Chapter 5

Quantum Statistical Mechanics: Systems of Identical Particles

5.1 The correct enumeration of states

In the previous chapter we had seen that unphysical results can arise, if in counting the states, the particles are treated as classically distinguishable.

In a system of N *localized* spins (which have no motional degree of freedom) the individual spins are *distinguishable* since each one can be thought of as sitting on a different, distinguishable site of the lattice. This gives each spin its own identity. The lattice site can be identified in principle, e.g. by absorbing a γ quantum and thereby going to an excited state which distinguishes that site from the others.

By contrast, particles of the same kind in a gas or liquid sharing the same volume cannot be distinguished: Suppose the particles number 1 and number 2, p_1, p_2, are of the same kind, i.e. they have no internal quantum number(s) which would allow to distinguish them. Then there is no experiment - not even in principle - which would allow to distinguish the two-particle state $|a, b\rangle$ with p_1 in the single-particle state $|a\rangle$ and p_2 in the single-particle state $|b\rangle$ from the state $|b, a\rangle$ where p_1 is in the state $|b\rangle$ and p_2 is in the state $|a\rangle$. Hence the particles p_1, p_2 are indistinguishable. The states $|a, b\rangle$ and $|b, a\rangle$ can differ only by a "$-$" sign (in

3 spatial dimensions), as discussed in many-particle quantum mechanics.

As a first step, we will consider only non-interacting particles (ideal systems). The general case will be discussed in suceeding chapters.

In the correct enumeration of states for indistinguishable particles, states which "differ" only by a permutation (interchange) of particles *must not be counted as being different*. The correct counting is conveniently done not in the coordinate representation (where the coordinates and other quantum numbers are specified for each particle) but rather in the occupation number representation (where first a complete basis of single-particle states $\{|\alpha\rangle\}$ is chosen and then the number n_α of particles in each single-particle state $|\alpha\rangle$ is specified):

$$|\Phi\rangle = |n_{\alpha_1}, n_{\alpha_2}, \ldots\rangle \tag{5.1}$$

In this representation the double counting of identical states is automatically avoided.

Enumerating the states by the occupation numbers n_α is, however, difficult in the canonical ensemble, because here the total number of particles is fixed;

$$N = n_{\alpha_1} + n_{\alpha_2} + n_{\alpha_3} + \ldots, \tag{5.2}$$

and thus the summations over the occupation numbers n_{α_i} cannot be done independently of each other. Therefore, in quantum statistics, it is convenient to calculate in the grand canonical ensemble, which is equivalent in the thermodynamic limit. Since the grand canonical ensemble contains all the states with arbitrary total particle numbers, $N = 0, 1, 2, 3, \ldots, \infty$, the sums over the occupation numbers n_{α_i} are independent of each other.

5.2 The ideal Fermi gas

5.2.1 General expressions

Because of the antisymmetry of the total wave function with respect to particle exchange the occupation numbers of a single-particle state are restricted to

$n_{\alpha_i} = 0, 1$ with $i = 1, 2, \ldots$.

The total energy eigenvalues of the many-particle system are

$$E(n_{\alpha_1}, n_{\alpha_2}, \ldots) = \sum_{i=1}^{\infty} n_{\alpha_i} E_{\alpha_i} \tag{5.3}$$

where E_{α_i} = energy of the single-particle state $|\alpha_i\rangle$.

The grand canonical partition function is

$$\begin{aligned} Z_{\text{GC}} &= \sum_{\substack{n_{\alpha_i}=0,1 \\ i=1,2,3,\ldots}} e^{-\frac{E(\{n_{\alpha_i}\})-\mu N}{k_B T}} && (5.4) \\ &= \prod_{i=1}^{\infty} \left(\sum_{n_{\alpha_i}=0,1} e^{-\frac{n_{\alpha_i}(E_{\alpha_i}-\mu)}{k_B T}} \right) && (5.5) \\ &\equiv \prod_{i=1}^{\infty} Z_{\text{GC},1}(\alpha_i, \mu, T) && (5.6) \\ &= \prod_{i=1}^{\infty} \left(1 + e^{-\frac{E_{\alpha_i}-\mu}{k_B T}} \right) && (5.7) \end{aligned}$$

where $N = \sum_{i=1}^{\infty} n_{\alpha_i}$.

The grand canonical potential is:

$$\Omega = -k_B T \ln Z_{\text{GC}} = -k_B T \sum_{i=1}^{\infty} \ln Z_{\text{GC},1}(\alpha_i, \mu, T). \tag{5.8}$$

The average occupation number of the single particle state $|\alpha_i\rangle$ is computed as,

$$\begin{aligned} \langle n_{\alpha_i} \rangle &= \sum_{\substack{n_{\alpha_j}=0,1 \\ j=1,2,\ldots}} n_{\alpha_i} W_{\text{GC}}(\{\alpha_j\}) = \sum_{n_{\alpha_i}=0,1} n_{\alpha_i} \frac{e^{-\frac{n_{\alpha_i}(E_{\alpha_i}-\mu)}{k_B T}}}{Z_{\text{GC},1}(\alpha_i, \mu, T)} && (5.9) \\ &= -k_B T \frac{\partial}{\partial E_{\alpha_i}} \ln Z_{\text{GC},1}(\alpha_i, \mu, T) && (5.10) \\ &= \frac{e^{-\frac{E_{\alpha_i}-\mu}{k_B T}}}{1 + e^{-\frac{E_{\alpha_i}-\mu}{k_B T}}} \qquad = \frac{1}{e^{\frac{E_{\alpha_i}-\mu}{k_B T}} + 1} && (5.11) \end{aligned}$$

$$\boxed{\langle n_{\alpha_i} \rangle = \frac{1}{e^{\beta(E_{\alpha_i}-\mu)}+1} \equiv f(E_{\alpha_i}), \quad \beta = \frac{1}{k_B T}} \quad \text{Fermi distribution function} \tag{5.12}$$

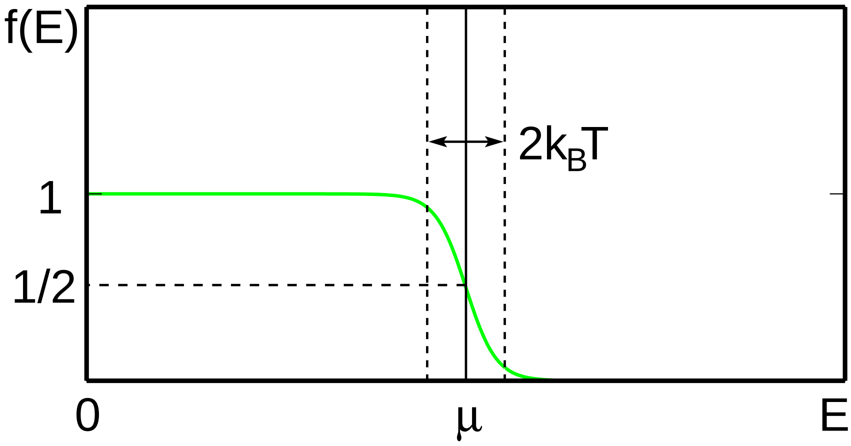

Figure 5.1: Fermi-Dirac distribution function

$$\langle n_{\alpha_i} \rangle = \frac{1}{2}\left\{1 - \tanh\left(\frac{1}{2}\beta(E_{\alpha_i}-\mu)\right)\right\} \tag{5.13}$$

$$\langle n_{\alpha_i} \rangle \xrightarrow{T\to 0} \theta(\mu - E_{\alpha_i}) \tag{5.14}$$

Note the difference:
The Boltzmann distribution $\frac{1}{Z_{\mathrm{GC}}} e^{\frac{E-\mu N}{k_B T}}$ is the probability that a *many-particle state* with energy E and average total particle number N is realized in the grand canonical ensemble.
The Fermi distribution $f_\mu(E_{\alpha_i})$ is the average occupation number $\langle n_{\alpha_i} \rangle$ (or occupation probability) of a *single-particle state* $|\alpha_i\rangle$ within a many-particle state.

The correct counting of indistinguishable particles and the restriction $n_{\alpha_i} = 0, 1$ induces the non-trivial form of $f(E_{\alpha_i})$.

In the limit $T \to 0$ $\quad \mu$ is called Fermi energy:

$$\mu(T = 0) \equiv \varepsilon_F \ . \tag{5.15}$$

According to Equation (5.15) it is the energy up to which the single-particle states are occupied in a Fermi gas with total particle number N at $T = 0$. The Fermi momentum p_F is the momentum of the highest occupied single-particle state, i.e. defined by $\varepsilon_F = p_F^2/2m$.

The chemical potential μ is determined so as to fix the average total particle number:

$$\langle N \rangle = \sum_{i=1}^{\infty} f_\mu(E_{\alpha_i}) = \int \mathrm{d}E \rho(E) f_\mu(E), \tag{5.16}$$

where $\rho(E) = \sum_{i=1}^{\infty} \delta(E - E_{\alpha_i})$ is the density of states (DOS).

This is an implicit equation for μ.

The occupation number fluctuations in state α are (with $n_\alpha^2 = n_\alpha$ for fermions),

$$\begin{aligned} \left\langle (n_\alpha - \langle n_\alpha \rangle)^2 \right\rangle &= \left\langle n_\alpha^2 \right\rangle - \langle n_\alpha \rangle^2 && (5.17) \\ &= \langle n_\alpha \rangle - \langle n_\alpha \rangle^2 && (5.18) \\ &= f(E_\alpha)\left(1 - f(E_\alpha)\right) && (5.19) \end{aligned}$$

The relative fluctuations of the total particle number are, thus,

$$\frac{\sqrt{\langle \Delta N^2 \rangle}}{\langle N \rangle} = \frac{\left[\int \mathrm{d}E \rho(E) f(E)\left(1 - f(E)\right)\right]^{1/2}}{\int \mathrm{d}E \rho(E) f(E)} \sim \frac{1}{\sqrt{V}} \overset{V \to \infty}{\longrightarrow} 0 \tag{5.20}$$

since $\rho(E) \sim V$.

This shows that grand canonical and canonical ensembles are equivalent in the thermodynamic limit $V \to \infty$: Although the formulas for physical quantities may look different in the canonical and in the grand canonical treatment, their numerical values are the same in both treatments.

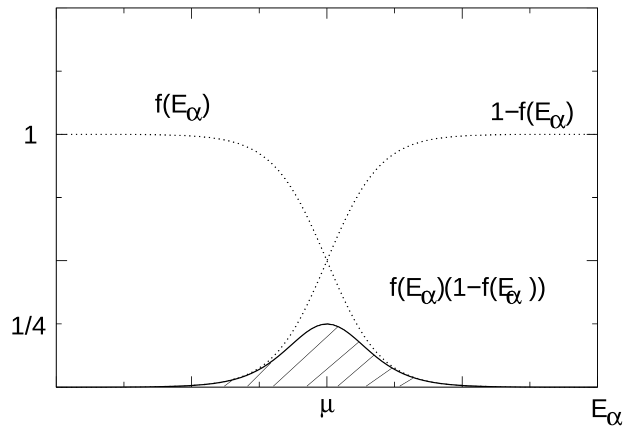

Figure 5.2: Occupation number fluctuations in a Fermi gas

Thermodynamic properties of the free electron gas

To be specific, we will consider the free electron gas with single-particle energies

$$E_{\vec{p},\sigma} = \frac{\vec{p}^2}{2m} \tag{5.21}$$
$$\vec{p} = \frac{2\pi\hbar}{L}[m_x\widehat{e}_x + m_y\widehat{e}_y + m_z\widehat{e}_z] \tag{5.22}$$
$$L = \text{system length.} \tag{5.23}$$

The DOS per spin orientation is

$$\rho_\sigma(E)\mathrm{d}E = \frac{4\pi p^2 \mathrm{d}p}{\frac{(2\pi\hbar)^3}{V}} = \frac{4\pi p^2 \left(\frac{\mathrm{d}E_{\vec{p}\sigma}}{\mathrm{d}p}\right)^{-1}}{(2\pi\hbar)^3} V\mathrm{d}E \tag{5.24}$$
$$\rho_\sigma(E) = \frac{mp(E)}{2\pi^2\hbar^3}V = V\frac{m^{3/2}}{\sqrt{2}\pi^2\hbar^3}\sqrt{E} = Vc_3\sqrt{E}. \tag{5.25}$$

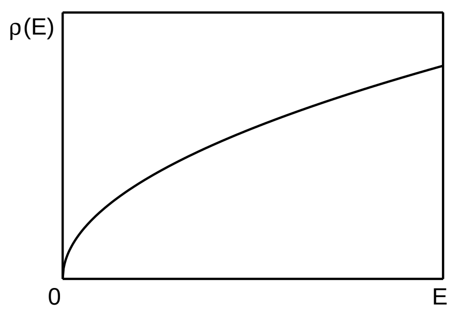

Figure 5.3: Density of states (DOS) of the free electron gas in d_3 dimensions

For the free electron gas (spin 1/2) in $d = 3$ dimensions the Fermi energy ε_F is determined by

$$N = 2Vc_3 \int_0^{\varepsilon_F} dE\sqrt{E} = 2Vc_3 \frac{2}{3}\varepsilon_F^{3/2} \tag{5.26}$$

$$\varepsilon_F = \left(\frac{3n}{4c_3}\right)^{2/3} = (3\pi^2 n)^{2/3}\frac{\hbar^2}{2m} \tag{5.27}$$

with the particle density $n = N/V$.

The density of states per spin orientation and volume is then, expressing c_3 in Eq. (5.25) using Eq. (5.27),

$$\frac{\rho_\sigma(E)}{V} = \frac{3}{4} n \frac{1}{\varepsilon_F}\sqrt{\frac{E}{\varepsilon_F}} \tag{5.28}$$

It can be expressed in units of the Fermi energy ε_F, the only characteristic energy scale of the free Fermi gas, and in terms of the particle density n only.

- **Extensitivity in the grand canonical ensemble:**
  Since $\rho_\sigma(E) \sim V$ and quantities like the grand potential Ω involving a sum over all single-particle eigenstates can be written as $\sum_\alpha(\ldots) = \sum_\sigma \int \mathrm{d}E \rho_\sigma(E)$, these quantities are explicitly extensive.

- **Entropy, internal energy and specific heat:**
Using the grand potential

$$\Omega = -k_B T \ln Z_{\mathrm{GC}} = -k_B T \sum_\alpha \ln\left(1 + e^{-\frac{E_\alpha - \mu}{k_B T}}\right) \tag{5.29}$$

the entropy of the Fermi gas is obtained as (with α =single-particle eigenstate)

$$\begin{aligned}
S &= -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} && (5.30)\\
&= k_B \sum_\alpha \left[\ln\left(1 + e^{-\frac{E_\alpha-\mu}{k_B T}}\right) + \frac{E_\alpha - \mu}{k_B T}\frac{e^{-\frac{E_\alpha-\mu}{k_B T}}}{1 + e^{-\frac{E_\alpha-\mu}{k_B T}}}\right] && (5.31)\\
&= -k_B \sum_\alpha \left[\frac{E_\alpha - \mu}{k_B T}\left[1 - f(E_\alpha)\right] + \ln\left(f(E_\alpha)\right)\right] \geq 0 && (5.32)\\
S &= -\frac{\Omega}{T} + k_B \sum_\alpha \frac{E_\alpha - \mu}{k_B T} f(E_\alpha) && (5.33)
\end{aligned}$$

The internal energy (for a fixed volume V) is then using $N = \langle N \rangle = \sum_\alpha f(E_\alpha)$ in the thermodynamic limit,

$$\begin{aligned}
U &= \Omega + TS + \mu N && (5.34)\\
&= \sum_\alpha (E_\alpha - \mu) f(E_\alpha) + \mu N = \sum_\alpha E_\alpha f(E_\alpha) = \langle E \rangle && (5.35)
\end{aligned}$$

This agrees with the expression used for calculating $\langle E \rangle$ from the average occupation numbers $f(E_\alpha)$.

The specific heat (for constant volume) is:

$$\begin{aligned}
c_V &= \left(\frac{\delta Q}{\mathrm{d}T}\right)_{V,\mu} = -T\left(\frac{\partial S}{\partial T}\right)_{V,\mu} && (5.36)\\
&= T\Bigg\{\frac{\Omega}{T^2} - k_B \sum_\alpha \frac{E_\alpha - \mu}{k_B T^2} f(E_\alpha) - \frac{1}{T}\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} && (5.37)\\
&\quad + k_B \sum_\alpha \frac{E_\alpha - \mu}{k_B T}\left(\frac{\partial f(E_\alpha)}{\partial T}\right)_{V,\mu}\Bigg\}\\
&= -S - \left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} + \sum_\alpha (E_\alpha - \mu)\frac{\partial f(E_\alpha)}{\partial T}. && (5.38)
\end{aligned}$$

where we made in equation (5.36) use of equation (5.32).

Note that in this development μ is kept constant according to the grand canonical treatment, i.e. the T-dependence of μ is *not* taken into account in taking the T derivative.

Using the general expression for the entropy, $\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = -S$ we have

$$\begin{aligned} c_V &= \sum_\alpha (E_\alpha - \mu) \frac{\partial f(E_\alpha)}{\partial T} = \left(\frac{\partial}{\partial T} \langle E - \mu \rangle\right)_{V,\mu=\text{const.}} && (5.39) \\ &= \frac{\partial}{\partial T} \langle E \rangle = \left(\frac{\partial U}{\partial T}\right)_{V,\mu} && (5.40) \end{aligned}$$

The specific heat for constant volume is the T-derivative of the (internal) energy of the system, measured relative to the (constant) chemical potential μ. Since $\langle \mu \rangle = \text{const.}(T)$, this shows that the grand canonical and the canonical calculation of c_V are equivalent.

c_V obeys the following properties:

1. $c_V \geq 0$:

$$\begin{aligned} \frac{\partial f(E)}{T} &= \left(-\left(\frac{\partial f(E)}{\partial E}\right) k_B T \cdot \frac{E-\mu}{k_B T^2}\right. && (5.41) \\ &= \underbrace{\left(-\frac{\partial f(E)}{\partial E}\right)}_{>0} \frac{E-\mu}{T} && (5.42) \\ \Rightarrow \quad c_V &= \frac{1}{T} \sum_\alpha (E_\alpha - \mu)^2 \left(-\frac{\partial f(E)}{\partial E}\right) \geq 0. && (5.43) \end{aligned}$$

2. $T = 0$ limit:

$$\begin{aligned} \left(-\frac{\partial f(E)}{\partial E}\right)_{T=0} &= -\frac{\mathrm{d}}{\mathrm{d}E} \theta(\mu - E) = \delta(E - \mu) && (5.44) \\ \Rightarrow \quad c_V (T=0) &= 0. && (5.45) \end{aligned}$$

- **Pressure:**
  In calculating the pressure $p = -(\partial\Omega/\partial V)_{T,\mu}$ from the grand potential Ω,

$$\begin{aligned}\Omega &= -k_BT\sum_\alpha \ln\left(1+e^{-\frac{E_\alpha-\mu}{k_BT}}\right) &(5.46)\\ &= -k_BT\sum_\sigma\int \mathrm{d}E_\alpha\rho_\sigma(E_\alpha)\ln\left(1+e^{-\frac{E_\alpha-\mu}{k_BT}}\right), &(5.47)\end{aligned}$$

  one can either use the first expression, taking into account the dependence of the eigenenergies on the volume V,

$$\begin{aligned} E_\alpha &= \frac{1}{2m}\frac{(2\pi\hbar)^2}{V^{2/3}}\left(n_x^2+n_y^2+n_z^2\right) &(5.48)\\ \text{with}\quad \alpha &= (n_x,n_y,n_z) &(5.49)\\ L &= V^{1/3}\,, &(5.50)\end{aligned}$$

  or the second expression, where E is a volume independent integration variable and $\rho_\sigma(E)$ is explicitly proportional to V.

  Hence, one obtains:

$$p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = -\frac{\Omega}{V} > 0 \tag{5.51}$$

  This should be compared to the pressure of the ideal Boltzmann gas:

$$p = \frac{Nk_BT}{V} = \frac{\frac{2}{3}U^{\text{classical}}}{V} \tag{5.52}$$

  with $U^{\text{classical}} = \frac{3}{2}Nk_BT$.

- **The spin susceptibility of the electron gas $\left(s=\frac{1}{2}\right)$:**
  is defined as,

$$\chi = \left(\frac{\partial M}{\partial B}\right)_{T,\mu} \tag{5.53}$$

with the spin magnetization,

$$M = 2\mu_0 \sum_{\alpha} \sigma f(E_\alpha) \tag{5.54}$$

$$= \mu_0 \sum_{\vec{k}} \left[f\left(E_{\vec{k}\uparrow}\right) - f\left(E_{\vec{k}\downarrow}\right) \right] \tag{5.55}$$

and

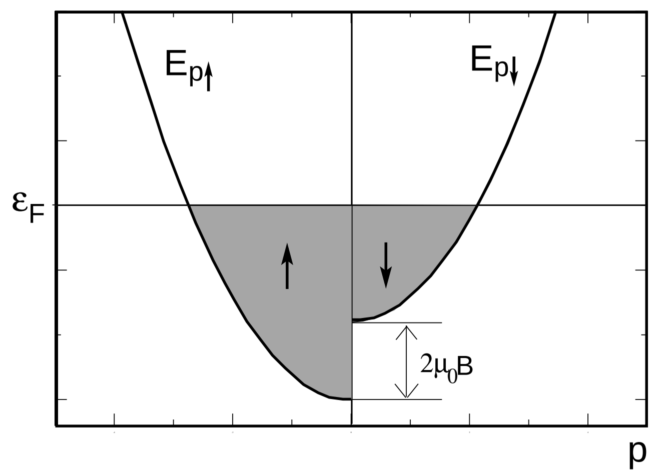

Figure 5.4: Spin magnetization of a free electron gas

$$\alpha = \left(\vec{k}, \sigma\right): \quad \text{single-particle quantum number} \tag{5.56}$$

$$\sigma = \pm\frac{1}{2}: \quad \text{spin orientation of one electron} \tag{5.57}$$

$$E_{\vec{k}\sigma} = E_{\vec{k}}(B=0) - 2\sigma\mu_0 B = E_{\vec{k}}(0) \mp \mu_0 B \tag{5.58}$$

$E_{\vec{k}\sigma}$ is the energy of an electron in the magnetic field B with Zeeman splitting $\Delta = 2\mu_0 B$

Note that orbital effects ("Lorentz force", Landau levels) have been neglected in $E_{\vec{k}\sigma}$. These would lead to diamagnetism and are not considered here.

For small magnetic field ($B \ll \varepsilon_\mathrm{F},\ k_B T$) we have:

$$
\begin{aligned}
M &= 2\mu_0^2 B \sum_{\vec{k}} \left(-\frac{\partial f\left(E_{\vec{k}}(B=0)\right)}{\partial E_{\vec{k}}} \right) + \mathcal{O}(B^3) && (5.59)\\
\chi &= 2\mu_0^2 \sum_{\vec{k}} \left(-\frac{\partial f(E_{\vec{k}})}{\partial E_{\vec{k}}} \right)\Bigg|_{B=0} = 2\mu_0^2 \int \mathrm{d}E \underset{\nearrow}{\rho(E)} \left(-\frac{\partial f}{\partial E} \right)\Bigg|_{B=0} && (5.60)
\end{aligned}
$$

DOS per spin orientation

5.2.2 The low-temperature region $k_BT \ll \varepsilon_\mathrm{F}$

From the expressions derived in section 4.2.1 it is clear that physical quantities of Fermi systems usually involve integrals over the Fermi distribution or its derivative (e.g. $\langle E\rangle$ or M).

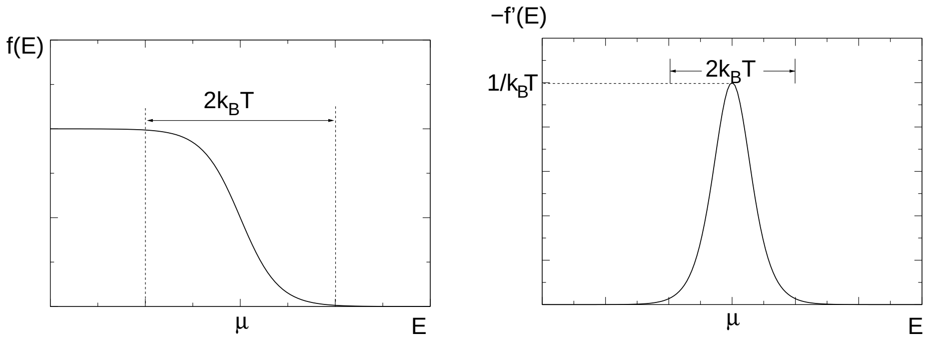

Figure 5.5: Fermi distribution and its derivative

Knowing that for $k_BT \ll \varepsilon_\mathrm{F}$ $f(E)$ is essentially a constant function except near the Fermi edge $E = \mu \approx \varepsilon_\mathrm{F}$, we see that partial integration transforms the integrand from $f(E)$ to $\frac{\partial f(E)}{\partial E}$ which is strongly peaked near $E = \mu$.

Therefore, the integrals are effectively limited to the region of width $2k_BT$ around ε_F. This demonstrates that for Fermi systems all physical properties are dominated by contributions from the Fermi edge only.

This observation can be formalized to develop a low-temperature expansion in the width $2k_BT$, the so-called *Sommerfeld expansion.*

We perform the Sommerfeld expansion for the grand potential Ω and then derive the low-T behaviour of physical quantities from it.

The expression

$$\Omega = -k_BT\sum_\sigma\int_{-\infty}^{+\infty} \mathrm{d}E\rho_\sigma(E)\ln\left[1+e^{-\frac{E-\mu}{k_BT}}\right] \tag{5.61}$$

requires one partial integration to bring out $f(E)$:

$$\Omega = -\sum_\sigma \int_{-\infty}^{+\infty} \mathrm{d}E\, a_\sigma(E) f(E) \tag{5.62}$$

$$\text{where} \qquad a_\sigma(E) = \int_{-\infty}^{E} \mathrm{d}\varepsilon\, \rho_\sigma(\varepsilon) \tag{5.63}$$

$$\frac{\partial}{\partial E} \ln\left[1 + e^{-\frac{E-\mu}{k_B T}}\right] = -\frac{1}{k_B T} f(E) \tag{5.64}$$

and the boundary terms vanish because $a(E) = 0$ for $E < 0$ (lower band edge) and $\ln\left(1 + e^{-\frac{E-\mu}{k_B T}}\right) \to 0$ for $E \to \infty$.

One more partial integration yields

$$\Omega = -\sum_\sigma \int_{-\infty}^{+\infty} \mathrm{d}E\, b(E) \left(-\frac{\partial f(E)}{\partial E}\right) \tag{5.65}$$

$$\text{with} \quad b_\sigma(E) = \int_{-\infty}^{E} \mathrm{d}\varepsilon' a_\sigma(\varepsilon') = \int_{-\infty}^{E} \mathrm{d}\varepsilon' \int_{-\infty}^{\varepsilon'} \mathrm{d}\varepsilon\, \rho_\sigma(\varepsilon). \tag{5.66}$$

The double integral $b(E)$ is a weakly varying function compared to $\frac{\partial f}{\partial E}$ for $k_B T \ll \varepsilon_\mathrm{F}$ and can therefore be expanded with respect to $E = \mu \approx \varepsilon_\mathrm{F}$:

$$b_\sigma(E) = b_\sigma(\mu) + b_\sigma'(\mu)(E-\mu) + \frac{1}{2} b_\sigma''(\mu)(E-\mu)^2 + \ldots \tag{5.67}$$

$$= b_\sigma(\mu) + a_\sigma(\mu)(E-\mu) + \frac{1}{2} \rho_\sigma(\mu)(E-\mu)^2 \tag{5.68}$$

Using the *Fermi integrals* (derived using function theory):

$$I_n = \int_{-\infty}^{+\infty} \mathrm{d}E (E-\mu)^n \left(-\frac{\partial f(E)}{\partial E}\right) \tag{5.69}$$

$$= \begin{cases} 1 & , \quad n = 0 \\ \frac{\pi^2}{3}(k_B T)^2 & , \quad n = 2 \\ \frac{7\pi^4}{15}(k_B T)^4 & , \quad n = 4 \\ 0 & , \quad n = 1, 3, 5, \ldots \end{cases} \tag{5.70}$$

We can write the Sommerfeld expansion of Ω as:

$$
\boxed{\begin{aligned} \Omega &= \sum_\sigma \left\{ -b_{\sigma(\mu)} - \frac{\pi^2}{6}\rho_\sigma(\mu)(k_B T)^2 + \mathcal{O}\left[(k_B T)^4\right] \right\} \\ &= -pV \end{aligned}} \tag{5.71}
$$

The chemical potential $\mu(T)$ is T-dependent as well (see below). However, when taking thermodynamic derivatives of Ω, μ is kept constant. Therefore one can put $\mu = \mu(0) = \varepsilon_\mathrm{F}$ in the above expression for Ω.

- **Chemical potential (for fixed particle number N)**:
  It is evident from figure 37 that $\mu(T)$ is a decreasing function if the DOS $\rho_\sigma(E)$ is a monotonically increasing function of energy E:

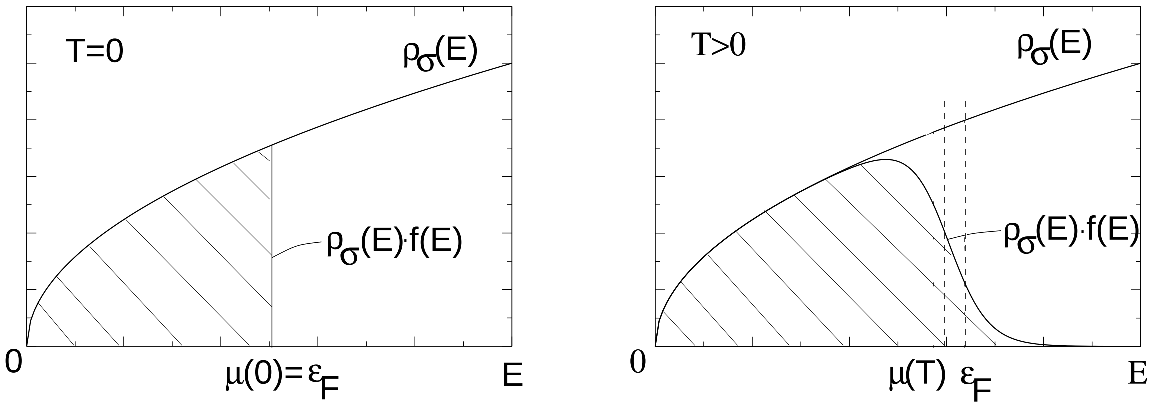

Figure 5.6: The temperature dependence of the chemical potential in a Fermi gas

The shaded area represents the particle number

$$
N = \sum_\sigma \int \mathrm{d}E \rho_\sigma(E) f(E) \tag{5.72}
$$

and must stay constant as function of T.

$$
\Rightarrow \quad \mu(T > 0) < \mu(T = 0). \tag{5.73}
$$

The low-T expansion of $\mu(T)$ follows as

$$N = \text{const.} = -\frac{\partial \Omega}{\partial \mu} = 2\left[\frac{\partial b(\mu)}{\partial \mu} + \frac{\pi^2}{6}\frac{\partial \rho(\mu)}{\partial \mu}(k_B T)^2 + \ldots\right] \tag{5.74}$$

where we have assumed spin degeneracy,

$$\begin{aligned}
b_\sigma(\mu) &\equiv b(\mu), && (5.75)\\
\rho_\sigma(\mu) &\equiv \rho(\mu), && (5.76)\\
\sum_\sigma(\ldots) &= 2(\ldots). && (5.77)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial b}{\partial \mu} &= a(\mu) && (5.78)\\
&= a(\varepsilon_{\mathrm{F}}) + a^{'}(\varepsilon_{\mathrm{F}})(\mu(T) - \varepsilon_{\mathrm{F}}) && (5.79)\\
&= a(\varepsilon_{\mathrm{F}}) + \rho(\varepsilon_{\mathrm{F}})(\mu(T) - \varepsilon_{\mathrm{F}}), && (5.80)
\end{aligned}$$

where

$$a^{'}(\varepsilon_{\mathrm{F}}) = \frac{\partial}{\partial E}\int_{-\infty}^{E} \mathrm{d}\varepsilon\, \rho(\varepsilon)\Big|_{\varepsilon_{\mathrm{F}}}, \qquad a(\varepsilon_{\mathrm{F}}) = \underset{\substack{\uparrow \\ \text{spin!}}}{\tfrac{1}{2}} \quad N \tag{5.81}$$

Inserting this into N and solving for μ we obtain:

$$0 = 2\rho(\varepsilon_{\mathrm{F}})\left(\mu(T) - \varepsilon_{\mathrm{F}}\right) + \frac{\pi^2}{3}\frac{\partial \rho(\varepsilon_{\mathrm{F}})}{\partial \varepsilon_{\mathrm{F}}}(k_B T)^2 + \mathcal{O}\left((k_B T)^4\right) \tag{5.82}$$

$$\boxed{\mu(T) = \varepsilon_{\mathrm{F}} - \frac{\pi^2}{6}\frac{1}{\rho(\varepsilon_{\mathrm{F}})}\frac{\partial \rho(\varepsilon_{\mathrm{F}})}{\partial \varepsilon_{\mathrm{F}}}(k_B T)^2 + \mathcal{O}\left((k_B T)^4\right)} \tag{5.83}$$

- **Entropy**:

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = 2\frac{\pi^2}{3}\rho(\varepsilon_{\mathrm{F}})k_B^2 T \tag{5.84}$$

explicitly extensive → Gibbs paradox resolved

- **Specific heat**:

$$\boxed{\begin{aligned} c_V &= T\left(\frac{\partial S}{\partial T}\right)_{V,\mu} \equiv S \\ &= 2\frac{\pi^2}{3}\rho(\varepsilon_{\mathrm{F}})k_B^2 T \\ &= \gamma T + \mathcal{O}(T^2) \end{aligned}} \tag{5.85}$$

The linear temperature coefficient of c_V is a measure of the DOS at the Fermi energy in a Fermi gas.
Physically: $U(t) \sim E(\text{ex. state}) \cdot n(\text{ex. states}) \sim T \cdot T \Rightarrow c_V \sim T$

- **Magnetization and spin susceptibility**:

$$M = 2\mu_0^2 B \int \mathrm{d}E\, \rho(E)\left(-\frac{\partial f}{\partial E}\right) \tag{5.86}$$

$$\rho(E) = \rho(\mu) + \rho^{'}(\mu)(E-\mu) + \frac{1}{2}\rho^{''}(\mu)(E-\mu)^2 + \dots \tag{5.87}$$

$$M = 2\mu_0^2 B\left[\rho(\mu) + \rho^{''}(\mu)\cdot\frac{\pi^2}{6}(k_B T)^2 + \mathcal{O}(T^4)\right] \tag{5.88}$$

$$\begin{aligned} &= 2\mu_0^2 B\Big[\rho(\varepsilon_{\mathrm{F}}) - \frac{\pi^2}{6}\frac{1}{\rho(\varepsilon_{\mathrm{F}})}\left[\rho^{'}(\varepsilon_{\mathrm{F}})\right]^2 (k_B T)^2 \\ &\quad + \frac{\pi^2}{6}\rho^{''}(\varepsilon_{\mathrm{F}})(k_B T)^2 + \mathcal{O}(T^4)\Big] \end{aligned} \tag{5.89}$$

$$= 2\mu_0^2 B\left[\rho(\varepsilon_{\mathrm{F}}) - \frac{\pi^2}{6}\underbrace{\left[\frac{1}{\rho(\varepsilon_{\mathrm{F}})}\left[\rho^{'}(\varepsilon_{\mathrm{F}})\right]^2 - \rho^{''}(\varepsilon_{\mathrm{F}})\right]}_{>0}(k_B T)^2\right] \tag{5.90}$$

$$\boxed{\begin{aligned}\chi &= \left(\frac{\partial M}{\partial B}\right)_{T,\mu} \\ &= 2\mu_0^2\rho(\varepsilon_\mathrm{F}) - \frac{\pi^2}{3}\left[\frac{1}{\rho(\varepsilon_\mathrm{F})}\left[\rho^{'}(\varepsilon_\mathrm{F})\right]^2 - \rho^{''}(\varepsilon_\mathrm{F})\right](k_BT)^2 \\ &= \chi(T=0) - \mathcal{O}(T^2).\end{aligned}} \tag{5.91}$$

Pauli susceptibility

For indistinguishable (mobile) fermionic spins the susceptibility is $\chi(0) = \text{const.}$ for $T \to 0$ (Pauli behaviour).

For distinguishable (localized) spins the susceptibility diverges $\chi(T) \sim \frac{1}{T}$ for $T \to 0$ (Curie behaviour)

5.2.3 The high-temperature region $k_BT \gg \varepsilon_\mathrm{F}$ (Classical or Boltzmann limit)

In the limit $T \to \infty$ the Fermi distribution

$$f(E) = \frac{1}{\exp\left((E-\mu)/k_BT\right)+1} \to \frac{1}{2} \quad \text{for all energies E} \tag{5.92}$$

which differ from μ by a *finite* amount (less than k_BT). In order to keep the average particle number finite, the chemical potential μ must therefore approach $-\infty$ faster than $-T$. This means that for any possible single-particle energy $E \geq 0$, the average occupation number of a single-particle state becomes a Boltzmann factor:

$$\boxed{f(E) = \frac{1}{e^{\frac{E-\mu}{k_BT}}+1} \xrightarrow{T\to\infty} e^{-\frac{E-\mu}{k_BT}}} \tag{5.93}$$

with $E \geq 0 \quad T \gg \varepsilon_\mathrm{F} \quad \text{or} \quad \lambda_T \ll a_0$.

Anticipating this limiting behaviour of $f(E)$, the T-dependence of μ can be given explicitly.

$$N = \sum_\sigma \int dE\ \rho_\sigma(E) f(E) \to 2\int dE\ \rho_\sigma(E) e^{-\frac{E-\mu}{k_B T}} \tag{5.94}$$

With $\rho_\sigma(E) = V\frac{m^{\frac{3}{2}}}{\sqrt{2}\pi^2\hbar^3}\sqrt{E} = V\frac{3}{4}\frac{n}{\varepsilon_F}\sqrt{\frac{\varepsilon}{\varepsilon_F}}$ in d=3 dimensions we obtain ($x = \frac{E}{k_B T}$),

$$\begin{aligned} N &= 2e^{\frac{\mu}{k_B T}}(k_B T)^{\frac{3}{2}}\frac{3}{4}\frac{Vn}{\varepsilon_F^{\frac{3}{2}}}\int_0^\infty dx\sqrt{x}e^{-x} && (5.95)\\ &= N\frac{3}{2}\frac{\sqrt{\pi}}{2}e^{\frac{\mu}{k_B T}}\left(\frac{k_B T}{\varepsilon_F}\right)^{\frac{3}{2}} && (5.96)\end{aligned}$$

and:

$$\boxed{\mu(T) = -\frac{3}{2}k_B T\ \ln\left(\left(\frac{3\sqrt{\pi}}{4}\right)^{\frac{2}{3}}\frac{k_B T}{\varepsilon_F}\right) \quad , k_B T \gg \varepsilon_F} \tag{5.97}$$

It is seen that $\mu(T) \to -\infty$ faster than -T, in agreement with the argument above.

In the high-T limit all other quantities cross over to the behaviour of the classical Boltzmann gas, using $f(E) \to e^{-\frac{E-\mu}{k_B T}} \ll 1$ for $E \geq 0$.

The grand potential Ω is:

$$\begin{aligned} \Omega &= -k_B T \cdot 2\int dE\ \rho_\sigma(E)\ln\left(1 + e^{-\frac{E-\mu}{k_B T}}\right) && (5.98)\\ &\approx -k_B T \cdot 2\int dE\ \rho_\sigma(E)e^{-\frac{E-\mu}{k_B T}} + \mathcal{O}\left(e^{-\frac{E-\mu}{k_B T}}\right)^2 && (5.99)\\ &\approx -k_B T \cdot 2\int dE\ \rho_\sigma(E) f(E) = -N k_B T && (5.100)\end{aligned}$$

Using the thermodynamic relation

$$\Omega = U - TS - \mu N \equiv -pV \tag{5.101}$$

the ideal gas follows:

$$\boxed{pV = N k_B T} \tag{5.102}$$

- **Internal energy in d=1,2,3 dimensions**

$$U \approx 2 \int dE\ \rho_{d,\sigma}(E) E \cdot e^{-\frac{E-\mu}{k_B T}} \tag{5.103}$$

with

$$\rho_{d\sigma}(E) = c_d E^{\frac{d}{2}-1} \left\{ \begin{array}{ll} \sim \sqrt{E}, & d=3 \\ \sim 0, & d=2 \\ \sim \frac{1}{\sqrt{E}}, & d=1 \end{array} \right\}. \tag{5.104}$$

Using the substitution $x = \frac{E}{k_B T}$ and the partial integration

$$\begin{aligned} \int_0^\infty dx\ d^{\alpha-1} e^{-x} &= \frac{1}{\alpha} \int_0^\infty dx\ \frac{d}{dx} x^\alpha e^{-x} && (5.105) \\ &= \frac{1}{\alpha} \int_0^\infty dx\ x^\alpha e^{-x} && (5.106) \end{aligned}$$

U can be reduced to the integral of the particle number (with $\alpha = \frac{d}{2}$)

$$\boxed{U = (k_B T) \frac{d}{2} 2 \int dE\ c_d\, E^{\frac{d}{2}-1} e^{-\frac{E-\mu}{k_B T}} = \frac{d}{2} N k_B T}\,, \tag{5.107}$$

in agreement with expression for classical gas.

- **Entropy**
Since in the grand canonical ensemble the particle number N is not a fixed quantity, its T-dependence for fixed μ must be taken into account when taking the T-derivative

$$\begin{aligned} S &= -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = \frac{d}{dT}(N k_B T) = N k_B + k_B T \left(\frac{\partial N}{\partial T}\right)_{V,\mu} && (5.108) \\ &= N k_B + k_B T \int dE\ \rho_\sigma(E) \frac{\partial}{\partial T} \left(e^{\frac{E-\mu}{k_B T}}\right)_{V,\mu} && (5.109) \\ &= N k_B + \int dE\ \rho_\sigma(E) \frac{E-\mu}{T} e^{-\frac{E-\mu}{k_B T}} && (5.110) \\ &= N k_B + \frac{U}{T} - \frac{\mu}{T} N && (5.111) \end{aligned}$$

$$\boxed{S = N k_B \left[\frac{d}{2} + 1 - \frac{\mu}{k_B T}\right] \equiv \frac{d}{2} N k_B \ln\left(\frac{k_B T}{\varepsilon F}\right) + const.} \tag{5.112}$$

where the first term ist the grand canonical expression with $N = N(T, V, \mu)$ and the second term is the canonical expression with $N = const.$

- **Specific heat**

(a) *Grand canonical evaluation* (process with changing $N, \mu = const.$)

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_{V,\mu} = T\left(\frac{\partial N}{\partial T}\right)_{V,\mu} k_B\left[\frac{d}{2}+1-\frac{\mu}{k_BT}\right]+Nk_B\frac{\mu}{k_BT} \quad (5.113)$$

Note concerning thermodynamic derivatives:

In $\frac{\partial}{\partial T}$ μ is kept const. according to the grand canonical ensemble.
With $\left(\frac{\partial N}{\partial T}\right)_{V,\mu}$ as above:

$$\begin{aligned} c_V &= \left(\frac{U}{T}-\frac{\mu}{T}N\right)\left[\frac{d}{2}+1-\frac{\mu}{k_BT}\right]+Nk_B\frac{\mu}{k_BT} && (5.114)\\ &= Nk_B\left[\frac{d}{2}\left(\frac{d}{2}+1\right)-d\frac{\mu}{k_BT}+\frac{\mu^2}{(k_BT)^2}\right] && (5.115)\end{aligned}$$

$$\boxed{c_V = \frac{d}{2}\left(\frac{d}{2}+1\right)Nk_B + \mathcal{O}\left(\frac{1}{T}\right)} \quad (5.116)$$

By increasing T the Fermi gas takes up additional energy, if there is particle exchange with $\mu = const.$

(b) **Canoncial evaluation**
Alternatively, we can conceive the expression for S as obtained in the canonical ensemble, i.e. we keep N fixed, but take the T-dependence of $\mu(T)$ into account in $\frac{\partial}{\partial T}$. Then we have

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = T\frac{\partial}{\partial T}\left(\frac{d}{2}Nk_B\ln\frac{k_BT}{\varepsilon_F}\right) = \frac{d}{2}Nk_B \equiv \left(\frac{\partial U}{\partial T}\right)_{V,N} \quad (5.117)$$

in explicit agreement with the classical result.

- **Spin susceptibility and magnetization**

$$
\begin{aligned}
M &= 2\mu_0^2 B \int dE\ \rho_\sigma(E) \left(-\frac{\partial f}{\partial E}\right) && (5.118)\\
&\approx 2\mu_0^2 B \int dE\ \rho_\sigma(E) \frac{1}{k_B T} e^{-\frac{E-\mu}{k_B T}} && (5.119)\\
&= 2N\mu_0^2 B \frac{1}{k_B T} && (5.120)\\
X(B=0) &= \left(\frac{\partial M}{\partial B}\right)_{B=0} = 2N\frac{\mu_0^2}{k_B T} && (5.121)
\end{aligned}
$$

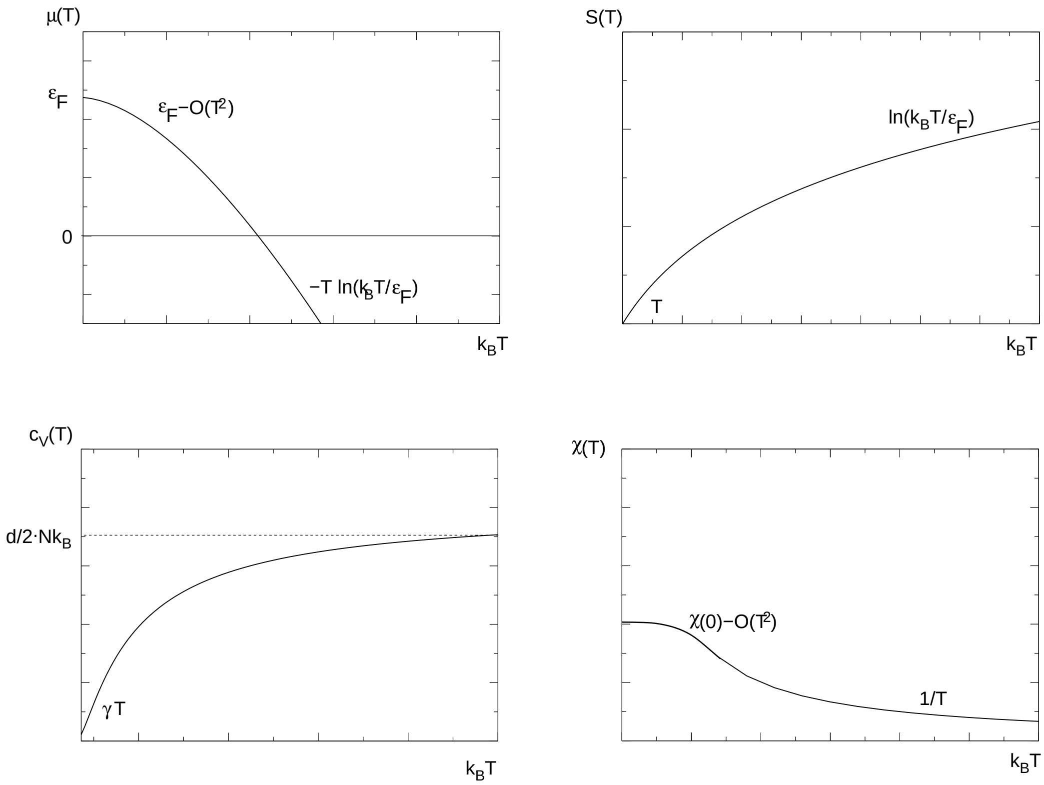

Figure 5.7: T-dependence of $\mu(T), S(T), c_V(T), and \chi(T)$

5.3 The ideal Bose gas

Fermion number conservation and Boson number non-conservation:
In any closed system there does not exist any interaction process which would only create or destroy a single fermion, because this would change the total angular momentum J of the system by a half-integer value, while J is a conserved quantity (Fermion number conservation). Therefore, in an isolated system the fermion number N is fixed (canonical ensemble) and in a system with particle number $\langle N \rangle$ is fixed by means of the Lagragne multiplier μ (grand canonical ensemble). This has been naturally assumed in section 4.2.
By contrast, creating or destroying a boson changes the total angular momentum J=L+S by an integer value. This can be compensated by a corresponding integer change of the orbital angular momentum $\vec{L}$ of the system. Hence, it is not forbidden that a bosonic particle is destroyed or created, e.g. absorbed or emitted by the wall of the container. The (integer) spin of the boson is then taken up as an orbital angular momentum of the container.
Indeed, there exists two types of bosonic particles, (1) those with conserved particle number N, whose average number $\langle N \rangle$ is fixed by a chemical potential μ in the grand canonical ensemble, and (2) those whose particle number is not conserved and which, therefore, do not have a chemical potential, i.e. $\mu = 0$ in the grand canoncial ensemble. These different constraints lead to different thermodynamical behaviour.

Statistical behaviour of particles:

1. *Fermions* (half integer spin):
   $n_\alpha = 0, 1$ occupation number of single-particle state
   N conserved implied by angular momentum conservation
   $\rightarrow \mu(T)$

   Examples: Electrons, atoms with half-integer total spin, ^{3}He, neutrons

2. *Bosons* (integer spin)
   $n_\alpha = 0, 1, 2, ...$

   (a) N conserved in a physical process
   $\rightarrow \mu(T)$

Example: Atoms, ^{4}He

(b) N not conserved
$\mu \equiv 0$

Example: Photons, oscillator quanta of a h.o. (phonons), quantized collective excitations in a solid (magnons etc.)

5.3.1 Bosons with conserved particle number: Bose-Einstein condensation

We calculate the grand canonical partition sum with arbitrary occupation number n_{α_i} of the single-particle states $|\alpha_i\rangle$ with energies E_{α_i}

$$\begin{aligned} Z_{GC} &= \sum_{n_{\alpha_i}=0,1,2,..} e^{-\frac{\sum_{j=1}^{\infty}(E_{\alpha_j}-\mu)n_{\alpha_j}}{k_BT}} && (5.122)\\ &= \prod_{i=1}^{\infty}\sum_{n=0}^{\infty} e^{-\frac{(E_{\alpha_i}-\mu)n}{k_BT}} && (5.123)\\ &= \prod_{i=1}^{\infty}\frac{1}{1-e^{-\frac{E_{\alpha_i}-\mu}{k_BT}}} \equiv \prod_{i=1}^{\infty} Z_{GC,1}(\alpha_i) && (5.124)\end{aligned}$$

i.e. Z_{GC} factorizes again into a product of the single-particle partition sums

$$\boxed{Z_{GC,1}(\alpha_i) = \sum_{n=0}^{\infty} e^{-\frac{(E_{\alpha_i}-\mu)n}{k_BT}} = \frac{1}{1-e^{-\frac{E_{\alpha_i}-\mu}{k_BT}}}} \qquad (5.125)$$

In order for this geometrical series to converge, one must have

$$E_{\alpha_i} - \mu \geq 0 \qquad \forall\, |\alpha_i\rangle \qquad (5.126)$$

which means for $E_{\alpha_i} \in [0, \infty[$:

$$\boxed{\mu(T) \leq 0} \quad \text{for bosonic systems} \qquad (5.127)$$

The grand potential is

$$\Omega = -k_B T \ln Z_{GC} = -k_B T \ln \left(\frac{1}{1 - e^{-\frac{E_\alpha - \mu}{k_B T}}} \right) \tag{5.128}$$

$$\boxed{\Omega = k_B T \sum_\alpha \ln \left(1 - e^{-\frac{E_\alpha - \mu}{k_B T}} \right)} \tag{5.129}$$

The sum runs over all single-particle states.

The average occupation number of the single-particle state $|\alpha_i\rangle$ is

$$\langle n_{\alpha_i} \rangle = \sum_{\substack{n_{\alpha_j}=0 \\ j=0,1,2,..}}^{\infty} n_{\alpha_i} \underbrace{\prod_{k=0}^{\infty} \frac{e^{-\frac{E_{\alpha_k}-\mu}{k_B T} n_{\alpha_k}}}{Z_{GC,1}(\alpha_k)}}_{W_{GC}(\{n_{\alpha_k}\})} \tag{5.130}$$

$$= \sum_{n_{\alpha_i}=0}^{\infty} n_{\alpha_i} \frac{e^{-\frac{E_{\alpha_i}-\mu}{k_B T} n_{\alpha_i}}}{Z_{GC,1}(\alpha_i)} \tag{5.131}$$

$$= -\frac{\partial}{\partial(\beta(E_{\alpha_i} - \mu))} \ln Z_{GC,1}(\alpha_i) \tag{5.132}$$

$$\boxed{\langle n_{\alpha_i} \rangle = \frac{1}{e^{\frac{E_{\alpha_i}-\mu}{k_B T}} - 1} \equiv b(E_{\alpha_i})} \quad \text{Bose-Einstein distribution} \tag{5.133}$$

The *entropy* and the *internal energy* are

$$S = -\left(\frac{\partial \Omega}{\partial T} \right)_{V,\mu} = -\frac{\Omega}{T} + \sum_\alpha \frac{E_\alpha - \mu}{T} b(E_\alpha) \tag{5.134}$$

$$U = \Omega + TS + \mu N = \sum_\alpha (E_\alpha - \mu)\, b(E_\alpha) = \sum_\alpha E_\alpha\, b(E_\alpha) \tag{5.135}$$

with

$$N = \sum_\alpha b(E_\alpha). \tag{5.136}$$

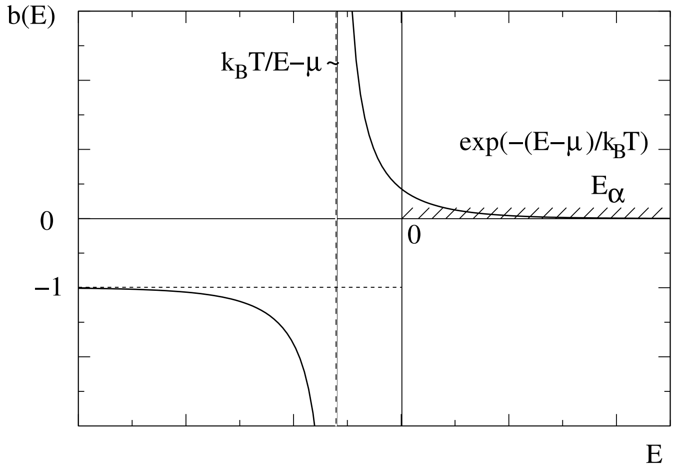

Figure 5.8: Bose-Einstein distribution function

T-dependence of the chemical potential $\mu(T)$ and Bose-Einstein condensation

We expect generally that quantum effects due to indistinguishability become important when the wavelength $\lambda_T = \frac{2\pi}{k}$ of a particle with typical thermal excitation energy $E_k = \frac{(\hbar k)^2}{2m} = k_B T$ becomes longer than the average spacing a_0 between the particles, i.e. when the thermal wavelength

$$\lambda_T = \frac{2\pi\hbar}{\sqrt{2mk_BT}} \gtrsim a_0 = \left(\frac{V}{N}\right)^{\frac{1}{3}} = n^{-\frac{1}{3}} \quad (*) \tag{5.137}$$

the condition for quantum behaviour.

This is because the length scale within which a particle can be localized in principle by a scattering experiment is at best its wavelength λ_T.
If $\lambda_T < a_0$ the particles can be identified in space (by a scattering experiment), i.e. they behave classically as distinguishable particles.
If $\lambda_T \geq a_0$ the regions in which a particle can be localized necessarily overlap, the particles become indistinguishable and quantum statistical effects become important.

$$\left[\begin{array}{lll} \text{Fermi system:} & \lambda_T \gg a_0 & \text{degenerate Fermi gas} \\ \text{Bose system:} & \lambda_T \gg a_0 & \text{Bose condensation} \end{array}\right]$$

Note: The wave functions still penetrate each other for $\lambda_T < a_0$, since they are

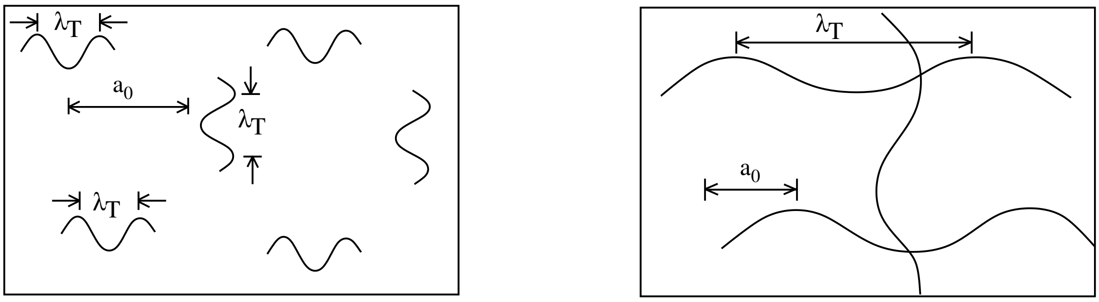

Figure 5.9: Classical regime $\lambda_T < a_0$ and quantum regime $\lambda_T > a_0$ of a gas

extended over the whole system, but a scattering experiment can localize them.

For low temeratures, deep in the quantum regime of a Bose gas (spin 0) we have

$$\lambda_T \gg a_0 \quad \text{or} \quad k_B T \ll \frac{2\pi\hbar^2}{2ma_0^2} \tag{5.138}$$

and the particle density is

$$n = \frac{N}{V} = \frac{1}{V}\sum_k \frac{1}{e^{\frac{E_k-\mu}{k_BT}}-1} \tag{5.139}$$

$$\overset{V\to\infty}{=} \frac{N_0(T)}{V} + \frac{1}{V}\int_0^\infty dE\ \rho(E)\frac{1}{e^{\frac{E-\mu}{k_BT}}-1} \tag{5.140}$$

where $N_0(T) = \langle n_{k=0}\rangle$ is the occupation number of the lowest single-particle state ($\vec{k}=0, \vec{E}_k = 0$ for a free Bose gas).

In going over to the thermodynamic limit, $V \to \infty$, the energies $E_{\vec{k}}$ become continuous and the sum $\sum_k$ can be replaced by the integral $\int_0^\infty dE\ \rho(E)(...)^n$, *if* the spacing of successive energy levels $\Delta E_k \ll E_k$. In the thermodynamic limit this is always achieved for $E_k > 0$, since $\Delta E_k \sim \frac{1}{V}$.

However, it can never be achieved for the lowest state $E_0 = 0$. Therefore, the occupation number n of the $E_0 = 0$ state must be counted separately in the above expression. For massive bosons (m>0) in d=3 dimensions $\rho(E) = Vc_3\sqrt{E}$ (as for electrons), and one can estimate the number of particles in the *excited* states as

$$
\begin{aligned}
N_{ex} &= \int dE\, \rho(E) \frac{1}{e^{\frac{E-\mu}{k_B T}} - 1} \leq \int dE\, \rho(E) \frac{1}{e^{\frac{E}{k_B T}} - 1} && (5.141) \\
&= V c_3 (k_B T)^{\frac{3}{2}} \int_0^{\infty} dx \underbrace{\frac{\sqrt{x}}{e^x - 1}}_{\sqrt{x} e^{-x}(1+e^{-x}+..)} \quad \left(\text{using } \lambda_T^3 = \frac{2\pi}{c_3^3}\right) && (5.142) \\
&= \frac{2\pi V}{\lambda_T^3} \zeta\left(\frac{3}{2}\right) \approx 2,612\, \frac{2\pi V}{\lambda_T^3} \sim T^{\frac{3}{2}} \stackrel{T \to 0}{\longrightarrow} 0! && (5.143)
\end{aligned}
$$

For high T ($\lambda_T \ll a_0$) the total number of particles in excited states is $N_{ex} \gg n_0$,

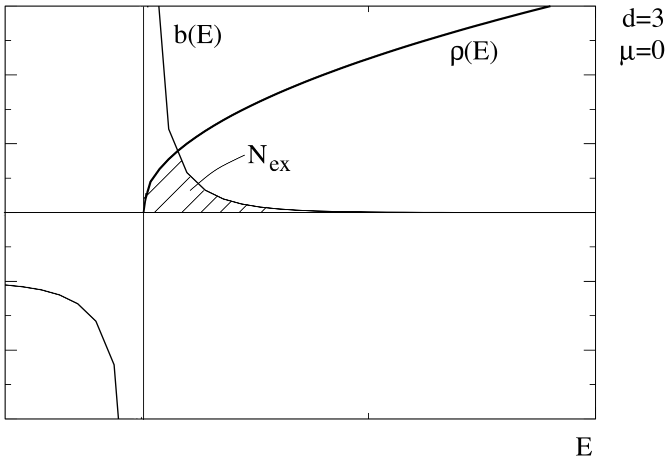

Figure 5.10: Number of particles N_{ex} in the excited single-particle states of a free Bose gas

i.e. $n_0 \approx 1 \approx V$ (non-extensive) and can be neglected for $V \to \infty$.

Then $N = N_{ex}$ for $V \to \infty$. However, below a critical temperature $T < T_0$ the fixed N particles of the system cannot all be fit into the excited states, and n_0 must become an extensive quantity $N_0 \sim V$, i.e. the lowest single-particle state (single-particle ground state) becomes macroscopically occupied.

$$
n = \frac{N_0}{V} + \frac{2\pi}{\lambda_T^3} \zeta\left(\frac{3}{2}\right) = \frac{N}{V} \equiv \frac{1}{a_0^3} \tag{5.144}
$$

Thus, one obtains for the ground state occupation

$$\boxed{n_0 \equiv \frac{N_0}{V} = n\left[1 - 2\pi\zeta\left(\frac{3}{2}\right)\frac{a_0^3}{\lambda_T^3}\right] = n\left[1 - \left(\frac{T}{T_0}\right)^{\frac{3}{2}}\right]} \tag{5.145}$$

with $\lambda_T = \frac{2\pi\hbar}{\sqrt{2mk_BT}}$ and $T < T_0$.

Hence, the critical temperature T_0 below which $n_0 = \left.\frac{N_0}{V}\right|_{V\to\infty} > 0$ is

$$\left(\frac{T}{T_0}\right)^{\frac{3}{2}} = 2\pi\zeta\left(\frac{3}{2}\right)\left(\frac{a_0}{\lambda_T}\right)^3 \tag{5.146}$$

$$\boxed{k_BT_0 = \frac{1}{\left[2\pi\zeta\left(\frac{3}{2}\right)\right]^{\frac{2}{3}}}\frac{\hbar^2\left(\frac{2\pi}{a_0}\right)^2}{2m}} \quad \text{Bose-Einstein condensation temperature} \tag{5.147}$$

The state in which the single-particle ground state is macroscopically occupied, i.e. its occupation number scales with the system volume, $n_0 = \frac{N_0}{V} > 0$, is called *Bose-Einstein-condensate*. The T-dependence of the chemical potential for $T \geq T_0$ is extracted from the condition

$$N = \int d\varepsilon\, \rho(\varepsilon) b(\varepsilon) = const. \tag{5.148}$$

by implicit differentiation:

$$0 = \int d\varepsilon\, \rho(\varepsilon)\frac{db}{dT} = \int d\varepsilon\, \rho(\varepsilon)\frac{-e^{\frac{E-\mu}{k_BT}}}{\left(e^{\frac{E-\mu}{k_BT}} - 1\right)^2}\left[-\frac{\varepsilon-\mu}{k_BT^2} - \frac{\frac{d\mu}{dT}}{k_BT}\right] \tag{5.149}$$

$$\frac{d\mu}{dT} = -\frac{1}{T}\frac{\int d\varepsilon\, \rho(\varepsilon)\frac{\varepsilon-\mu}{4\sinh^2\left(\frac{(\varepsilon-\mu)}{2k_BT}\right)}}{\int d\varepsilon\, \rho(\varepsilon)\frac{1}{4\sinh^2\left(\frac{(\varepsilon-\mu)}{2k_BT}\right)}} \quad (\text{for } T \to T_c + 0,\ \mu \to 0 - 0) \tag{5.150}$$

$$\to -\frac{1}{T}\frac{\int_0^\infty d\varepsilon\, \varepsilon^{\frac{3}{2}}\frac{1}{\sinh^2\left(\frac{\varepsilon}{2k_BT_c}\right)}}{\int_0^\infty d\varepsilon\, \varepsilon^{\frac{1}{2}}\frac{1}{\sinh^2\left(\frac{\varepsilon}{2k_BT_c}\right)}} = 0 \tag{5.151}$$

2nd implicit differentiation yields a finite value of $\frac{d^2\mu}{dT^2} < 0$ at $T = T_c$. For $T \to +\infty$ $b(\varepsilon) \to e^{-\frac{\varepsilon-\mu(T)}{k_B T}}$ for the same reason as for fermions, and $\mu(T) \to -T \ln T$ takes on the same classical behavior.

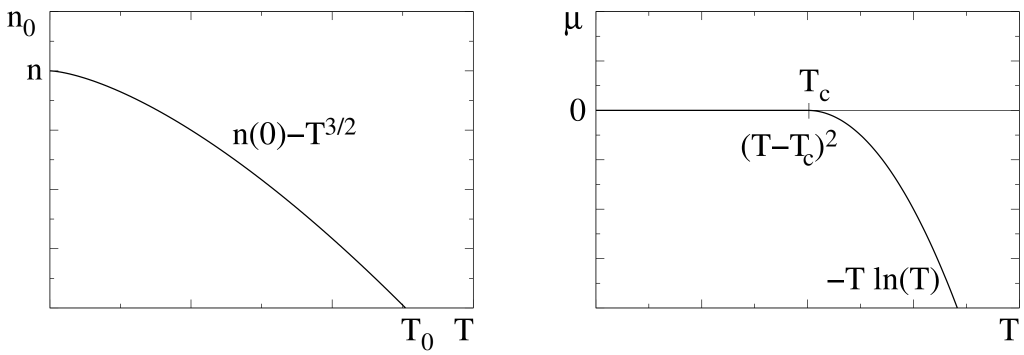

Figure 5.11: Verlauf μ gegen T

Properties of the Bose-Einstein-condensate

1. The Bose condensation transition occurs when $\lambda_T \approx a_0$, i.e. when the bosons become indistinguishable in space. This can be seen from equation (**).

2. The Bose condensate is described by a *macroscopic wave function* $\psi_0(\vec{x})$ with a *single*, macroscopic phase ϕ:
   In position representation, the condensate state $|n_0\rangle$ is a simple product wave function

$$\psi_0(x_1, \ldots, x_{N_0}) = \langle x_1 \ldots x_{N_0} | n_0 \rangle \tag{5.152}$$

$$= \prod_{i=1}^{N_0} \varphi_0(x_i) e^{i\phi_i} \tag{5.153}$$

$$= e^{i \sum_{i=1}^{N_0} \phi_i} \prod_{i=1}^{N_0} \varphi_0(x_i) \tag{5.154}$$

   where $\varphi_0(x_i)e^{i\phi_i}$ is the ground state wave fuction of particle i with

- an arbitrary phase ϕ_i
- $\varphi_0(x)$ the same wave function for all particles and
- $\phi = \sum_{i=1}^{N_0} \varphi_i$ the macroscopic phase.

The expectation value of any single-particle operator $\widehat{F}(x_1, \ldots, x_{N_0}) = \sum_{i=1}^{N_0} \widehat{f}(x_i)$ in the condensate is

$$\langle\psi_0\{x_i\}| \sum_i \widehat{f}(x_i)|\psi_0\{x_i\}\rangle = N_0\langle\varphi_0(x)|\widehat{f}(x)|\varphi_0(x)\rangle \; . \tag{5.155}$$

Therefore, $\psi_0\{x_i\}$ can be written as

$$\boxed{\psi_0(x) = \sqrt{N_0}e^{i\phi}\varphi_0(x)} \tag{5.156}$$

with a single, macroscopic coordinate x and a macroscopic phase ϕ.
$\psi_0(x)$ is normalized to N_0, the occupation number of the condensate. It leads to the same expectation values of single-particle operators as the many-particle wave function of the condensate.[1]

3. The Bose condensation depends on the spatial dimension. For massive particles, $E_p = \frac{p^2}{2m}$, there is no condensation transition in $d = 1, 2$ for $T > 0$:
   In dimensions $d = 1, 2$ the integral

   $$N_{ex} = Vc_d \int_0^\infty d\varepsilon\, \varepsilon^{\frac{d}{2}-1} \frac{1}{e^{\frac{\varepsilon}{k_B T}}-1} \tag{5.157}$$

   diverges, i.e. an arbitrary number of particles can be put into the excited states, and the ground state is not macroscopically occupied for any finite temperature $T > 0$.

4. The place wherence of all particles in the condensate implies that there is no scattering in the condensate; the condensate has viscosity 0.

Entropy and specific heat of the Bose gas
Grand canonical potential:

$$\Omega = k_B T \int dE\, \rho(E) \ln\left(1 - e^{-\frac{E-\mu}{k_B T}}\right) \tag{5.158}$$

[1] For a free Bose gas $\varphi_0(x)$ is the $\vec{k} = 0$ wave function, $\varphi_0(x) = const.$, and $\psi_0(x) \equiv \psi_0$ is a single complex number.

Entropy:

$$
\begin{aligned}
S &= -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} && (5.159)\\
&= -k_B \int dE\,\rho(E)\ln\left(1-e^{\frac{E-\mu}{k_B T}}\right) && (5.160)\\
&\quad -k_B T \int dE\,\rho(E)(-b(E))\left(\frac{E-\mu}{k_B T^2}\right) && (5.161)\\
&= -\frac{\Omega}{T}+\frac{\langle E\rangle}{T}-\frac{\mu}{T}N && (5.162)
\end{aligned}
$$

in agreement with the general thermodynamic relation $\Omega = U - TS - \mu N$.

For $T < T_0$ only the excited states contribute to the entropy, since the condensate state ψ_0 is unique and, thus, has entropy $S_0 = 0$. Therefore, the summation over states in the above expression can be written as an integral, neglecting the ground state. One can show for massive particles with dispersion $E_p = \frac{p^2}{2m}$ in $d = 3$ dimensions ($\rho(E) \sim \sqrt{E}$):

$$S(T) \sim T^{\frac{3}{2}} \qquad \text{for } T \to 0. \tag{5.163}$$

The specific heat for fixed volume V and particle number N is

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} \tag{5.164}$$

Remark:

In calculating S from the grand canonical potential Ω, μ is kept fixed (i.e. not differentiation wrt. T), since Ω is a function of μ by definition (thermodynamic derivative). S is a general function of T, both through the explicit dependence and through the implicit dependence of $\mu(T)$ on T. In calculating c_V one can, therefore choose to keep N fixed (as is usually done) and differentiate $\frac{\partial\mu}{\partial T}$. Since $\frac{\partial^2\mu}{\partial T^2} = \begin{cases} 0 & , \quad T < T_0 \\ < 0 & , \quad T > T_0 \end{cases}$ discontinuous at $T = T_0$, the T-derivative of c_V has a discontinuity at the condensation transition:

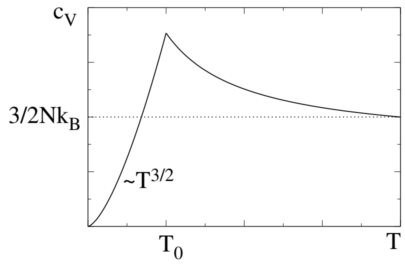

Figure 5.12: Verlauf c_V gegen T

5.3.2 Bosons without particle number conservation: Black body radiation

Photons are an example of bosons (spin 1) which can be absorbed or emitted e.g. by the walls of a container, i.e. whose particle number is not conserved: $\mu = 0$. A body which can absorb or emit photons with equal probability for *all frequencies* is called *black body*. We consider a system of photons (the electromagnetic field) in thermodynamic equilibrium with a black body at temperature T and calculate its spectral energy density $\frac{dE_\omega}{d\omega}|_\omega$, i.e. the energy content dE_ω in a given photon frequency interval $d\omega$ at frequency ω:

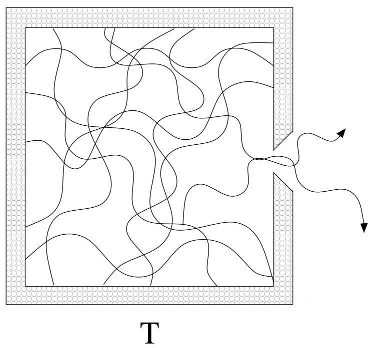

Figure 5.13: Black body radiation

For $d = 3$ and $\omega = ck$ the photon density of states is

$$\rho(\omega)d\omega = \underbrace{2}_{\text{Polarization}} \frac{4\pi k^2}{\frac{(2\pi)^3}{V}} \cdot dk = V\frac{\omega^2}{\pi^2 c^3} d\omega \tag{5.165}$$

and with $x = \frac{\hbar\omega}{k_B T}$

$$\Omega = V\frac{(k_B T)^4}{\pi^2(\hbar c)^3} \underbrace{\int_0^\infty dx\, x^2 \ln[1 - e^{-x}]}_{-\frac{\pi^4}{45}} = -\gamma V T^4 \tag{5.166}$$

with $\gamma = \frac{\pi^2 k_B^4}{45(\hbar c)^3}$. The pressure of the photon gas (radiation pressure) is

$$P_{ph} = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = -\gamma T^4 \,, \tag{5.167}$$

and the spectral energy density

$$\boxed{\frac{dE_\omega}{d\omega} = \rho(\omega)\hbar\omega b(\hbar\omega) = V\frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1}} \tag{5.168}$$

The radiation law has been historically one of the first signatures of the quantum

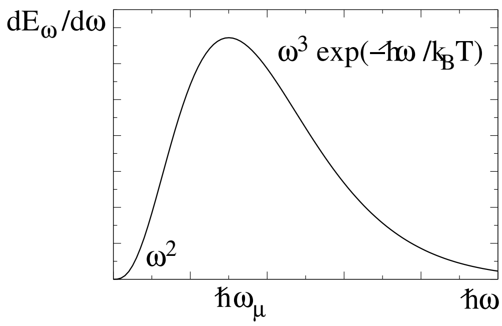

Figure 5.14: Planck's radiation law with maximum at $\hbar\omega_M = 2.822\, k_B T$

nature of light. It lead Planck to postulate the light quantum with energy $\hbar\omega$ for light of frequency ω.
Measuring the Planck radiation law of e.g. light from a distant star, one can measure the star's surface temperature.