3.2 Using annihilation and creation operators

We can go on without algebraic devices to compute various expectation values, but in any case, we must be familiar with the so-called second quantization formalism, so the needed device is introduced in the most efficient way.

Since we are studying indistinguishable particle systems, any microstate may be uniquely specified by the occupation numbers \( n_k \) of one particle energy states \( k \). That is, \( \{n_k\} \) is a complete specification of a microstate of the system. Let us introduce a normalized ket \( |n_k\rangle \) describing the state that the one-particle \( k \)-th energy level is occupied by \( n_k \) particles. All the possible states allowed to the \( k \)-th single energy level is completely described by \( n_k \) and the states with different occupation numbers can never be observed simultaneously, so we may assume that \( \{|n_k\rangle \}_{n_k=0,1,...} \) is an orthonormal complete set to describe this single energy level system. If we introduce a direct product ket \( \{|n_k\rangle = |n_1\rangle|n_2\rangle \cdots \) , we may assume that the totality of such kets makes a complete orthonormal system for the whole system. To describe the microstates choosing these kets as the basis is called number representation.

Consider a representative single one-particle energy level (the state name \( k \) is omitted for simplicity), and write the state with \( n \) particles on that level to be \( |n\rangle \) without a suffix for simplicity. Let us define\(^7\) a linear operator called the creation operator \( a^+ \) by

\[
a^+|n\rangle = c_{n+1}|n+1\rangle.
\]

(3.2.1)

Here, \( c_{n+1} \) is a complex number we can choose conveniently. The adjoint of \( a^+ \) is denoted by \( a \):

\[
\langle n|a = c_{n+1}^*\langle n+1|.
\]

(3.2.2)

(3.2.1) and (3.2.2) yield

\[
\langle n|a|n+1\rangle = c_{n+1}^*\langle n+1|n+1\rangle = c_{n+1}^*.
\]

(3.2.3)

For other combinations of bras and kets, this is zero. Therefore, \( a|n+1\rangle \) must be parallel to \( |n\rangle \): to be consistent with (3.2.3):

\[
a|n+1\rangle = c_{n+1}^*|n\rangle.
\]

(3.2.4)

\(^7\)A linear operator on a certain vector space is defined if we specify all the matrix components with respect to a complete orthonormal set like \( \{|n\rangle \} \). Thus, we can freely design an operator. Of course, whether it is useful or not is another matter.
This implies that $a$ may be called the *annihilation operator*. Since we cannot remove any particle from $|0\rangle$, we demand $c_0 = 0$:

$$a|0\rangle = 0.$$  \hspace{1cm} (3.2.5)

(3.2.1) and (3.2.4) imply

$$a^+ a |n\rangle = |c_n|^2 |n\rangle.$$  \hspace{1cm} (3.2.6)

**Boson case**

Now, we assume that $n$ is without upper bound, so $\{|n\rangle\}_{n \in \mathbb{N}}$ makes a complete orthonormal set. To define the operators we can freely choose $\{c_n\}$. A convenient choice is $c_n = \sqrt{n}$

$$a^+ a |n\rangle = n|n\rangle.$$  \hspace{1cm} (3.2.7)

With this choice $\hat{n} = a^+ a$ is called the *number operator*. We see

$$aa^+ - a^+ a = [a, a^+] = 1.$$  \hspace{1cm} (3.2.8)

We can summarize the boson annihilation and creation operator as follows:

$$a^+ |n\rangle = \sqrt{n + 1} |n + 1\rangle,$$

$$a|n\rangle = \sqrt{n} |n - 1\rangle,$$

$$\hat{n} = a^+ a.$$  \hspace{1cm} (3.2.9 - 3.2.11)

The following commutation relations are useful:

$$[a, a^+] = 1, \ [a, a] = [a^+, a^+] = 0.$$  \hspace{1cm} (3.2.12)

**Fermion case**

Pauli’s principle tells us that $\{|0\rangle, |1\rangle\}$ is a complete set, so we may regard this as a complete orthonormal set. We may introduce a creation operator $a^+$ by

$$a^+ |0\rangle = |1\rangle, \ a^+ |1\rangle = 0.$$  \hspace{1cm} (3.2.13)

The adjoint becomes an annihilation operator

$$a|0\rangle = 0, \ a|1\rangle = |0\rangle.$$  \hspace{1cm} (3.2.14)

This defines $a$ and $a^+$ completely. We could write as

$$a^+ |n\rangle = \sqrt{1 - n} |n + 1\rangle, \ a|n\rangle = \sqrt{n} |n - 1\rangle.$$  \hspace{1cm} (3.2.15)
It is easy to see $\hat{n} = a^+a$ is the number operator. Since
\[
(aa^+ + a^+a)|0\rangle = |0\rangle, \quad (3.2.16)
\]
\[
(aa^+ + a^+a)|1\rangle = |1\rangle, \quad (3.2.17)
\]
in terms of anticommutator $[A, B]_+ = AB + BA$,
\[
[a, a^+]_+ = 1, \quad [a, a]_+ = [a^+, a^+]_+ = 0. \quad (3.2.18)
\]

We must extend the above formalism to many one-particle energy state cases. Let $a_j$ and $a_j^+$ be the annihilation and creation operators for the $j$-th (one particle) energy state. To the end, we must specify the relation between $x_i x'_j$ and $x'_j x_i$, where $x$ and $x'$ are the creation or annihilation operators. The physical effect of these operations must be the same. We can freely choose the phase factor, so we "uniformize" the rule:

Creation and annihilation operators: SUMMARY

**Bosons:**

\[
a_i^+|n_1,\cdots,n_i,\cdots\rangle = \sqrt{n_i + 1}|n_1,\cdots,n_i + 1,\cdots\rangle, \quad (3.2.19)
\]
\[
a_i|n_1,\cdots,n_i,\cdots\rangle = \sqrt{n_i}|n_1,\cdots,n_i - 1,\cdots\rangle. \quad (3.2.20)
\]

The commutation relations are
\[
[a_i, a_j] = [a_i^+, a_j^+] = 0, \quad [a_i, a_j^+] = \delta_{ij}. \quad (3.2.21)
\]
\[
|n_1, n_2, \cdots\rangle = \prod_{k=1}^{\infty} \frac{1}{\sqrt{n_k!}} (a_k^+)^{n_k} |0\rangle \quad (3.2.22)
\]

makes a complete orthonormal set of a vector space called the *Fock space*.

**Fermions:**

\[
a_i^+|n_1,\cdots,n_i,\cdots\rangle = \sqrt{1-n_i}|n_1,\cdots,n_i + 1,\cdots\rangle, \quad (3.2.23)
\]
\[
a_i|n_1,\cdots,n_i,\cdots\rangle = \sqrt{n_i}|n_1,\cdots,n_i - 1,\cdots\rangle. \quad (3.2.24)
\]

These operators satisfy the following *anti-commutation* relations:
\[
[a_i, a_j]_+ = [a_i^+, a_j^+]_+ = 0, \quad [a_i, a_j^+]_+ = \delta_{ij}. \quad (3.2.25)
\]

Analogous to (3.2.22), the space spanned by the orthonormal basis vectors
\[
|n_1, n_2, \cdots\rangle = \prod_{k=1}^{\infty} (a_k^+)^{n_k} |0\rangle \quad (3.2.26)
\]
3.2. USING ANNIHILATION AND CREATION OPERATORS

is also called a Fock space.

Let \( \psi_k(x) = \langle x|1_k \rangle \) be the (normalized) one particle wave function for the \( k \)-th state. Then,

\[
\psi^+(x) = \sum_k \psi^*_k(x)a^+_k
\]

(3.2.27)
is an operator to create a particle at \( x \). For bosons,

\[
[\psi(x), \psi^+(y)] = \sum_k \psi_k(x)\psi^*_k(y) = \delta(x - y),
\]

(3.2.28)
because \{\( \psi_k \)\} is an orthonormal complete system (this is just Parseval’s equality). All other commutators vanish. Needless to say, its fermion analogue holds with the anticommutator.

The Hamiltonian of the ideal system may be written as

\[
H = \sum_r \varepsilon_r \hat{n}_r.
\]

(3.2.29)

Since the total number of particles \( N = \sum_r \hat{n}_r \), the grand partition function may be written as

\[
\Xi = Tr e^{-\beta(H - \mu N)} = Tr \prod_r e^{-\beta(\varepsilon_r - \mu)\hat{n}_r}.
\]

(3.2.30)

Here, \( \hat{n}_r \)'s commute, so we can factorize the product.

If we wish to compute \( \langle \hat{n}_r \rangle \) we have only to compute

\[
\langle \hat{n}_r \rangle = \frac{1}{\Xi_r} Tr \left[ \hat{n}_r e^{-\beta(\varepsilon_r - \mu)\hat{n}_r} \right],
\]

(3.2.31)

where \( \Xi_r \) is the normalization constant. To compute this we use the following useful formulas (correct for both bosons and fermions) (the suffix \( r \) is omitted for simplicity):

\[
e^{A\hat{n}} a = a e^{A\hat{n}} e^{-A},
\]

(3.2.32)

\[
e^{A\hat{n}} a^+ = a^+ e^{A\hat{n}} e^A.
\]

(3.2.33)

Here, \( A \) is anything commutative with the creation/annihilation operators. This implies

\[
\langle aB \rangle = e^{\beta(\varepsilon - \mu)} \langle Ba \rangle,
\]

(3.2.34)

\[
\langle a^+B \rangle = e^{-\beta(\varepsilon - \mu)} \langle Ba^+ \rangle.
\]

(3.2.35)
Here, $B$ is an arbitrary operator. To show (3.2.34) we have only to compute

$$Tr \left[ aB e^{-\beta(\epsilon-\mu)n} \right] = Tr \left[ Be^{-\beta(\epsilon-\mu)n} a \right] = e^{\beta(\epsilon-\mu)} Tr \left[ Be^{-\beta(\epsilon-\mu)n} a \right]$$

(3.2.36)

Here, we have used the cyclic permutation invariance of $Tr(AB \cdots YZ) = Tr(ZAB \cdots Y)$.

For the boson case (if obvious the hat of the number operator may be dropped.)

$$1 = a_r a_r^+ - a_r^+ a_r \Rightarrow 1 = \langle a_r a_r^+ \rangle - \langle n_r \rangle.$$  (3.2.37)

Thanks to (3.2.33)

$$\langle a_r a_r^+ \rangle = e^{\beta(\epsilon_r-\mu)} \langle n_r \rangle.$$  (3.2.38)

Therefore, (3.2.37) becomes

$$1 = e^{\beta(\epsilon_r-\mu)} \langle n_r \rangle - \langle n_r \rangle.$$  (3.2.39)

That is,

$$\langle n_r \rangle = \frac{1}{e^{\beta(\epsilon_r-\mu)} - 1}.$$  (3.2.40)

For fermions, the anti-commutation relation tells us

$$1 = a_r a_r^+ + a_r^+ a_r \Rightarrow 1 = \langle a_r a_r^+ \rangle + \langle n_r \rangle.$$  (3.2.41)

Therefore,

$$\langle n_r \rangle = \frac{1}{e^{\beta(\epsilon_r-\mu)} + 1}.$$  (3.2.42)

The expectation values of the products of creation and annihilation operators for noninteracting particle systems may be systematically reduced to the calculation of the average of number operators. The general formula is called the Bloch-de Dominicis theorem. In practice, the following iterative rule implied by the theorem is enough. Let $A_i$ be $a_i$ or $a_i^+$ (annihilation or creation operators). For fermions

$$\langle A_1 A_2 \cdots A_{2n} \rangle = \langle A_1 A_2 \rangle \langle A_3 \cdots A_{2n} \rangle - \langle A_1 A_3 \rangle \langle A_2 A_4 \cdots A_{2n} \rangle + \langle A_1 A_4 \rangle \langle A_2 A_3 A_5 \cdots A_{2n} \rangle + \cdots \pm \langle A_1 A_{2n} \rangle \langle A_2 \cdots A_{2n-1} \rangle.$$  (3.2.43)

For bosons — signs must be all +. For example, for the fermion case

$$\langle A_1 A_2 A_3 A_4 A_5 A_6 \rangle = \langle A_1 A_2 \rangle \langle A_3 A_4 A_5 A_6 \rangle - \langle A_1 A_3 \rangle \langle A_2 A_4 A_5 A_6 \rangle + \langle A_1 A_4 \rangle \langle A_2 A_3 A_5 A_6 \rangle - \langle A_1 A_5 \rangle \langle A_2 A_3 A_4 A_6 \rangle + \langle A_1 A_6 \rangle \langle A_2 A_3 A_4 A_5 \rangle$$  (3.2.44)
and the 4-operator product can be reduced as
\[ \langle A_1 A_2 A_3 A_4 \rangle = \langle A_1 A_2 \rangle \langle A_3 A_4 \rangle - \langle A_1 A_3 \rangle \langle A_2 A_4 \rangle + \langle A_1 A_4 \rangle \langle A_2 A_3 \rangle. \] (3.2.45)

We can easily compute the variance of the occupation number (let us write \( \langle \hat{n} \rangle = n \)). For bosons
\[ \langle \hat{n}^2 \rangle = \langle a^+ a a^+ a \rangle = \langle a^+ a \rangle \langle a^+ a \rangle + \langle a^+ a \rangle \langle a a \rangle + \langle a^+ a \rangle \langle a a \rangle, \] (3.2.46)
\[ = n^2 + n \langle a a \rangle = n^2 + n(1 + n) = 2n^2 + n, \] (3.2.47)
so
\[ \langle \delta n^2 \rangle = n + n^2. \] (3.2.48)

For fermions, we can use the same method, but since \( \hat{n}^2 = \hat{n} \), we immediately obtain
\[ \langle \delta n^2 \rangle = n - n^2 = n(1 - n). \] (3.2.49)

For the classical case \( n \ll 1 \) for any one particle state, so
\[ \langle \delta n^2 \rangle = n. \] (3.2.50)

This is in agreement with the result of the Poisson distribution as we already discussed in Chapter 1.

The Bloch-de Dominicis theorem
Here is the ‘official statement’ of the Bloch-de Dominicis theorem
Let \( A_i \) be \( a_i \) or \( a_i^+ \) (annihilation or creation operators for fermions). Then, we have for the canonical or grand canonical ensemble average of noninteracting (ideal) fermion systems (for boson systems \( \text{sgn}(P) \) is simply replaced by unity everywhere; it is formally the same as Wick’s theorem for Gaussian random variables.)
\[ \langle A_1 A_2 \cdots A_{2n} \rangle = \sum_P \text{sgn}(P) \langle A_{i_1} A_{i_2} \rangle \langle A_{i_3} A_{i_4} \rangle \cdots \langle A_{i_{2n-1}} A_{i_{2n}} \rangle, \] (3.2.51)
where \( \text{sgn}(P) \) is the sign of the permutation of \( i_1, i_2, \cdots, i_{2n} \), and
\[ i_1 < i_2, \quad i_3 < i_4 \quad \cdots, \quad i_{2n-1} < i_{2n}, \]
\[ i_1 < i_3 < \cdots i_{2n-1}. \] (3.2.52) (3.2.53)
\( \langle A_{i_1} A_{i_2} \rangle \) are called contractions and the sum in (3.2.51) is over all the ways to make contractions choosing pairs with the constraints above.
Here, we demonstrate the theorem for fermions. The case with bosons is analogous.
We may assume
\[ A_i A_j + A_j A_i = c(i, j), \] (3.2.54)
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where \( c(i, j) \) is an ordinary number calculated by the anti-commutation relations.

Let \( \langle \rangle \) be the canonical or grand canonical average. Then,

\[
\langle A_1 A_2 \cdots A_{2n} \rangle = \langle [c(1, 2) - A_2 A_1] \cdots A_{2n} \rangle, \quad (3.2.55)
\]

\[
= c(1, 2) \langle A_3 \cdots A_{2n} \rangle - \langle A_2 A_1 A_3 \cdots A_{2n} \rangle, \quad (3.2.56)
\]

\[
= c(1, 2) \langle A_3 \cdots A_{2n} \rangle - \langle A_2 [c(1, 3) - A_3 A_1] \cdots A_{2n} \rangle, \quad (3.2.57)
\]

\[= \cdots. \quad (3.2.58)\]

Therefore, eventually, we obtain

\[
\langle A_1 A_2 \cdots A_{2n} \rangle = c(1, 2) \langle A_3 \cdots A_{2n} \rangle - c(1, 3) \langle A_2 A_4 \cdots A_{2n} \rangle + \cdots + c(1, 2n) \langle A_2 \cdots A_{2n-1} \rangle - \langle A_2 A_3 \cdots A_{2n} A_1 \rangle. \quad (3.2.59)
\]

Now, let us assume that the average above is about the canonical or grand canonical ensemble and that the particles are non-interacting. That is, the system Hamiltonian is of the following form

\[
H = \sum_{r} \varepsilon_r n_r. \quad (3.2.60)
\]

and (in the following for the grand canonical ensemble replace \( \varepsilon_r \) with \( \varepsilon_r - \mu \))

\[
(A_2 A_3 \cdots A_{2n} A_1) = \frac{1}{Z} \text{Tr}(A_2 A_3 \cdots A_{2n} A_1 e^{-\beta H}). \quad (3.2.61)
\]

Let \( A_1 = a_1^+ \), where \( a_1^- = a_1 \). Then,

\[
a_1^+ e^{-\beta H} = e^{-\beta H} e^{\pm \beta \varepsilon_1} a_1^+. \quad (3.2.62)
\]

Therefore, using the cyclic permutation invariance of the trace operation, we have

\[
\langle A_2 A_3 \cdots A_{2n} a_1^+ \rangle = e^{\pm \beta \varepsilon_1} \langle a_1^+ A_2 A_3 \cdots A_{2n} \rangle. \quad (3.2.63)
\]

Therefore, \((3.2.59)\) reads

\[
(1 + e^{\pm \beta \varepsilon_1}) \langle A_1 A_2 \cdots A_{2n} \rangle = c(1, 2) \langle A_3 \cdots A_{2n} \rangle - c(1, 3) \langle A_2 A_4 \cdots A_{2n} \rangle + \cdots + c(1, 2n) \langle A_2 \cdots A_{2n-1} \rangle. \quad (3.2.64)
\]

Now, consider

\[
c(1, 2)/(1 + e^{\pm \beta \varepsilon_1}). \quad (3.2.65)
\]

If \( A_1 = a_1^+ \), then \( c(1, 2) \neq 0 \) only when \( A_2 = a_1 \). \( \langle A_1 A_2 \rangle \neq 0 \) only when \( A_2 = a_1 \). If \( A_2 = a_1 \), then \( c(1, 2) = 1 \) and

\[
\langle A_1 A_2 \rangle = \frac{1}{e^{\beta \varepsilon_1} + 1} = \frac{c(1, 2)}{e^{\beta \varepsilon_1} + 1}. \quad (3.2.66)
\]

If \( A_1 = a_1 \), then \( c(1, 2) \neq 0 \) only when \( A_2 = a_1^+ \). \( \langle A_1 A_2 \rangle \neq 0 \) only when \( A_2 = a_1^+ \). If \( A_2 = a_1^+ \), then \( c(1, 2) = 1 \) and

\[
\langle A_1 A_2 \rangle = 1 - \frac{1}{e^{\beta \varepsilon_1} + 1} = \frac{c(1, 2)}{e^{-\beta \varepsilon_1} + 1}. \quad (3.2.67)
\]
Therefore,
\[ c(1, 2)/(1 + e^{\pm \beta_1}) = \langle a_1^\pm A_2 \rangle \]  
(3.2.68)

for all cases. Thus, in (3.2.59) we may formally ignore the last term and replace all \( c(1, j) \) with \( \langle A_1 A_j \rangle \). It is obvious that we can repeat the same argument for smaller \( n \), so the proof is essentially over.

Maxwell derived his distribution function based on the detailed balance argument. Its essence is: if two particles in states \( r \) and \( r' \) collide and make two particles in states \( s \) and \( s' \), there must also be the reversed process as frequently as the original process (thanks to time reversal symmetry of mechanics). The collision process may be described by the interaction Hamiltonian

\[ H_I = \sum A_{s', s, r, r'}^* a_{s'}^+ a_r^+ a_s a_{s'} \]  
(3.2.69)

The representative term expresses a binary collision: \( r \) and \( r' \) states are destroyed and \( s \) and \( s' \) states are created. When particles satisfying the conditions collide, the probability amplitude for such a process actually happens is described by \( A_{s', s, r, r'}^* \). If the initial ket is \( |i\rangle = |\{n_k\}\rangle \), and if \( r, r', s, \) and \( s' \) are all distinct (i.e., the generic case),

\[ \langle f | H_I | i \rangle = A_{s', s, r, r'}^* \sqrt{(n_s + 1)(n_{s'} + 1)n_r n_{r'}.} \]  
(3.2.70)

Since \( H_I \) is self-adjoint, it must also contain the term

\[ A_{s', s, r, r'}^* a_{s'}^+ a_r^+ a_s a_{s'} \]  
(3.2.71)

This contributes

\[ \langle f | A_{s', s, r, r'}^* a_{s'}^+ a_r^+ a_s a_{s'} | i \rangle = A_{s', s, r, r'}^* \sqrt{(n_r + 1)(n_{r'} + 1)n_s n_{s'}.} \]  
(3.2.72)

In equilibrium if a transition \( A \rightarrow B \) can occur, then the opposite transition \( B \rightarrow A \) also can occur with the same probability (detailed balance). Therefore, (3.2.70) and (3.2.72) must have the same absolute value, or

\[ (n_s + 1)(n_{s'} + 1)n_r n_{r'} = (n_{r'} + 1)(n_r + 1)n_s n_{s'}. \]  
(3.2.73)

This implies

\[ \frac{n_{s'}}{n_{s'} + 1} \frac{n_s}{n_s + 1} = \frac{n_r}{n_r + 1} \frac{n_{r'}}{n_{r'} + 1}. \]  
(3.2.74)

That is,

\[ q_s = \log \frac{n_s}{n_s + 1} \]  
(3.2.75)
is an additive invariant of the binary interaction (collision). Therefore, it is natural to assume that this is a linear function of energy:

\[
\frac{n_s}{n_s + 1} = e^{-\beta(\varepsilon - \mu)}.
\] (3.2.76)

This is exactly the Bose-Einstein distribution.

For fermions we have

\[
\langle f | H \rangle | i \rangle = A_{s's', rr'} \sqrt{(1 - n_s)(1 - n_s')n_r n_{r'}}.
\] (3.2.77)

The detailed balance condition implies

\[
(1 - n_s)(1 - n_s')n_r n_{r'} = (1 - n_r)(1 - n_{r'})n_s n_{s'}.
\] (3.2.78)

The same logic as before gives the Fermi-Dirac distribution.

The Maxwell’s original case is \( n_s n_{s'} = n_r n_{r'} \). This is consistent with the above quantum cases, because \( n_s \ll 1 \) for any state \( s \) in the classical limit.

### 3.3 Ideal Fermion Systems

Let us summarize what we know.

The creation/annihilation operators:

\[
[a_i, a_j^+]^+ = [a_i^+, a_j^+]^+ = 0, \quad [a_i, a_j^+]^+ = \delta_{ij},
\] (3.3.1)

and the particle number operator is

\[
\hat{n}_j = a_j^+ a_j
\] (3.3.2)

with

\[
f(\varepsilon) \equiv \langle \hat{n} \rangle = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1},
\] (3.3.3)

where \( \varepsilon \) is the energy of a particular one particle state (an eigenvalue of the single body Hamiltonian describing each particle) and \( \mu \) is the chemical potential. The chemical potential (also called the Fermi energy or Fermi level) must be positive, if
the temperature is sufficiently low, but is a monotone decreasing function of temperature.

The pressure is obtained with the aid of Kramers’ \( q \):

\[
q = \frac{PV}{T} = k_B \sum_r \log(1 + e^{-\beta(\varepsilon_r - \mu)}). \tag{3.3.4}
\]

Since \( G = N\mu \),

\[
A = G - PV = N\mu - k_BT \sum_r \log(1 + e^{-\beta(\varepsilon_r - \mu)}). \tag{3.3.5}
\]

Also

\[
N = \sum_r \langle n_r \rangle = \sum_r f(\varepsilon_r), \tag{3.3.6}
\]

\[
E = \sum_r \varepsilon_r \langle n_r \rangle = \sum_r \varepsilon_r f(\varepsilon_r). \tag{3.3.7}
\]

If we know the density of state, i.e., the density distribution function for the eigenvalues of the one particle Hamiltonian, \( D_t(\varepsilon) \)

\[
A = N\mu - k_BT \int d\varepsilon gD_t(\varepsilon) \log(1 + e^{-\beta(\varepsilon - \mu)}), \tag{3.3.8}
\]

\[
N = \int d\varepsilon gD_t(\varepsilon)f(\varepsilon), \tag{3.3.9}
\]

\[
E = \int d\varepsilon gD_t(\varepsilon)\varepsilon f(\varepsilon), \tag{3.3.10}
\]

where \( g \) is the multiplicity due to internal degrees of freedom (\( g = 2 \) for electrons due to spin).

Intuitively, we may think that the total entropy is the sum of the contributions due to individual single particle states:

\[
S = \sum_k S_k. \tag{3.3.11}
\]

For each single state, \( \langle n_k \rangle \) is the occupation probability, so we may guess with the aid of the Gibbs-Shannon formula:

\[
S_k = -k_B[\langle n_k \rangle \log \langle n_k \rangle + (1 - \langle n_k \rangle) \log(1 - \langle n_k \rangle)]. \tag{3.3.12}
\]
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That is,

\[ S = -k_B \int d\varepsilon g D_t(\varepsilon) \left[ f(\varepsilon) \log f(\varepsilon) + (1 - f(\varepsilon)) \log (1 - f(\varepsilon)) \right]. \quad (3.3.13) \]

Our guess is correct. Let us derive the formula thermodynamically.

\[
ST = E - A = \int d\varepsilon g D_t(\varepsilon) \varepsilon f(\varepsilon) - \mu \int d\varepsilon g D_t(\varepsilon) f(\varepsilon) + k_B T \int d\varepsilon g D_t(\varepsilon) \log (1 + e^{-\beta(\varepsilon - \mu)}),
\]

\[
= \int d\varepsilon g D_t(\varepsilon) (\varepsilon - \mu) f(\varepsilon) + k_B T \int d\varepsilon g D_t(\varepsilon) \log f(\varepsilon) - \int d\varepsilon g D_t(\varepsilon) (\varepsilon - \mu). \quad (3.3.14)
\]

Here, \( k_B T \log (f(\varepsilon)^{-1} - 1) = \varepsilon - \mu \), so

\[
ST = -k_B T \int d\varepsilon g D_t(\varepsilon) (1 - f(\varepsilon)) \log \frac{1 - f(\varepsilon)}{f(\varepsilon)} - k_B T \int d\varepsilon g D_t(\varepsilon) \log f(\varepsilon). \quad (3.3.16)
\]

Our guess is right.

Topics of some interest of the ideal fermion system may be:
(1) Qualitative feature of \( f(\varepsilon) \) as a function of \( T \).
(2) Properties at \( T = 0 \),
(3) Finite temperature corrections for small \( T \).
The reader should be able to sketch (1) and (3).

Let us sketch \( D_y(\varepsilon) f(\varepsilon) \) for various temperatures.
The Fermi energy at $T = 0$ is implicitly defined by ($D_t$ is (3.1.28))

$$N = \int_{\mu(0)}^{\mu(0)} gD_t(\varepsilon)f(\varepsilon) = V\frac{4}{3}\pi g \left(\frac{2m\mu(0)}{\hbar^2}\right)^{3/2}. \quad (3.3.17)$$

The main feature is $n \propto \mu(0)^{3/2}$, which is equal to the number of one particle states below $\mu(0)$ and is proportional to the volume of the 3-ball of radium $\propto \sqrt[6]{\mu(0)}$. (3.3.17) implies

$$\mu(0) = \frac{h^2}{2m} \left(\frac{3n}{4\pi g}\right)^{2/3}. \quad (3.3.18)$$

The density of states may be written as

$$gD_t(\varepsilon) = V\frac{3}{2} n \left(\frac{\varepsilon}{\mu(0)^3}\right)^{1/2}. \quad (3.3.19)$$

We know $D_t$ must be proportional to $\varepsilon^{1/2}$ and its dimension must be 1/energy, so $1/\mu(0)^{3/2}$ is required.

The internal energy at $T = 0$ must be $\propto n\mu(0)$ per volume. Indeed,

$$e(0) = \frac{1}{V} \int_0^{\mu(0)} \varepsilon gD_t(\varepsilon) d\varepsilon = \frac{3}{2} n\mu(0)^{-3/2} \int_0^{\mu(0)} \varepsilon^{3/2} d\varepsilon = \frac{3}{5} \mu(0)n. \quad (3.3.20)$$
This can be derived quickly from the form $D_t = A \varepsilon^{1/2}$ ($A$ is a constant independent of $\varepsilon$); $N = (2/3)A\mu(0)^{3/2}$ and $E = (2/5)A\mu(0)^{5/2}$, so $E = (3/5)\mu(0)N$. $E/V$ immediately gives us the pressure at $T = 0$

$$PV = \frac{2}{5} \mu(0)N. \quad (3.3.21)$$

Now, we must compute the correction due to small $T$ for various quantities. The basic idea is that at low temperatures, the cliff of the Fermi distribution is steep, so its derivative is close to a $\delta$-function around $\mu$.

![Fig. 3.3.2 The derivative of the Fermi distribution. Its width is about $5k_B T$. and the height is $\beta/4$.](image)

Thus,

$$J = \int_0^\infty d\varepsilon \phi(\varepsilon) \left( -\frac{df}{d\varepsilon} \right) \simeq \phi(\mu). \quad (3.3.22)$$

To improve this approximation we Taylor expand $\phi$ around $\mu$ as

$$J = -\int_{-\infty}^{+\infty} d\varepsilon \left[ \phi(\mu) + (\varepsilon - \mu)\phi'(\mu) + \frac{1}{2}(\varepsilon - \mu)^2\phi''(\mu) + \cdots \right] \frac{df}{d\varepsilon}. \quad (3.3.23)$$

Exchanging the order of integration and expansion, we have only to compute the integral of the power $(\varepsilon - \mu)^n$. $df/d\varepsilon$ is symmetric around $\mu$, so the odd powers vanish. The result is a useful formula for $J$:

$$-\int_{-\infty}^{+\infty} d\varepsilon \phi(\varepsilon) \frac{df(\varepsilon)}{d\varepsilon} = \phi(\mu) + (k_B T)^2 \zeta(2)\phi''(\mu) + \cdots. \quad (3.3.24)$$

Here, $\zeta$ is the zeta function: $\zeta(2) = \pi^2/6$.

Analogously, we should be able to expand the following integral, if $\phi(0) = 0$ and the asymptotic increase rate of $\phi$ is at most algebraic:

$$\int_0^{+\infty} d\varepsilon \phi(\varepsilon)f(\varepsilon) = \int_0^{\mu} \phi(x)dx + (k_B T)^2 \zeta(2)\phi'(\mu) + \cdots. \quad (3.3.25)$$
The full expansion formula

\[ J = - \int_{-\infty}^{+\infty} \left[ \phi(\varepsilon) \frac{dJ(\varepsilon)}{d\varepsilon} \right] d\varepsilon = \phi(\mu) + \sum_{r=1}^{\infty} 2 (1 - 2^{1-2r}) \zeta(2r) \phi(2r)(\mu)(k_B T)^{2r} \]  

(3.3.26)

may be obtained as follows. Taylor-expanding \( \phi \), we obtain

\[ J = \phi(\mu) - \sum_{n=1}^{\infty} \int_{-\infty}^{+\infty} d\varepsilon \frac{1}{n!} (\varepsilon - \mu)^n \frac{d\phi(n)}{d\varepsilon} (\mu) = \phi(\mu) + \sum_{n=1}^{\infty} (k_B T)^n \frac{1}{n!} K_n \phi(n)(\mu). \]  

(3.3.27)

Here,

\[ K_n = - \int_{-\infty}^{+\infty} d\varepsilon (\varepsilon - \mu)^n \frac{dJ(\varepsilon)}{d\varepsilon}. \]  

(3.3.28)

This is zero for odd \( n \). We have

\[ K_n = -2(k_B T)^n \int_{0}^{\infty} dy y^n \frac{d}{dy} \frac{1}{e^y + 1} = 2n(k_B T)^n \int_{0}^{\infty} dy y^{n-1} \frac{1}{e^y + 1}. \]  

(3.3.29)

for even \( n > 0 \). To compute this we use the following expansion

\[ \frac{1}{e^y + 1} = \frac{e^{-y}}{1 + e^{-y}} = \sum_{k=0}^{\infty} (-1)^k e^{-(k+1)y}, \]  

(3.3.30)

and the integral and this expansion may be exchanged: we can use

\[ \int_{0}^{\infty} dy y^{n-1} e^{-(k+1)y} = \frac{\Gamma(n)}{(k+1)^n}. \]  

(3.3.31)

Therefore,

\[ K_n = 2(k_B T)^n n! \sum_{k=0}^{\infty} (-1)^k \frac{1}{(k+1)^n}. \]  

(3.3.32)

The sum can be computed as

\[ \sum_{k=0}^{\infty} (-1)^k \frac{1}{(k+1)^n} = \sum_{\text{even}} \frac{1}{(k+1)^n} - \sum_{\text{odd}} \frac{1}{(k+1)^n} = \sum_{\text{odd}} \frac{1}{k^n} - \sum_{\text{even} \geq 0} \frac{1}{k^n} \]  

(3.3.33)

\[ = \sum_{k=0}^{\infty} \frac{1}{(2k+1)^n} - \sum_{k=1}^{\infty} \frac{1}{(2k)^n} = \sum_{k=1}^{\infty} \frac{1}{k^n} - 2 \sum_{k=1}^{\infty} \frac{1}{(2k)^n} \]  

(3.3.34)

\[ = \zeta(n) - 2^{1-n} \zeta(n). \]  

(3.3.35)

Therefore,

\[ K_n = 2(k_B T)^n n! (1 - 2^{1-n}) \zeta(n). \]  

(3.3.36)
We may apply (3.3.25) to \( N \) because \( D_t \) grows only algebraically (\( \zeta(2) = \pi^2/6 \)):

\[
N = \int_0^\infty d\varepsilon gD_t(\varepsilon) f(\varepsilon) = \int_0^\mu dx gD_t(x) + \zeta(2) \left. \frac{dD_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu} (k_B T)^2 + \cdots. \tag{3.3.37}
\]

The Fermi level \( \mu(0) \) at \( T = 0 \) has already been computed with the aid of

\[
N = \int_0^{\mu(0)} gD_t(\varepsilon)d\varepsilon. \tag{3.3.38}
\]

Therefore, combining with (6.3.71), we can find \( \mu \) as a function of \( T \): First, we see

\[
\int_0^{\mu(0)} gD_t(\varepsilon)d\varepsilon = \int_0^\mu dx gD_t(x) + \zeta(2) \left. \frac{dD_t(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu} (k_B T)^2 + \cdots. \tag{3.3.39}
\]

We can guess \( \mu = \mu(0) + a(k_B T)^2 + \cdots \), so substituting this relation in the above formula to fix \( a \), we obtain the low temperature formula for the Fermi level:

\[
\mu(T) = \mu(0) - \frac{\pi^2}{6} \frac{d}{d\varepsilon} \log gD_t(\varepsilon) \left|_{\varepsilon=\mu(0)} \right. (k_B T)^2 + \cdots. \tag{3.3.40}
\]

This may be streamlined as follows for sufficiently low temperature:

\[
\mu(T) = \mu(0) \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 \right]. \tag{3.3.41}
\]

Here, \( T_F = \mu(0)/k_B \) is the Fermi temperature.\(^8\) This behavior can be guessed from (i) no change of any thermodynamic potential (per particle) at \( T = 0 \) (hence, no first order derivative wrt \( T \) is nonzero) and (ii) for \( T > 0 \) \( \mu \) is a decreasing function of \( T \).

(3.3.25) allows us to calculate temperature corrections such as

\[
E = \int d\varepsilon gD_t(\varepsilon) \varepsilon f(\varepsilon) \tag{3.3.42}
\]

\[
= \int_0^\mu d\varepsilon gD_t(\varepsilon) \varepsilon + \zeta(2)(k_B T)^2 \left. \frac{dD_t(\varepsilon)}{d\varepsilon} \right|_\mu \varepsilon + \cdots. \tag{3.3.43}
\]

\(^8\)Representative values: Li \( 5.5 \times 10^4 \)K (4.7 eV); Cu \( 8.2 \times 10^4 \)K (8.2 eV); Au \( 5.5 \times 10^4 \)K (5.5 eV).
Therefore, introducing \((3.3.40)\) and expanding the integral around \(\mu(0)\), we obtain (notice that \(D'_t(\varepsilon)\varepsilon = D_t(\varepsilon)/2\))

\[
E = E_0 + \zeta(2)gD_t(\mu(0))(k_B T)^2 + \cdots,
\]

(3.3.44)

where \(E_0 = V\varepsilon(0)\) is the zero-point energy. A more streamlined low temperature formula for the internal energy density reads

\[
e(T) = \frac{3}{5} n\mu(0) \left\{ 1 + \frac{5\pi^2}{12} \left( \frac{T}{T_F} \right)^2 + \cdots \right\},
\]

(3.3.45)

Its high temperature asymptote reads

\[
e(T) \simeq \frac{3}{2} nk_B T,
\]

(3.3.46)

so we may sketch \(E(T)\) as Fig. 3.3.3.

Fig. 3.3.3 Internal energy of ideal Fermi gas as a function of \(T\).

From the internal energy obtained in \((3.3.45)\), it is easy to see that the low temperature specific heat reads

\[
C_V \simeq \frac{\pi^2}{3} k_B^2 T gD_t(\mu(0)).
\]

(3.3.47)

This reads

\[
C_V \simeq \frac{1}{2} \frac{\pi^2}{2} nk_B^2 T/\mu(0) = \frac{1}{2} \frac{\pi^2}{2} nk_B \frac{T}{T_F}
\]

(3.3.48)

for ideal Fermi gas, where \(T_F\) is the Fermi temperature; the dependence on spin is only through \(T_F\). \(C_V \sim T/T_F\) can easily be guessed dimensionally analytically as well.
Specific heat is proportional to the number of thermally excitable degrees of freedom (in ideal gas this is proportional to the number of thermally excitable particles); the reader must be able to explain $\propto T$ intuitively. For ordinary metals, however, it is not easy to see this linear behavior, because $T_F$ is very high and easily masked by the phonon contribution.

It is wise to use the specific heat to compute the $T$ dependence of entropy:

$$S(T) = \int_0^T \frac{C_V}{T} dT.$$  \hfill (3.3.49)

Therefore, at low temperatures

$$S(T) \simeq C_V(T).$$  \hfill (3.3.50)

For sufficiently low temperatures, we can use the formula for internal energy (3.3.45) to obtain the equation of state.

$$PV = \frac{2}{5} N k_B T_F \left( 1 + \frac{5}{12} \pi^2 \left( \frac{T}{T_F} \right)^2 + \cdots \right).$$  \hfill (3.3.51)

Clearly recognize that this is extremely large for metals.

For sufficiently high temperatures (or rather, for sufficiently low chemical potential close to classical limit) fugacity $z = e^{\beta \mu}$ is very small, so we wish to expand $PV$ and $N, T$ in powers of fugacity. $PV$ in terms of the fugacity $z$ is:

$$\frac{PV}{k_B T} = \int d\varepsilon g D_t(\varepsilon) \log(1 + ze^{-\beta \varepsilon}) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1} z^n}{n} \int d\varepsilon e^{-n\beta \varepsilon} g D_t(\varepsilon),$$  \hfill (3.3.52)

and

$$N = \int d\varepsilon g D_t(\varepsilon) \frac{1}{1 + e^{\beta \varepsilon}/z} = \sum_{n=1}^{\infty} (-1)^{n-1} z^n \int d\varepsilon e^{-n\beta \varepsilon} g D_t(\varepsilon).$$  \hfill (3.3.53)

Both are analytic functions of $z$ along the positive real $z$-axis.\footnote{Hence, there is no phase transition. See Chapter 5.} Solving $z$ in powers of number density $n$, we can obtain the virial expansion of the equation of state for the ideal Fermi gas:

$$\frac{PV}{NRT} = 1 + \frac{1}{2^{5/2} g n_Q} + \cdots.$$  \hfill (3.3.54)

Here, $g$ is the spin degeneracy, and $n_Q = (2\pi m k_B T/h^2)^{3/2}$ as before.
3.4 Ideal Boson Systems

The creation/annihilation operators (→ Section 3.2):

\[ [a_i, a_j] = [a_i^+, a_j^+] = 0, \quad [a_i, a_j^*] = \delta_{ij}, \]  

(3.4.1)

and the particle number operator is

\[ \hat{n}_j = a_j^* a_j \]  

(3.4.2)

with

\[ \langle \hat{n}_j \rangle = \frac{1}{e^{\beta (\epsilon_j - \mu)} - 1}. \]  

(3.4.3)

The chemical potential \( \mu \) is a monotone decreasing function of \( T \) and cannot be larger than the one-particle ground-state energy, because \( \langle n(\epsilon) \rangle \) must be positive.

The pressure is obtained by

\[ q = \frac{PV}{T} = -k_B \sum_r \log(1 - e^{\beta (\epsilon_r - \mu)}). \]  

(3.4.4)

Since \( G = N\mu \),

\[ A = G - PV = N\mu + k_B T \sum_r \log(1 - e^{-\beta (\epsilon_r - \mu)}). \]  

(3.4.5)

Also

\[ N = \sum_r \langle n_r \rangle = \sum_r f(\epsilon_r), \]  

(3.4.6)

\[ E = \sum_r \epsilon_r \langle n_r \rangle = \sum_r \epsilon_r f(\epsilon_r), \]  

(3.4.7)

where

\[ f(\epsilon) = \frac{1}{e^{\beta (\epsilon - \mu)} - 1}. \]  

(3.4.8)

\( \mu \) must be a function of \( N \) and \( T \) for a canonical ensemble. We know

\[ PV = \frac{2}{3} E \]  

(3.4.9)
is true for any (non-relativistic) ideal gas in 3-space.

Intuitively, we may think that the total entropy is the sum of the contributions due to each one particle state:

\[ S = \sum_k S_k, \]  

(3.4.10)

where \( S_k \) is the entropy contribution by a one particle energy state \( k \) with energy \( \varepsilon_k \). Let \( f = \langle \hat{n}_k \rangle \). The Gibbs-Shannon formula tells us that

\[ S_k/k_B = -\sum_n p_n \log p_n, \]  

(3.4.11)

where \( p_n \) is the probability for this energy state to have \( n \) bosons. This can be computed as (suffixes \( k \) are omitted for simplicity)

\[ p_n = e^{-n\beta(\varepsilon-\mu)}/(1 + e^{-\beta(\varepsilon-\mu)} + e^{-2\beta(\varepsilon-\mu)} + \cdots) = \frac{1}{1 + f} \left( \frac{f}{1 + f} \right)^n. \]  

(3.4.12)

Putting this into (3.4.11), we obtain

\[ S_k/k_B = -\sum_n \frac{1}{1 + f} \left( \frac{f}{1 + f} \right)^n \left[ -\log(1 + f) + n \log \frac{f}{1 + f} \right] \]

\[ = \log(1 + f) - f \log \frac{f}{1 + f} = (1 + f) \log(1 + f) - f \log f. \]  

(3.4.13)

That is (compare the following result with (3.3.13)),

\[ S = -k_B \sum_k \left[ f(\varepsilon_k) \log f(\varepsilon_k) - (1 + f(\varepsilon_k)) \log(1 + f(\varepsilon_k)) \right]. \]  

(3.4.14)

This indeed agrees with the thermodynamic result:

\[ ST = E - A = \sum_k \varepsilon_k f(\varepsilon_k) - \mu \sum_k f(\varepsilon_k) - k_B T \sum_k \log(1 - e^{-\beta(\varepsilon_k-\mu)}) \]

\[ = -k_B T \sum_k \left\{ f(\varepsilon_k) \log \frac{f(\varepsilon_k)}{1 + f(\varepsilon_k)} + \log \frac{1}{1 + f(\varepsilon_k)} \right\}. \]  

(3.4.15)

(3.4.16)

We have already noted that rewriting the sum \( \sum_k \to \int d\varepsilon D(\varepsilon) \) may not be correct for bosons. Let us explicitly see why. Let us formally rewrite the formula for \( N \) as

\[ N_1(T, \mu) = \frac{V}{\hbar^3} \int_0^\infty \frac{1}{e^{\beta(p^2/2m-\mu)} - 1} 4\pi p^2 dp. \]  

(3.4.17)
This integral is a monotone increasing function of $\mu$, so its upper bound can be evaluated as

$$N_1(T, \mu) \leq N_1(T, 0) = \frac{V}{\hbar^3} \int_0^\infty \frac{1}{e^{\beta p^2/2m} - 1} 4\pi p^2 dp = AVT^{3/2}, \quad (3.4.18)$$

where $A$ is a positive constant. Thus, if $T$ is sufficiently low $N_1 < N$. That is, the integral approximation cannot describe the number of particles correctly. Let us plot $n_1(T, \mu) = N_1/V$ as a function of $T$ (Fig. 3.4.1).

![Figure 3.4.1 Qualitative behavior of $n_1(T, \mu)$, the integral approximation = the number density of particles in excited states. If the temperature is higher than $T_c$ as $T_1$, we may choose a negative chemical potential such that $n = n_1$. If $T < T_c$ such as $T_2$, then $\mu = 0$, but then $n_0 > 0$ is possible and $n_1 + n_0 = n$ can be satisfied.](image)

We must write the contribution of the ground state explicitly as

$$N = \frac{1}{e^{-\beta \mu} - 1} + N_1(T, \mu). \quad (3.4.19)$$

Let us write the number densities with the lower case letters as $n_1 = N_1/V$, etc.

(i) If $n_1(T, 0) > n = N/V$, $\mu(T) < 0$ is required, but then $N_0$ cannot be macroscopic, so we must choose a negative chemical potential such that $n_1 = n$.

(ii) As we lower the temperature, to fulfill the equality $n_1 = n$, we must increase $\mu$. This is sketched in Fig. 3.4.1.

(iii) As we increase $\mu$, we hit $\mu = 0$ at $T = T_c$. Below this temperature $n_1 < n$, so (one particle) ground state is occupied by a macroscopic number of particles. This is called the Bose-Einstein condensation.\(^\text{10}\)

Below $T_c$, the number density of the condensate is

$$n_0(T) = n - n_1(T, 0) = n \left( 1 - \left( \frac{T}{T_c} \right)^{3/2} \right). \quad (3.4.20)$$

\(^\text{10}\)This was discovered by Einstein; Bose has nothing to do with this discovery.
For small $T - T_c$ $n_0 \propto (T_c - T)$. To get $T_c$ we must solve $n_1(T_c, 0) = n$; from (3.4.18)

$$n_1(T_c, 0) = \frac{1}{h^3} \int_0^\infty \frac{1}{e^{\beta p^2/2m} - 1} 4\pi p^2 dp = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F_{3/2}(0) \quad (3.4.21)$$

with

$$F_{3/2}(0) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{t^{1/2}}{e^t - 1} dt = \zeta(3/2) \simeq 2.61. \quad (3.4.22)$$

Therefore,

$$T_c = \frac{h^2}{2\pi k_B m} \left(\frac{n}{2.61}\right)^{2/3} \propto \frac{n^{2/3}}{m}. \quad (3.4.23)$$

$1/m$ can be seen from the combination of $\beta p^2/2m$ in the Boltzmann factor.

Let us confirm that in the pressure formula we may replace the summation (3.1.16) with the integration (3.1.22). The grand canonical partition function $\Xi_0$ for the lowest energy state $\varepsilon = 0$ is given by

$$\Xi_0 = \sum_{n=0}^\infty e^{n\beta\mu} = \frac{1}{1 - e^{\beta\mu}} = e^{-\beta\mu}\langle N_0 \rangle. \quad (3.4.24)$$

Below $T_c$ $\mu$ is almost zero (really zero in the thermodynamic limit):

$$\langle N_0 \rangle = \frac{1}{e^{-\mu} - 1} \simeq \frac{k_B T}{|\mu|}. \quad (3.4.25)$$

Because $\Xi_0 = 1/(1 - e^{\beta\mu}) = N_0 e^{1/N_0}$, the contribution of the ground state to pressure reads $P_0 \simeq (k_B T/V) \log N_0$. That is, it is $O[(\log N)/N]$. Therefore, we may use integration in macroscopic systems to obtain pressure (and internal energy).

Below $T_c$ $\mu = 0$ so thermodynamic quantities depends on $T$ in a clean fashion. This fact is worth memorizing. For example,

$$E = \int d\varepsilon g_D(\varepsilon) \frac{\varepsilon}{e^{\beta\varepsilon} - 1} = \frac{3}{2} k_B T V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \zeta(5/2) \propto V T^{5/2}, \quad (3.4.26)$$

so

$$C_V \propto T^{3/2}. \quad (3.4.27)$$
For $T > T_c$ we must pay attention to $\mu(T)$ as well, so it is not very easy to demonstrate that $C_V$ is monotone decreasing (explicit calculation is needed; see the problem for this Chapter).

Fig. 3.4.2q Specific heat has a cusp at $T_c$. To see the behavior above $T_c$, we need a detailed calculation (see a problem at the end of the chapter).

The integral in (3.4.18) for $d \leq 2$ dimensional space diverges, so $n_1 = n$ can always be satisfied by choosing an appropriate $\mu(T)$. Therefore, there is no Bose-Einstein condensation in low dimensional spaces.

When superfluidity was found (around 1938 explicitly by Kapitza\textsuperscript{11}),\textsuperscript{12} London suggested this is related to the Bose-Einstein condensation.

To consider this problem, we must reflect on what ‘superfluidity’ means. Charged superfluidity is superconductivity. We know that supercurrent and the Meissner effect are two major characteristic features of superconductivity. We have already seen that the Bohr-van Leeuwen theorem should imply that the Meissner effect is a purely quantum effect. Furthermore, the rotation-vector potential analogy implies that there is a counterpart of the Meissner effect, the nonclassical rotational inertia (NCRI) for non-charged superfluid (Section 1.7). Therefore, as Leggett stresses, NCRI and supercurrent should be the characteristic features of superfluidity.

To exhibit NCRI the system must have a certain quantum coherence over a macro-

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\textsuperscript{11}Kamerlingh-Onnes found a singularity in the density in 1911, but Kapitza was the first to realize superfluidity: Nature, 141, 74 (1938).

\textsuperscript{12}In 1911 Rutherford proposed his atom model. G. Mahler died; Amundsen reached the South Pole. In 1938 Hahn et al. discovered nuclear fission. Kemal Atatürk died; Carel Chapek died (who coined the word ‘robot’). Anschluss; Kristallnacht.
scopic range, because non-commutativity of the canonical variables is crucial. However, NCRI does not require the Bose-Einstein condensation.\textsuperscript{13} For the existence of supercurrent, the state with flow must be metastable thermodynamically, so we must consider the barrier between different flow states. Again, some sort of quantum coherence is needed,\textsuperscript{14} but its direct relation to the Bose-Einstein condensation does not exist.\textsuperscript{15}

### 3.5 Phonons and photons

Photons and phonons are obtained through quantization of the systems that can be described as a collection of harmonic oscillators.\textsuperscript{16} Possible energy levels for the \(i\)-th mode whose angular frequency is \(\omega_i\)\textsuperscript{17} are \((n + 1/2)\hbar \omega_i\). The canonical partition function of the whole systems is given by

\[
Z(\beta) = \prod_i \left( \sum_{n_i} e^{-\beta(n_i+1/2)\hbar \omega_i} \right),
\]

(3.5.1)

since no modes interact each other. Here, the product is over all the modes. The sum in the parentheses gives the canonical partition function for a single harmonic oscillator we have already encountered in (2.2.12). The canonical partition function may be rewritten as:

\[
Z(\beta) = \prod_i \left( e^{-\beta\hbar \omega_i/2} \right) \Xi(\beta, 0).
\]

(3.5.2)


\textsuperscript{15}A natural conclusion is that superfluidity and the Bose-Einstein condensation are caused in 4He liquid by a deeper common reason, the special topology of the many-body wave function.

\textsuperscript{16}That is, the system whose Hamiltonian is quadratic in canonical coordinates (quantum mechanically in the corresponding operators).

\textsuperscript{17}A system with a quadratic Hamiltonian may be described in terms of canonical coordinates (or corresponding operators) that makes the Hamiltonian diagonal. In other words, the system may be described as a collection of independent harmonic oscillators. The motion corresponding to each such harmonic oscillator is called a mode. If more than one modes have identical angular frequencies, modes cannot be uniquely chosen, but this does not cause any problem to us because partition functions need the system energies and their degeneracies only.