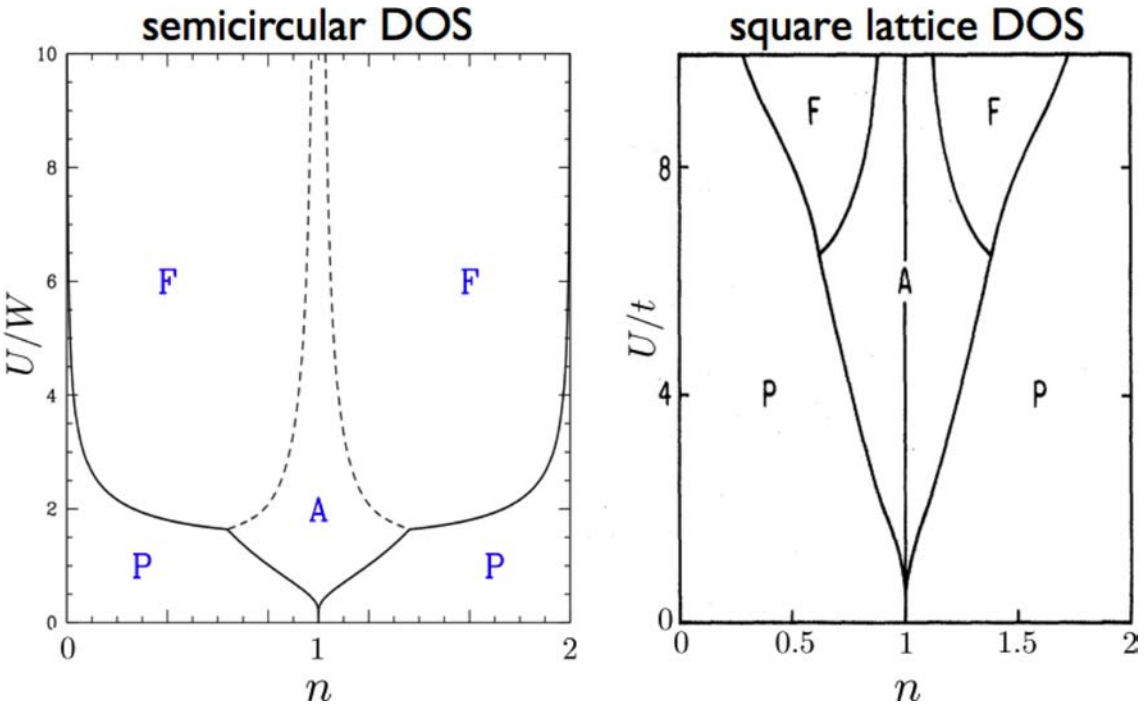

Figure 5.17: Mean field phase diagram of the Hubbard model, including paramagnetic (P), ferromagnetic (F), and antiferromagnetic (A) phases. Left panel: results using a semicircular density of states function of half-bandwidth W. Right panel: results using a two-dimensional square lattice density of states with nearest neighbor hopping t, from J. E. Hirsch, *Phys. Rev. B* **31**, 4403 (1985). The phase boundary between F and A phases is first order.

Model exhibits no ferromagnetism for any n up to $U = 10$. Furthermore, he found the antiferromagnetic phase to be entirely confined to the vertical line $n = 1$. For $n \neq 1$ and $0 \leq U \leq 10$, the system is a paramagnet[23]. These results were state-of-the art at the time, but both computing power as well as numerical algorithms for interacting quantum systems have advanced considerably since 1985. Yet as of 2018, we *still* don't have a clear understanding of the $d = 2$ Hubbard model's $T = 0$ phase diagram! There is an emerging body of numerical evidence[24] that in the underdoped ($n < 1$) regime, there are portions of the phase diagram which exhibit a *stripe* ordering, in which antiferromagnetic order is interrupted by a parallel array of line defects containing excess holes (*i.e.* the absence of an electron)[25]. This problem has turned out to be unexpectedly rich, complex, and numerically difficult to resolve due to the presence of *competing ordered states*, such as d-wave superconductivity and spiral magnetic phases, which lie nearby in energy with respect to the putative stripe ground state.

In order to achieve a ferromagnetic solution, it appears necessary to introduce geometric frustration, either by including a next-nearest-neighbor hopping amplitude t' or by defining the model on non-bipartite lattices. Numerical work by M. Ulmke (1997) showed the existence of a ferromagnetic phase at

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[23] A theorem due to Nagaoka establishes that the ground state is ferromagnetic for the case of a single hole in the $U = \infty$ system on bipartite lattices.

[24] See J. P. F. LeBlanc *et al.*, *Phys. Rev. X* **5**, 041041 (2015) and B. Zheng *et al.*, *Science* **358**, 1155 (2017).

[25] The best case for stripe order has been made at $T = 0$, $U/t = 8$, and hold doping $x = \frac{1}{8}$ (*i.e.* $n = \frac{7}{8}$).

$T = 0$ on the FCC lattice Hubbard model for $U = 6$ and $n \in [0.15, 0.87]$ (approximately).

5.8.7 White dwarf stars

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

The electron density is then

$$n = \frac{N}{V} = \frac{2 \cdot M/4m_\text{p}}{V} = \frac{\rho}{2m_\text{p}} \approx 10^{30}\,\text{cm}^{-3} \quad , \tag{5.291}$$

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

$$\begin{aligned} k_\text{F} &= (3\pi^2 n)^{1/3} = 2.14 \times 10^{10}\,\text{cm}^{-1} \\ p_\text{F} &= \hbar k_\text{F} = 2.26 \times 10^{-17}\,\text{g cm/s} \\ mc &= (9.1 \times 10^{-28}\,\text{g})(3 \times 10^{10}\,\text{m/s}) = 2.7 \times 10^{-17}\,\text{g cm/s} \quad . \end{aligned} \tag{5.292}$$

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

The kinetic energy is given by

$$\varepsilon(\boldsymbol{p}) = \sqrt{\boldsymbol{p}^2 c^2 + m^2 c^4} - mc^2 \quad . \tag{5.293}$$

The velocity is

$$\boldsymbol{v} = \frac{\partial \varepsilon}{\partial \boldsymbol{p}} = \frac{\boldsymbol{p} c^2}{\sqrt{p^2 c^2 + m^2 c^4}} \quad . \tag{5.294}$$

The pressure in the ground state is

$$\begin{aligned} p_0 = \tfrac{1}{3} n \langle \boldsymbol{p} \cdot \boldsymbol{v} \rangle &= \frac{1}{3\pi^2 \hbar^3} \int\limits_0^{p_\text{F}} dp\, p^2 \cdot \frac{p^2 c^2}{\sqrt{p^2 c^2 + m^2 c^4}} \\ &= \frac{m^4 c^5}{3\pi^2 \hbar^3} \int\limits_0^{\theta_\text{F}} d\theta\, \sinh^4\!\theta = \frac{m^4 c^5}{96\pi^2 \hbar^3} \big(\sinh(4\theta_\text{F}) - 8 \sinh(2\theta_\text{F}) + 12\, \theta_\text{F} \big) \quad , \end{aligned} \tag{5.295}$$

where we use the substitution

$$p = mc \sinh\theta \quad , \quad v = c \tanh\theta \quad \Longrightarrow \quad \theta = \tfrac{1}{2} \ln\!\bigg(\frac{c+v}{c-v}\bigg) \quad . \tag{5.296}$$

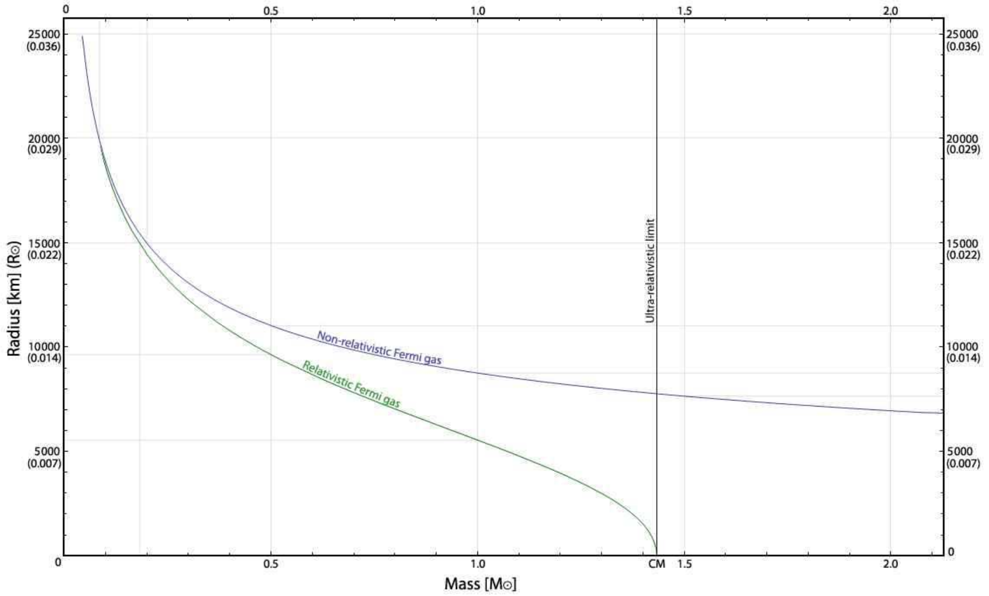

Figure 5.18: Mass-radius relationship for white dwarf stars. (*Source: Wikipedia*).

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

$$n = \frac{M}{2m_{\rm p}V} \qquad \Longrightarrow \qquad 3\pi^2 n = \frac{9\pi}{8}\,\frac{M}{R^3\,m_{\rm p}} \quad . \tag{5.297}$$

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

$$dE_0 = -p_0\,dV = -p_0(R)\cdot 4\pi R^2\,dR \quad . \tag{5.298}$$

This must be balanced by gravity:

$$dE_{\rm g} = \gamma \cdot \frac{GM^2}{R^2}\,dR \quad , \tag{5.299}$$

where γ depends on the radial mass distribution. Equilibrium then implies

$$p_0(R) = \frac{\gamma}{4\pi}\,\frac{GM^2}{R^4} \quad . \tag{5.300}$$

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

$$\frac{\gamma}{4\pi}\,\frac{gM^2}{R^4} = \frac{m^4c^5}{96\pi^2\hbar^3}\big(\sinh(4\theta_{\rm F}) - 8\sinh(2\theta_{\rm F}) + 12\,\theta_{\rm F}\big) \quad . \tag{5.301}$$

Note that

$$\sinh(4\theta_{\rm F}) - 8\sinh(2\theta_{\rm F}) + 12\theta_{\rm F} = \begin{cases} \frac{96}{15}\,\theta_{\rm F}^5 & \theta_{\rm F}\to 0 \\ \frac{1}{2}\,e^{4\theta_{\rm F}} & \theta_{\rm F}\to\infty \quad . \end{cases} \tag{5.302}$$

Thus, we may write

$$p_0(R) = \frac{\gamma}{4\pi}\,\frac{gM^2}{R^4} = \begin{cases} \frac{\hbar^2}{15\pi^2 m}\left(\frac{9\pi}{8}\,\frac{M}{R^3\,m_{\rm p}}\right)^{5/3} & \theta_{\rm F}\to 0 \\ \frac{\hbar c}{12\pi^2}\left(\frac{9\pi}{8}\,\frac{M}{R^3\,m_{\rm p}}\right)^{4/3} & \theta_{\rm F}\to\infty \quad . \end{cases} \tag{5.303}$$

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

$$R = \tfrac{3}{40\gamma}\,(9\pi)^{2/3}\,\frac{\hbar^2}{G\,m_{\rm p}^{5/3}\,m\,M^{1/3}} \propto M^{-1/3} \quad . \tag{5.304}$$

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

$$M = M_0 = \frac{9}{64}\left(\frac{3\pi}{\gamma^3}\right)^{1/2}\left(\frac{\hbar c}{G}\right)^{3/2}\frac{1}{m_{\rm p}^2} \quad . \tag{5.305}$$

To find the R dependence, we must go beyond the lowest order expansion of eqn. 5.302, in which case we find

$$R = \left(\frac{9\pi}{8}\right)^{1/3}\left(\frac{\hbar}{mc}\right)\left(\frac{M}{m_{\rm p}}\right)^{1/3}\left[1-\left(\frac{M}{M_0}\right)^{2/3}\right]^{1/2} \quad . \tag{5.306}$$

The value M_0 is the limiting size for a white dwarf. It is called the *Chandrasekhar limit*.

5.9 Appendix I : Second Quantization

5.9.1 Basis states and creation/annihilation operators

Second quantization is a convenient scheme to label basis states of a many particle quantum system. We are ultimately interested in solutions of the many-body Schrödinger equation,

$$\hat{H}\Psi(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = E\,\Psi(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) \tag{5.307}$$

where the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^N \boldsymbol{\nabla}_i^2 + \sum_{j<k}^N V(\boldsymbol{x}_j-\boldsymbol{x}_k) \quad . \tag{5.308}$$

To the coordinate labels $\{\boldsymbol{x}_1,\ldots\boldsymbol{x}_N\}$ we may also append labels for internal degrees of freedom, such as spin polarization, denoted $\{\zeta_1,\ldots,\zeta_N\}$. Since $\big[\hat{H},\sigma\big]=0$ for all permutations $\sigma\in S_N$, the many-body wavefunctions may be chosen to transform according to irreducible representations of the symmetric group S_N. Thus, for any $\sigma\in S_N$,

$$\Psi\big(\boldsymbol{x}_{\sigma(1)},\ldots,\boldsymbol{x}_{\sigma(N)}\big) = \begin{Bmatrix} 1 \\ \mathsf{sgn}(\sigma)\end{Bmatrix}\Psi(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) \quad , \tag{5.309}$$

where the upper choice is for Bose-Einstein statistics and the lower sign for Fermi-Dirac statistics. Here $\boldsymbol{x}_j$ may include not only the spatial coordinates of particle j, but its internal quantum number(s) as well, such as ζ_j.

A convenient basis for the many body states is obtained from the single-particle eigenstates $\big\{|\alpha\rangle\big\}$ of some single-particle Hamiltonian $\hat{H}_0$, with $\langle\, \boldsymbol{x} \,|\, \alpha \,\rangle = \varphi_\alpha(\boldsymbol{x})$ and $\hat{H}_0\,|\alpha\rangle = \varepsilon_\alpha\,|\alpha\rangle$. The basis may be taken as orthonormal, *i.e.* $\big\langle\, \alpha \,\big|\, \alpha' \,\big\rangle = \delta_{\alpha\alpha'}$. Now define

$$\Psi_{\alpha_1,\ldots,\alpha_N}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = \frac{1}{\sqrt{N!\prod_\alpha n_\alpha!}} \sum_{\sigma\in S_N} \begin{Bmatrix} 1 \\ \mathsf{sgn}(\sigma) \end{Bmatrix} \varphi_{\alpha_{\sigma(1)}}(\boldsymbol{x}_1)\cdots\varphi_{\alpha_{\sigma(N)}}(\boldsymbol{x}_N) \quad . \tag{5.310}$$

Here n_α is the number of times the index α appears among the set $\{\alpha_1,\ldots,\alpha_N\}$. For BE statistics, $n_\alpha \in \{0,1,2,\ldots\}$, whereas for FD statistics, $n_\alpha \in \{0,1\}$. Note that the above states are normalized[26]:

$$\begin{aligned} \int\! d^dx_1 \cdots \!\int\! d^dx_N\, \big|\Psi_{\alpha_1\cdots\alpha_N}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)\big|^2 &= \frac{1}{N!\prod_\alpha n_\alpha!} \sum_{\sigma,\mu\in S_N} \begin{Bmatrix} 1 \\ \mathsf{sgn}(\sigma\mu) \end{Bmatrix} \prod_{j=1}^N \int\! d^dx_j\, \varphi^*_{\alpha_{\sigma(j)}}(\boldsymbol{x}_j)\, \varphi_{\alpha_{\mu(j)}}(\boldsymbol{x}_j) \\ &= \frac{1}{\prod_\alpha n_\alpha!} \sum_{\sigma\in S_N} \prod_{j=1}^N \delta_{\alpha_j,\alpha_{\sigma(j)}} = 1 \quad . \end{aligned} \tag{5.311}$$

Note that

$$\begin{aligned} \sum_{\sigma\in S_N} \varphi_{\alpha_{\sigma(1)}}(\boldsymbol{x}_1)\cdots\varphi_{\alpha_{\sigma(N)}}(\boldsymbol{x}_N) &\equiv \mathsf{per}\big\{\varphi_{\alpha_i}(\boldsymbol{x}_j)\big\} \\ \sum_{\sigma\in S_N} \mathsf{sgn}(\sigma)\, \varphi_{\alpha_{\sigma(1)}}(\boldsymbol{x}_1)\cdots\varphi_{\alpha_{\sigma(N)}}(\boldsymbol{x}_N) &\equiv \mathsf{det}\big\{\varphi_{\alpha_i}(\boldsymbol{x}_j)\big\} \quad , \end{aligned} \tag{5.312}$$

which stand for *permanent* and *determinant*, respectively. We may now write

$$\Psi_{\alpha_1\cdots\,\alpha_N}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = \big\langle\, \boldsymbol{x}_1,\cdots,\boldsymbol{x}_N \,\big|\, \alpha_1\cdots\alpha_N \,\big\rangle \quad , \tag{5.313}$$

where

$$\big|\, \alpha_1\cdots\,\alpha_N \,\big\rangle = \frac{1}{\sqrt{N!\prod_\alpha n_\alpha!}} \sum_{\sigma\in S_N} \begin{Bmatrix} 1 \\ \mathsf{sgn}(\sigma) \end{Bmatrix} \big|\, \alpha_{\sigma(1)} \,\big\rangle \otimes \big|\, \alpha_{\sigma(2)} \,\big\rangle \otimes \cdots \otimes \big|\, \alpha_{\sigma(N)} \,\big\rangle \quad . \tag{5.314}$$

Note that $\big|\, \alpha_{\sigma(1)}\cdots\alpha_{\sigma(N)} \,\big\rangle = (\pm 1)^\sigma\, \big|\, \alpha_1\cdots\alpha_N \,\big\rangle$, where by $(\pm1)^\sigma$ we mean 1 in the case of BE statistics and $\mathrm{sgn}\,(\sigma)$ in the case of FD statistics.

We may express $\big|\, \alpha_1\cdots\alpha_N \,\big\rangle$ as a product of creation operators acting on a vacuum $\big|\, 0 \,\big\rangle$ in *Fock space*. For bosons,

$$\big|\, \alpha_1\cdots\,\alpha_N \,\big\rangle = \prod_\alpha \frac{(b^\dagger_\alpha)^{n_\alpha}}{\sqrt{n_\alpha!}}\, \big|\, 0 \,\big\rangle \equiv \big|\, \{n_\alpha\} \,\big\rangle \quad , \tag{5.315}$$

with

$$\big[b_\alpha\,,\,b_\beta\big] = 0 \qquad , \qquad \big[b^\dagger_\alpha\,,\,b^\dagger_\beta\big] = 0 \qquad , \qquad \big[b_\alpha\,,\,b^\dagger_\beta\big] = \delta_{\alpha\beta} \quad , \tag{5.316}$$

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[26] In the normalization integrals, each $\int d^dx$ implicitly includes a sum $\sum_\zeta$ over any internal indices that may be present.

where $[\,\bullet\,,\bullet\,]$ is the commutator. For fermions,

$$\big|\,\alpha_1\cdots\,\alpha_N\,\big\rangle = c^\dagger_{\alpha_1} c^\dagger_{\alpha_2}\cdots\, c^\dagger_{\alpha_N}\,\big|\,0\,\big\rangle \equiv \big|\,\{n_\alpha\}\,\big\rangle \quad , \tag{5.317}$$

with

$$\big\{c_\alpha\,,\,c_\beta\big\} = 0 \qquad , \qquad \big\{c^\dagger_\alpha\,,\,c^\dagger_\beta\big\} = 0 \qquad , \qquad \big\{c_\alpha\,,\,c^\dagger_\beta\big\} = \delta_{\alpha\beta} \quad , \tag{5.318}$$

where $\{\bullet\,,\bullet\}$ is the anticommutator.

5.9.2 Second quantized operators

Now consider the action of permutation-symmetric first quantized operators such as $\hat{T} = -\frac{\hbar^2}{2m}\sum_{i=1}^N \boldsymbol{\nabla}_i^2$ and $\hat{V} = \sum_{i<j}^N \hat{v}(\boldsymbol{x}_i - \boldsymbol{x}_j)$. For a one-body operator such as $\hat{T}$, we have

$$\begin{aligned}\big\langle\,\alpha_1\cdots\,\alpha_N\,\big|\,\hat{T}\,\big|\,\alpha'_1\cdots\,\alpha'_N\,\big\rangle &= \int\! d^d\!x_1\cdots\!\int\! d^d\!x_N\,\Big(\prod_\alpha n_\alpha!\Big)^{-1/2}\Big(\prod_\alpha n'_\alpha!\Big)^{-1/2} \\ &\qquad\qquad \times \sum_{\sigma\in S_N}(\pm 1)^\sigma\,\varphi^*_{\alpha_{\sigma(1)}}(\boldsymbol{x}_1)\cdots\varphi^*_{\alpha_{\sigma(N)}}(\boldsymbol{x}_N)\,\sum_{k=1}^N \hat{T}_i\,\varphi_{\alpha'_{\sigma(1)}}(\boldsymbol{x}_1)\cdots\varphi_{\alpha'_{\sigma(N)}} \\ &= \sum_{\sigma\in S_N}(\pm 1)^\sigma\,\Big(\prod_\alpha n_\alpha!\,n'_\alpha!\Big)^{-1/2}\sum_{i=1}^N\prod_{\substack{j\\(j\neq i)}}\delta_{\alpha_j,\alpha'_{\sigma(j)}}\int\! d^d\!x_1\,\varphi^*_{\alpha_i}(\boldsymbol{x}_1)\,\hat{T}_1\,\varphi_{\alpha'_{\sigma(i)}}(\boldsymbol{x}_1) \quad .\end{aligned} \tag{5.319}$$

One may verify that any permutation-symmetric one-body operator such as $\hat{T}$ is faithfully represented by the second quantized expression,

$$\hat{T} = \sum_{\alpha,\beta}\big\langle\,\alpha\,\big|\,\hat{T}\,\big|\,\beta\,\big\rangle\,\psi^\dagger_\alpha\,\psi_\beta \quad , \tag{5.320}$$

where $\psi^\dagger_\alpha$ is $b^\dagger_\alpha$ or $c^\dagger_\alpha$ as the application determines, and

$$\big\langle\,\alpha\,\big|\,\hat{T}\,\big|\,\beta\,\big\rangle = \int\! d^d\!x_1\,\varphi^*_\alpha(\boldsymbol{x}_1)\,\hat{T}_1\,\varphi_\beta(\boldsymbol{x}_1) \quad . \tag{5.321}$$

Similarly, two-body operators such as $\hat{V}$ are represented as

$$\hat{V} = \tfrac{1}{2}\sum_{\alpha,\beta,\gamma,\delta}\big\langle\,\alpha\beta\,\big|\,\hat{V}\,\big|\,\gamma\delta\,\big\rangle\,\psi^\dagger_\alpha\,\psi^\dagger_\beta\,\psi_\delta\,\psi_\gamma \quad , \tag{5.322}$$

where

$$\big\langle\,\alpha\beta\,\big|\,\hat{V}\,\big|\,\gamma\delta\,\big\rangle = \int\! d^d\!x_1\!\int\! d^d\!x_2\,\varphi^*_\alpha(\boldsymbol{x}_1)\,\varphi^*_\beta(\boldsymbol{x}_2)\,v(\boldsymbol{x}_1-\boldsymbol{x}_2)\,\varphi_\delta(\boldsymbol{x}_2)\,\varphi_\gamma(\boldsymbol{x}_1) \quad . \tag{5.323}$$

The general form for an n-body operator is then

$$\hat{R} = \frac{1}{n!}\sum_{\substack{\alpha_1\cdots\,\alpha_n\\ \beta_1\cdots\,\beta_n}}\big\langle\,\alpha_1\cdots\,\alpha_n\,\big|\,\hat{R}\,\big|\,\beta_1\cdots\,\beta_n\,\big\rangle\,\psi^\dagger_{\alpha_n}\cdots\psi^\dagger_{\alpha_n}\,\psi_{\beta_n}\cdots\psi_{\beta_1} \quad . \tag{5.324}$$

Finally, if the Hamiltonian is noninteracting, consisting solely of one-body operators $\hat{H} = \sum_{i=1}^{N} \hat{h}_i$, then

$$\hat{H} = \sum_\alpha \varepsilon_\alpha \, \psi^\dagger_\alpha \, \psi_\alpha \quad , \tag{5.325}$$

where $\{\varepsilon_\alpha\}$ is the spectrum of each single particle Hamiltonian $\hat{h}_i$.

5.10 Appendix II : Ideal Bose Gas Condensation

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

$$K = \sum_{\boldsymbol{k}} (\varepsilon_{\boldsymbol{k}} - \mu)\, b^\dagger_{\boldsymbol{k}} b_{\boldsymbol{k}} - \sqrt{N} \sum_{\boldsymbol{k}} \big(\nu_{\boldsymbol{k}}\, b^\dagger_{\boldsymbol{k}} + \bar{\nu}_{\boldsymbol{k}}\, b_{\boldsymbol{k}}\big) \quad . \tag{5.326}$$

Here $b^\dagger_{\boldsymbol{k}}$ is the creation operator for a boson in a state of wavevector $\boldsymbol{k}$, hence $\big[b_{\boldsymbol{k}} \, , \, b^\dagger_{\boldsymbol{k}'}\big] = \delta_{\boldsymbol{k}\boldsymbol{k}'}$. The dispersion relation is given by the function $\varepsilon_{\boldsymbol{k}}$, which is the energy of a particle with wavevector $\boldsymbol{k}$. We must have $\varepsilon_{\boldsymbol{k}} - \mu \geq 0$ for all $\boldsymbol{k}$, lest the spectrum of K be unbounded from below. The fields $\{\nu_{\boldsymbol{k}}, \bar{\nu}_{\boldsymbol{k}}\}$ break a global 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 $N \to \infty$. 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 $\exp\big(iN_l\, \boldsymbol{k} \cdot \boldsymbol{a}_l\big) = 1$ for all $l \in \{1, \ldots, d\}$, where $\boldsymbol{a}_l$ is the l^{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 $\boldsymbol{k} = \sum_l (2\pi n_l/N_l)\, \boldsymbol{b}_l$, where $\boldsymbol{b}_l$ is the l^{th} elementary reciprocal lattice vector ($\boldsymbol{a}_l \cdot \boldsymbol{b}_{l'} = 2\pi\delta_{ll'}$) 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

$$K = \sum_{\boldsymbol{k}} (\varepsilon_{\boldsymbol{k}} - \mu)\, \beta^\dagger_{\boldsymbol{k}} \beta_{\boldsymbol{k}} - N \sum_{\boldsymbol{k}} \frac{|\nu_{\boldsymbol{k}}|^2}{\varepsilon_{\boldsymbol{k}} - \mu} \quad , \tag{5.327}$$

where

$$\beta_{\boldsymbol{k}} = b_{\boldsymbol{k}} - \frac{\sqrt{N}\, \nu_{\boldsymbol{k}}}{\varepsilon_{\boldsymbol{k}} - \mu} \quad , \quad \beta^\dagger_{\boldsymbol{k}} = b^\dagger_{\boldsymbol{k}} - \frac{\sqrt{N}\, \bar{\nu}_{\boldsymbol{k}}}{\varepsilon_{\boldsymbol{k}} - \mu} \quad . \tag{5.328}$$

Note that $\big[\beta_{\boldsymbol{k}} \, , \, \beta^\dagger_{\boldsymbol{k}'}\big] = \delta_{\boldsymbol{k}\boldsymbol{k}'}$ so the above transformation is canonical. The Landau free energy $\Omega = -k_{\rm B} T \ln \Xi$, where $\Xi = \text{Tr } e^{-K/k_{\rm B}T}$, is given by

$$\Omega = N k_{\rm B} T \int\limits_{-\infty}^{\infty} \! d\varepsilon \; g(\varepsilon) \; \ln\big(1 - e^{(\mu - \varepsilon)/k_{\rm b}T}\big) - N \sum_{\boldsymbol{k}} \frac{|\nu_{\boldsymbol{k}}|^2}{\varepsilon_{\boldsymbol{k}} - \mu} \quad , \tag{5.329}$$

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

$$g(\varepsilon) = \frac{1}{N} \sum_{\boldsymbol{k}} \delta\big(\varepsilon - \varepsilon_{\boldsymbol{k}}\big) \xrightarrow[N\to\infty]{} \int\limits_{\hat{\Omega}} \frac{d^d\!k}{(2\pi)^d}\, \delta\big(\varepsilon - \varepsilon_{\boldsymbol{k}}\big) \quad . \tag{5.330}$$

Note that

$$\psi_{\boldsymbol{k}} \equiv \frac{1}{\sqrt{N}} \langle b_{\boldsymbol{k}} \rangle = -\frac{1}{N} \frac{\partial \Omega}{\partial \bar{\nu}_{\boldsymbol{k}}} = \frac{\nu_{\boldsymbol{k}}}{\varepsilon_{\boldsymbol{k}} - \mu} \quad . \tag{5.331}$$

In the condensed phase, $\psi_{\boldsymbol{k}}$ is nonzero.

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

$$Y(T, N, \mu, \psi, \bar{\psi}) = \Omega(T, N, \mu, \nu, \bar{\nu}) + N \sum_{\boldsymbol{k}} \big(\nu_{\boldsymbol{k}} \bar{\psi}_{\boldsymbol{k}} + \bar{\nu}_{\boldsymbol{k}} \psi_{\boldsymbol{k}}\big) \quad . \tag{5.332}$$

Note that

$$\frac{\partial Y}{\partial \bar{\nu}_{\boldsymbol{k}}} = \frac{\partial \Omega}{\partial \bar{\nu}_{\boldsymbol{k}}} + N \psi_{\boldsymbol{k}} = 0 \quad , \tag{5.333}$$

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

$$Y(T, N, \mu, \psi, \bar{\psi}) = N k_\mathrm{B} T \int\limits_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, \ln\big(1 - e^{(\mu - \varepsilon)/k_\mathrm{b} T}\big) + N \sum_{\boldsymbol{k}} (\varepsilon_{\boldsymbol{k}} - \mu)\, |\psi_{\boldsymbol{k}}|^2 \quad . \tag{5.334}$$

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

$$n = \frac{N_b}{N} = -\frac{1}{N} \frac{\partial Y}{\partial \mu} = \sum_{\boldsymbol{k}} |\psi_{\boldsymbol{k}}|^2 + \int\limits_{-\infty}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{(\varepsilon - \mu)/k_\mathrm{B} T} - 1} \quad , \tag{5.335}$$

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

$$\nu_{\boldsymbol{k}} = \frac{1}{N} \frac{\partial Y}{\partial \bar{\psi}_{\boldsymbol{k}}} = (\varepsilon_{\boldsymbol{k}} - \mu)\, \psi_{\boldsymbol{k}} \quad . \tag{5.336}$$

Recall that $\nu_{\boldsymbol{k}}$ 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,

$$n(T, \mu) = \int\limits_{-\infty}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{(\varepsilon - \mu)/k_\mathrm{B} T} - 1} \quad , \tag{5.337}$$

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

$$n(T, \mu = 0) = \overbrace{\sum_{\boldsymbol{K}} |\psi_{\boldsymbol{K}}|^2}^{n_0} + \overbrace{\int\limits_{-\infty}^{\infty} d\varepsilon \, \frac{g(\varepsilon)}{e^{\varepsilon/k_{\mathrm{B}}T} - 1}}^{n_>(T)} \quad , \tag{5.338}$$

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 $n_0 = \sum_{\boldsymbol{K}} |\psi_{\boldsymbol{K}}|^2$ is the dimensionless condensate density. If the integral $n_>(T)$ in eqn. 5.338 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. 5.337 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_{c} for which $n = n_>(T_{\mathrm{c}})$. For $T < T_{\mathrm{c}}$, eqn. 5.337 has no solution for any μ and we must appeal to eqn. 5.338. 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 ψ inherits its phase from the external field ν, 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.

5.11 Appendix III : Example Bose Condensation Problem

`PROBLEM:` A three-dimensional gas of noninteracting bosonic particles obeys the dispersion relation $\varepsilon(\boldsymbol{k}) = A \left|\boldsymbol{k}\right|^{1/2}$.

(a) Obtain an expression for the density $n(T, z)$ where $z = \exp(\mu/k_{\mathrm{B}}T)$ 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

$$\mathrm{Li}_{\nu}(z) \equiv \frac{1}{\Gamma(\nu)} \int\limits_0^{\infty} dt \, \frac{t^{\nu-1}}{z^{-1}\, e^{t} - 1} = \sum_{k=1}^{\infty} \frac{z^k}{k^{\nu}} \quad . \tag{5.339}$$

Note $\mathrm{Li}_{\nu}(z)(1) = \zeta(\nu)$, 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

$$\begin{aligned} n(T,z) &= \int\!\frac{d^3\!k}{(2\pi)^3}\,\frac{1}{z^{-1}\,\exp(Ak^{1/2}/k_{\rm B}T)-1} \\ &= \frac{1}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}\int\limits_0^\infty\!ds\,\frac{s^5}{z^{-1}\,e^s-1} = \frac{120}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}\,{\rm Li}_6(z)\quad , \end{aligned} \tag{5.340}$$

where we have changed integration variables from k to $s = Ak^{1/2}/k_{\rm B}T$, and we have defined the functions ${\rm Li}_\nu(z)$ as above, in eqn. 5.339. Note ${\rm Li}_\nu(1) = \zeta(\nu)$, the Riemann zeta function.

(b) Bose condensation sets in for $z = 1$, *i.e.* $\mu = 0$. Thus, the critical temperature $T_{\rm c}$ and the density n are related by

$$n = \frac{120\,\zeta(6)}{\pi^2}\bigg(\frac{k_{\rm B}T_{\rm c}}{A}\bigg)^{\!6}, \tag{5.341}$$

or

$$T_{\rm c}(n) = \frac{A}{k_{\rm B}}\bigg(\frac{\pi^2\,n}{120\,\zeta(6)}\bigg)^{\!1/6}\quad . \tag{5.342}$$

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

$$n = n_0 + \frac{120\,\zeta(6)}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6} = n_0 + \bigg(\frac{T}{T_{\rm c}}\bigg)^{\!6}\,n\quad , \tag{5.343}$$

where n_0 is the condensate density. Thus, at $T = \frac{1}{2}\,T_{\rm c}$,

$$n_0\big(T = \tfrac{1}{2}T_{\rm c}\big) = \tfrac{63}{64}\,n. \tag{5.344}$$

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

$$p = nk_{\rm B}T\Big(1 + B_2(T)\,n + B_3(T)\,n^2 + \ldots\Big)\quad . \tag{5.345}$$

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 $p(T,z)$:

$$\begin{aligned} p(T,z) &= -k_{\rm B}T\!\int\!\frac{d^3\!k}{(2\pi)^3}\,\ln\Big(1 - z\,\exp(-Ak^{1/2}/k_{\rm B}T)\Big) \\ &= -\frac{k_{\rm B}T}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}\int\limits_0^\infty\!ds\,s^5\,\ln\big(1 - z\,e^{-s}\big) = \frac{120\,k_{\rm B}T}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}{\rm Li}_7(z). \end{aligned} \tag{5.346}$$

Expanding in powers of the fugacity, we have

$$\begin{aligned} n &= \frac{120}{\pi^2}\left(\frac{k_{\rm B}T}{A}\right)^6 \left\{ z + \frac{z^2}{2^6} + \frac{z^3}{3^6} + \ldots \right\} \\ \frac{p}{k_{\rm B}T} &= \frac{120}{\pi^2}\left(\frac{k_{\rm B}T}{A}\right)^6 \left\{ z + \frac{z^2}{2^7} + \frac{z^3}{3^7} + \ldots \right\} \quad . \end{aligned} \tag{5.347}$$

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

$$z = \left(\frac{\pi^2 A^6\, n}{120\,(k_{\rm B}T)^6}\right) - \frac{1}{2^6}\left(\frac{\pi^2 A^6\, n}{120\,(k_{\rm B}T)^6}\right)^2 + \mathcal{O}(n^3) \quad . \tag{5.348}$$

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

$$B_2(T) = -\frac{\pi^2}{15360}\left(\frac{A}{k_{\rm B}T}\right)^6 \quad , \tag{5.349}$$

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

5.12 Appendix IV : $C_{p,N}$ for the Ideal Bose Gas

The phase diagram for the ideal Bose gas in the (T,p) plane was considered in §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 $p = p_{\rm c}(T) = \zeta(5/2)\, k_{\rm B}T/\lambda_T^3$. We found that when the fugacity $z = \exp(\mu/k_{\rm B}T)$ is larger than one, then the density and pressure are given by

$$n(z,T) = {\rm Li}_{3/2}(z)\,\lambda_T^{-3} \qquad , \qquad p(z,T) = {\rm Li}_{5/2}(z)\,k_{\rm B}T\,\lambda_T^{-3} \quad . \tag{5.350}$$

The energy is $E = \frac{3}{2}pV$, as we obtained in eqn. 5.162.

To obtain $C_{p,N}$, we first set $dp = 0$, which is of course equivalent to setting $d\ln p = 0$:

$$d\ln p = 0 = \frac{{\rm Li}_{3/2}(z)}{{\rm Li}_{5/2}(z)}\, d\ln z + \tfrac{5}{2}\, d\ln T \quad \Rightarrow \quad \left(\frac{\partial \ln z}{\partial \ln T}\right)_p = -\frac{5\,{\rm Li}_{5/2}(z)}{3\,{\rm Li}_{3/2}(z)} \quad . \tag{5.351}$$

We wish to evaluate

$$C_{p,N} = \left(\frac{\partial E}{\partial T}\right)_{p,N} + p\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{5}{2}\,p\left(\frac{\partial V}{\partial T}\right)_{p,N} \quad . \tag{5.352}$$

Thus, we need

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_{p,N} &= \left(\frac{\partial N/n}{\partial T}\right)_{p,N} = -\frac{N}{n}\left(\frac{\partial \ln n}{\partial T}\right)_{p,N} \\ &= -\frac{N}{nT}\left\{\frac{{\rm Li}_{1/2}(z)}{{\rm Li}_{3/2}(z)}\left(\frac{\partial \ln z}{\partial \ln T}\right)_p + \frac{3}{2}\right\} = \frac{N}{nT}\left\{\frac{5\,{\rm Li}_{5/2}(z)\,{\rm Li}_{1/2}(z)}{2\,{\rm Li}_{3/2}^2(z)} - \frac{3}{2}\right\} \quad . \end{aligned} \tag{5.353}$$

Thus, we have

$$c_{p,N} \equiv \frac{N_{\rm A}\, C_{p,N}}{N} = \frac{25R}{4}\,\frac{\textsf{Li}_{5/2}(z)}{\textsf{Li}_{3/2}(z)}\left\{\frac{\textsf{Li}_{5/2}(z)\,\textsf{Li}_{1/2}(z)}{\textsf{Li}^2_{3/2}(z)} - \frac{3}{5}\right\} \quad , \tag{5.354}$$

where $R = N_{\rm A} k_{\rm B}$ is the gas constant.

As we approach the critical line $p = p_{\rm c}(T)$, the fugacity approaches unity: $z \to 1$. In this limit we have $\textsf{Li}_{3/2}(z \to 1) = \zeta(3/2)$ and $\textsf{Li}_{5/2}(z \to 1) = \zeta(5/2)$, but $\textsf{Li}_{1/2}(z \to 1)$ is divergent. We write $z \equiv \exp(-\epsilon)$, with

$$\frac{p}{p_{\rm c}(T)} = \frac{\textsf{Li}_{5/2}(z)}{\zeta(5/2)} = 1 - \zeta(3/2)\,\epsilon + \ldots \tag{5.355}$$

allows us to write

$$\epsilon = \frac{1}{\zeta(3/2)}\left(1 - \frac{p}{p_{\rm c}(T)}\right) \quad . \tag{5.356}$$

Here we have appealed to the expansion in eqn. 5.49, which also gives

$$\textsf{Li}_{1/2}(e^{-\epsilon}) = \sqrt{\pi}\left[\frac{p_{\rm c}(T) - p}{\zeta(3/2)\, p_{\rm c}(T)}\right] + \ldots \quad . \tag{5.357}$$

Thus, from eqn. 5.353, we have that $c_{p,N}$ diverges as we approach $p = p_{\rm c}(T)$ from below as

$$c_{p,N}(T,p) = \frac{25\sqrt{\pi}}{4}\,\frac{\zeta^2(5/2)}{\zeta^{5/2}(3/2)}\left(\frac{p_{\rm c}(T) - p}{p_{\rm c}(T)}\right)^{-1/2} + \ldots \quad . \tag{5.358}$$

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

$$c_{p,N}(T,p) \propto \big|p - p_{\rm c}(T)\big|^{-1/2} \quad , \quad c_{p,N}(T,p) \propto \big|T - T_{\rm c}(p)\big|^{-1/2} \quad . \tag{5.359}$$

In other words, the critical exponent is $\alpha = \frac{1}{2}$. and unlike $c_{V,N}(T,n)$ which has a cusp at $T = T_{\rm c}(n)$ yet remains finite, the specific heat at constant pressure diverges[27].

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[27] 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.