Chapter 3

Quantum Models

In classical statistical mechanics we did not know the exact microscopic state of the system (location in the phase space). We made use of the ergodic hypothesis and replaced the time average of a physical quantity with an ensemble average, i.e., an average over many equivalent systems.

In quantum statistical mechanics the situation is similar.

3.1 Quantum Statistics

In this Chapter we will first introduce the density matrix and then make an introduction to the Bose condensation.

In *quantum mechanics*, the energy levels are discrete and the state of the system is described by a wavefunction. Let us first assume that we know the dynamical state (wavefunction) $|\psi\rangle$ of the whole system and the *complete* set of stationary states $|n\rangle$ which are the eigenstates of the full Hamiltonian of the compound system,

$$\mathcal{H}|n\rangle = E_n|n\rangle. \tag{3.1}$$

(We assume that the states $|n\rangle$ are normalized.) n denotes the quantum states (e.g., momenta) of all particles in the system. E_n is the total energy of all particles of the system in the compound state n. Any dynamical state of the system can be expressed as a linear combination of these eigenstates,

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle, \tag{3.2}$$

The coefficients $c_n(t)$ define a point in the (Hilbert) space of wavefunctions $|n\rangle$. The (time-dependent) wavefunction $|\psi(t)\rangle$ which obeys the Schrödinger equation

$$i\hbar\frac{d|\psi\rangle}{dt} = \mathcal{H}|\psi\rangle \tag{3.3}$$

is thus the quantum-mechanical analogue of the point in phase space of classical statistical mechanics. The expectation value of a physical quantity A (which does not necessarily commute with $\mathcal{H}$) is:

$$\langle A(t)\rangle = \langle\psi(t)|A|\psi(t)\rangle = \sum_{m,n} c_n^* c_m \langle n|A|m\rangle$$

$$\tag{3.4}$$

The last expression holds for any complete set of states $|n\rangle$, also if they are not the eigenstates of the full Hamiltonian.

3.1.1 The Density Matrix

As the number of particles in the system increases, the separation between the energy levels decreases rapidly, and, in the thermodynamic limit, it becomes extremely high. On the other hand, the energy levels are never completely sharp. They are broadened for many reasons, including the uncertainty principle. In a macroscopic system (with extremely dense energy levels), the levels will thus always overlap. Consequently, a macroscopic system will never be in a strictly stationary quantum state, it will always be in a *dynamical* state, in a time-dependent *mixture* of stationary states.

It is neither feasible nor possible to find a complete description of such a system. Like in *classical statistical mechanics*, we first assume that the system is *ergodic*, we replace the time average by an ensemble average over many quantum systems at the same instance. We talk about probabilities of finding the system in the states $|n\rangle$. The dynamical state is no longer a unique quantum state but is a *statistical mixture of quantum states*. We introduce the *density matrix* as the ensemble average of $c_m^* c_n$:

$$\begin{aligned}\rho &= |m\rangle \rho_{m,n} \langle n| \\ \rho_{m,n} &\equiv \langle m|\rho|n\rangle = \frac{1}{\Omega}\sum_{i=1}^{\Omega} c_n^{i\,*} c_m^i.\end{aligned} \tag{3.5}$$

The sum over i runs over Ω configurations of the system, $|\psi^i\rangle$, all being part of the same ensemble, and $c_m^i = \langle m|\psi^i\rangle$. We do an ensemble average because our information on the system is not complete.

The density matrix is a statistical operator with the following important properties:

- The density matrix completely defines an ensemble of quantum systems and it carries all the information that is available for a quantum statistical ensemble.

- Its diagonal elements $\rho_{n,n}$ tell the probability that the system is in the state $|n\rangle$ whereas its non-diagonal elements $\rho_{m,n}$ tell the probability of a transition from the state $|n\rangle$ to the state $|m\rangle$. For stationary states, thus, ρ has to be diagonal, it commutes with the Hamiltonian.

- The density matrix is normalized,

$$\mathrm{Tr}(\rho) = 1. \tag{3.6}$$

The trace runs over any complete set of states $|n\rangle$ and is independent of the choice of the basis set.

- The (ensemble and quantum-mechanical) average value $\langle A \rangle$ of any physical quantity A is equal to:

$$\langle A \rangle = \langle \psi | A | \psi \rangle = \sum_{n,m} \rho_{m,n} \langle n|A|m \rangle = \mathrm{Tr}(\rho A) = \mathrm{Tr}(A\rho). \tag{3.7}$$

The trace in quantum statistical mechanics plays the role of integration over the whole available phase space in classical statistical mechanics.

- The dynamics of the system is completely described by:

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho]. \tag{3.8}$$

This is the "Schrödinger equation" of the density matrix.

3.1.2 Ensembles in Quantum Statistical Mechanics

Now, we shall specify the density matrix and its relation to thermodynamic quantities.

- *Quantum Microcanonical ensemble.*

  The energy of systems belonging to a microcanonical ensemble is fixed, therefore it is convenient to use the energy eigenstates as a basis. Then the density matrix is diagonal. According to the postulate of equal weights, all the states $|n\rangle$ with the energy E_n between E and $E + \Delta E$ are equally probable and let there be $\Delta\Omega$ such states. For a quantum system, $\Delta\Omega$ is an integer number. The probability for the system being in one of these states is $p = 1/\Delta\Omega$ and the entropy is equal to:

$$S = -k_B \langle \ln p \rangle. \tag{3.9}$$

  In general, we must use the density matrix instead of simple probabilities p and the entropy of a quantum system is:

$$\boxed{S = -k_B \langle \ln \rho \rangle = -k_B \, \text{Tr}(\rho \ln \rho)}. \tag{3.10}$$

  Again, the average $\langle \ \rangle$ means ensemble *and* quantum average – both averages cannot be separated.

- *Canonical ensemble.* In the energy representation ρ is diagonal and we can use the same arguments as in the case of classical canonical distributions. The matrix elements are equal to:

$$\rho_{m,m} = \frac{1}{Z} \, e^{-\beta E_m}, \tag{3.11}$$

  where the normalization constant is (again) the partition function

$$Z = \sum_m e^{-\beta E_m}. \tag{3.12}$$

  In an arbitrary basis, the density matrix can be written more generally as

$$\boxed{\rho = \frac{1}{Z} \, e^{-\beta \mathcal{H}}} \quad \text{with} \quad \boxed{Z = \text{Tr} \, e^{-\beta \mathcal{H}}} \tag{3.13}$$

  (ρ and $\mathcal{H}$ are operators!). Thus, for a canonical ensemble, the average (thermal and quantum- mechanical) of an operator A is:

$$\langle A \rangle = \text{Tr}\,(\rho A) = \frac{1}{Z} \, \text{Tr}\,(e^{-\beta \mathcal{H}} A) \tag{3.14}$$

In particular, the internal energy is

$$E = \langle \mathcal{H} \rangle = \frac{1}{Z} \mathrm{Tr} \left(\mathcal{H} \mathrm{e}^{-\beta \mathcal{H}} \right) = -\frac{\partial}{\partial \beta} \ln \mathrm{Tr} \, \mathrm{e}^{-\beta \mathcal{H}}$$

$$E = -\frac{\partial}{\partial \beta} \ln Z. \tag{3.15}$$

The free energy is

$$F = -k_B T \ln \, Z. \tag{3.16}$$

All the thermodynamic relations are the same as before (Tables I - III are still valid), the only difference is that now we have to calculate the partition function as the trace of the density matrix.

The entropy in a canonical ensemble, S, is the ensemble average over all (energy) states of the microcanonical entropy S:

$$S = -\langle k_B \ln \, \rho \rangle = -k_B \mathrm{Tr}(\rho \ln \rho). \tag{3.17}$$

- *Grand canonical ensemble.* In the grand canonical ensemble the operator ρ operates on a generalized Hilbert space which is the direct sum of all Hilbert spaces with fixed number of particles. The density matrix is:

$$\boxed{\rho = \frac{1}{\Xi} \, \mathrm{e}^{-\beta(\mathcal{H} - \mu N)},}$$

where the grand partition function is

$$\Xi(T, V, \mu) = \mathrm{Tr} \, \mathrm{e}^{-\beta(\mathcal{H} - \mu N)}.$$

Notice that now N is an operator in the generalized Hilbert space. As in the classical case, Ξ is equal to the canonical partition function Z, weighted by the fugacity $z = \exp(\beta \mu)$ and summed over N. The ensemble average of an operator A in the grand canonical ensemble is

$$\langle A \rangle = \frac{1}{\Xi} \mathrm{Tr}(A \, \mathrm{e}^{-\beta(\mathcal{H} - \mu N)}).$$

3.2 Bose Systems

3.2.1 Ideal Bose Gas

Now we shall consider the properties of an ideal gas of particles with integer spin and mass $m > 0$. As usually for ideal gases, we neglect the interaction between the particles. The Hamiltonian of the ideal Bose gas is:

$$\mathcal{H} = \sum_{\vec{p}} \frac{p^2}{2m} \, n_{\vec{p}}.$$

$n_{\vec{p}}$ is the number of particles in the state with momentum $\vec{p}$. Because we are dealing with Bosons, $n_{\vec{p}}$ can also be > 1. We want to study condensation where two phases come into contact, the number of particles in one phase is not fixed, therefore we must work with the grand-canonical distribution. The grand-canonical partition function of ideal Bose gas is:

$$\Xi = \sum_{\{n_{\vec{p}}\}} e^{-\beta \sum_{\vec{p}} (p^2/2m) \, n_{\vec{p}} + \beta \mu N}, \qquad N = \sum_{\vec{p}} n_{\vec{p}}.$$

(Here we will disregard the $(2S + 1)$ factor which comes from the spin degeneracy.) In the grand partition function, each sum over $n_{\vec{p}}$ is over all non-negative integers and, since the particles do not interact, we can split the partition function into a product:

$$\Xi = \sum_{n_0=0}^{\infty} \sum_{n_1=0}^{\infty} \cdots \left\{ \left[e^{\beta\mu} \right]^{n_0} \left[e^{-\beta(p_1^2/2m-\mu)} \right]^{n_1} \left[e^{-\beta(p_2^2/2m-\mu)} \right]^{n_2} \cdots \right\} = \quad (3.18)$$

$$= \prod_{\vec{p}} \left\{ \sum_{n} \left[e^{-\beta(p^2/2m-\mu)} \right]^{n} \right\} = \prod_{\vec{p}} \frac{1}{1 - z e^{-\beta p^2/2m}}.$$

Here we have introduced the *fugacity* $z = e^{\beta\mu}$. The equation of state of an ideal Bose gas is (see Table I):

$$PV = k_B T \ln \Xi(T, V, \mu)$$

$$\boxed{\frac{PV}{k_B T} = -\sum_{\vec{p}} \ln \left[1 - e^{-\beta(p^2/2m-\mu)} \right]} \qquad (3.19)$$

The thermal average of N is determined by the chemical potential μ (see Tables):

$$\langle N \rangle = -\frac{1}{\beta} \frac{\partial \ln \Xi}{\partial \mu} = \sum_{\vec{p}} \frac{1}{e^{\beta(p^2/2m-\mu)} - 1}. \tag{3.20}$$

We can write $\langle N \rangle = \sum_{\vec{p}} n_{\vec{p}}$ where

$$n_{\vec{p}} = \frac{1}{e^{\beta(p^2/2m-\mu)} - 1} \tag{3.21}$$

is the Bose-Einstein distribution function, which tells the occupation probability of a given (non-degenerate) state $\vec{p}$. For $\langle N \rangle$ to be finite and positive, the second term in the denominator has to be < 1 for any $\vec{p}$, in particular for $p = 0$. This means that μ must be < 0 and $0 < z < 1$.

For large V we replace the sum by an integral:

$$\sum_{\vec{p}} \rightarrow \frac{4\pi V}{h^3} \int_0^\infty p^2 \, dp \tag{3.22}$$

and we get:

$$\langle N \rangle = \frac{4\pi V}{h^3} \int_0^\infty p^2 \, dp \, \frac{1}{e^{\beta(p^2/2m-\mu)} - 1}$$
$$= V g_{3/2}(z) \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} = \frac{V}{\lambda^3} g_{3/2}(z), \tag{3.23}$$

where

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{e^x z^{-1} - 1} = \sum_{l=1}^\infty \frac{z^l}{l^\nu} \tag{3.24}$$

and λ is the thermal wavelength,

$$\lambda = \left(\frac{2\pi\hbar^2}{mk_B T}\right)^{1/2}.$$

The functions $g_{3/2}(z)$ and $g_{5/2}(z)$ are shown in Fig 3.1. For later use: $g_{3/2}(1) \approx 2.612$ and $g_{5/2}(1) \approx 1.342$. The pressure is:

$$P = \left(\frac{m}{2\pi\hbar^2}\right)(k_B T)^{5/3} g_{5/2}(z) = \frac{k_B T}{\lambda^3} g_{5/2}(z). \tag{3.25}$$
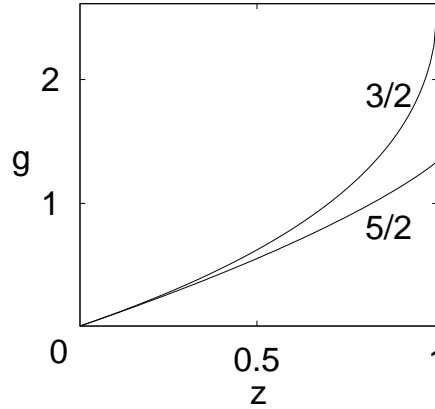
Figure 3.1: The functions $g_{3/2}(z)$ and $g_{5/2}(z)$.

Now let us start increasing the pressure at fixed (high enough) T. This increases the chemical potential, the fugacity, and the density of particles, $\langle N \rangle / V$. However, we know that z must be < 1. What happens when $z \to 1$? Can we further increase the pressure or the density of particles?

To answer this question we must go back to Eq. (3.20). The term with $\vec{p} = 0$ which was not included in (3.23) (The density of states $n(E)$ has a $\sqrt{E}$ dependence on E and vanishes as $E \to 0$.) becomes singular (divergent) when $\mu \to 0$ and it has to be treated separately. This divergence has very important consequences for a Bose gas, as we shall show now. Instead of Eq. (3.20) we must write:

$$\langle N \rangle = \sum_{\vec{p} \neq 0} \frac{1}{e^{\beta(p^2/2m - \mu)} - 1} + \frac{z}{1 - z} = \frac{V}{\lambda^3} g_{3/2}(z) + \frac{z}{1 - z} \qquad (3.26)$$

and the equation of state is:

$$\frac{PV}{k_B T} = -\frac{4\pi V}{h^3} \int_0^\infty p^2 \, dp \ln \left[1 - z e^{-\beta p^2/2m} \right] - \ln(1 - z)$$

$$\boxed{\frac{P}{k_B T} = \frac{1}{\lambda^3} g_{5/2}(z) - \frac{1}{V} \ln(1 - z),} \qquad (3.27)$$

The last terms in Eqs. (3.26) and (3.27) come from the term $p = 0$ and correspond to the particles in the lowest energy, in the ground state. In the thermodynamic limit the last term in (3.27) vanishes whereas it remains finite in (3.26). We will denote

$$\langle N \rangle = \langle N' \rangle + \langle N_0 \rangle, \tag{3.28}$$

where $\langle N' \rangle$ is the average number of bosons in the continuum (excited, $p > 0$) states,

$$\langle N' \rangle = \frac{V}{\lambda^3} g_{3/2}(z) \tag{3.29}$$

and $\langle N_0 \rangle$ the average number of bosons in the ground state,

$$\langle N_0 \rangle = \frac{z}{1 - z}. \tag{3.30}$$

The average density of bosons in the continuum states reaches its maximum value when $g_{3/2}(z)$ is maximal, that is for $z \to 1$ ($\mu \to 0$),

$$\frac{\langle N'_{max}(T) \rangle}{V} = g_{3/2}(1) \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \propto T^{3/2}. \tag{3.31}$$

The fact that $\langle N' \rangle$ is limited and cannot exceed $\langle N'_{max} \rangle$ has its origin in the quantum-mechanical and statistical nature of the system. The number of available states in a box with volume V is finite and is equal to $\frac{V}{\lambda^3}$. Each state, on the average, accommodates $n_{\vec{p}}$ particles, where $n_{\vec{p}}$ is given by the Bose-Einstein distribution function, Eq. (3.21). If there are more than $\langle N' \rangle$ particles in the system, they are *pushed* into the ground state.

3.2.2   Bose Einstein Condensation

We will now investigate the behaviour of *ideal* Bose gases, described by Eqs. (3.26, 3.27). Let us consider a system of N bosons in a volume V.

At high enough temperature, $\langle N'_{max} \rangle$ is so large that $N < \langle N'_{max} \rangle$ and the chemical potential is determined from

$$N = \langle N' \rangle = V \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} g_{3/2}(z). \tag{3.32}$$

This means that $z < 1$ and $\mu < 0$. The density of particles in the ground state is

$$\langle N_0 \rangle / V = z/(1-z)/V \to 0 \quad \text{as} \quad V \to \infty. \tag{3.33}$$

Almost all the particles are in the $|\vec{p}| > 0$ states and the ground state is macroscopically empty. The equation of state simplifies to

$$\frac{P}{k_B T} = \frac{g_{5/2}(z)}{\lambda^3} \tag{3.34}$$

At very high T, $g_{3/2}(z)$ and $g_{5/2}(z)$ are $\ll 1$ and we approximate [see the series for g_n, Eq. (3.24)]:

$$g_{5/2}(z) \approx g_{3/2} \approx z \tag{3.35}$$

and the equation of state becomes:

$$\frac{P}{k_B T} = g_{5/2}(z) \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \approx z \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} = \frac{z}{\lambda^3}. \tag{3.36}$$

z is determined by the density of particles:

$$\frac{N}{V} = g_{3/2}(z) \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \approx z \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} = \frac{z}{\lambda^3}. \tag{3.37}$$

The fugacity $z = \langle N \rangle \lambda^3 / V$ vanishes as $T^{-3/2}$ at high T and for fixed density. This justifies the approximation (3.35). Eliminating z from the last two equations yields the equation of state of the ideal Bose gas at high T:

$$\boxed{PV = <N> k_B T} \tag{3.38}$$

which is identical to the equation of state of a classical ideal gas (as it should be at high T!).

Now we lower the temperature by keeping N and V fixed. Eq. (3.32) tells us that $g_{3/2}(z)$ must increase. This means that z and μ also increase. Eventually, a temperature is reached, where z reaches its maximum value ($z \to 1$, $N = \langle N'_{max} \rangle$). This is the transition temperature T_C and is determined by the condition

$$\frac{N}{V} = g_{3/2}(1) \left(\frac{m k_B T_C}{2\pi \hbar^2} \right)^{3/2} \tag{3.39}$$

from which we find:

$$T_C = \frac{2\pi\hbar^2}{k_B m \left[g_{3/2}(1)\right]^{2/3}} \left(\frac{N}{V}\right)^{2/3}.$$

(3.40)

If we insert this expression into the equation of state, Eq. (3.34), we obtain the pressure at which the transition takes place:

$$P_C = k_B T_C^{5/2} g_{5/2}(1) \left(\frac{m k_B}{2\pi\hbar^2}\right)^{3/2} \propto T_C^{5/2}.$$

(3.41)

At T_C, the ensemble average of the density of particles in the continuum states reaches its maximum value whereas the ground state is still empty, $\langle N_0\rangle/V = 0$.

Below T_C, $\langle N'_{max}\rangle$ further decreases and becomes $< N$ (we keep N fixed). The chemical potential further approaches zero (μ cannot be exactly $= 0$, because that would mean that $N = \infty$) and $z \to 1$ in such a way that the total number of particles is kept constant. z is very close to 1, we can put $g_n(z) \approx g_n(1)$ and the number of particles in the continuum states is

$$\langle N'\rangle = V \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2} g_{3/2}(1).$$

(3.42)

When $\langle N'\rangle < N$, the ground state starts to fill, $\langle N_0\rangle$ increases. Below T_C, thus, only a part of the particles can be accommodated in the continuum states. The rest must go into the ground state! The number of bosons in the ground state is:

$$\langle N_0\rangle = N - \langle N'\rangle = N - V \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2} g_{3/2}(1)$$

from which we get:

$$\frac{\langle N_0\rangle}{N} = 1 - \left(\frac{T}{T_C}\right)^{3/2}.$$

(3.43)

$\langle N_0\rangle/N$ is finite, the state with $\vec{p} = 0$ is occupied with a *macroscopic* number of particles, the particles *condense* in the *momentum* space into the zero-momentum
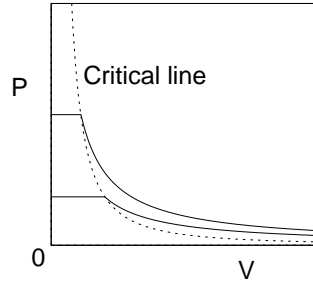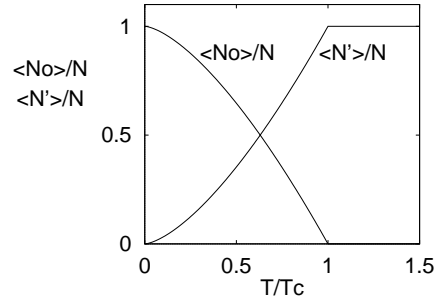
63

Figure 3.2: Isotherms of the ideal Bose gas.

Figure 3.3: Temperature dependence of the relative number of bosons in the ground ($\langle N_0 \rangle/N$) and excited ($\langle N' \rangle/N$) states.

state. This is the *Bose-Einstein condensation*. The fugacity is, from Eq. (3.30): $z = \langle N_0 \rangle/(\langle N_0 \rangle + 1)$. In the thermodynamic limit, when V and $\langle N_0 \rangle \rightarrow \infty$, $z = 1$ and $\mu = 0$ below T_C. The equation of state is:

$$P = g_{5/2}(1) \left(\frac{mk_BT}{2\pi\hbar^2} \right)^{3/2} k_BT = \frac{g_{5/2}(1)}{g_{3/2}(1)} \frac{\langle N' \rangle}{V} k_BT. \tag{3.44}$$

Only the particles in the continuum states (in the gas phase) contribute to pressure. The particles in the ground state (condensate) are at rest, they cannot exert any pressure. If the density is increased, the extra particles fall into the ground state and the pressure does not increase. At fixed $T < T_C$ the density of particles in the gas phase is constant and P is independent of V, see Fig. 3.2. The temperature dependence of $\langle N_0 \rangle$ is shown in Fig. 3.3. In the limit $T \rightarrow 0$, $\langle N'_{max} \rangle \rightarrow 0$ and all the particles are in the ground state, $N = \langle N_0 \rangle$.
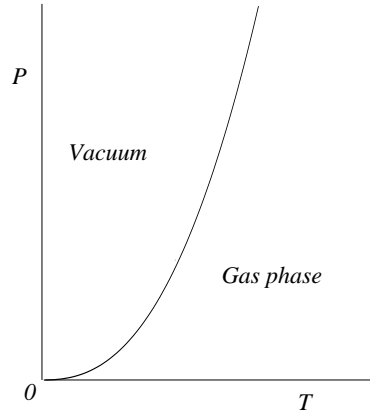
Figure 3.4: Phase diagram of an ideal Bose gas.

The corresponding *phase diagram* is shown in Fig. 3.4. The normal, gas phase exists for $T > T_C$, i.e., to the right of the transition line. On the line, given by (3.41), condensation takes place and since the particles in the ground state don't contribute to pressure, the condensate lies on the transition line itself. Notice that the "critical points" in Bose systems form a *line* in the P vs. T or in the P vs. V planes and are not in a single point like in van der Waals gases.

We now invert Eq. (3.44),

$$V = \frac{g_{5/2}(1)}{g_{3/2}(1)} \frac{\langle N' \rangle}{P} k_B T. \tag{3.45}$$

As $T \to 0$, also $\langle N' \rangle \to 0$ and therefore $V \to 0$ at any finite pressure. The condensed phase does not occupy any volume. This means that the ideal Bose gas can be compressed to zero volume without any increase in pressure.

Some comments: The condensate (ground state) contributes neither to E, nor to C_V, P, or V! At low T, C_V vanishes like $T^{3/2}$ in contrast to the photon gas, where $C_V \propto T^3$. They differ because the density of states is different in both cases. There are more excited states available for particles than for photons and the specific heat is greater.

Of course, this, and infinite compressibility are the artifacts of the ideal gas model. In reality, because of atomic repulsion, the volume of the condensed phase does not vanish and the compressibility does not diverge. The equation of state of a non-ideal Bose gas is shown in Fig. 3.5.
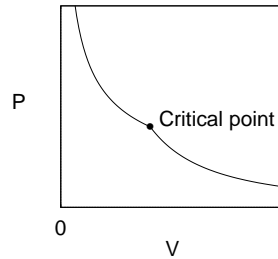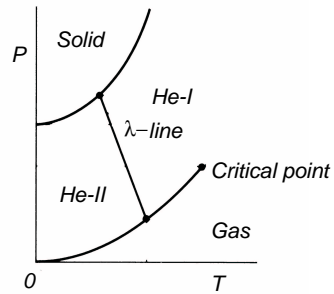
Figure 3.5: An isotherm of a non-ideal Bose gas.

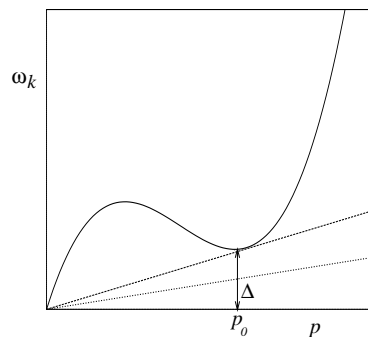Figure 3.6: Phase diagram of ^{4}He. He I is the normal, and He II the superfluid phase.

Figure 3.7: Dispersion curve of elementary excitations in liquid ^{4}He. The excitations around the minimum at p_0 are called rotons.

3.3 Liquid ^{4}He

A candidate for the Bose-Einstein condensation at low T is liquid ^{4}He. The phase diagram is shown in Fig. 3.6. He I is the normal liquid and He II exhibits super-fluid behaviour. From the fact that the line separating the solid and the fluid phases is horizontal at $T \to 0$, we conclude with the help of the Clausius-Clapeyron equation,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = 0 = \frac{S_{\text{fluid}} - S_{\text{solid}}}{V_{\text{fluid}} - V_{\text{solid}}} \tag{3.46}$$

that liquid He II at $T \to 0$ has no more entropy than solid helium, which is highly ordered, of course. We conclude that the particles in the ground state ($T \to 0$) have already the highest possible degree of order although they are in the fluid and not in the solid phase. We interpret the He II phase as a mixture of two fluids, a normal fluid with final viscosity and a super-fluid (formed of particles in the ground state) with zero viscosity. Characteristic for the superfluid state is also a very large heat conductivity (as a consequence, He II does not boil, the atoms only evaporate from the surface). What is the ground state of He II and what are the excitations?

We shall first discuss possible excitations above the ground state of liquid ^{4}He and only then the properties of the ground state. In the liquid, the atoms are close together, they are strongly interacting (exchanging momenta). A state of an atom with fixed momentum is not an eigenstate of the Hamiltonian, the atoms are subject to a *collective motion*. The elementary excitations in the system are collective excitations, *quasiparticles*, *phonons* (longitudinal because it is a liquid) and *rotons* (see Fig. 3.7). At low momenta, the excitations are phonons with a linear dispersion relation,

$$\epsilon_p = cp. \tag{3.47}$$

At high momenta (short wavelengths), the interaction between the atoms causes a minimum in the dispersion curve. Elementary excitations around this minimum are (for historical reasons) called rotons. Their energy is written in the form:

$$\epsilon_p = \Delta + \frac{(p - p_0)^2}{2m^*}, \tag{3.48}$$

where Δ is the energy gap, $\Delta/k_B = 8.6$K, and $m^* = 1.0 \times 10^{-27}$kg is the effective mass of rotons. $p_0 = 2.0 \times 10^{-24}$kg m/s. At low T, the density of these quasiparticles is low and they don't interact.

The grand canonical partition function for phonons ($\mu = 0$) is, in analogy with (3.18):

$$
\begin{aligned}
\ln \Xi_{ph} &= -\frac{4\pi V}{h^3} \int_0^\infty p^2 dp \ln(1 - e^{-\beta cp}) \\
&= \frac{4\pi V}{3(h\beta c)^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} \\
&= \frac{4\pi^5 V}{45(hc)^3}(k_B T)^3 \tag{3.49}
\end{aligned}
$$

The grand canonical partition function for rotons (also $\mu = 0$) is:

$$
\ln \Xi_{rot} = -\frac{4\pi V}{h^3} \int_0^\infty p^2 dp \ln(1 - e^{-\beta\Delta - \beta(p-p_0)^2/2m^*})
$$

At low T (large β), $e^{-\beta\Delta - \beta(p-p_0)^2/2m^*}$ is small and we approximate $\ln(1 - x) \approx -x$. (This is equivalent to using the Maxwell-Boltzmann distribution.)

$$
\begin{aligned}
\ln \Xi_{rot} &= \frac{4\pi V}{h^3} e^{-\beta\Delta} \int_0^\infty p^2 dp\, e^{-\beta(p-p_0)^2/2m^*} \\
&\approx \frac{4\pi V}{h^3} e^{-\beta\Delta} \int_{-\infty}^\infty p^2 dp\, e^{-\beta(p-p_0)^2/2m^*} \\
&= \frac{4\pi V}{h^3} \sqrt{\frac{2\pi m^*}{\beta}} \left(p_0^2 + \frac{m^*}{\beta} \right) e^{-\beta\Delta} \tag{3.50}
\end{aligned}
$$

From these equations, one can calculate the specific heat (and other thermodynamic quantities) at low temperatures.

3.3.1 Superfluidity

Consider an isolated system (in which energy and momentum are conserved) composed of a long cylindrical capillary filled with liquid ^{4}He at $T = 0$. Initially, let the capillary tube rotate along the symmetry axis with the tangential velocity v_0 and let the fluid be at rest. We would expect that - because of friction - energy would be transferred from the tube to the fluid and that the fluid will gradually be excited out of the ground state. Let us check under which conditions the energy and momentum can be transferred to the fluid. Immediately after the tube started to rotate, the tube had the kinetic energy $Mv_0^2/2$ (M is the mass of the tube) and the fluid was at rest and had the ground-state energy E_0. At a later time, we expect the tube velocity to decrease by Δv (because we consider an isolated system) and

that in the fluid an (at least one) elementary excitation with energy ϵ_p and momentum $\vec{p}$ is created. The conservation laws demand that the energy at a later time is:

$$\frac{1}{2}M(v_0 - \Delta v)^2 + \epsilon_p + E_0 = \frac{1}{2}Mv_0^2 + E_0$$

(3.51)

and that the momentum is:

$$M(v_0 - \Delta v) + p_t = Mv_0 \qquad \Rightarrow \qquad M\Delta v = p_t \qquad (3.52)$$

where p_t is the excitation momentum in the tangential direction. For $\Delta v \neq 0$, the first equation gives the inequality

$$\epsilon_p = Mv_0\Delta v - \frac{1}{2}M(\Delta v)^2 < Mv_0\Delta v. \qquad (3.53)$$

After eliminating $M\Delta v$, the conservation laws tell us that

$$\vec{v} \cdot \vec{p} > \epsilon_p. \qquad (3.54)$$

Inspection of Fig. 3.7 shows that this is only possible if v is larger than a threshold velocity v_c. At small relative velocity between the tube and the fluid, the rotons are not excited, the momentum is not transferred to the fluid, the fluid will stay at rest. This means that there is no friction, no viscosity - this is the superfluid phase. (As we will see later, roton excitations are not responsible for the excitation out of the ground state. Vortices have higher energy, but lower ϵ/p ratio.)

3.3.2 Vortex Excitations

There are other collective excitations in liquid ^{4}He that have higher energies than phonons or rotons, but which nonetheless have much lower energy to momentum ratio than rotons. The creation of these excitations allows energy and momentum to be transferred to the fluid at a much lower critical velocity than in the case of rotons.

Let us now discuss such excitations of the condensate. The wave function of an excited collective state is

$$\Psi = \psi e^{i\phi(r)}, \qquad (3.55)$$

the (mass) current density is

$$\vec{j} = \frac{i\hbar}{2}\left[\Psi\vec{\nabla}\Psi^* - \Psi^*\vec{\nabla}\Psi\right] = \hbar\psi^2\vec{\nabla}\phi(\vec{r}). \qquad (3.56)$$

On the other hand,

$$\vec{j} = \frac{N}{V} m \vec{v} \tag{3.57}$$

where $N/V = \rho = \psi^2$. From the two equations we get for the particle velocity

$$\vec{v} = \frac{\hbar}{m} \vec{\nabla} \phi(\vec{r}). \tag{3.58}$$

The wavefunction must be single-valued and the phase ϕ is determined modulo 2π, therefore the closed-path integral of the momentum is

$$m \oint \vec{v} \cdot d\vec{l} = \hbar \oint \vec{\nabla} \phi d\vec{l} = nh, \tag{3.59}$$

where h is the Planck's constant and n an arbitrary integer.

To understand the nature of these excited states it is best to consider liquid ^{4}He within a small rotating bucket. If the bucket is slowly brought into rotation, the liquid will behave in the following way. At small angular velocities of the bucket, the liquid will remain at rest. If the angular velocity is increased beyond some threshold angular velocity, the energy is transferred to the fluid, and the fluid will make an abrupt transition to a state in which there is a *vortex line* running from top to bottom, parallel to the axis of rotation. The vortex line looks like a small whirlpool, the fluid flows around the line with the velocity that decreases with distance from the line. The *vorticity*, defined as the line integral of the momentum along any path encircling the vortex line, Eq. (3.59), is quantized. As the angular velocity is increased, more and more quantized vortex lines are created. Once a vortex line is created, the macroscopically occupied single-particle ground state is no longer a zero-momentum eigenstate. It is a quantum state with a flow pattern that includes the vortex lines. When there are many vortex lines, they will distribute themselves in a pattern so that the average fluid velocity (averaged over many vortices) is the same as in the case of rigid-body rotation.

To summarize, the quantization of vortices is related to the phase factor of the condensate wave function, defined in Eq. (3.60). In the lowest-energy state, ψ and ϕ do not depend on $\vec{r}$, they are constant. The state in which ϕ varies with $\vec{r}$ is an excited state which describes the fluid with one or several vortices.

3.3.3   Order Parameter

A superfluid can be considered as a mixture of two coexisting fluids, of a normal component and of a superfluid component. At a first glance, one would choose

the density of particles in the ground (superfluid) state as the order parameter, because it is $\neq 0$ in the low-temperature phase and vanishes at T_C. However, in an interacting system, the *operator* N_0 doesn't commute with $\mathcal{H}$, the single-particle momenta are not good quantum numbers. On the other hand we already know that the ground state is a state with zero momentum $\vec{p} = 0 = -i\hbar\vec{\nabla} \Rightarrow \vec{\nabla} = 0$. This means that the *wavefunction* is a constant in the ground state. Therefore we choose for the order parameter the *statistical average of the ground-state wave function* which commutes with $\mathcal{H}$ and which can be written in the form:

$$\langle \Psi \rangle = \frac{1}{\Xi} \text{Tr} \left[\Psi e^{-\beta(\mathcal{H} - \mu N)} \right] = \psi e^{i\phi} \tag{3.60}$$

(ψ is the amplitude and ϕ the phase of the wavefunction). The density of the superfluid component is $\langle N_0 \rangle / V = \psi^2 = $ constant. In the superfluid phase, a *macroscopically occupied single-particle quantum-mechanical ground state with zero momentum extends through the whole volume available to the fluid. Each atom is not at any particular place, it is simultaneously everywhere in the macroscopic volume!* This is the meaning of the order parameter defined in (3.60).

Symmetry breaking. There is a strong parallel between $\langle \Psi \rangle$ and the spontaneous magnetization $\langle \vec{M} \rangle$ in ferromagnets,

$$\langle \vec{M} \rangle = \frac{1}{Z} \text{Tr} \left(\vec{M} e^{-\beta\mathcal{H}} \right), \tag{3.61}$$

where $\vec{M}$ is the (operator for the) total magnetic moment and

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j.$$

In the absence of an external magnetic field, thus, $\mathcal{H}$ is invariant under rotations, $\vec{M}$ and $-\vec{M}$ occur with equal probability and therefore $\langle \vec{M} \rangle$ is always zero. But we know that the ferromagnets do have spontaneous magnetization at low T. The resolution lies in "spontaneous symmetry breaking" - the ground state of a Hamiltonian does *not* possess the full symmetry of the Hamiltonian. The ground state wavefunction is not rotationally invariant, because $\langle \vec{M} \rangle$ points along a definite direction in space whereas $\mathcal{H}$ is rotationally invariant. In the case of ferromagnets, thus, the transition corresponds to spontaneous breaking of the rotational symmetry. One must therefore redefine $\langle \vec{M} \rangle$ in such a way that $+\vec{M}$ and $-\vec{M}$ are not both included in the partition function with equal weights. This is most easily done by imposing an infinitesimal external field H:

$$\langle \vec{M} \rangle = \lim_{H \to 0} \lim_{V \to \infty} \frac{1}{Z} \text{Tr} M e^{-\beta(\mathcal{H} - \vec{M} \cdot \vec{H})}. \tag{3.62}$$

Returning to Bose systems, the Hamiltonian has a *global gauge invariance*, the wave functions are invariant with respect to the phase shift,

$$\Psi(\vec{r}) \rightarrow e^{i\phi(\vec{r})}\Psi(\vec{r}) \tag{3.63}$$

where ϕ is an arbitrary phase factor (real number). Bose condensation corresponds to a *spontaneous breaking of global gauge invariance*. When calculating the order parameter, we imagine, like in magnetic systems that the system is subjected to an (infinitesimal) external field η which couples linearly to the order parameter. We calculate the statistical average of $\Psi(\vec{r})$ in the thermodynamic limit:

$$\langle \Psi(\vec{r}) \rangle = \lim_{\eta \to 0} \lim_{V \to \infty} \frac{1}{\Xi} \mathrm{Tr}\Psi(\vec{r}) e^{-\beta \mathcal{E}}, \tag{3.64}$$

where

$$\mathcal{E} = \mathcal{H} - \mu N - \int d^3 r [\Psi(\vec{r})\eta(\vec{r}) + \Psi^\dagger(\vec{r})\eta^\dagger(\vec{r})]. \tag{3.65}$$

The only essential difference with the ferromagnetic case is that the external field here is fictitious, it cannot be realized experimentally.