Lecture Notes on Statistical Mechanics

Stefano Giorgini
University of Trento

September 25, 2017

Contents

Chapter 1

Second Quantization

Second quantization is a formal development of the theoretical description of many-body systems in terms of quantized fields that is particularly suitable when dealing with interacting systems with many degrees of freedom. The representation of relevant physical operators, such as the Hamiltonian, in terms of quantized fields is formally similar to the usual Schrödinger representation in terms of wave functions. This theoretical treatment where fields, such as the electromagnetic field as well as matter fields represented by wave functions, are upgraded to space dependent operators is referred to as second quantization in analogy with the first quantization scheme where physical observables are upgraded to operators. We stress, however, that the second quantization formalism becomes truly crucial only when dealing with relativistic processes where particles can be created and annihilated, whereas in non-relativistic quantum many-body physics it provides a convenient formal scheme to treat systems in the grand-canonical ensemble. The chapter is organized as follows:

- Single-particle states and review of bra-ket formalism.
- Two-particle states and symmetric/antisymmetric states.
- Fully symmetric/antisymmetric many-particle states and indistinguishability principle.
- Fock space and creation/annihilation operators.
- Representation of one-body and two-body operators in terms of quantized fields.

1.1 Fock space and creation/annihilation operators

1.1.1 Single-particle Hilbert space

The single-particle Hilbert space is denoted by $\mathcal{H}_1$: states belonging to $\mathcal{H}_1$ are specified by a complete set of quantum numbers. We consider states forming a complete orthonormal basis of $\mathcal{H}_1$.

The basis can be:

- discrete: $|\alpha\rangle \to \langle\alpha|\beta\rangle = \delta_{\alpha,\beta}$ and $\sum_\alpha |\alpha\rangle\langle\alpha| = 1$
- continuous: $|\mathbf{r}\rangle \to \langle\mathbf{r}|\mathbf{r}'\rangle = \delta(\mathbf{r}-\mathbf{r}')$ and $\int d\mathbf{r}|\mathbf{r}\rangle\langle\mathbf{r}| = 1$

The single-particle wave function in coordinate space is given by:

$$\varphi_\alpha(\mathbf{r}) = \langle\mathbf{r}|\alpha\rangle \ .$$

-)Example: particle in a cubic box with periodic boundary conditions (p.b.c). States are labeled by the wave vector $\mathbf{k}$

$$|\mathbf{k}\rangle \to \varphi_{\mathbf{k}}(\mathbf{r}) = \langle\mathbf{r}|\mathbf{k}\rangle = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}} \ ,$$

where $V = L^3$ is the volume of the box. The possible values of $\mathbf{k}$ are

$$\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \ \text{ where } \ n_{x,y,z} = 0, \pm1, \pm2, ...$$

such that

$$e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1 \ .$$

One verifies the following properties:

- orthonormality

$$\langle\mathbf{k}|\mathbf{k}'\rangle = \int d\mathbf{r}\langle\mathbf{k}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{k}'\rangle = \frac{1}{V}\int d\mathbf{r}e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} = \delta_{\mathbf{k},\mathbf{k}'}$$

- completeness

$$\langle\mathbf{r}|\mathbf{r}'\rangle = \sum_{\mathbf{k}}\langle\mathbf{r}|\mathbf{k}\rangle\langle\mathbf{k}|\mathbf{r}'\rangle = \frac{1}{V}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \delta(\mathbf{r}-\mathbf{r}') \ ,$$

where the last identity follows from the properties of Fourier series. From the Fourier decomposition of the δ-function: $\delta(\mathbf{r}-\mathbf{r}') = 1/(2\pi)^3 \int d\mathbf{k} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}$, one derives the following relation

$$\frac{1}{V}\sum_{\mathbf{k}} = \frac{1}{(2\pi)^3}\int d\mathbf{k} \ ,$$

that will be used when taking the thermodynamic limit $V \to \infty$.

- representation of operators

a) The states $|\mathbf{k}\rangle$ are eigenstates of the kinetic energy: $T_1|\mathbf{k}\rangle = (\hbar^2 k^2/2m)|\mathbf{k}\rangle$. Thus, the single-particle kinetic energy is diagonal in momentum space

$$\langle \mathbf{k}'|T_1|\mathbf{k}\rangle = \delta_{\mathbf{k},\mathbf{k}'}\frac{\hbar^2 k^2}{2m} \ .$$

One gets

$$\begin{aligned}\delta_{\mathbf{k},\mathbf{k}'}\frac{\hbar^2 k^2}{2m} &= \int d\mathbf{r}' \int d\mathbf{r} \langle \mathbf{k}'|\mathbf{r}'\rangle\langle \mathbf{r}'|T_1|\mathbf{r}\rangle\langle \mathbf{r}|\mathbf{k}\rangle \\ &= \int d\mathbf{r}' \int d\mathbf{r} \frac{1}{\sqrt{V}} e^{-i\mathbf{k}'\cdot\mathbf{r}'}\langle \mathbf{r}'|T_1|\mathbf{r}\rangle \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}\end{aligned}$$

from which we have the well-known coordinate representation of the kinetic-energy operator

$$\langle \mathbf{r}'|T_1|\mathbf{r}\rangle = \delta(\mathbf{r}-\mathbf{r}')\left(\frac{-\hbar^2\nabla^2}{2m}\right) \ .$$

Notice that an equivalent result for $\langle \mathbf{r}'|T_1|\mathbf{r}\rangle$ that can be derived by inserting two closure relations $\sum_{\mathbf{k}} |\mathbf{k}\rangle\langle\mathbf{k}|$ in the matrix element is given by $\langle \mathbf{r}'|T_1|\mathbf{r}\rangle = \left(-\hbar^2\nabla^2/(2m)\delta(\mathbf{r}-\mathbf{r}')\right)$.

b) The states $|\mathbf{r}\rangle$ are eigenstates of the potential energy: $U_1|\mathbf{r}\rangle = U(\mathbf{r})|\mathbf{r}\rangle$, and U_1 is diagonal in coordinate space

$$\langle \mathbf{r}'|U_1|\mathbf{r}\rangle = \delta(\mathbf{r}-\mathbf{r}')U(\mathbf{r}) \ .$$

In momentum space the matrix elements of U_1 are given by the Fourier transform of the function $U(\mathbf{r})$

$$\langle \mathbf{k}'|U_1|\mathbf{k}\rangle = \frac{1}{V}\int d\mathbf{r} U(\mathbf{r}) e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}} \equiv \frac{1}{V}U_{\mathbf{k}'-\mathbf{k}} \ .$$

If the particle possesses spin s, the total wave function should also include a spinor χ_σ spanning a space with $2s+1$ dimensions. For example, in the case of spin 1/2, the wave function is given by

$$\varphi_{\mathbf{k}\uparrow}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \begin{pmatrix} 1 \\ 0 \end{pmatrix} .$$

We label by $|x\rangle$ the states $|\mathbf{r},\sigma\rangle$ having space coordinate $\mathbf{r}$ and component of the spin σ and we use the notation

$$\int dx = \int d\mathbf{r} \sum_\sigma \quad \text{and} \quad \delta(x-x') = \delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma,\sigma'}$$

such that

$$\int dx |x\rangle\langle x| = 1 \quad \text{and} \quad \langle x|x'\rangle = \delta(x-x') .$$

1.1.2 Two-particle Hilbert space

The two-particle Hilbert space is denoted by $\mathcal{H}_2 = \mathcal{H}_1 \otimes \mathcal{H}_1$, tensor product of two single-particle Hilbert space $\mathcal{H}_1$.

A complete basis of the space $\mathcal{H}_2$ is formed by the states

$$|\alpha_1\alpha_2\rangle = |\alpha_1\rangle|\alpha_2\rangle \quad \text{and} \quad \langle\alpha_1\alpha_2| = \langle\alpha_1|\langle\alpha_2| ,$$

where $|\alpha_1\rangle$ refer to particle 1 and $\alpha_2\rangle$ to particle 2. They satisfy the following properties

- orthogonality

$$\langle\alpha_1\alpha_2|\alpha_1'\alpha_2'\rangle = \langle\alpha_1|\alpha_1'\rangle\langle\alpha_2|\alpha_2'\rangle$$

- completeness

$$\sum_{\alpha_1\alpha_2} |\alpha_1\alpha_2\rangle\langle\alpha_1\alpha_2| = \sum_{\alpha_1} |\alpha_1\rangle\langle\alpha_1| \sum_{\alpha_2} |\alpha_2\rangle\langle\alpha_2| = 1$$

The wave functions in coordinate space (*e.g.* for particles in a cubic box with p.b.c.) are given by

$$\varphi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{V} e^{i\mathbf{k}_1\cdot\mathbf{r}_1} e^{i\mathbf{k}_2\cdot\mathbf{r}_2} ,$$

where particle 1 has wave vector $\mathbf{k}_1$ and particle 2 wave vector $\mathbf{k}_2$.

States can be symmetric or antisymmetric with respect to particle exchange

$$\begin{aligned} S|\alpha_1\alpha_2\rangle &= \frac{1}{2}\left(|\alpha_1\alpha_2\rangle + |\alpha_2\alpha_1\rangle\right) \\ A|\alpha_1\alpha_2\rangle &= \frac{1}{2}\left(|\alpha_1\alpha_2\rangle - |\alpha_2\alpha_1\rangle\right) \ , \end{aligned}$$

where S and A are respectively the symmetrizing and antisymmetrizing operators.

- If $|\alpha_1\alpha_2\rangle$ is a complete system in $\mathcal{H}_2$ then
  - a) $S|\alpha_1\alpha_2\rangle$ is a complete system in the symmetric subspace $\mathcal{H}_2^S$

    Proof:

    $$1 = S = SS = SS^\dagger = \sum_{\alpha_1\alpha_2} S|\alpha_1\alpha_2\rangle\langle\alpha_1\alpha_2|S^\dagger$$

    where we used the following properties of the symmetrizing operator
    - S is the identity in $\mathcal{H}_2^S$
    - S is a projector on $\mathcal{H}_2^S$ ($SS = S$)
    - S is hermitian ($S = S^\dagger$)

      as one can prove using: $\langle\alpha_1\alpha_2|S^\dagger|\alpha_1'\alpha_2'\rangle = \langle\alpha_1'\alpha_2'|S|\alpha_1\alpha_2\rangle^* = \langle\alpha_1\alpha_2|S|\alpha_1'\alpha_2'\rangle$.
  - b) $A|\alpha_1\alpha_2\rangle$ is a complete system in the antisymmetric subspace $\mathcal{H}_2^A$

    Proof: same as for S since A and S have the same properties.
- The states $S|\alpha_1\alpha_2\rangle$ and $A|\alpha_1\alpha_2\rangle$ are orthogonal but not normalized
  - a) Symmetric states

$$\begin{aligned} \langle\alpha_1'\alpha_2'|SS|\alpha_1\alpha_2\rangle &= \langle\alpha_1'\alpha_2'|\frac{1}{2}\Big(|\alpha_1\alpha_2\rangle + |\alpha_2\alpha_1\rangle\Big) \\ &= \frac{1}{2}\left(\delta_{\alpha_1',\alpha_1}\delta_{\alpha_2',\alpha_2} + \delta_{\alpha_1',\alpha_2}\delta_{\alpha_2',\alpha_1}\right) \\ &= \begin{cases} (1+\delta_{\alpha_1,\alpha_2})/2 & \text{if } \alpha_{1(2)}' = \alpha_{1(2)} \text{ or } \alpha_{1(2)}' = \alpha_{2(1)} \\ 0 & \text{otherwise} \end{cases} \end{aligned}$$

- b) Antisymmetric states

$$\begin{aligned}\langle\alpha_1'\alpha_2'|AA|\alpha_1\alpha_2\rangle &= \langle\alpha_1'\alpha_2'|\frac{1}{2}\left(|\alpha_1\alpha_2\rangle - |\alpha_2\alpha_1\rangle\right) \\ &= \frac{1}{2}\left(\delta_{\alpha_1',\alpha_1}\delta_{\alpha_2',\alpha_2} - \delta_{\alpha_1',\alpha_2}\delta_{\alpha_2',\alpha_1}\right) \\ &= \begin{cases} 1/2 & \text{if } \alpha'_{1(2)} = \alpha_{1(2)} \text{ and } \alpha_1 \neq \alpha_2 \\ -1/2 & \text{if } \alpha'_{1(2)} = \alpha_{2(1)} \text{ and } \alpha_1 \neq \alpha_2 \\ 0 & \text{otherwise} \end{cases}\end{aligned}$$

- Orthonormal basis in $\mathcal{H}_2^S$ and $\mathcal{H}_2^A$ are given by the following expressions:
  - a) Symmetric states

$$|\alpha_1\alpha_2\rangle_S = \sqrt{\frac{2}{1+\delta_{\alpha_1,\alpha_2}}}S|\alpha_1\alpha_2\rangle$$

  - b) Antisymmetric states

$$|\alpha_1\alpha_2\rangle_A = \sqrt{2}A|\alpha_1\alpha_2\rangle$$

The completeness condition now reads

$$\begin{aligned}\sum_{\alpha_1\alpha_2}\left(\frac{1+\delta_{\alpha_1,\alpha_2}}{2}\right)|\alpha_1\alpha_2\rangle_{SS}\langle\alpha_1\alpha_2| &= 1 \\ \sum_{\alpha_1\alpha_2}\frac{1}{2}|\alpha_1\alpha_2\rangle_{AA}\langle\alpha_1\alpha_2| &= 1\end{aligned}$$

- Normalized wave functions in coordinate space have the form
  - a) Symmetric states

$$\langle\mathbf{r}_1\mathbf{r}_2|\alpha_1\alpha_2\rangle_S = \frac{1}{\sqrt{2(1+\delta_{\alpha_1,\alpha_2})}}\Big(\varphi_{\alpha_1}(\mathbf{r}_1)\varphi_{\alpha_2}(\mathbf{r}_2) + \varphi_{\alpha_1}(\mathbf{r}_2)\varphi_{\alpha_2}(\mathbf{r}_1)\Big)$$

  - b) Antisymmetric states

$$\langle\mathbf{r}_1\mathbf{r}_2|\alpha_1\alpha_2\rangle_A = \frac{1}{\sqrt{2}}\Big(\varphi_{\alpha_1}(\mathbf{r}_1)\varphi_{\alpha_2}(\mathbf{r}_2) - \varphi_{\alpha_1}(\mathbf{r}_2)\varphi_{\alpha_2}(\mathbf{r}_1)\Big)$$

Notice that in the antisymmetric case the wave function vanishes if $\alpha_1 = \alpha_2$.

1.1.3 N-particle Hilbert space

The N-particle Hilbert space is defined by the tensor product of N single-particle Hilbert space $\mathcal{H}_1$: $\mathcal{H}_N = \mathcal{H}_1 \otimes \mathcal{H}_1 \otimes ... \otimes \mathcal{H}_1$. In analogy with the two-particle Hilbert space, a complete basis of $\mathcal{H}_N$ is formed by the states

$$|\alpha_1\alpha_2...\alpha_N\rangle = |\alpha_1\rangle|\alpha_2\rangle...|\alpha_N\rangle \ .$$

The general symmetrizing and antisymmetrizing operators in $\mathcal{H}_N$ are defined as

$$\begin{aligned} S &= \frac{1}{N!}\sum_P P \\ A &= \frac{1}{N!}\sum_P (-1)^P P \ , \end{aligned}$$

where P are the permutations of the particle labels and $(-1)^P$ is the parity of the permutation (P even or P odd).

- Complete orthonormal basis in the subspaces $\mathcal{H}_N^S$ (completely symmetric) and $\mathcal{H}_N^A$ (completely antisymmetric) are given by
  - a) Symmetric states

$$\begin{aligned} |\alpha_1\alpha_2...\alpha_N\rangle_S &= \sqrt{\frac{N!}{n_\alpha! n_\beta! ... n_\omega!}} S|\alpha_1\alpha_2...\alpha_N\rangle \\ &= \frac{1}{\sqrt{N! n_\alpha! n_\beta! ... n_\omega!}} \sum_P |\alpha_{P_1}\alpha_{P_2}...\alpha_{P_N}\rangle \\ &\equiv |n_\alpha n_\beta ... n_\omega\rangle \end{aligned}$$

  - b) Antisymmetric states

$$\begin{aligned} |\alpha_1\alpha_2...\alpha_N\rangle_A &= \sqrt{N!} A|\alpha_1\alpha_2...\alpha_N\rangle \\ &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P |\alpha_{P_1}\alpha_{P_2}...\alpha_{P_N}\rangle \\ &\equiv |n_\alpha n_\beta ... n_\omega\rangle \end{aligned}$$

We introduced the occupation numbers n_α, n_β of the single-particle states $|\alpha\rangle$ and $|\beta\rangle$, satisfying the normalization condition

$$\sum_\alpha n_\alpha = N \ .$$

The representation of N-particle states in terms of occupation numbers counts the number of particles occupying a given single-particle state, instead of specifying the single particle-state occupied by a given particle. This representation is in general more convenient, especially within the Fock space (see later), where the total number of particles is not fixed. Notice also that the product $\prod_\alpha n_\alpha!$ of factorials of occupation numbers extends to the case of N particles the factor $(1 + \delta_{\alpha_1,\alpha_2})$ introduced for the $N = 2$ case.

- The closure relations in $\mathcal{H}_N^S$ and $\mathcal{H}_N^A$ read
  - a) Symmetric states

$$\sum_{\alpha_1 ... \alpha_N} \frac{n_\alpha! n_\beta! ... n_\omega!}{N!} |\alpha_1 ... \alpha_N\rangle_{SS}\langle\alpha_1 ... \alpha_N| = 1$$

  - b) Antisymmetric states

$$\sum_{\alpha_1 ... \alpha_N} \frac{1}{N!} |\alpha_1 ... \alpha_N\rangle_{AA}\langle\alpha_1 ... \alpha_N| = 1$$

- Completely symmetric and antisymmetric wave functions of N particles are given by
  - a) Symmetric states

$$\langle \mathbf{r}_1 ... \mathbf{r}_N | \alpha_1 ... \alpha_N\rangle_S = \frac{1}{\sqrt{N! n_\alpha! n_\beta! ... n_\omega!}} \sum_P \varphi_{\alpha_{P_1}}(\mathbf{r}_1) ... \varphi_{\alpha_{P_N}}(\mathbf{r}_N)$$

  The above sum over permutations of the particle labels is called a permanent. The corresponding occupation numbers can take any integer value $n_\alpha \geq 0$.

- b) Antisymmetric states

$$
\begin{aligned}
\langle \mathbf{r}_1 ... \mathbf{r}_N | \alpha_1 ... \alpha_N \rangle_A &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \varphi_{\alpha_{P_1}}(\mathbf{r}_1) ... \varphi_{\alpha_{P_N}}(\mathbf{r}_N) \\
&= \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \varphi_{\alpha_1}(\mathbf{r}_1) & ... & \varphi_{\alpha_1}(\mathbf{r}_N) \\ : & & : \\ \varphi_{\alpha_N}(\mathbf{r}_1) & ... & \varphi_{\alpha_N}(\mathbf{r}_N) \end{pmatrix}
\end{aligned}
$$

  The above sum over permutations of the particle labels is a determinant (Slater determinant). Notice that, if two particles occupy the same single-particle state ($\alpha_i = \alpha_j$), two lines of the determinant will be equal and the wave function will consequently vanish (Pauli principle). The corresponding occupation numbers can either be $n_\alpha = 0$ or $n_\alpha = 1$.

1.1.4 Principle of particles indistinguishability

- Physical states of N particles, denoted by $|\alpha_1 ... \alpha_N\rangle_{ps}$, do not depend on the exchange of particles i and j

$$
P_{ij} |\alpha_1 .. \alpha_i .. \alpha_j .. \alpha_N\rangle_{ps} = |\alpha_1 .. \alpha_j .. \alpha_i .. \alpha_N\rangle_{ps} = e^{i\gamma} |\alpha_1 .. \alpha_i .. \alpha_j .. \alpha_N\rangle_{ps} \ ,
$$

  where $e^{i\gamma}$ is a phase factor.

  Since $P_{ij} P_{ij} = 1 \rightarrow e^{i2\gamma} = 1 \rightarrow \gamma = 0, \pi$

  - if $\gamma = 0$ then $P_{ij} |\alpha_1 .. \alpha_i .. \alpha_j .. \alpha_N\rangle_{ps} = |\alpha_1 .. \alpha_i .. \alpha_j .. \alpha_N\rangle_{ps}$ for the elementary permutation P_{ij}. Then, for a generic permutation $P = \prod P_{ij}$, one finds

    $P|\alpha_1 ... \alpha_N\rangle_{ps} = |\alpha_{P_1} ... \alpha_{P_N}\rangle_{ps} = |\alpha_1 ... \alpha_N\rangle_{ps}$.

    These states belong to the completely symmetric subspace $\mathcal{H}_N^S$, such that $S|\alpha_1 ... \alpha_N\rangle_{ps} = |\alpha_1 ... \alpha_N\rangle_{ps}$, and describe bosonic particles.

  - if $\gamma = \pi$ then $P_{ij} |\alpha_1 .. \alpha_i .. \alpha_j .. \alpha_N\rangle_{ps} = -|\alpha_1 .. \alpha_i .. \alpha_j .. \alpha_N\rangle_{ps}$ for the elementary permutation P_{ij}. Then, for a generic permutation $P = \prod P_{ij}$, one finds

    $P|\alpha_1 ... \alpha_N\rangle_{ps} = |\alpha_{P_1} ... \alpha_{P_N}\rangle_{ps} = (-1)^P |\alpha_1 ... \alpha_N\rangle_{ps}$.

    These states belong to the completely antisymmetric subspace $\mathcal{H}_N^A$, such that $A|\alpha_1 ... \alpha_N\rangle_{ps} = |\alpha_1 ... \alpha_N\rangle_{ps}$, and describe fermionic particles.

- Physical operators are invariant with respect to permutations of the particle indexes

  $$\big[O, P\big] = 0 \ ,$$

  for a generic observable O and a generic permutation P. In particular, $[H, P] = 0$ for the Hamiltonian H and, consequently, one has

  $$\big[H, S\big] = \big[H, A\big] = 0 \ .$$

  → Eigenstates of H are also eigenstates of S and A. The operator S (A), being a projector, has eigenvalue 1 if the eigenstate belongs to $\mathcal{H}_N^S$ ($\mathcal{H}_N^A$) or eigenvalue 0 if the eigenstate belongs to the complementary space of $\mathcal{H}_N^S$ ($\mathcal{H}_N^A$).

  → The eigenstates of H corresponding to physical systems are the ones belonging to the subspaces $\mathcal{H}_N^S$ and $\mathcal{H}_N^A$ (see Fig. 1.1) and can be written as linear combinations of the states $|n_\alpha ... n_\omega\rangle$ forming a basis in the corresponding subspace $\mathcal{H}_N^S$ and $\mathcal{H}_N^A$.

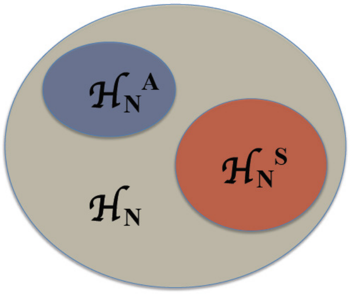

Figure 1.1: Representation of the completely symmetric and completely antisymmetric subspaces inside $\mathcal{H}_N$.

1.1.5 Fock space

The Fock space $\mathcal{F}$ is defined as the direct sum of the N-particle Hilbert spaces $\mathcal{H}_N$ for $N = 0, 1, 2, ...$

$$\mathcal{F} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus ...$$

- The space $\mathcal{H}_0$ is generated by the state $|0\rangle$, the vacuum state, for which we require the normalization $\langle 0|0\rangle = 1$.

- The creation and annihilation operators are defined as follows

$$\begin{aligned}
|n_\alpha ... n_\omega\rangle &= \frac{1}{\sqrt{n_\alpha! ... n_\omega!}}\,(a^\dagger_\alpha)^{n_\alpha} ... (a^\dagger_\omega)^{n_\omega}|0\rangle \\
\langle n_\alpha ... n_\omega| &= \frac{1}{\sqrt{n_\alpha! ... n_\omega!}}\,\langle 0|(a_\omega)^{n_\omega} ... (a_\alpha)^{n_\alpha}
\end{aligned}$$

and

$$0 = a_\alpha|0\rangle = \langle 0|a^\dagger_\alpha \ .$$

For a two-particle state one can write: $(\sqrt{1+\delta_{\alpha,\beta}})|\alpha\beta\rangle_{S(A)} = a^\dagger_\alpha a^\dagger_\beta|0\rangle = \pm a^\dagger_\beta a^\dagger_\alpha|0\rangle$,

where the upper sign refers to bosons and the lower sign to fermions. The above relation implies the following result for the commutator (anticommutator) of bosonic (fermionic) operators

$$\begin{aligned}
\Big[a^\dagger_\alpha, a^\dagger_\beta\Big]_\mp &\equiv a^\dagger_\alpha a^\dagger_\beta \mp a^\dagger_\beta a^\dagger_\alpha = 0 \\
\Big[a_\alpha, a_\beta\Big]_\mp &\equiv a_\alpha a_\beta \mp a_\beta a_\alpha = 0
\end{aligned}$$

In the case of fermionic operators the anticommutation relations entail that: $(a_\alpha)^2 = (a^\dagger_\alpha)^2 = 0$. Furthermore, the following relation holds:

$\delta_{\alpha,\beta} = \langle\alpha|\beta\rangle = \langle 0|a_\alpha a^\dagger_\beta|0\rangle = \langle 0|a_\alpha a^\dagger_\beta \mp a^\dagger_\beta a_\alpha|0\rangle$, from which a convenient choice for the (anti)commutation rule between annihilation and creation operators is provided by

$$\Big[a_\alpha, a^\dagger_\beta\Big]_\mp = \delta_{\alpha,\beta} \ .$$

As we will see below, this choice allows one to obtain a simple expression for the operator giving the number of particles in a single-particle state.

By using the identity $[a_\alpha, (a^\dagger_\alpha)^{n_\alpha}]_\mp = n_\alpha (a^\dagger_\alpha)^{n_\alpha - 1}$, holding for $n_\alpha = 1$ in the case of fermions and for $n_\alpha > 0$ in the case of bosons, it is easy to verify that the states $|n_\alpha ... n_\omega\rangle$ and $\langle n_\alpha ... n_\omega|$ defined above verify the normalization condition $\langle n_\alpha ... n_\omega | n_\alpha ... n_\omega\rangle = 1$.

When acting on a state $|n_\alpha ... n_\omega\rangle$ the creation and annihilation operators give the following results

$$\begin{aligned} a_\lambda^\dagger|n_\alpha..n_\lambda..n_\omega\rangle &= (\pm 1)^m\sqrt{n_\lambda+1}\;|n_\alpha..n_\lambda+1..n_\omega\rangle \\ a_\lambda|n_\alpha..n_\lambda..n_\omega\rangle &= (\pm 1)^m\sqrt{n_\lambda}\;|n_\alpha..n_\lambda-1..n_\omega\rangle\ , \end{aligned}$$

where the upper sign refers to bosons and the lower sign to fermions and $m = n_\alpha + n_\beta + ... + n_{\lambda-1}$. Notice that in the case of fermions the first equation holds only if $n_\lambda = 0$, otherwise the right hand side vanishes since $(a_\lambda^\dagger)^2 = 0$. For both bosons and fermions one finds the result

$$a_\lambda^\dagger a_\lambda|n_\alpha..n_\lambda..n_\omega\rangle = n_\lambda|n_\alpha..n_\lambda..n_\omega\rangle\ .$$

The states $|n_\alpha...n_\omega\rangle$ are thus eigenstates of the operator $a_\lambda^\dagger a_\lambda$ with eigenvalue given by the occupation number n_λ. They are also eigenstates of the operator $\sum_\alpha a_\alpha^\dagger a_\alpha$ with eigenvalue $\sum_\alpha n_\alpha = N$, corresponding to the total number of particles.

- In a change of the single-particle basis:

  $|\alpha\rangle = \sum_i \langle i|\alpha\rangle|i\rangle \to a_\alpha^\dagger|0\rangle = \sum_i \langle i|\alpha\rangle a_i^\dagger|0\rangle$

  the creation/annihilation operators behave as follows

$$\begin{cases} a_\alpha^\dagger = \sum_i \langle i|\alpha\rangle a_i^\dagger \\ \\ a_\alpha = \sum_i \langle \alpha|i\rangle a_i \end{cases}$$

- By using the above relations for a general change of single-particle basis we introduce the creation/annihilation operators of a particle at space position $\mathbf{r}$:

$$\begin{aligned} \psi^\dagger(\mathbf{r}) &= \sum_\alpha \langle\alpha|\mathbf{r}\rangle a_\alpha^\dagger = \sum_\alpha \varphi_\alpha^*(\mathbf{r}) a_\alpha^\dagger \\ \psi(\mathbf{r}) &= \sum_\alpha \langle\mathbf{r}|\alpha\rangle a_\alpha = \sum_\alpha \varphi_\alpha(\mathbf{r}) a_\alpha\ . \end{aligned}$$

It is straightforward to show that $\psi(\mathbf{r})|0\rangle = \langle 0|\psi^\dagger(\mathbf{r}) = 0$. Furthermore, the bosonic (fermionic) field operators satisfy commutation (anticommutation) relations as given by

$$\Big[\psi(\mathbf{r}), \psi(\mathbf{r}')\Big]_{\mp} = \Big[\psi^\dagger(\mathbf{r}), \psi^\dagger(\mathbf{r}')\Big]_{\mp} = 0$$

$$\Big[\psi(\mathbf{r}), \psi^\dagger(\mathbf{r}')\Big]_{\mp} = \delta(\mathbf{r}-\mathbf{r}') \ ,$$

where we used the commutation (anticommutation) relations of the operators a_α, $a^\dagger_\alpha$.

We write down explicitly the transformation laws of particle fields in coordinate/momentum space and viceversa for particles in a cubic box with p.b.c.

$$\left\{ \begin{array}{l} a_{\mathbf{k}} = \frac{1}{\sqrt{V}} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \psi(\mathbf{r}) \\ a^\dagger_{\mathbf{k}} = \frac{1}{\sqrt{V}} \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \psi^\dagger(\mathbf{r}) \end{array} \right. \qquad \left\{ \begin{array}{l} \psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} a_{\mathbf{k}} \\ \psi^\dagger(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} a^\dagger_{\mathbf{k}} \end{array} \right. .$$

- A generic many-body state $|\phi\rangle$ is written in terms of quantized fields in the form

$$|\phi\rangle = \frac{1}{\sqrt{N!}} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \phi(\mathbf{r}_1, \dots, \mathbf{r}_N) \psi^\dagger(\mathbf{r}_1) \dots \psi^\dagger(\mathbf{r}_N) |0\rangle \ ,$$

which defines the many-body wave function $\phi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ in coordinate space. This expression holds both for bosons and fermions, is properly normalized as one can check from

$$\langle\phi|\phi\rangle = \frac{1}{N!} \int d\mathbf{R}\ d\mathbf{R}' \phi^*(\mathbf{R}') \phi(\mathbf{R})\ \langle 0|\psi(\mathbf{r}'_N) \dots \psi(\mathbf{r}'_1) \psi^\dagger(\mathbf{r}_1) \dots \psi^\dagger(\mathbf{r}_N)|0\rangle = 1 \ ,$$

where we introduced the compact notation $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ for the 3N coordinate vector. The action of the annihilation operator on the state $|\phi\rangle$ is given by

$$\psi(\mathbf{r})|\phi\rangle = \frac{\sqrt{N}}{\sqrt{(N-1)!}} \int d\mathbf{r}_2 \dots d\mathbf{r}_N \phi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi^\dagger(\mathbf{r}_2) \dots \psi^\dagger(\mathbf{r}_N)|0\rangle \ .$$

1.2 Representation of one-body and two-body operators

1.2.1 One-body operators

Let F_1 be a physical observable described by a one-body operator acting on $\mathcal{H}_1$ and let the states $|i\rangle$ be its eigenstates with f_i the corresponding eigenvalues: $F_1 = \sum_i f_i |i\rangle\langle i|$. In terms of the general basis $|\alpha\rangle$ of $\mathcal{H}_1$ we can write

$$F_1 = \sum_{\alpha\beta} |\alpha\rangle\langle\alpha|F_1|\beta\rangle\langle\beta| \; .$$

The operator acting on the N-particle space $\mathcal{H}_N$ must be invariant with respect to a permutation P of the particle indices and therefore can only be defined as the sum

$$F_N = \sum_{n=1}^{N} F_1^{(n)} \; ,$$

where $F_1^{(n)}$ acts on the n-th particle: $F_1^{(n)}|\beta_1..\beta_n..\beta_N\rangle = \sum_\alpha \langle\alpha|F_1|\beta_n\rangle|\beta_1..\alpha..\beta_N\rangle$. One gets thus

$$F_N|\beta_1..\beta_n..\beta_N\rangle = \sum_{n=1}^{N}\sum_{\alpha_n}\langle\alpha_n|F_1|\beta_n\rangle|\beta_1..\alpha_n..\beta_N\rangle \; .$$

The above result remains valid if one applies the operator F_N to a state $P|\beta_1...\beta_N\rangle$, where P is a generic permutation. As a consequence, the result holds also for the symmetric (antisymmetric) physical states $|\beta_1...\beta_N\rangle_{S(A)}$.

The corresponding operator acting on the Fock space $\mathcal{F}$ is given by

$$F = \sum_{\alpha\beta}\langle\alpha|F_1|\beta\rangle a^\dagger_\alpha a_\beta \tag{1.1}$$

in terms of the creation and annihilation operators. To show this we proceed as follows:

- The generic symmetric (antisymmetric) states forming a basis in the Fock space $\mathcal{F}$ can be written as $|\beta_1...\beta_N\rangle_{S(A)} = C_{S(A)} a^\dagger_{\beta_1}...a^\dagger_{\beta_N}|0\rangle$, where $C_{S(A)}$ is a normalization factor.

- The commutator between F given by (1.1) and a creation operator is given by: $[F, a^\dagger_\beta] = \sum_\alpha \langle\alpha|F_1|\beta\rangle a^\dagger_\alpha$

- By acting with F on the state $|n_\alpha ... n_\omega\rangle$ one finds:

$$\begin{aligned} F|\beta_1..\beta_n..\beta_N\rangle_{S(A)} &= C_{S(A)}\left(\left[F, a^\dagger_{\beta_1}\right] a^\dagger_{\beta_2}..a^\dagger_{\beta_N}|0\rangle + ... + a^\dagger_{\beta_1}..a^\dagger_{\beta_{N-1}}\left[F, a^\dagger_{\beta_N}\right]|0\rangle\right) \\ &= C_{S(A)}\sum_{n=1}^{N}\sum_{\alpha_n}\langle\alpha_n|F_1|\beta_n\rangle a^\dagger_{\beta_1}..a^\dagger_{\alpha_n}..a^\dagger_{\beta_N}|0\rangle \\ &= \sum_{n=1}^{N}\sum_{\alpha_n}\langle\alpha_n|F_1|\beta_n\rangle|\beta_1..\alpha_n..\beta_N\rangle_{S(A)} \; . \end{aligned}$$

Thus, the action of F given by (1.1) on any state of a complete basis of $\mathcal{H}_N^{S(A)}$ is identical to the action of F_N, implying the identity of the operators.

-) **Examples of one-body operators**

- Kinetic energy

  In coordinate space: $T = \int d\mathbf{r} \int d\mathbf{r}' \delta(\mathbf{r}-\mathbf{r}')\left(-\frac{\hbar^2\nabla^2}{2m}\right)\psi^\dagger(\mathbf{r}')\psi(\mathbf{r}) = \int d\mathbf{r}\; \psi^\dagger(\mathbf{r})\left(-\frac{\hbar^2\nabla^2}{2m}\right)\psi(\mathbf{r})$

  In momentum space: $T = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} a^\dagger_{\mathbf{k}} a_{\mathbf{k}}$

- Potential energy

  In coordinate space: $U = \int d\mathbf{r}\; U(\mathbf{r})\psi^\dagger(\mathbf{r})\psi(\mathbf{r})$

  In momentum space: $U = 1/V \sum_{\mathbf{k},\mathbf{k}'} U_{\mathbf{k}'-\mathbf{k}} a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} = 1/V \sum_{\mathbf{k},\mathbf{q}} U_{\mathbf{q}} a^\dagger_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}}$

- Number of particles: $N = \sum_{n=1}^{N} 1$

  In coordinate space: $N = \int d\mathbf{r}\; \psi^\dagger(\mathbf{r})\psi(\mathbf{r})$

  In momentum space: $N = \sum_{\mathbf{k}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}}$

- Total momentum: $\mathbf{P} = \sum_{n=1}^{N} \mathbf{p}_n$

  In coordinate space: $\mathbf{P} = -i\hbar \int d\mathbf{r}\; \psi^\dagger(\mathbf{r})\nabla\psi(\mathbf{r})$

  In momentum space: $\mathbf{P} = \sum_{\mathbf{k}} \hbar\mathbf{k} a^\dagger_{\mathbf{k}} a_{\mathbf{k}}$

- Particle density: $n(\mathbf{r}) = \sum_{n=1}^{N} \delta(\mathbf{r}-\mathbf{r}_n)$

  In coordinate space: $n(\mathbf{r}) = \psi^\dagger(\mathbf{r})\psi(\mathbf{r})$

  resulting from $n(\mathbf{r}) = \int d\mathbf{r}_2 \int d\mathbf{r}_1 \delta(\mathbf{r}_1-\mathbf{r}_2)\delta(\mathbf{r}-\mathbf{r}_1)\psi^\dagger(\mathbf{r}_2)\psi(\mathbf{r}_1)$.

In momentum space: $n(\mathbf{r}) = 1/V \sum_{\mathbf{k},\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}} \equiv 1/V \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \rho_{\mathbf{q}}$,

where $\rho_{\mathbf{q}} = \sum_{\mathbf{k}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}}$ is the density fluctuation operator with wave vector $\mathbf{q}$.

- Current density: $j(\mathbf{r}) = 1/2 \sum_{n=1}^{N} \big(\mathbf{p}_n \delta(\mathbf{r}-\mathbf{r}_n) + \delta(\mathbf{r}-\mathbf{r}_n)\mathbf{p}_n\big)$

  In coordinate space: $j(\mathbf{r}) = -i\hbar/2 \Big[\psi^\dagger(\mathbf{r})\nabla\psi(\mathbf{r}) - \big(\nabla\psi^\dagger(\mathbf{r})\big)\psi(\mathbf{r})\Big]$

  resulting from $j(\mathbf{r}) = 1/2 \int d\mathbf{r}_2 \int d\mathbf{r}_1 \delta(\mathbf{r}_1 - \mathbf{r}_2) \Big[\delta(\mathbf{r}-\mathbf{r}_1)(-i\hbar\nabla_1) + (-i\hbar\nabla_1)\delta(\mathbf{r}-\mathbf{r}_1)\Big] \psi^\dagger(\mathbf{r}_2)\psi(\mathbf{r}_1)$ and using integration by parts for the second term.

  In momentum space: $j(\mathbf{r}) = 1/V \sum_{\mathbf{k},\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \hbar(2\mathbf{k}+\mathbf{q})/2 \; a^\dagger_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}} \equiv 1/V \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} j_{\mathbf{q}}$

  where $j_{\mathbf{q}} = \sum_{\mathbf{k}} \hbar(2\mathbf{k}+\mathbf{q})/2 \; a^\dagger_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}}$ is the current-density fluctuation operator with wave vector $\mathbf{q}$.

We notice that, if one substitutes the single-particle wave function $\psi(\mathbf{r})$ and $\psi^*(\mathbf{r})$ respectively for the particle field $\psi(\mathbf{r})$ and $\psi^\dagger(\mathbf{r})$ in the above equations for the operators in the coordinate representation, the resulting expressions are formally identical to the expectation values over the state described by the wave function $\psi(\mathbf{r})$ in the Hilbert space of single-particle states. For this reason, to the formalism of creation/annihilation operators in the Fock space is given the name of second quantization.

1.2.2 Two-body operators

Let V_2 be a symmetric two-body operator acting on $\mathcal{H}_2$. Its general form is given by

$$V_2 = \sum_{\alpha\beta\gamma\delta} |\alpha\beta\rangle\langle\alpha\beta|V_2|\gamma\delta\rangle\langle\gamma\delta| \; .$$

where the matrix elements do not depend on the ordering of particle 1 and 2: $\langle\alpha\beta|V_2|\gamma\delta\rangle = \langle\beta\alpha|V_2|\delta\gamma\rangle$. On $\mathcal{H}_N$ we define the symmetric combination

$$V_N = V_2^{(1,2)} + V_2^{(1,3)} + ... = \sum_{n<m=2}^{N} V_2^{(n,m)} \; ,$$

where $V_2^{n,m}$ acts on the n-th and the m-th particle:

$V_2^{(n,m)}|\beta_1..\beta_n..\beta_m..\beta_N\rangle = \sum_{\alpha_n\alpha_m}\langle\alpha_n\alpha_m|V_2|\beta_n\beta_m\rangle|\beta_1..\alpha_n..\alpha_m..\beta_N\rangle$. One finds the result

$$V_N|\beta_1..\beta_n..\beta_m..\beta_N\rangle = \sum_{n<m=2}^{N}\sum_{\alpha_n\alpha_m}\langle\alpha_n\alpha_m|V_2|\beta_n\beta_m\rangle|\beta_1..\alpha_n..\alpha_m..\beta_N\rangle \ ,$$

holding also for symmetric (antisymmetric) states $|\beta_1...\beta_N\rangle_{S(A)}$.

The second quantization expression of the operator V_N has the following form:

$$V = \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\langle\alpha\beta|V_2|\gamma\delta\rangle a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma \ ,$$

notice the inverted order of the two annihilation operators. To prove the above equation we proceed similarly to the case of the one-body operator:

- For the commutator one finds:

  $[V, a^\dagger_\beta] = 1/2\sum_{\alpha\gamma\delta}\Big(\langle\alpha\gamma|V_2|\beta\delta\rangle + \langle\gamma\alpha|V_2|\delta\beta\rangle\Big)a^\dagger_\alpha a^\dagger_\gamma a_\delta = \sum_{\alpha\gamma\delta}\langle\alpha\gamma|V_2|\beta\delta\rangle a^\dagger_\alpha a^\dagger_\gamma a_\delta,$

- By applying V to the state $|n_\alpha...n_\omega\rangle$, the result is:

$$\begin{aligned}
V|\beta_1..\beta_n..\beta_m..\beta_N\rangle_{S(A)} &= C_{S(A)}\Big(\Big[V, a^\dagger_{\beta_1}\Big]a^\dagger_{\beta_2}..a^\dagger_{\beta_N}|0\rangle + ... + a^\dagger_{\beta_1}..a^\dagger_{\beta_{N-1}}\Big[V, a^\dagger_{\beta_N}\Big]|0\rangle\Big) \\
&= C_{S(A)}\sum_{n=1}^{N-1}\sum_{\alpha_n\gamma_n\delta_n}\langle\alpha_n\gamma_n|V_2|\beta_n\delta_n\rangle a^\dagger_{\beta_1}..a^\dagger_{\alpha_n}a^\dagger_{\gamma_n}a_{\delta_n}..a^\dagger_{\beta_N}|0\rangle \\
&= C_{S(A)}\sum_{n=1}^{N-1}\sum_{m>n}^{N}\sum_{\alpha_n\alpha_m}\langle\alpha_n\alpha_m|V_2|\beta_n\beta_m\rangle a^\dagger_{\beta_1}..a^\dagger_{\alpha_n}..a^\dagger_{\alpha_m}..a^\dagger_{\beta_N}|0\rangle \\
&= \sum_{n<m=2}^{N}\sum_{\alpha_n\alpha_m}\langle\alpha_n\alpha_m|V_2|\beta_n\beta_m\rangle|\beta_1..\alpha_n..\alpha_m..\beta_N\rangle_{S(A)} \ ,
\end{aligned}$$

  which is identical to the result for V_N.

-) **Examples of two-body operators**

- Interaction energy

  The action of V_2 on the states of $\mathcal{H}_2$ in the coordinate representation is defined as:

  $V_2|\mathbf{r}_1\mathbf{r}_2\rangle = V(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{r}_1\mathbf{r}_2\rangle$.

  This definition involves the interaction potential $V(\mathbf{r}_1,\mathbf{r}_2)$ that depends on the coordinates $\mathbf{r}_1$, $\mathbf{r}_2$ of the two particles. The corresponding matrix elements are given by:

$\langle \mathbf{r}_1\mathbf{r}_2|V_2|\mathbf{r}'_1\mathbf{r}'_2\rangle = \delta(\mathbf{r}_1-\mathbf{r}'_1)\delta(\mathbf{r}_2-\mathbf{r}'_2)V(\mathbf{r}_1,\mathbf{r}_2)$

If the system is homogeneous then the interaction potential can only depend on the difference between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$: $V(\mathbf{r}_1,\mathbf{r}_2) = V(\mathbf{r}_1-\mathbf{r}_2)$. In this case we find:

In coordinate space: $V = 1/2\int d\mathbf{r}_1\int d\mathbf{r}_2\psi^\dagger(\mathbf{r}_1)\psi^\dagger(\mathbf{r}_2)V(\mathbf{r}_1-\mathbf{r}_2)\psi(\mathbf{r}_2)\psi(\mathbf{r}_1)$

notice that the inverted order in the product of annihilation operators is crucial to make V hermitian. By introducing the center of mass and relative coordinate: $\mathbf{R} = (\mathbf{r}_1+\mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_1-\mathbf{r}_2$, we can rewrite the above integral in the following form

$V = 1/2\int d\mathbf{R}\int d\mathbf{r}\psi^\dagger(\mathbf{R}+\mathbf{r}/2)\psi^\dagger(\mathbf{R}-\mathbf{r}/2)V(\mathbf{r})\psi(\mathbf{R}-\mathbf{r}/2)\psi(\mathbf{R}+\mathbf{r}/2)$

In momentum space: $V = 1/(2V)\sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} V_{\mathbf{q}} a^\dagger_{\mathbf{k}} a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}'} a_{\mathbf{k}-\mathbf{q}}$,

where $V_{\mathbf{q}} = V^*_{-\mathbf{q}} = \int d\mathbf{r}V(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}$ is the Fourier transform of the interaction potential.

1.2.3 N-body operators

The generalization to symmetric N-body operators is straightforward. For example, for a symmetric three-body operator W_3 one constructs the symmetric combination in $\mathcal{H}_N$

$$W_N = \sum_{i<j<k=3}^{N} W_3^{(i,j,k)} \ ,$$

which has the following representation in the Fock space $\mathcal{F}$

$$W = \frac{1}{6}\sum_{\alpha\beta\gamma}\sum_{\alpha'\beta'\gamma'} a^\dagger_\alpha a^\dagger_\beta a^\dagger_\gamma \langle\alpha\beta\gamma|W_3|\alpha'\beta'\gamma'\rangle a_{\gamma'}a_{\beta'}a_{\alpha'} \ .$$

1.3 Problems

- 1. Show that the Hamiltonian

  $H = \int d\mathbf{r}\; \psi^\dagger(\mathbf{r}) \left(-\hbar^2\nabla^2/2m\right) \psi(\mathbf{r}) + (1/2) \int d\mathbf{r} \int d\mathbf{r}' \psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')V(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})$

  of an interacting system commutes with the number of particles operator $N = \int d\mathbf{r}\psi^\dagger(\mathbf{r})\psi(\mathbf{r})$.

  Solution: If we write the total Hamiltonian as the sum of the kinetic and interaction energy parts, $H = T + V$, the separate contributions to the commutator with N are given by

  $$[T, N] = \int d\mathbf{r}\; d\mathbf{r}' \left[\psi^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \delta(\mathbf{r}-\mathbf{r}')\psi(\mathbf{r}') - \psi^\dagger(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}') \left(-\frac{\hbar^2}{2m}\nabla^2\right) \psi(\mathbf{r})\right] = 0\ ,$$

  and

  $$\begin{aligned} [V, N] &= \int d\mathbf{r}\; d\mathbf{r}'\; d\mathbf{r}'' V(\mathbf{r}-\mathbf{r}') \Big[\delta(\mathbf{r}-\mathbf{r}'') \Big(\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r}'') - \psi^\dagger(\mathbf{r}'')\psi^\dagger(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})\Big) \\ &+ \delta(\mathbf{r}'-\mathbf{r}'') \Big(\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')\psi(\mathbf{r}'')\psi(\mathbf{r}) - \psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}'')\psi(\mathbf{r}')\psi(\mathbf{r})\Big)\Big] = 0\ , \end{aligned}$$

  where in the first equation we used twice integration by parts of one of the two terms in the square bracket.

- 2. Determine the representation in the Fock space of the displacement operator $\mathbf{R} = \sum_i \mathbf{r}_i$, where i runs over the particles, both in the coordinate and in the momentum space. Calculate the commutator [$\mathbf{R}$,$\mathbf{P}$] with the total momentum operator $\mathbf{P}$.

  Solution: In the coordinate representation we have: $\mathbf{R} = \int d\mathbf{r}\;\; \psi^\dagger(\mathbf{r})\mathbf{r}\psi(\mathbf{r})$ and in momentum space $\mathbf{R} = 1/V \sum_{\mathbf{k},\mathbf{q}} \int d\mathbf{r}\; \mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} a^\dagger_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}}$. Given the total momentum operator $\mathbf{P} = \sum_{\mathbf{k}} \hbar\mathbf{k} a^\dagger_{\mathbf{k}} a_{\mathbf{k}}$, the calculation of the commutator yields $[\mathbf{R}, \mathbf{P}] = -\hbar \sum_{\mathbf{k},\mathbf{q}} (1/V) \int d\mathbf{r}\; \mathbf{r}\mathbf{q} e^{-i\mathbf{q}\cdot\mathbf{r}} a^\dagger_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}}$. The integral can be rewritten as $i/V \int d\mathbf{r}\; \mathbf{r}\nabla e^{-i\mathbf{q}\cdot\mathbf{r}}$ and after integration by parts as $-i/V \int d\mathbf{r}\;\; e^{-i\mathbf{q}\cdot\mathbf{r}} = -i\delta_{\mathbf{q},0}$. The commutator gives thus $[\mathbf{R}, \mathbf{P}] = i\hbar N$ as expected.

- 3. Consider the Hamiltonian of free particles $H = \sum_{ij} \langle i|H_1|j\rangle a^\dagger_i a_j$. Perform a change of the single-particle basis such that H_1 becomes diagonal and determine the expression of H and the time evolution of the corresponding creation and annihilation operators. (Use Heisenberg's equation $i\hbar dO/dt = [O, H]$, holding for a generic operator O.)

  Solution: In the diagonal representation $H = \sum_\alpha \epsilon_\alpha a^\dagger_\alpha a_\alpha$. The commutators of a_α, $a^\dagger_\alpha$ with H give respectively: $[a_\alpha, H] = \epsilon_\alpha a_\alpha$ and $[a^\dagger_\alpha, H] = -\epsilon_\alpha a^\dagger_\alpha$ both for fermions and bosons. From Heisenberg's equation we obtain therefore: $a_\alpha(t) = e^{-i\epsilon_\alpha t/\hbar} a_\alpha$ and $a^\dagger_\alpha(t) = e^{i\epsilon_\alpha t/\hbar} a^\dagger_\alpha$.

- 4. Consider a system of free particles described by the following Hamiltonian in momentum space $H = \sum_{\mathbf{k}} \hbar^2 k^2/(2m) a^\dagger_{\mathbf{k}} a_{\mathbf{k}}$. Show that $[\rho^\dagger_{\mathbf{q}}, [H, \rho_{\mathbf{q}}]] = N\hbar^2 q^2/m$ where $\rho_{\mathbf{q}} = \sum_{\mathbf{k}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}}$ and N is the total number of particles (f-sum rule).

Solution: The commutator between H and $\rho_{\mathbf{q}}$ gives $[H, \rho_{\mathbf{q}}] = \sum_{\mathbf{k}} \hbar^2 k^2/(2m)(a^\dagger_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}} - a^\dagger_{\mathbf{k}-\mathbf{q}} a_{\mathbf{k}})$. From the double commutator one gets after some algebra: $[\rho^\dagger_{\mathbf{q}}, [H, \rho_{\mathbf{q}}]] = \sum_{\mathbf{k}} \hbar^2 k^2/(2m)(a^\dagger_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}+\mathbf{q}} + a^\dagger_{\mathbf{k}-\mathbf{q}} a_{\mathbf{k}-\mathbf{q}} - 2a^\dagger_{\mathbf{k}} a_{\mathbf{k}}) = (\hbar^2 q^2/m) \sum_{\mathbf{k}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}}$, finally giving the f-sum rule. Notice that the above derivation holds both for bosons and fermions.

- 5. Show that the f-sum rule remains valid also for interacting systems with a two-body interaction potential $V = 1/(2V) \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} V_{\mathbf{q}} a^\dagger_{\mathbf{k}} a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}'} a_{\mathbf{k}-\mathbf{q}}$.

Solution: We notice that the interaction potential can be conveniently written in the form

$$V = \frac{1}{2V} \sum_{\mathbf{q}} V_{\mathbf{q}} \left(\rho^\dagger_{\mathbf{q}} \rho_{\mathbf{q}} - N \right) \ ,$$

vald both for bosons and fermions. For the operators $\rho_{\mathbf{q}}$ we have the following commutation relations independent of statistics: $[\rho_{\mathbf{q}}, \rho_{\mathbf{k}}] = 0$ and $[\rho_{\mathbf{q}}, \rho^\dagger_{\mathbf{k}}] = 0$ given that $\rho^\dagger_{\mathbf{k}} = \rho_{-\mathbf{k}}$. One finds then trivially $[V, \rho_{\mathbf{q}}] = 0$ and the interaction potential does not contribute to the f-sum rule.

- 6. Consider a system of free particles confined by a harmonic potential $U(\mathbf{r}) = m/2(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)$. Determine the expression of the Hamiltonian in the basis where H_1 is diagonal and the expressions of the dipole operator $F = \sum_i z_i$ and of the monopole operator $G = \sum_i r_i^2$, where the index i runs over the particles, in terms of the creation and annihilation operators.

Solution: The energy levels of the harmonic oscillator are given by

$$\epsilon_{n_x n_y n_z} = \hbar\omega_x(n_x + 1/2) + \hbar\omega_y(n_y + 1/2) + \hbar\omega_z(n_z + 1/2) \ ,$$

and the Hamiltonian in this representation is written as

$$H = \sum_{n_x, n_y, n_z} \epsilon_{n_x n_y n_z} a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z} \ ,$$

where $n_{x,y,z} = 0, 1, 2, ...$ are non negative integers. From the elementary quantum mechanical treatment of the harmonic oscillator we have that the matrix elements of the one-body z and z^2 operators are given by

$$\begin{aligned}
\langle n_x n_y n_z | z | n_x' n_y' n_z' \rangle &= \frac{a_z}{\sqrt{2}} \delta_{n_x,n_x'} \delta_{n_y,n_y'} \left(\sqrt{n_z'+1}\, \delta_{n_z,n_z'+1} + \sqrt{n_z'}\, \delta_{n_z,n_z'-1} \right) \\
\langle n_x n_y n_z | z^2 | n_x' n_y' n_z' \rangle &= \frac{a_z^2}{2} \delta_{n_x,n_x'} \delta_{n_y,n_y'} \left(\sqrt{n_z'+2}\sqrt{n_z'+1}\, \delta_{n_z,n_z'+2} + (2n_z'+1)\delta_{n_z,n_z'} \right. \\
&+ \left. \sqrt{n_z'}\sqrt{n_z'-1}\, \delta_{n_z,n_z'-2} \right) ,
\end{aligned}$$

where $a_z = \sqrt{\hbar/m\omega_z}$ is the harmonic oscillator length in the z-direction. The operator F is then given by

$$F = \frac{a_z}{\sqrt{2}} \sum_{n_x n_y n_z} \sqrt{n_z} \left(a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z - 1} + \text{h.c.} \right) .$$

The operator G, instead, is written as

$$\begin{aligned}
G = \sum_{n_x n_y n_z} \quad & \tfrac{a_x^2}{2} \quad \left[(2n_x+1) a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z} + \sqrt{n_x(n_x-1)} \left(a^\dagger_{n_x n_y n_z} a_{n_x-2\, n_y n_z} + \text{h.c.} \right) \right] \\
& \tfrac{a_y^2}{2} \quad \left[(2n_y+1) a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z} + \sqrt{n_y(n_y-1)} \left(a^\dagger_{n_x n_y n_z} a_{n_x n_y-2\, n_z} + \text{h.c.} \right) \right] \\
& \tfrac{a_z^2}{2} \quad \left[(2n_z+1) a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z} + \sqrt{n_z(n_z-1)} \left(a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z-2} + \text{h.c.} \right) \right] ,
\end{aligned}$$

where we used the fact that $r^2 = x^2 + y^2 + z^2$ and we introduced the oscillator length scales $a_{x(y)} = \sqrt{\hbar/m\omega_{x(y)}}$ associated with the x and y-direction.

- 7. Show that for the problem 6 the dipole operator satisfies the analog of the f-sum rule $[F,[H,F]] = N\hbar^2(2m)$.

Solution: The commutator between H and the operator F from problem 6 is given by

$$\begin{aligned}
[H,F] &= \frac{a_z}{2} \sum_{n_x n_y n_z} \sqrt{n_z} \left(\epsilon_{n_x n_y n_z} - \epsilon_{n_x n_y n_z - 1} \right) \left(a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z-1} - a^\dagger_{n_x n_y n_z-1} a_{n_x n_y n_z} \right) \\
&= \frac{a_z}{2} \hbar\omega_z \sum_{n_x n_y n_z} \sqrt{n_z} \left(a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z-1} - a^\dagger_{n_x n_y n_z-1} a_{n_x n_y n_z} \right) .
\end{aligned}$$

If we write $F = \tilde{F} + \tilde{F}^\dagger$, then one has that $[H,F] = \hbar\omega_z(\tilde{F} - \tilde{F}^\dagger)$. One gets then the relation $[F,[H,F]] = 2\hbar\omega_z[\tilde{F}^\dagger, \tilde{F}]$ and by calculating the commutator between the operator

$$\tilde{F} = \frac{a_z}{2} \sum_{n_x n_y n_z} \sqrt{n_z}\, a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z-1}$$

and its adjoint $\tilde{F}^\dagger$ one finds the required result

$$[F,[H,F]] = \frac{\hbar^2}{2m} \sum_{n_x n_y n_z} a^\dagger_{n_x n_y n_z} a_{n_x n_y n_z} = N \frac{\hbar^2}{2m} .$$

Chapter 2

Phase transitions and critical phenomena

The structure of the chapter is as follows:

- Introduction to general aspects of phase transitions
- Ising model.
    - Spin Hamiltonian and ferromagnetic transition
    - Mean-field solution:
        - Transition temperature.
        - Order parameter and susceptibility.
    - Exact solution in 1D:
        - Calculation of the partition function.
        - Magnetization and absence of phase transition.
- Landau theory of phase transitions.
    - Ising model again: Gibbs free energy.
    - Second order phase transitions:
        - Order parameter and expansion of Gibbs free energy.

    - Thermodynamic properties and critical exponents
- Phase transition in the presence of an external field.
- Van der Waals equation of state and gas-liquid critical point.
- Inhomogeneous order parameter:
    - Role of fluctuations and correlation functions.
    - Ginzburg criterium and critical dimensions.

2.1 Phase transitions: general aspects

Phase transitions occur in many substances we are familiar with in our everyday life. One example is provided by the different phases of water: liquid, solid and vapour.

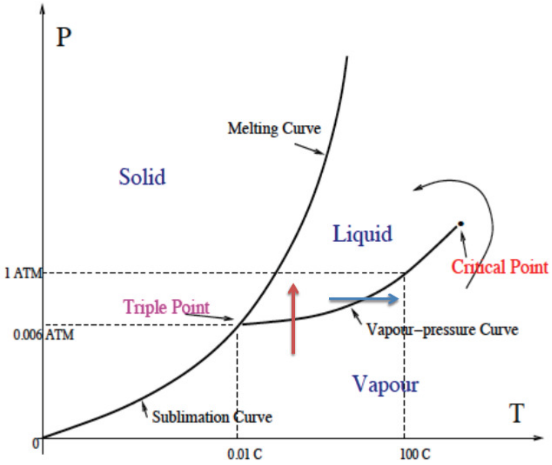

Figure 2.1: Sketch of typical phase diagram. Values on the liquid-vapour curve refers to water.

A typical phase diagram in the p-T plane is sketched in Fig. 2.1. The lines correspond to values of pressure and temperature where two phases coexist (at the triple point all three phases coexist). By crossing the vapour-pressure line at constant T (red arrow) the vapour condenses into liquid and the volume per particle $v = V/N$ undergoes a jump being larger in the gas than in the liquid ($v_G > v_L$). Upon crossing the same line at constant pressure (blue arrow), the liquid evaporates into gas and the entropy per particle $s = S/N$ undergoes a jump ($s_L < s_G$). The latent heat of evaporation $\lambda_{ev} = NT(s_G - s_L)$, where T is the temperature on the vapour-pressure line, is absorbed by the system. By approaching the critical point the discontinuities Δv and Δs both vanish with a power-law dependence on the distance from the critical point: $\Delta v \propto \Delta s \propto (T_c - T)^\beta$, where T_c is the temperature of the critical point (critical temperature). At the critical point there is no difference between the vapour and the liquid phase. Along the vapour-pressure line the isothermal compressibility of the gas $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ diverges with a power-law of the distance from T_c: $\kappa_T \propto (T_c - T)^{-\gamma}$. Close to the critical point the fluid is no longer transparent to light because density fluctuations occur over large length scales, on the order and larger than the wavelength of visible light. This phenomenon is called critical opalescence. A similar behavior takes place when crossing the melting curve which separates the solid from the liquid phase. Contrary to the vapour-pressure curve, however, the melting curve does not end at a critical point and the transition from liquid to solid is always associated with a discontinuous change of v and with the release of the latent heat of solidification.

Analogous features are observed in all substances characterized by a similar phase diagram. In Fig. 2.2 the phase diagram of ^{4}He is shown in the $p-T$ plane. Here some peculiar aspects are present: there is no tricritical point of coexistence of the three phases and below a critical pressure the system remains in the liquid state down to zero temperature. In addition, the lambda line separates two distinct liquid phases where the fluid behaves normally (He I) and where instead superfluidity, in the sense of vanishing viscosity, occurs (He II). Transition points along the lambda line share a similar behavior with the critical point of the liquid-gas transition: the entropy is continuous at the transition whereas the specific heat at constant pressure C_p exhibits a discontinuity. Another example of phase transition is provided in Fig. 2.8 which refers to the ferromagnetic transition of solids like Fe or Ni in the plane spanned by temperature and external magnetic field. By crossing the transition line at fixed T, as the external field along a given direction changes sign, the magnetization M of the system parallel to the field jumps discontinuously from a positive to a negative value. This behavior is similar to the jump of the volume per particle when crossing the vapour-pressure curve in the liquid-gas transition. Instead, if one moves along the temperature axis at $h = 0$ the magnetization decreases continuously until it vanishes at T_c following the law $M \propto (T_c - T)^\beta$, in the same way as the gaps Δv and Δs vanish when approaching the critical point along the vapour-pressure curve. One also has that the magnetic susceptibility of the gas $\chi = \frac{1}{V}\left(\frac{\partial M}{\partial h}\right)_T$ diverges at the critical temperature as $\chi \propto (T_c - T)^{-\gamma}$, similarly to the behavior of the compressibility along the vapour-pressure line.

Historically phase transitions are classified according to the following definitions due to P. Ehrenfest.

- Ehrenfest's classification of phase transitions
  1. First-order phase transition: at least one first derivative of the free energy is discontinuous at the transition. Examples are: i) The liquid-gas and the liquid-solid transitions where both the entropy and the volume per particle are discontinuous. ii) The ferromagnetic transition at fixed temperature where the magnetization is discontinuous.
  2. Second-order phase transitions: all first derivatives of the free energy are continuous, but

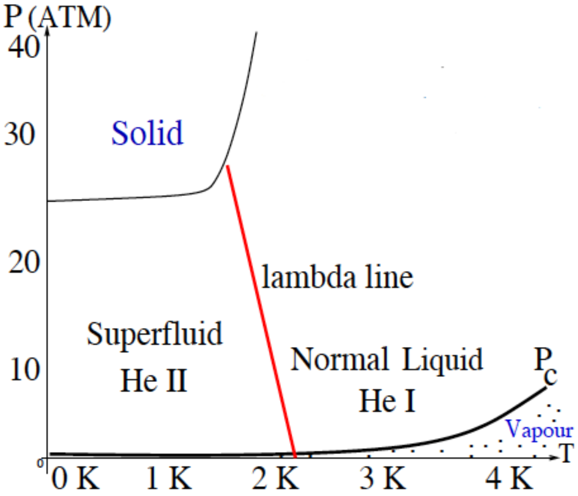

Figure 2.2: Phase diagram of ^{4}He.

at least one second derivative is discontinuous at the transition. Examples are: i) The lambda transition in ^{4}He where there is no release or absorption of latent heat, but the heat capacity is discontinuous. ii) The ferromagnetic transition at zero external field where the magnetization is continuous, but the heat capacity is discontinuous. iii) The liquid-gas transition at the critical point where there is no latent heat nor jump in the volume per particle, but the specific heat is again discontinuous.

3. Higher nth-order phase transitions: there is a discontinuity in at least one nth-order derivative of the free energy, while all lower order derivatives are continuous at the transition.

It is useful at this point to list a series of important features characterizing in general phase transitions:

- Phase transitions are associated with the non-analytic behavior of thermodynamic quantities (discontinuities or divergences). For a finite-N system *all* thermodynamic quantities are by definition analytic functions of their variables. Thus, strictly speaking, phase transitions occur only in the thermodynamic limit ($N \to \infty$); in the wording of P.W. Anderson: *more is different*.

- Phase transitions are associated with the breaking of a symmetry which is present in the ordered (low temperature) phase and is absent in the disordered (high temperature) phase. For example, translational symmetry is broken in the liquid to solid transition; rotational symmetry is broken in the paramagnetic to ferromagnetic transition; U(1) gauge symmetry is broken in the superfluid transition of ^{4}He. In the case of ferromagnets with a preferential direction of magnetization (well described by the Ising model), the discrete Z_2 symmetry is broken in the transition from the paramagnetic to the ferromagnetic state. The same Z_2 symmetry is also broken in the liquid-gas transition: in fact the difference $v - v_c$ between the volume per particle and its value at the critical point can have any value in the fluid phase corresponding to $T > T_c$ or $p > p_c$, but $v - v_c > 0$ in the gas phase for $T < T_c$ below the vapour-pressure curve and $v - v_c < 0$ in the liquid phase for $p < p_c$ above the vapour-pressure line.

- Phase transitions are characterized by an order parameter which vanishes in the disordered phase and is finite in the ordered phase. Examples are the scalar magnetization M in the Ising model of ferromagnetism and the difference of volume per particle $v_G - v_L$ in the liquid-gas transition. The order parameter can be more complex than a simple scalar, such as a vector or a matrix, and represents a new thermodynamic variable necessary to describe the ordered phase.

- A more modern classification of phase transitions based on the behavior of the associated order parameter distinguishes between first-order transitions, where the order parameter jumps discontinuously at the transition, from continuous transitions, where instead the order parameter vanishes at the transition in a continuous fashion.

- In a continuous transition the typical fluctuation length (known as correlation length) diverges at the critical point. As a consequence, the thermodynamic variables scale in the vicinity of the critical point with specific power laws of the reduced temperature $t = \frac{T - T_c}{T_c}$, the exponents being known as critical indexes. Some examples, taken from the ferromagnetic transition, are as follows: i) order parameter $M \sim |t|^\beta$, ii) susceptibility associated with the order parameter $\chi \sim |t|^{-\gamma}$, iii) specific heat $C \sim |t|^{-\alpha}$, iv) order parameter at the critical point as a function of the external field $M \sim h^{1/\delta}$. The values of the critical indexes are universal within a class of phase transitions, which is defined by the dimensionality of the system and by the number of components of the order parameter.

2.2 Ising model and ferromagnetic transition

We consider a model of magnetism in solids where magnetic moments are coupled. As opposed to the Langevin theory describing the paramagnetic behavior of independent magnetic moments, this model captures the main features of the ferromagnetic transition.

The main source of coupling between spins in a crystal is provided by exchange interactions. A simple model, which contains the relevant physics, is realized by considering the spin states of just two electrons. If the corresponding protons are far apart, the spin states of the two electrons form a four-fold degenerate manifold: $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$. By bringing the two protons closer together, interactions become more important providing to lowest order an energy splitting $E_S - E_T$ between the singlet state and the three-fold degenerate manifold corresponding to the triplet state. The square of the total spin of the system, $\mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2$, has eigenvalue 0 in the singlet and 2 in the triplet state. Since $\mathbf{S}_i^2 = 3/4$ for each spin, the eigenvalue of $\mathbf{S}_1 \cdot \mathbf{S}_2$ must be -3/4 in the singlet and 1/4 in the triplet state. Consequently, the operator

$$H^{spin} = \frac{1}{4}(E_S + 3E_T) - (E_S - E_T)\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{2.1}$$

has eigenvalue E_S in the singlet state and E_T in each of the three triplet states. This shows that the splitting between singlet and triplet states can be described in terms of coupling between spins. Of course, for the He atom problem $E_S < E_T$, because the triplet state corresponds to an antisymmetric spatial wave function with higher energy compared to the nodeless symmetric wave function of the singlet state. However, if one considers two valence electrons belonging to two multielectron atoms, the effective Hamiltonian can still be described by (2.1) with possibly $E_T < E_S$.

By following the above discussion one is led to introduce the most general Hamiltonian of interacting spins on a lattice

$$H = -\frac{1}{2}\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j \ , \tag{2.2}$$

where the indices i and j run over the lattice sites and $\mathbf{S}_i$ are spin operators defined on the lattice site and obeying to the usual on-site commutation rules $[S_i^\alpha, S_i^\beta] = i\epsilon_{\alpha\beta\gamma}S_i^\gamma$, while spins on different lattice sites commute, $[S_i^\alpha, S_j^\beta] = 0 \ \forall \alpha, \beta$ if $i \neq j$ (notice that spin operators are here dimensionless). The indices α, β, γ indicate the three spatial components of the spin and $\epsilon_{\alpha\beta\gamma}$ is the completely antisymmetric tensor with $\epsilon_{xyz} = 1$. The factor 1/2 in (3.1) ensures that each pair of spins is countend only once. The interaction matrix J_{ij} is symmetric, $J_{ij} = J_{ji}$, and the diagonal terms are zero ($J_{ii} = 0$) in order to avoid self-interaction of the spins. The above spin Hamiltonian is known as Heisenberg model: the coupling parameters J_{ij} arise from exchange interactions between the spins, it can favor parallel alignment of the spins ($J_{ij} > 0$) or antiparallel alignment of the spins ($J_{ij} < 0$).

The Ising model is a version of the Heisenberg Hamiltonian (3.1) simplified in three respects:

- the rotational symmetry is broken corresponding to a crystal with a preferential direction,
- interactions favor spin alignment and are limited to nearest neighbors on a cubic lattice,
- spins are two-level systems $S_i^z = \pm 1$.

The resulting Hamiltonian is given by

$$H = -\frac{1}{2}\sum_{\langle ij \rangle} J \, S_i^z S_j^z - h \sum_i S_i^z \ , \tag{2.3}$$

where $J > 0$ and $\langle ij \rangle$ indicates the sum over the lattice sites i, while j runs over the nearest neighbors of site i. The number of nearest neighbors, called the coordination number z, is determined by the geometry and by the dimensionality of the lattice: in a cubic lattice $z = 2$ in 1D, $z = 4$ in 2D and $z = 6$ in 3D. In the Hamiltonian (2.3) we also introduced a uniform external field $h > 0$ (with the dimension of energy) which tends to align the spins in the positive direction of the z-axis.

We notice that the Ising Hamiltonian (2.3) is diagonal in the spin eigenstates of S_i^z. These are given by the general product states $| \pm 1 \pm 1 ... \pm 1\rangle$ of N spin variables, where N is the number of lattice sites. The average magnetization is defined as

$$\langle M \rangle = \sum_{i=1}^{N} \langle S_i \rangle = N \langle S \rangle \ , \tag{2.4}$$

where for notational convenience we removed the superscript z from the spin operator. We also notice that the Heisenberg Hamiltonian (3.1) is invariant under rotations as it depends on the scalar quantity $\mathbf{S}_i \cdot \mathbf{S}_j$. Since the Ising Hamiltonian (2.3) has a preferential direction, it is no longer invariant under rotations but it is still invariant under the parity transformation $\mathbf{r} \to -\mathbf{r}$.

The ground state of the Ising Hamiltonian (2.3) is ferromagnetic, with all the spins aligned in one direction. Its energy is given by (we assume $N \gg 1$)

- $E_0 = -JNz/2$ and $\langle M \rangle = \pm N$ if $h = 0$,
- $E_0 = -JNz/2 - hN$ and $\langle M \rangle = N$ if $h > 0$.

The relevant question concerning the model concerns the possible existence of a ferromagnetic phase at $T \neq 0$. In other words:

- can $\langle M \rangle \neq 0$ even if $h = 0$?

The Ising Hamiltonian (2.3) can be solved exactly in 1D (Ising 1925), also in the presence of the external field h, and in 2D (Onsager 1944) only in the case $h = 0$. In all other cases one must resort to numerical simulations. The answer to the above question is negative in 1D and positive in 2D and 3D.

2.2.1 Mean-field solution

An extremely powerful tool to study many-body problems is provided by the mean-field theory. In general, it amounts to an approximate treatment of interaction terms so that the Hamiltonian is reduced to an effective one of independent particles immersed in an external field produced by the interaction with all the other particles. The solution is then determined self consistently.

For the problem at hand, the mean-field treatment consists in writing the interaction term $S_i S_j$ as

$$\begin{aligned} S_i S_j &= S_i \langle S_j \rangle + \langle S_i \rangle S_j - \langle S_i \rangle \langle S_j \rangle \\ &= S_i \langle S \rangle + S_j \langle S \rangle - \langle S \rangle^2 , \end{aligned} \tag{2.5}$$

where $\langle S \rangle = \langle M \rangle / N$ is the uniform average magnetization density. The above prescription neglects correlations between spin operators in different lattice sites in the sense that $\langle S_i S_j \rangle = \langle S \rangle^2$. Notice that the last term on the right hand side of eq. (2.5) avoids double counting when calculating $\langle S_i S_j \rangle$. By using the above expression for the product $S_i S_j$ in (2.3) on gets the effective mean-field

Hamiltonian

$$\begin{aligned} H_{\mathrm{MF}} &= \frac{1}{2} JzN\langle S\rangle^2 - \sum_i \left(Jz\langle S\rangle + h\right) S_i \\ &= E_0^{\mathrm{MF}} + \sum_i H_i \ , \end{aligned} \tag{2.6}$$

where, in the last equation, we introduced the constant term $E_0^{\mathrm{MF}} = JzN\langle S\rangle^2/2$ and the single-site Hamiltonian $H_i = -(Jz\langle S\rangle + h)S_i$. As anticipated, the effective Hamiltonian H_{MF} describes independent spins S_i subject to the external field $Jz\langle S\rangle + h$.

The canonical partition function can be readily calculated using the definition $Z_C = Tr(e^{-\beta H})$. By using as a basis the eigenstates of the operators S_i corresponding to the eigenvalues $\sigma_i = \pm 1$ we get

$$\begin{aligned} Z_C &= \sum_{\sigma_1=\pm 1} \ldots \sum_{\sigma_N=\pm 1} \langle \sigma_1 \ldots \sigma_N | e^{-\beta H_{\mathrm{MF}}} | \sigma_1 \ldots \sigma_N \rangle \\ &= e^{-\beta E_0^{\mathrm{MF}}} \sum_{\sigma_1=\pm 1} \langle \sigma_1 | e^{-\beta H_1} | \sigma_1 \rangle \ \ldots \sum_{\sigma_N=\pm 1} \langle \sigma_N | e^{-\beta H_N} | \sigma_N \rangle \\ &= e^{-\beta E_0^{\mathrm{MF}}} \left(Z_1\right)^N \ , \end{aligned} \tag{2.7}$$

where

$$Z_1 = \sum_{\sigma=\pm 1} e^{\frac{\tilde{J}\langle S\rangle + h}{k_B T}\sigma} = 2\cosh\left(\frac{\tilde{J}\langle S\rangle + h}{k_B T}\right) \tag{2.8}$$

is the partition function of the single spin. Here we introduced the notation $\tilde{J} = Jz$ accounting for the coordination number in different dimensions.

From the partition function one can straightforwardly obtain all relevant thermodynamic functions:

- Free energy

$$F = -k_B T \log Z_C = E_0^{\mathrm{MF}} - N k_B T \log\left[2\cosh\left(\frac{\tilde{J}\langle S\rangle + h}{k_B T}\right)\right] \ . \tag{2.9}$$

- Magnetization

$$\langle M\rangle = -\left(\frac{\partial F}{\partial h}\right)_{TN} = N\tanh\left(\frac{\tilde{J}\langle S\rangle + h}{k_B T}\right) \ . \tag{2.10}$$

The above eq. (2.10) provides us with the sought equation for the magnetization density

$$\langle S \rangle = \tanh \left(\frac{\tilde{J}\langle S \rangle + h}{k_B T} \right) \ . \tag{2.11}$$

For $h = 0$ it reduces to the transcendental equation

$$\langle S \rangle = \tanh \left(\frac{\tilde{J}\langle S \rangle}{k_B T} \right) \ , \tag{2.12}$$

which has the trivial solution $\langle S \rangle = 0$ and, for $k_B T < \tilde{J}$, also a non trivial solution $\langle S \rangle \neq 0$ as shown in Fig. 2.3.

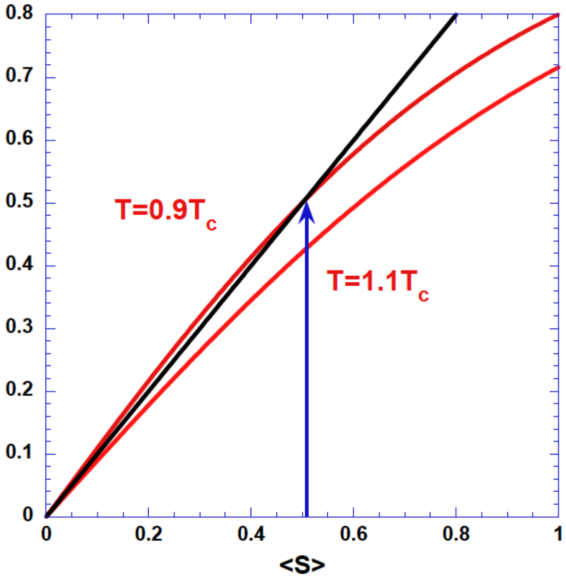

Figure 2.3: Graphical solution of eq. (2.12). For $T = 1.1T_c$ the curve $\tanh(T_c\langle S \rangle/T)$ does not intercept the straight line $\langle S \rangle$ unless if $\langle S \rangle = 0$. It does instead if $T = 0.9T_c$ as shown by the blue arrow.

By setting $T_c = \tilde{J}/k_B$, we conclude then

- if $T > T_c$ one finds $\langle S \rangle = 0$ and the system is paramagnetic,
- if $T < T_c$ one finds $\langle S \rangle \neq 0$ and the system is ferromagnetic.

The value of $\langle S \rangle$ can be calculated explicitly from eq. (2.12) in the limit $T \to 0$ and $T \to T_c^-$. By expanding the argument of the tanh one finds

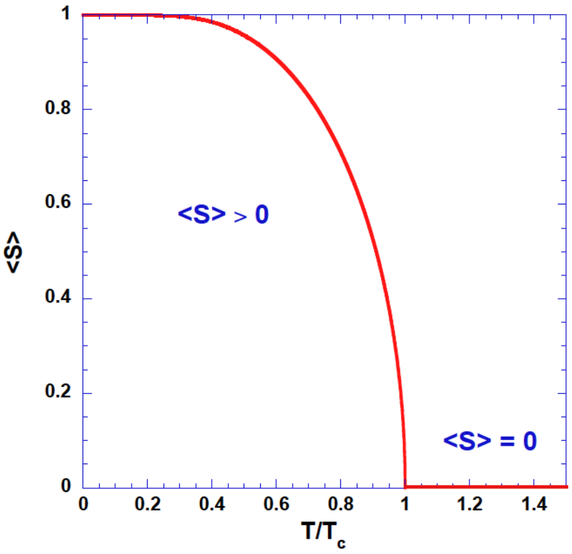

Figure 2.4: Temperature dependence of the magnetization density. Below the transition temperature T_c the magnetization density is different from zero.

- $T \to 0$: $\langle S \rangle \simeq 1 - 2e^{-2T_c/T}$, showing that deviations from the saturated magnetization are exponentially small at $T = 0$.
- $T \to T_c^-$: $\langle S \rangle \simeq \langle S \rangle T_c/T - (\langle S \rangle T_c/T)^3/3 \simeq \sqrt{3}\sqrt{(T_c - T)/T_c}$, showing that the magnetization density approaches zero with the law $\sqrt{T_c - T}$.

The temperature dependence of $\langle S \rangle$ is shown in Fig. 2.4. The magnetization density $\langle S \rangle$ is the order parameter of the ferromagnetic transition. Some general remarks are in order here:

- The order parameter is equal to zero above the transition temperature and different from zero below T_c.
- The transition is continuous as the order parameter grows continuously from zero for $T < T_c$.
- The original symmetry $z \to -z$ of the Ising Hamiltonian (2.3) is broken when $\langle S \rangle \neq 0$. The system spontaneously chooses one of the two possible degenerate directions: $\langle S \rangle > 0$ or $\langle S \rangle < 0$. The appearance of an order parameter is always related to the spontaneous breaking of a symmetry present in the Hamiltonian.

An important property of the system is provided by the magnetic susceptibility. The magnetic susceptibility is defined as the rate of change of $\langle M\rangle$ by an increase of the external field h

$$\chi = \frac{1}{N}\lim_{h\to 0}\frac{\langle M\rangle}{h} = \lim_{h\to 0}\frac{\langle S\rangle}{h}\ . \tag{2.13}$$

- $T > T_c$: By expanding eq. (2.11) keeping terms linear in $\langle S\rangle$ and h we find

  $$\langle S\rangle \simeq \frac{\tilde{J}\langle S\rangle + h}{k_B T} = \frac{h}{k_B(T - T_c)}\ , \tag{2.14}$$

  yielding the result

  $$\chi = \frac{1}{k_B(T - T_c)}\ . \tag{2.15}$$

  When approaching T_c from above χ diverges as $1/(T - T_c)$, while at high temperatures one recovers the standard Curie's law $\chi = 1/k_B T$.

- $T < T_c$: By differentiating with respect to h both left and right hand side of eq. (2.11) one gets

  $$\frac{d\langle S\rangle}{dh}|_{h=0} = \chi = \left(1 - \tanh^2\frac{\tilde{J}\langle S\rangle_{h=0}}{k_B T}\right)\left(\frac{\tilde{J}\chi}{k_B T} + \frac{1}{k_B T}\right)\ , \tag{2.16}$$

  yielding the result

  $$\chi = \frac{1 - \tanh^2\frac{T_c\langle S\rangle_{h=0}}{T}}{k_B T - k_B T_c\left(1 - \tanh^2\frac{T_c\langle S\rangle_{h=0}}{T}\right)}\ . \tag{2.17}$$

  Two limiting regimes are worth investigating in more details:

  - $T \to T_c^-$: By substituting $\langle S\rangle = \sqrt{3(T_c - T)/T_c}$ one finds the diverging result

    $$\chi = \frac{1}{2k_B(T_c - T)}\ . \tag{2.18}$$

  - $T \to 0$: By substituting $\langle S\rangle = 1 - 2e^{-2T_c/T}$ one finds the exponentially small value

    $$\chi = \frac{4e^{-2T_c/T}}{k_B T}\ . \tag{2.19}$$

The behavior of the susceptibility χ close to the transition point is of great importance in understanding the onset of ferromagnetism. In fact, due to its divergence, infinitesimally small fields can produce finite magnetization densities over large regions. Thermal fluctuations can always produce some finite values of $\langle S \rangle$ in spatial regions that are large on a microscopic scale, but still much smaller compared to the size of the system. Furthermore, if the temperature is close to T_c, the field produced by these small magnetic domains can trigger the magnetization of even larger domains, finally inducing the ferromagnetic transition over the whole system.

2.2.2 Exact solution in 1D

The mean-field solution of the Ising model discussed in the previous section is essentially insensitive to the dimensionality of the system, the only change being the coordination number z entering in the parameter $\tilde{J}$. In particular, a ferromagnetic transition is predicted in any dimensionality. An exact solution of the model can be easily obtained for the 1D case and, as we will see, no finite transition temperature is obtained in contrast to the mean-field prediction. This is a frequent drawback of the mean-field theory in low dimensions. The reason is that thermal fluctuations, neglected in the mean-field treatment, have an increased role in lower dimensions.

In 1D with periodic boundary conditions on the string, $S_i = S_{i+N}$, the Ising Hamiltonian (2.3) can be recast in the following form

$$H = -\sum_{i=1}^{N} \left(J S_i S_{i+1} + h S_i \right) \ . \tag{2.20}$$

The partition function can be conveniently written in the following form

$$Z_C = \sum_{\sigma_1 = \pm 1} \dots \sum_{\sigma_N = \pm 1} K(\sigma_1, \sigma_2) K(\sigma_2, \sigma_3) \dots K(\sigma_{N-1}, \sigma_N) K(\sigma_N, \sigma_1) \ , \tag{2.21}$$

where the pair function K is defined as

$$K(\sigma_i, \sigma_{i+1}) = e^{\frac{J}{k_B T} \sigma_i \sigma_{i+1} + \frac{h}{2 k_B T} (\sigma_i + \sigma_{i+1})} \ . \tag{2.22}$$

We introduce the two-state vectors

$$\sigma^{+} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \sigma^{-} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \ , \tag{2.23}$$

satisfying the completeness relation in dimension two

$$\sum_{\alpha=\pm} \sigma^{\alpha}(\sigma^{\alpha})^T = \begin{pmatrix} 1 \\ 0 \end{pmatrix} (1\ 0) + \begin{pmatrix} 0 \\ 1 \end{pmatrix} (0\ 1) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} , \tag{2.24}$$

and the 2×2 matrix

$$K = \begin{pmatrix} e^{\bar{J}+\bar{h}} & e^{-\bar{J}} \\ e^{-\bar{J}} & e^{\bar{J}-\bar{h}} \end{pmatrix} , \tag{2.25}$$

where $\bar{J} = J/k_BT$ and $\bar{h} = h/k_BT$. One can readily show the following identities: $K(1,1) = e^{\bar{J}+\bar{h}} = (\sigma^+)^T K\sigma^+$, $K(1,-1) = e^{-\bar{J}} = (\sigma^+)^T K\sigma^-$, $K(-1,1) = e^{-\bar{J}} = (\sigma^-)^T K\sigma^+$ and $K(-1,-1) = e^{\bar{J}-\bar{h}} = (\sigma^-)^T K\sigma^-$. By using the two-state formalism introduced above the calculation of the partition function (2.21) can be efficiently carried out giving the result

$$\begin{aligned} Z_C &= \sum_{\alpha_1=\pm} ... \sum_{\alpha_N=\pm} (\sigma^{\alpha_1})^T K\sigma^{\alpha_2}(\sigma^{\alpha_2})^T K\sigma^{\alpha_3} ... \,(\sigma^{\alpha_N})^T K\sigma^{\alpha_1} \\ &= \sum_{\alpha_1=\pm} (\sigma^{\alpha_1})^T K^N \sigma^{\alpha_1} = Tr(K^N) \,. \end{aligned} \tag{2.26}$$

The matrix K, being symmetric, can be diagonalized using a unitary matrix U

$$K = U^T \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} U \quad \text{and} \quad K^N = U^T \begin{pmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{pmatrix} U \,, \tag{2.27}$$

and the result for the trace can be readily obtained

$$Tr(K^N) = Tr \begin{pmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{pmatrix} = \lambda_1^N + \lambda_2^N \,. \tag{2.28}$$

The eigenvalues $\lambda_{1,2}$ of the matrix K are given by

$$\lambda_{1,2} = e^{\bar{J}} \cosh \bar{h} \pm \sqrt{e^{2\bar{J}} \sinh^2 \bar{h} + e^{-2\bar{J}}} \,, \tag{2.29}$$

showing that they are both positive and $\lambda_1 > \lambda_2$. In the thermodynamic limit of a large number of spins ($N \gg 1$) one obtains $Z_C = \lambda_1^N(1+(\lambda_2/\lambda_1)^N) \simeq \lambda_1^N$ and thus

$$Z_C = \left(e^{\bar{J}}\cosh\bar{h} + \sqrt{e^{2\bar{J}}\sinh^2\bar{h} + e^{-2\bar{J}}}\right)^N \ . \tag{2.30}$$

From this result one can derive all relevant thermodynamic quantities:

- Magnetization

$$\langle M\rangle = Nk_BT\frac{1}{\lambda_1}\left(\frac{\partial\lambda_1}{\partial h}\right)_{TN} = N\frac{\sinh\bar{h}}{\sqrt{\sinh^2\bar{h} + e^{-4\bar{J}}}} \ . \tag{2.31}$$

  - In the limit $h \to 0$

$$\langle M\rangle = N\bar{h}e^{2\bar{J}} \to 0 \ , \tag{2.32}$$

    showing that no spontaneous magnetization can be supported at any finite temperature.

  - In the limit $T \to 0$

$$\langle M\rangle = N\frac{\sinh\bar{h}}{|\sinh\bar{h}|} = \pm N \ , \tag{2.33}$$

    showing that the ground state is indeed ferromagnetic and that an infinitesimally small magnetic field drives the saturated magnetization to point either in the positive or negative direction.

- Susceptibility

  From eq. (2.32)

$$\chi = \frac{1}{k_BT}e^{2\bar{J}} \ , \tag{2.34}$$

  which

  a) diverges as $T \to 0$, consistently with the ground state being ferromagnetic, and

  b) goes over to Curie's law $\chi = 1/k_BT$ for temperatures $T \gg J/k_B$.

- Free energy

$$F = -Nk_BT\log\lambda_1 = -Nk_BT\log\left(e^{\bar{J}}\cosh\bar{h} + \sqrt{e^{2\bar{J}}\sinh^2\bar{h} + e^{-2\bar{J}}}\right) \ , \tag{2.35}$$

  which for $h = 0$ reduces to

$$F = -Nk_BT\log\left(2\cosh\bar{J}\right) \ , \tag{2.36}$$

and for $T = 0$ to the ground-state energy $E_0 = -N(J + h)$. We notice that at $T = 0$ the mean-field result (2.9) reproduces the exact one, while in the high temperature regime ($k_B T \gg J$ and $k_B T \gg h$) the first gives $F_{\mathrm{MF}} = -N k_B T \log(2 + \bar{h}^2)$ to be compared with $F = -N k_B T \log(2 + \bar{h}^2 + \bar{J}^2)$ obtained by expanding (2.35). Thus, in 1D, the mean-field theory is unable to recover interaction effects not even to the lowest order in the coupling parameter J.

We conclude this section about exact solutions of the Ising model by mentioning that the exact solution in 2D gives indeed a ferromagnetic phase transition at $k_B T_c = 2.27J$. This result differs quantitatively from the mean-field prediction $k_B T_c = \tilde{J} = 4J$ and the values of the critical exponents also differ from their mean-field counterparts. However, in this case, the mean-field approach does capture the correct qualitative behavior of the system.

2.3 Landau theory of phase transitions

2.3.1 The Ising model again

Let us consider again the mean-field solution of the Ising model.

- Helmoltz free energy

  In magnetic systems the Helmoltz free energy is a function of temperature, volume and external magnetic field (see Supplement 2.4.1). In the Ising model the number N of spins determines the volume, given the fixed spacing of the lattice points, and we have $F = F(T, N, h)$. At fixed N its differential is given by $dF = -SdT - \langle M \rangle dh$ so that the average magnetization is the derivative of $-F$ with respect to h

  $$\langle M \rangle = -\left(\frac{\partial F}{\partial h}\right)_{TN} , \tag{2.37}$$

  and the susceptibility is the second derivative of $-F/N$ with respect to h

  $$\chi = \frac{1}{N}\left(\frac{\partial \langle M \rangle}{\partial h}\right)_{TN} = -\frac{1}{N}\left(\frac{\partial^2 F}{\partial h^2}\right)_{TN} . \tag{2.38}$$

  Since $\chi > 0$ it turns out that $-F/N$ is a concave function of h.

- Gibbs free energy

  The Gibbs free energy of a magnetic system depends on temperature, volume and magnetization (see Supplement 2.4.1). It is obtained as the sum $G = F + \langle M \rangle h$ and its differential is given by $dG = -SdT + hd\langle M \rangle$. Thus we have

  $$h = \left(\frac{\partial G}{\partial \langle M \rangle}\right)_{TN} , \tag{2.39}$$

  and

  $$\chi^{-1} = \left(\frac{\partial h}{\partial \langle S \rangle}\right)_{TN} = \frac{1}{N}\left(\frac{\partial^2 G}{\partial \langle S \rangle^2}\right)_{TN} , \tag{2.40}$$

  showing that G/N is a concave function of the magnetization density $\langle S \rangle$.

Let us derive the dependence of the Gibbs energy on $\langle S \rangle$ when the order parameter is small. To this purpose we use the mean-field equation (2.11) that we invert obtaining

$$\frac{\tilde{J}\langle S\rangle}{k_BT} + \frac{h}{k_BT} = \operatorname{atanh}(\langle S\rangle) \simeq \langle S\rangle + \frac{1}{3}\langle S\rangle^3 \, . \tag{2.41}$$

By solving for h we find the following result for the partial derivative of G

$$\frac{h}{k_BT} = \langle S\rangle\left(1 - \frac{T_c}{T}\right) + \frac{1}{3}\langle S\rangle^3 = \frac{1}{k_BTN}\left(\frac{\partial G}{\partial\langle S\rangle}\right)_{TN} \, , \tag{2.42}$$

and, finally, by integrating with respect to $\langle S\rangle$ we find the desired expansion in powers of the order parameter

$$G(T, N, \langle S\rangle) = G_0(T, N) + Nk_BT\left[\frac{1}{2}\langle S\rangle^2\left(1 - \frac{T_c}{T}\right) + \frac{1}{12}\langle S\rangle^4\right] \, , \tag{2.43}$$

holding in the limit $\langle S\rangle \ll 1$.

The mean-field solutions discussed in the previous section correspond to minima of the free energy (2.43). In fact, from the equation

$$\left(\frac{\partial G}{\partial\langle S\rangle}\right)_{TN} = 0 \, , \tag{2.44}$$

we obtain

- if $T > T_c$: $\langle S\rangle = 0$
- if $T < T_c$: $\langle S\rangle = \sqrt{3(T_c - T)/T_c}$,

in agreement with the findings of eq. (2.12).

The behavior of the function (2.43) close to T_c shows the peculiar transition from parabolic to mexican hat shape as one crosses the critical temperature (see Fig.2.5).

- $\underline{T > T_c}$:

  The function G exhibits a single minimum located at $\langle S\rangle = 0$. The second derivative of G, proportional to $1/\chi$, is positive and finite $\partial^2 G/\partial\langle S\rangle^2 > 0$.

- $\underline{T = T_c}$:

  The minimum of G is still at $\langle S\rangle = 0$, but $\partial^2 G/\partial\langle S\rangle^2 = 0$ and the curve is very flat near the bottom.

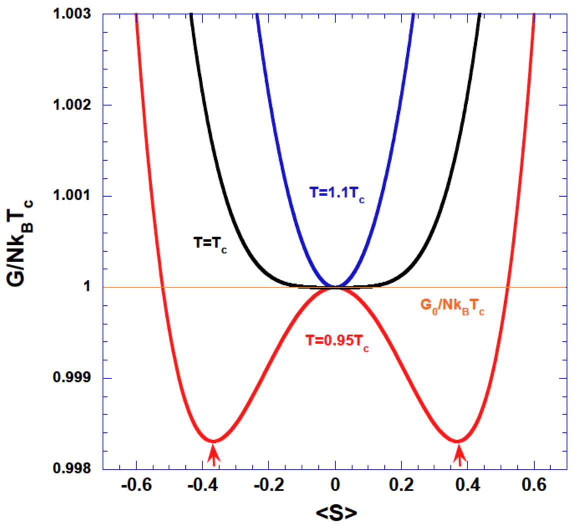

Figure 2.5: Gibbs free energy as a function of $\langle S\rangle$ above the transition ($T = 1.1T_c$), at the transition ($T = T_c$) and below the transition ($T = 0.95T_c$). The horizontal orange line is the arbitrary value of G_0/Nk_BT_c. The two arrows indicate the possible equilibrium values of $\langle S\rangle$ at $T = 0.95T_c$.

- $\underline{T < T_c:}$

  The value $\langle S\rangle = 0$ corresponds now to a maximum of G and two symmetric minima appear at $\langle S\rangle = \pm\sqrt{3(T_c - T)/T_c}$.

To the function of the order parameter given in eq. (2.43) can be attributed the meaning of the Gibbs free energy associated with a fluctuation of $\langle S\rangle$ for a given temperature and volume. The equilibrium state corresponds to the minimum of G, but the function describes quantitatively the increase of free energy following a change of the value of $\langle S\rangle$. For temperatures larger than T_c, thermal fluctuations can only provide tiny oscillations of the order parameter around the minimum value $\langle S\rangle = 0$. By approaching T_c large fluctuations cost little energy, consistently with a diverging magnetic susceptibility. Finally, at $T < T_c$, two degenerate minima at a finite value of $\langle S\rangle$ develop. The two phases with $\pm\langle S\rangle$ can coexist in equilibrium and domains will form, nevertheless in each domain, that is large on a microscopic scale, the system randomly chooses one of the two options breaking thus the parity symmetry.

2.3.2 Landau theory of second order phase transitions

We are now ready to discuss the general theory due to Landau of second order phase transitions. The main assumptions of the theory are:

- existence of a continuous transition,
- vicinity of the critical point.

The basis of the theory is an expansion of the Gibbs free energy in powers of the order parameter. Equilibrium states only correspond to minima, but the function is defined for any small value of the order parameter and it describes the increase in free energy associated with a fluctuation of the order parameter away from the equilibrium value.

We will consider general situations where the order parameter is written in terms of a vector with n components $\mathbf{m} = (m_1, m_2, ..., m_n)$. Examples of this category are:

- magnetization in Ising models: the order parameter is a scalar ($n = 1$);
- condensate wave function in superfluids: the order parameter is a complex number ($n = 2$)
- magnetization in ferromagnets: the order parameter is a vector ($n = 3$).

More complex order parameters are also possible, for example if there is a dependence on spin variables. In this case the most general order parameter is a $n \times n$ tensor.

The requirement of the Landau free energy possessing the same symmetries as the original Hamiltonian fixes some constraints on the general form of the expansion in terms of powers of the order parameter. For a fixed volume V we can write

$$\frac{G(T,V,\mathbf{m})}{V} = \frac{G_0(T,V)}{V} + a(T)m^2 + b(T)m^4 + ... \; , \tag{2.45}$$

where $G_0(T,V)$ is independent of the order parameter and $a(T)$ and $b(T)$ are functions of the temperature only. Notice that, in general, the coefficients a and b in the expansion (2.45) are also functions of the volume V as the order parameter $\mathbf{m}$ is assumed to be an intensive variable. We notice that G is invariant under rotations of the vector $\mathbf{m}$ as it should be for symmetry reasons and depends only on the modulus of the order parameter. According to general thermodynamic relations, the probability of a fluctuation $\mathbf{m}$ of the order parameter for given values of T and V is proportional to

$$\mathrm{Prob}[\mathbf{m}] \propto \exp\left(-\frac{G(T,V,\mathbf{m})}{k_B T}\right) , \tag{2.46}$$

consistently with the fact that equilibrium states correspond to minima of G.

Due to the vicinity of the critical point, one can expand the functions of temperature in eq. (2.45) as

$$\begin{aligned} a(T) &= a_0 + a_1 t + ... \\ b(T) &= b_0 + b_1 t + ... \end{aligned} \tag{2.47}$$

in terms of the reduced temperature $t = (T - T_c)/T_c$. Since we aim to describe a phase transition, it must happen that:

- at $T > T_c$ there is only one minimum for $m = 0$, implying $a(T) > 0$ and $b(T) > 0$;
- at $T < T_c$ there is a minimum for $m \neq 0$, implying $a(T) < 0$ and $b(T) > 0$.

Consequently, for $|t| << 1$, one can write

$$\frac{G(T,V,\mathbf{m})}{V} = \frac{G_0(T,V)}{V} + a_1 t m^2 + b_0 m^4 + ... , \tag{2.48}$$

with $a_1 > 0$ and $b_0 > 0$. Equilibrium states correspond to values of m fulfilling the equation

$$0 = \frac{1}{V}\left(\frac{\partial G}{\partial m}\right)_{TV} = 2a_1 t m + 4b_0 m^3 , \tag{2.49}$$

and are given by

$$\begin{aligned} &\text{a)} \qquad m = 0 \quad \text{if} \quad t > 0 \\ &\text{b)} \qquad m = \sqrt{\frac{a_1}{2b_0}}|t|^{1/2} \quad \text{if} \quad t < 0 . \end{aligned} \tag{2.50}$$

By comparing eq. (2.48) with the expansion (2.43), one can identify the parameters a_1 and b_0 in the case of the Ising model, finding $a_1 = \tilde{J}/2$ and $b_0 = \tilde{J}/12$. We also notice that the order parameter vanishes at the transition with the law $|t|^{1/2}$, showing that the prediction of Landau theory is always $\beta = 1/2$ for the critical exponent associated with the order parameter.

An important general consideration applies here to the ordered phase ($\mathbf{m} \neq 0$) if the dimensionality of the order parameter is larger than $n = 1$. In this case all states corresponding to different orientations of the order parameter, but with the same modulus m, are degenerate in energy and the phase transition signals the spontaneous breaking of a continuous symmetry.

Thermodynamic properties

- Entropy

  The entropy corresponding to equilibrium states is obtained from the thermodynamic relation $S = -(\partial G/\partial T)_V$ giving

  $$\frac{S}{V} = \frac{S_0}{V} - \frac{a_1}{T_c} m^2 \ , \tag{2.51}$$

  where $S_0 = -(\partial G_0/\partial T)_V$ is the entropy in the absence of m. We used the fact that $(\partial G/\partial m)(\partial m/\partial T)$ vanishes when m satisfies eq. (2.49). By using the solutions (2.50) for m^2 we find

  $$\text{a)} \qquad \frac{S}{V} = \frac{S_0}{V} \quad \text{if} \quad t > 0$$

  $$\text{b)} \qquad \frac{S}{V} = \frac{S_0}{V} - \frac{a_1}{2T_c b_0}|t| \quad \text{if} \quad t < 0 \ , \tag{2.52}$$

  showing that S is continuous at T_c and that the transition is not accompanied by the release of any latent heat. It also shows and that the entropy is lower in the ordered phase.

- Specific heat

  The specific heat at constant volume is defined as $C = T(\partial S/\partial T)_V$. One gets:

  $$\text{a)} \qquad \frac{C}{V} = \frac{C_0}{V} \quad \text{if} \quad t > 0$$

  $$\text{b)} \qquad \frac{C}{V} = \frac{C_0}{V} + \frac{a_1^2}{2T_c^2 b_0} T \quad \text{if} \quad t < 0 \ . \tag{2.53}$$

The specific heat exhibits a discontinuity at T_c given by $[C(T_c^+) - C(T_c^-)]/V = -a_1^2/(2b_0 T_c)$. According to the standard classification of phase transitions, the presence of a discontinuity in the second derivative of a thermodynamic potential identifies a second order phase transition. We also notice that the critical exponent associated with the specific heat, $C \sim 1/|t|^\alpha$, is predicted to have the value $\alpha = 0$ within this theory.

- Susceptibility

  In the presence of an external field $\mathbf{h} = h\hat{e}_1$, where $\hat{e}_1$ is a unit vector in the n-dimensional space of the order parameter, this latter is oriented along the direction of the field, $\mathbf{m} = m\hat{e}_1$, and the inverse susceptibility is given by $\chi^{-1} = (\partial h/\partial m)_{TV}$. Since by definition $h = (\partial(G/V)/\partial m)_{TV}$, using eq. (2.49) we obtain

  $$\chi = \frac{1}{2a_1 t + 12 b_0 m^2} \, , \tag{2.54}$$

  and finally through eq. (2.50):

  $$\text{a)} \qquad \chi = \frac{1}{2a_1 t} \quad \text{if} \quad t > 0$$

  $$\text{b)} \qquad \chi = \frac{1}{4a_1 |t|} \quad \text{if} \quad t < 0 \, . \tag{2.55}$$

  The corresponding critical exponent, $\chi \sim 1/|t|^\gamma$, is $\gamma = 1$.

- Critical field

  As the last thermodynamic relation, let us consider the behavior of the external field h at the critical point $T = T_c$. From eq. (2.49), by setting $t = 0$, we find the result

  $$h = 4 b_0 m^3 \, , \tag{2.56}$$

  determining the value $\delta = 3$ for the critical exponent defined by the relation $h \sim m^\delta$ or $m \sim h^{1/\delta}$ holding at T_c

An important remark concerning the Landau theory of phase transitions has to do with the universal validity of its results. The value of T_c is clearly not predicted by the theory, since it is a phenomenological input parameter. The same is true for the amplitudes of the various thermodynamic quantities, such as specific heat, susceptibility and order parameter. Their values depend on the phenomenological parameters a_1 and b_0 which are determined for each different phase transition by the details of the underlying microscopic Hamiltonian. The important predictions of the theory concern the values of the critical exponents, which are universally valid for all continuous phase transitions, irrespective of the dimensionality of the system and the number of components of the order parameter.

2.3.3 Phase transition in the presence of an external field

In the presence of an external field, $\mathbf{h} = h\hat{e}_1$, the order parameter is oriented along the direction of $\mathbf{h}$ giving $\mathbf{m} = m\hat{e}_1$ and the Landau free energy (2.48) is modified as follows

$$\frac{G(T, V, \mathbf{m}, \mathbf{h})}{V} = \frac{G_0(T, V)}{V} + a_1 t m^2 + b_0 m^4 - hm \ , \tag{2.57}$$

with an explicit dependence on the value of the applied field. The above expression ensures that equilibrium states are still determined by the minima of the free energy

$$\left(\frac{\partial G(T, V, \mathbf{m}, \mathbf{h})}{\partial m}\right)_{TV\mathbf{h}} = 0 \ . \tag{2.58}$$

This can be can immediately verified from the general relation $h = (\partial G(T, V, \mathbf{m})/\partial m)_{TV}$. We also notice that if we eliminate $\mathbf{m}$ in terms of $\mathbf{h}$ using the equilibrium relation, then eq. (2.57) recovers the expression of the Helmoltz free energy $F(T, V, \mathbf{h})$. Here, however, we aim to describe out-of-equilibrium situations where fluctuations of $\mathbf{m}$ are present under the action of the field $\mathbf{h}$.

Equation (2.58) gives

$$h = 2a_1 t m + 4b_0 m^3 \ . \tag{2.59}$$

From the above equation we notice that:

- a) For any temperature t the solution of eq. (2.59) yields $m \neq 0$. The disordered phase with $m = 0$ can only exist if $h = 0$.

- b) If $t > 0$, corresponding to $T > T_c$, the function of m on the right hand side of eq. (2.59) increases monotonously with its argument. For any value of h, there exists only one solution $\mathbf{m}$ that is parallel to the external field (see panel a) of Fig.2.6). In terms of the free energy (2.57), its minimum varies continuously from $m > 0$ (if $h > 0$) to $m < 0$ (if $h < 0$).

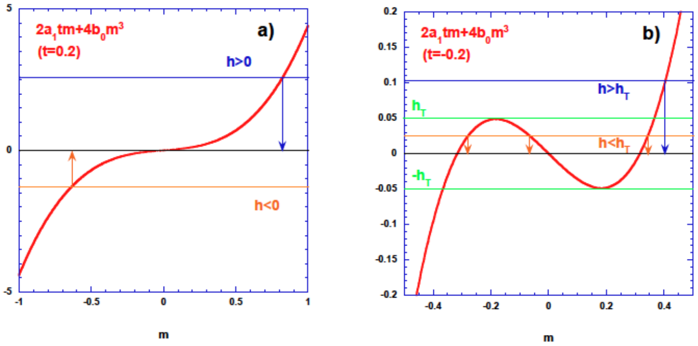

Figure 2.6: Panel a): Right hand side of eq (2.59) as a function of m for $t = 0.2$. The solutions corresponding to $h > 0$ and $h < 0$ are shown with arrows. Panel b): Same as panel a) for $t = -0.2$. The green horizontal lines show the threshold values $\pm h_T$ embracing the region of external fields where three solutions of eq. (2.59) exist. The values of a_1 and b_0 have been arbitrarily chosen as $a_1 = b_0 = 1$.

- c) If $t < 0$, corresponding to $T < T_c$, the right hand side of eq. (2.59) has the shape shown in panel b) of Fig.2.6. For some values of h, within the threshold values $-h_T < h < h_T$, there exist three solutions for $\mathbf{m}$, one parallel and two antiparallel to $\mathbf{h}$. For a given reduced temperature t, the threshold field takes the value $h_T = \sqrt{8a_1^2|t|^3/27b_0}$. It is determined from eq. (2.59), with m corresponding to the maximum of the function $2a_1tm + 4b_0m^3$, namely $m_T = -\sqrt{a_1|t|/6b_0}$.

  The physical meaning of the solutions of eq. (2.59) is best understood by looking at the behavior of the free energy (2.57) for a fixed value of the reduced temperature as shown in Fig.2.7.

  - If $h > h_T$, shown in panel a), there is only one minimum of G corresponding to $m > 0$.
  - If $0 < h < h_T$, shown in panel b), a relative minimum and a maximum appear at $m < 0$. They correspond to the other two solutions of eq. (2.59). The equilibrium state, corresponding to the absolute minimum, is still at $m > 0$, but a metastable state, corresponding to the relative minimum, appears at $m < 0$. The maximum represents instead an unstable state.
  - If $-h_T < h < 0$, shown in panel c), the situation is symmetric with respect to panel b).

The absolute minimum is now at $m < 0$.

- If $h < -h_T$, shown in panel d), the only minimum is at $m < 0$.
- If $h = 0$, the two minima of G correspond to $m = \pm\sqrt{a_1|t|/2b_0}$ and are degenerate in energy (as shown in Fig.2.5).

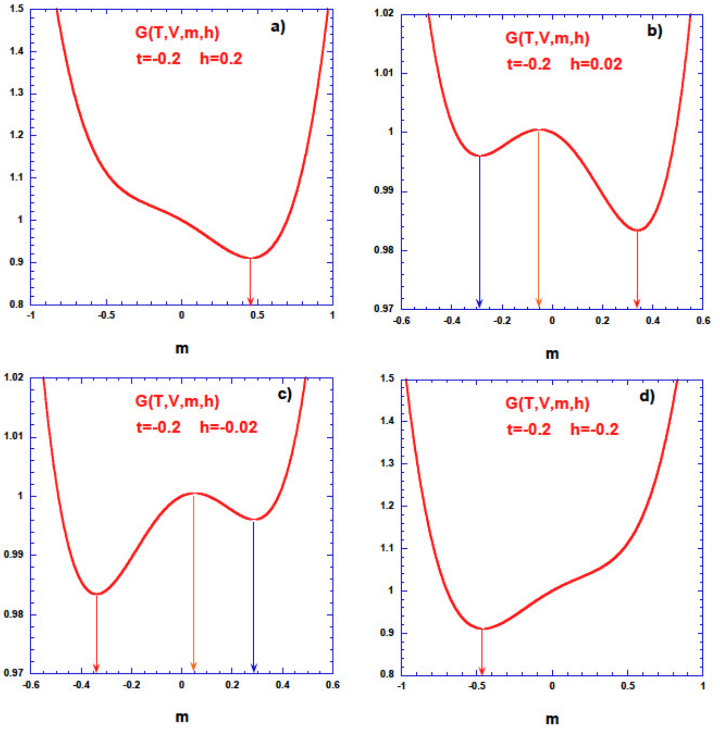

Figure 2.7: Gibbs free energy (2.57) for the value $t = -0.2$ of the reduced temperature and for different values of the field h. Units are such $G_0/V = 1$ and we have arbitrarily chosen $a_1 = b_0 = 1$.

By decreasing the intensity of the external field from positive values the equilibrium state corresponds to a positive order parameter, but a metastable state with $m < 0$ starts to appear if $h < h_T$. At $h = 0$ the two states having opposite m coexist in equilibrium and for small negative values of h the equilibrium state becomes the one with $m < 0$, while the one with $m > 0$ becomes metastable. Finally, for large negative external fields ($h < -h_T$), only one minimum at negative m survives.

We notice that the transition occurring at a given negative value of t when the external field crosses the $h = 0$ line, is different from the one taking place as a function of t in the absence of h. The transition is no longer continuous and the order parameter jumps discontinuously from $m = +\sqrt{a_1|t|/2b_0}$ to $m = -\sqrt{a_1|t|/2b_0}$. The derivative $(\partial F/\partial h)_{TV} = m$ exhibits a discontinuity and the transition is of first order. What is happening is that domains of the phase with negative m are nucleated and they coexist in equilibrium with the regions of positive m. These domains grow in size and the relative volume occupied by the new phase increases until it comprises the entire system and the phase with positive m has completely disappeared.

We notice also that for a given $t > 0$ there is no discontinuous jump. The order parameter follows the external field vanishing when $h = 0$. The phase diagram in the (T, h) plane is schematically shown in Fig.2.8.

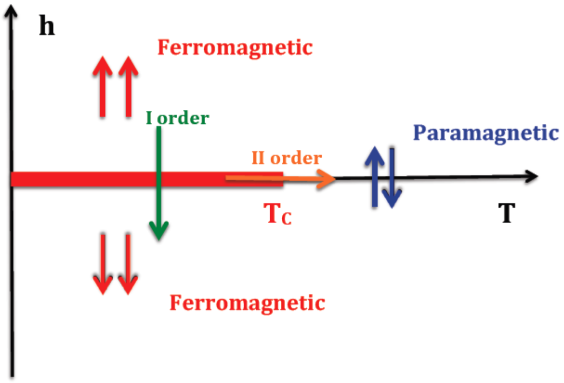

Figure 2.8: Schematic phase diagram in the (h, T) plane. The first and second order phase transitions are shown with arrows.

2.3.4 The Van der Waals equation of state and the gas-liquid critical point

The Van der Waals equation of state provides a model of the gas-liquid first order phase transition. It can be easily derived from the equation of state of an ideal gas

$$pv = k_B T \, , \tag{2.60}$$

where $v = V/N$ is the volume per particle, by making the following simple assumptions on the interparticle interactions:

- 1. The interatomic potential is strongly repulsive at short distances implying that two particles can not approach each other at distances below a certain threshold r_0. The excluded volume $b = (4/3)\pi r_0^3$ results in a reduction of the available volume per particle $v \to v - b$.

- 2. The interatomic potential is vanishingly small at large distances ($r \gg \sigma$) and is attractive at intermediate distances ($r_0 \lesssim r \lesssim \sigma$), where σ is a typical length scale. The amount of attraction felt by each particle scales as σ^3/v, *i.e.* the number of particles in a volume of size σ surrounding the particle.

- 3. In an ideal gas the pressure acting on the walls of the container originates from the kinetic energy of the particles, $p = p_{\rm kin}$. In a gas with attraction the same pressure is reduced by an amount $p = p_{\rm kin} - a/v^2$, arising from the density $1/v$ multiplied by the effect of attraction on a single particle. The pressure originating from the kinetic energy should thus be replaced by $p_{\rm kin} \to p_{\rm kin} + a/v^2$, where a is a positive constant.

- 4. The physical assumption made by Van der Waals is that the relation between $p_{\rm kin}$ and the available volume per particle is the same as for an ideal gas, leading to the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = k_B T \ , \tag{2.61}$$

  where a and b are positive parameters which depend on the type of gas.

The above equation is the famous Van der Waals equation of state of real gases. In a $p-v$ diagram the isothermal curves have the following properties:

- At high temperatures, $k_B T \gg a/v$, isotherms recover the hyperbolic form $p = k_B T/(v - b)$ of the ideal gas and $p(v)$ is a monotonous decreasing function of v.

- At low temperatures, $k_B T \ll a/v$, the function $p(v)$ exhibits two extremal points: a minimum at $v = v_1$ and a maximum at $v = v_2 > v_1$.

- The crossover between the above two behaviors takes place at the critical isotherm $T = T_c$, defined by the conditions $(\partial p/\partial v)_T = (\partial^2 p/\partial v^2)_T = 0$, where the two extremal points meet at v_c.

Critical isotherm and law of corresponding states

From the two equations

$$\begin{aligned}\left(\frac{\partial p}{\partial v}\right)_T &= -\frac{k_B T}{(v-b)^2} + \frac{2a}{v^3} = 0 \\ \left(\frac{\partial^2 p}{\partial v^2}\right)_T &= \frac{2k_B T}{(v-b)^3} - \frac{6a}{v^4} = 0 \ ,\end{aligned} \tag{2.62}$$

and from the equation of state (2.61) one can easily derive the critical values for volume, pressure and temperature in terms of the parameters a and b:

$$v_c = 3b \qquad p_c = \frac{a}{27b^2} \qquad k_B T_c = \frac{8a}{27b} \ . \tag{2.63}$$

It is useful to introduce the reduced variables: $\tilde{p} = p/p_c$, $\tilde{v} = v/v_c$ and $\tilde{T} = T/T_c$, in terms of which the equation of state (2.61) takes the dimensionless form

$$\tilde{p} = \frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2} \ . \tag{2.64}$$

This equation is universal, in the sense that it does not depend on the parameters a and b specific of a given substance, and it is called the *law of corresponding states.* The equation of state of many real gases, once expressed in terms of reduced variables, follows quite closely the above law of corresponding states, showing that Van der Waals theory captures correctly the physics of interacting gases.

Gas to liquid transition

In Fig. 2.9 some isotherms of the Van der Waals gas at and around the critical temperature T_c are shown in reduced units. In particular, the one corresponding to $T = 0.9T_c$ exhibits the peculiar features of the first order gas-liquid transition. These are:

1. The points in the BD interval of the Van der Waals curve have negative compressibility $\kappa_T = -(1/v)(\partial v/\partial p)_T$ and correspond to unphysical states because of the mechanic instability.

2. The physical line connecting points A and E is the horizontal orange line, where the liquid phase at density $1/v_A$ coexists with the gas phase at density $1/v_E$. Along this line only the relative volume between the two phases changes, varying from full liquid (point A) to full gas (point E). The line is determined by the condition that the area $ABCA$ and $CDEC$ should be

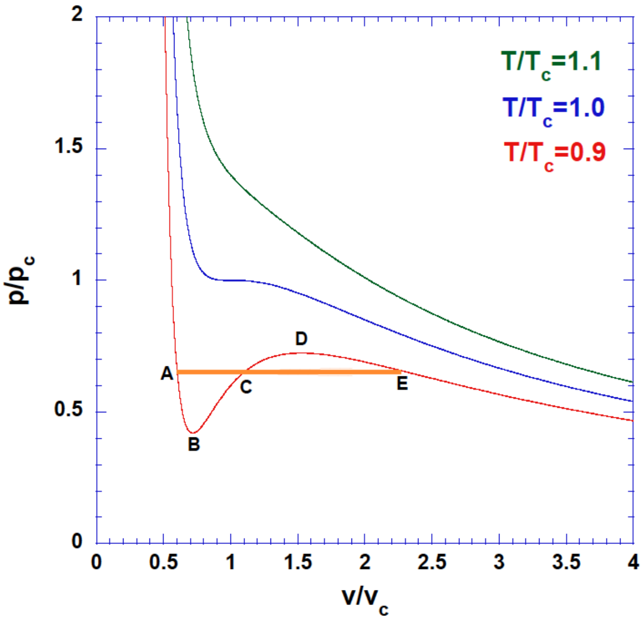

Figure 2.9: Van der Waals isotherms in reduced units. The horizontal orange line indicates the coexistence line between the gas and the liquid at volumes per particle corresponding respectively to point E and point A in the diagram.

equal (Maxwell construction). A simple way to see this is that the work done in an isothermal reversible cycle should be zero. Let's consider the reversible cycle $ABCDEA$, where we move from A to E along the Van der Waals curve and then we move back to A along the coexistence line. Since $ABCA$ contributes to the total work with the negative sign and $CDEC$ with the positive sign, the two areas must be equal. Notice in this respect that the cycle $ABCA$ is not reversible because at point C the unstable state belonging to the Van der Waals curve and the stable state on the coexistence line are connected by an irreversible transformation.

3. The physical states in the intervals AB and DE are metastable and correspond respectively to a supercooled liquid and to a superheated gas.

4. By reducing the volume v at fixed temperature starting from a gas state, the pressure increases along the Van der Waals curve up to the point E. Here, by further reducing the volume, the pressure remains unchanged and some liquid at density $1/v_A$ is nucleated. The fraction of liquid increases until at point A the system is fully in the liquid state. From point A a further reduction of v determines a large increase in pressure as it is typical of the liquid phase. During

the process from E to A the latent heat of condensation is released.

Connection to Landau theory and critical behavior

The relevant free energy is provided by the Gibbs free energy (see Supplement 2.4.1) where the dependence on V is left explicit: $G(T,p,V) = F(T,V) + pV$. Indeed, since $p = -(\partial F/\partial V)_T$, one has that equilibrium states correspond to the minima with respect to the volume of the Gibbs free energy at fixed temperature and number of particles

$$0 = \left(\frac{\partial}{\partial V} G(T,p,V)\right)_{T,N} \ . \tag{2.65}$$

In terms of reduced variables one can write $G/N = p_c v_c(\tilde{f} + \tilde{p}\tilde{v})$, where $\tilde{f} = F/(N p_c v_c)$. One can expand the equation of state (2.64) around the critical point using $\tilde{T} = 1 + t$, $\tilde{p} = 1 + \pi$ and $\tilde{v} = 1 + x$ up to cubic terms in the small parameter x:

$$\begin{aligned} 1 + \pi &\simeq 4(1+t)\left(1 - \frac{3}{2}x + \frac{9}{4}x^2 - \frac{27}{8}x^3\right) - 3(1 - 2x + 3x^2 - 4x^3) \\ &\simeq 1 + t(4 - 6x + 9x^2) - \frac{3}{2}x^3 \ , \end{aligned} \tag{2.66}$$

where in the last equation we neglected the term proportional to tx^3. From a direct integration of the relation $\tilde{p} = -\left(\partial\tilde{f}/\partial x\right)_{T,N}$, one gets the reduced free energy per particle

$$\tilde{f} = -x - t(4x - 3x^2 + 3x^3) + \frac{3}{8}x^4 + \alpha(t) \ , \tag{2.67}$$

where $\alpha(t)$ is an unknown function of the reduced temperature only. The reduced Gibbs free energy is then given by

$$\frac{G}{N p_c v_c} = \alpha(t) + 1 + \pi - (4t - \pi)x + 3tx^2 - 3tx^3 + \frac{3}{8}x^4 \ . \tag{2.68}$$

According to Eq. (2.65), we should look for minima of the above expression with respect to x, for given values of π and t. By the shift $x = y + 2t$ we can remove the cubic term in G/N and arrive at the simpler result

$$\frac{G}{N p_c v_c} = \alpha(t) + 1 + \pi - (4t - \pi)y + 3ty^2 + \frac{3}{8}y^4 \ , \tag{2.69}$$

where we kept only terms linear in t and π. We notice that the above expansion of the Gibbs free energy has the general form (2.57) predicted by Landau theory where the scalar quantity y plays the role of the order parameter and $4t - \pi$ of the external field h.

- If $t > 0$: There is only one minimum of Eq. (2.69) which has the same sign as the external field $h = 4t - \pi$.
- If $t < 0$: There is only one minimum having the same sign of the external field if $|4t - \pi| > h_T = 8|t|^{3/2}/3$. Two minima (one absolute and one relative) are present if $|4t - \pi| < h_T$. The absolute minimum has the sign of $4t - \pi$.
- If $t = 0$: There is one minimum at $y = x = (-2\pi/3)^{1/3}$ corresponding to a critical exponent $\delta = 3$.
- If $4t - \pi = 0$: Vapor-pressure curve, *i.e.* the projection of the equation of state on the $p - T$ plane at v_c. The transition is second order. Degenerate minima appear at $x \simeq y = \pm 2\sqrt{|t|}$. The critical exponent is thus $\beta = 1/2$.

It is important to discuss the isothermal compressibility κ_T, whose reciprocal is related to the second derivative of the Gibbs free energy with respect to the volume V

$$\kappa_T^{-1} = -V\left(\frac{\partial p}{\partial V}\right)_T = V\left(\frac{\partial^2 G(T,p,V)}{\partial V^2}\right)_T . \tag{2.70}$$

After some rearrangements specific of the neighborhood of the critical point we get the result

$$\kappa_T^{-1} = p_c\left(\frac{\partial^2}{\partial y^2}\frac{G(t,\pi,y)}{Np_cv_c}\right)_t = p_c\left(6t + \frac{9}{2}y^2\right) . \tag{2.71}$$

A divergence is found in κ_T as $|t| \to 0$ along the vapor-pressure curve, $4t - \pi = 0$, where the transition is second order. We have

$$\begin{aligned} \kappa_T &= \frac{1}{p_c 6t} \qquad \text{if } t > 0 \\ \kappa_T &= \frac{1}{p_c 12|t|} \qquad \text{if } t < 0 . \end{aligned} \tag{2.72}$$

The associated critical exponent is thus given by $\gamma = 1$. It is instructive to compare the values of the critical exponents as obtained from the Landau theory with the ones measured in experiments on real gases around the critical point. These give: $\beta \simeq 0.32$, $\gamma \simeq 1.2$ and $\delta \simeq 4.8$.

2.3.5 Role of fluctuations: correlation functions

The theory described above deals with situations where the value of the order parameter is uniform across the system. An important extension of the theoretical treatment includes a spatially varying external field $\mathbf{h}(\mathbf{r})$ and order parameter $\mathbf{m}(\mathbf{r})$. The Gibbs free energy (2.57) should be replaced in this case by the energy functional

$$G[\mathbf{m}(\mathbf{r})] = G_0 + \int d\mathbf{r} \left[a_1 t \mathbf{m}^2(\mathbf{r}) + b_0 \mathbf{m}^4(\mathbf{r}) + c_0(\nabla\mathbf{m}(\mathbf{r}))^2 - \mathbf{h}(\mathbf{r})\mathbf{m}(\mathbf{r})\right] \ , \tag{2.73}$$

where we only consider the explicit dependence on $\mathbf{m}(\mathbf{r})$ and we introduced the notation $(\nabla\mathbf{m})^2 = \partial_x\mathbf{m}\partial_x\mathbf{m} + \partial_y\mathbf{m}\partial_y\mathbf{m} + \partial_z\mathbf{m}\partial_z\mathbf{m}$. Here products of vectors mean scalar products over the n components of $\mathbf{m}$ and $\mathbf{h}$. Compared to the uniform case (2.57) the functional (2.73) contains a term that is invariant under rotations of $\mathbf{m}$, as required by symmetry reasons, and accounts to lowest order for its spatial variations. Higher order terms are of the form $(\nabla^2\mathbf{m})^2$. The coefficient c_0 is a phenomenological parameter depending on the microscopic physics, but it must be positive ($c_0 > 0$) because in general spatial modulation of the order parameter should cost some extra energy.

It is worth stressing that the Landau theory is aimed to provide an effective description of the low-energy physics of the system in terms of a number of phenomenological parameters deriving from the microscopic Hamiltonian once the contribution from fast, high-energy modes has been integrated out. The theory is capable to account correctly for the slow and long-wavelength modulations of the order parameter, which are expected to play a crucial role close to the phase transition, but contains an intrinsic high-momentum cut-off that limits its applicability on scales that are on the order of the interparticle distance.

The equilibrium or most probable configuration of $\mathbf{m}(\mathbf{r})$ is determined from the extremal condition

$$\frac{\delta G}{\delta\mathbf{m}} = \frac{G[\mathbf{m}+\delta\mathbf{m}] - G[\mathbf{m}]}{\delta\mathbf{m}} = 2\Big(a_1 t + 2b_0\mathbf{m}^2(\mathbf{r}) - c_0\nabla^2\Big)\mathbf{m}(\mathbf{r}) - \mathbf{h}(\mathbf{r}) = 0 \ , \tag{2.74}$$

where to obtain the term proportional to $\nabla^2\mathbf{m}$ we used integration by parts. For a constant external field $\mathbf{h} = h\hat{e}_1$, the order parameter is uniform $\mathbf{m}(\mathbf{r}) = m\hat{e}_1$ and the above equation reduces to eq. (2.59) or to eq. (2.49) if $h = 0$.

Let us now consider a situation where $\mathbf{h} = 0$ and the order parameter fluctuates by $\delta\mathbf{m}$ around the equilibrium value m_0 solution of eq. (2.49) and defined by the average $\langle \mathbf{m}(\mathbf{r}) \rangle = m_0 \hat{e}_1$. The fluctuating part is conveniently decomposed into a parallel component $\delta m_\parallel$, in the direction of the unit vector $\hat{e}_1$, and a transverse component $\delta\mathbf{m}_\perp$ orthogonal to $\hat{e}_1$ by writing

$$\mathbf{m}(\mathbf{r}) = m_0 \hat{e}_1 + \delta\mathbf{m}(\mathbf{r}) = \big(m_0 + \delta m_\parallel(\mathbf{r})\big)\hat{e}_1 + \delta\mathbf{m}_\perp(\mathbf{r}) \; . \tag{2.75}$$

The free energy associated with the order parameter configuration $\mathbf{m}(\mathbf{r})$ can be readily calculated from the expression (2.73) by including the fluctuating part up to second order. One finds

$$G[\mathbf{m}] = G(m_0) + \int d\mathbf{r} \Big[\big(a_1 t + 6 b_0 m_0^2\big) \delta m_\parallel^2 + \big(a_1 t + 2 b_0 m_0^2\big)\big(2 m_0 \delta m_\parallel + \delta\mathbf{m}_\perp^2\big) + c_0 \big(\nabla \delta\mathbf{m}\big)^2 \Big] \; , \tag{2.76}$$

where $G(m_0)$ is the free energy at the equilibrium point m_0.

Two cases should be treated separately:

- $T > T_c$

  In this case $m_0 = 0$ and the free energy (2.76) reads

$$\begin{aligned} G[\mathbf{m}] &= G(0) + \int d\mathbf{r} \Big[a_1 t \, \delta\mathbf{m}^2 + c_0 \big(\nabla\delta\mathbf{m}\big)^2 \Big] \\ &= G(0) + \sum_{\mathbf{k}} \big(a_1 t + c_0 k^2\big) |\mathbf{m}_{\mathbf{k}}|^2 \; . \end{aligned} \tag{2.77}$$

  The second of the above equations has been written in terms of the Fourier components of the fluctuation $\delta\mathbf{m}$ which are defined by

$$\delta\mathbf{m}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \mathbf{m}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \; , \tag{2.78}$$

  and satisfy the condition $\mathbf{m}_{\mathbf{k}}^* = \mathbf{m}_{-\mathbf{k}}$ because $\delta\mathbf{m}$ must be real.

  The probability of such a fluctuation to take place is provided by the exponential law

$$\mathrm{Prob}[\mathbf{m}(\mathbf{r})] = \frac{1}{Z_G} e^{-\beta G(m_0)} e^{-\beta \sum_{\mathbf{k}} |\mathbf{m}_{\mathbf{k}}|^2 (a_1 t + c_0 k^2)} \; , \tag{2.79}$$

where Z_G is the associated partition function

$$Z_G = e^{-\beta G(m_0)} \int \Big(\prod_{\mathbf{k}} d\mathbf{m}_{\mathbf{k}} \Big)\, e^{-\beta \sum_{\mathbf{k}} |\mathbf{m}_{\mathbf{k}}|^2 (a_1 t + c_0 k^2)} \ , \tag{2.80}$$

obtained by integrating the probability distribution (2.79) over all possible values of the Fourier components $\mathbf{m}_{\mathbf{k}}$. The Gaussian distribution (2.79) allows us to straightforwardly derive the average value of the square fluctuations $\mathbf{m}_{\mathbf{q}}\mathbf{m}_{-\mathbf{q}}$. One finds

$$\begin{aligned} \langle |\mathbf{m}_{\mathbf{q}}|^2 \rangle &= \frac{1}{Z_G} e^{-\beta G(m_0)} \int \Big(\prod_{\mathbf{k}} d\mathbf{m}_{\mathbf{k}} \Big)\, |\mathbf{m}_{\mathbf{q}}|^2 e^{-\beta \sum_{\mathbf{k}} |\mathbf{m}_{\mathbf{k}}|^2 (a_1 t + c_0 k^2)} \\ &= \frac{\int d\mathbf{m}'_{\mathbf{q}} d\mathbf{m}''_{\mathbf{q}}\ |\mathbf{m}_{\mathbf{q}}|^2 e^{-\beta |\mathbf{m}_{\mathbf{q}}|^2 2(a_1 t + c_0 q^2)}}{\int d\mathbf{m}'_{\mathbf{q}} d\mathbf{m}''_{\mathbf{q}}\ e^{-\beta |\mathbf{m}_{\mathbf{q}}|^2 2(a_1 t + c_0 q^2)}} = \frac{k_B T}{2(a_1 t + c_0 q^2)} \ , \end{aligned} \tag{2.81}$$

where we introduced the real and imaginary parts of $\mathbf{m}_{\mathbf{q}}$, respectively $\mathbf{m}'_{\mathbf{q}}$ and $\mathbf{m}''_{\mathbf{q}}$, in terms of which $|\mathbf{m}_{\mathbf{q}}|^2 = \mathbf{m}'^2_{\mathbf{q}} + \mathbf{m}''^2_{\mathbf{q}}$. The factor 1/2 in the final result comes from the ratio of Gaussian integrals $\int_{-\infty}^{+\infty} dx x^2 e^{-x^2} / \int_{-\infty}^{+\infty} dx e^{-x^2} = 1/2$. One can easily convince himself that the average of any other product of Fourier components vanishes identically: $\langle \mathbf{m}_{\mathbf{q}} \mathbf{m}_{\mathbf{q}'} \rangle = 0$ if $\mathbf{q}' \neq -\mathbf{q}$.

By using the inverse Fourier transform $\mathbf{m}_{\mathbf{k}} = (1/\sqrt{V}) \int d\mathbf{r} \delta\mathbf{m}(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}$, we find that the space average over the volume V of the mean square fluctuation is proportional to the susceptibility $\chi = 1/(2a_1 t)$, obtained from eq. (2.81) in the limit $q \to 0$. More precisely one gets the relevant result

$$\frac{1}{V} \int d\mathbf{r}\, d\mathbf{r}' \langle \delta\mathbf{m}(\mathbf{r}) \delta\mathbf{m}(\mathbf{r}') \rangle = \langle |\mathbf{m}_{\mathbf{q}=0}|^2 \rangle = k_B T \chi \ , \tag{2.82}$$

which is a static example of the so-called fluctuation-dissipation theorem relating, more in general, the spectrum of fluctuations with the dissipative part of response functions.

The result (2.81) for the mean square fluctuations in momentum space also allows us to calculate the behavior in real space of the correlation function defined as

$$G(r) = \langle \mathbf{m}(\mathbf{r}' + \mathbf{r}) \mathbf{m}(\mathbf{r}') \rangle \ , \tag{2.83}$$

and describing the behavior of statistical correlations between values of the order parameter in different spatial positions. Notice that, due to the spatial homogeneity of the system, the function G can only depend on the modulus of the displacement vector $\mathbf{r}$. Since $\mathbf{m}(\mathbf{r}) = \delta\mathbf{m}(\mathbf{r})$, the correlation function can be readily calculated using the momentum-space representation of $\delta\mathbf{m}$. In 3D one finds

$$G(r) = \frac{1}{V}\sum_{\mathbf{k}} \langle |\mathbf{m}_{\mathbf{k}}|^2 \rangle e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{k_B T}{8\pi c_0 r} e^{-r/\xi} \;, \tag{2.84}$$

where we used the formula $(1/V)\sum_{\mathbf{k}} = 1/(2\pi)^3 \int d\mathbf{k}$ converting the discrete sum over wave vectors into an integral and the result $1/(2\pi)^3 \int d\mathbf{k}\; e^{i\mathbf{k}\cdot\mathbf{r}}/(\xi^{-2} + k^2) = e^{-r/\xi}/(4\pi r)$. The expression (2.84) is called the Ornstein-Zernike correlation function. It involves the length scale $\xi = \sqrt{c_0/a_1 t}$, called the correlation length. An important remark concerns the behavior of ξ when T_c is approached from above ($t \to 0^+$): the correlation length diverges as $\xi \sim 1/t^{\nu}$, where $\nu = 1/2$ within the Landau theory.

We notice that the fluctuation-dissipation result (2.82) can be rewritten in terms of the spatial integral of the correlation function

$$\int d\mathbf{r}\; G(r) = k_B T \chi \;, \tag{2.85}$$

which diverges proportionally to χ when approaching the transition point.

- $T < T_c$

In this case $m_0^2 = a_1|t|/(2b_0)$ and the expression (2.76) reduces to

$$\begin{aligned} G[\mathbf{m}] &= G(m_0) + \int d\mathbf{r} \Big[2a_1|t|\; \delta m_{\parallel}^2 + c_0 \big(\nabla \delta\mathbf{m}\big)^2 \Big] \\ &= G(m_0) + \sum_{\mathbf{k}} \Big[\big(2a_1|t| + c_0 k^2\big) |m_{\parallel\mathbf{k}}|^2 + c_0 k^2 |\mathbf{m}_{\perp\mathbf{k}}|^2 \Big] \;, \end{aligned} \tag{2.86}$$

in terms of the parallel and transverse Fourier components of the fluctuation $\delta\mathbf{m}$. By performing similar calculations to the ones at $T > T_c$, the spatial average of the mean square fluctuations yields the fluctuation-dissipation result for the parallel component and a diverging result for the transverse component:

$$\frac{1}{V}\int d\mathbf{r}\, d\mathbf{r}' \langle \delta m_{\parallel}(\mathbf{r}) \delta m_{\parallel}(\mathbf{r}') \rangle = k_B T \chi \;, \tag{2.87}$$

$$\frac{1}{V}\int d\mathbf{r}\, d\mathbf{r}' \langle \delta \mathbf{m}_{\perp}(\mathbf{r}) \delta \mathbf{m}_{\perp}(\mathbf{r}') \rangle = \lim_{q\to 0} \frac{k_B T}{2c_0 q^2} \;. \tag{2.88}$$

These equations follow directly from the Gaussian integration in momentum space giving: $\langle |m_{\parallel\mathbf{q}}|^2 \rangle = k_B T/(4a_1|t| + 2c_0 q^2)$ and $\langle |\mathbf{m}_{\perp\mathbf{q}}|^2 \rangle = k_B T/(2c_0 q^2)$.

The mean square fluctuations of the transverse component demand a more detailed study as their contribution strongly depends on the dimensionality D of the system. First of all we notice from eq. (2.88) that the space average diverges in the thermodynamic limit at any temperature as $1/q^2 \sim V^{2/D}$. Furthermore, the local average can be obtained through an integral of the Fourier components

$$\langle \delta\mathbf{m}_\perp^2(\mathbf{r}) \rangle = \frac{1}{V} \sum_{\mathbf{q}} \langle |\mathbf{m}_{\perp\mathbf{q}}|^2 \rangle = \frac{1}{(2\pi)^D} \int d^D\mathbf{q} \frac{k_B T}{2c_0 q^2} \; . \tag{2.89}$$

One immediately notices that the above integral diverges in any dimension, although there is an essential difference if $D > 2$ or if $D \leq 2$. In the first case, the integral has an ultraviolet divergence at large wave vectors. This divergence is unphysical, being an artifact of the effective description of the low-energy physics provided by the Landau theory, and in a more microscopic theory it would be absent because of the occurrence of a natural cut-off at large momenta. In passing we notice that the same divergence is also present in the local fluctuations of the parallel component. In the latter case, instead, the integral is also plagued by an infrared divergence occurring at low wave vectors. Long wave-length fluctuations are correctly described by the Landau theory and the divergence is therefore a physical one. It implies that there can not exist an order parameter with $n \geq 2$ in dimensionality $D \leq 2$, due to the diverging behavior of transverse fluctuations.

In the ordered phase one should distinguish between a parallel and a transverse component of the correlation function for which we find the following results holding in 3D

$$\begin{aligned} G_\parallel(r) &= \langle m_\parallel(\mathbf{r}' + \mathbf{r}) m_\parallel(\mathbf{r}') \rangle - m_0^2 = \frac{k_B T}{8\pi c_0 r} e^{-r/\xi} \; , \\ G_\perp(r) &= \langle \mathbf{m}_\perp(\mathbf{r}' + \mathbf{r}) \mathbf{m}_\perp(\mathbf{r}') \rangle = \frac{k_B T}{8\pi c_0 r} \; . \end{aligned} \tag{2.90}$$

The parallel component exhibits the typical Ornstein-Zernike behavior with a correlation length given by $\xi = \sqrt{c_0/2a_1|t|}$. To determine the behavior of the transverse component one uses again the Fourier transform of the function $1/(\xi^{-2} + k^2)$ letting $\xi \to \infty$ at the end of the calculation.

The correlation length ξ sets the length scale where fluctuations of the order parameter are significative. This length scale diverges as $\xi \sim 1/|t|^{1/2}$ on approaching T_c both from above and from below, implying that fluctuations become more and more relevant close to the critical point. The same conclusion is drawn from the fluctuation-dissipation results (2.82) and (2.87), showing that the space average of the mean square fluctuations diverges at T_c proportionally to the susceptibility χ. On the other hand the space average of the order parameter also diverges at T_c proportionally to the relevant volume of fluctuations whose linear size is set by the correlation length. The competition between the two divergent behaviors depends on dimensionality and will be discussed in detail below as the basis of the Ginzburg criterium.

It is worth noticing that transverse fluctuations in the ordered phase are always critical. This behavior has a clear physical explanation if one considers the shape of the Gibbs free energy when the order parameter has more than one component ($n \geq 2$). In fact, the equilibrium state corresponds to a minimum of the free energy at some finite value m_0 of the order parameter along a specific direction $\hat{e}_1$ that the system chooses breaking spontaneously the rotational symmetry. In the directions perpendicular to $\hat{e}_1$ there is a continuous of states degenerate with the minimum and the free energy has the typical shape of a mexican hat. The order parameter can fluctuate almost freely in these directions because the energy price associated with the fluctuation scales as k^2 [see eq. (2.86)] and is small at small wavevectors. The transverse fluctuations of the order parameter are the Goldstone modes associated with the breaking of a continuous symmetry occurring at the phase transition. These modes are gapless as their energy becomes vanishingly small in the limit of long wavelengths.

2.3.6 Role of fluctuations: Ginzburg criterium

The Landau theory of phase transitions neglects fluctuations of the order parameter altogether. On the other hand, by taking into account fluctuations to the lowest order, we understood that they decay over a length scale on the order of the correlation length ξ and that this length scale diverges on approaching the transition point.

For the whole theory to be valid we should require that the mean square fluctuations of the order parameter are small compared to its equilibrium value. This is the essence of the Ginzburg criterium that yields a critical dimension above which the mean-field theory becomes exact and, for lower dimensions, a temperature region where the theory can be safely applied.

Let us consider the region of temperatures $T < T_c$: the square of the space average of $\mathbf{m}(\mathbf{r})$ integrated over a large volume V is given by $\bar{m}^2 = (\int d\mathbf{r}\ \mathbf{m}(\mathbf{r}))^2 = (a_1|t|/2b_0)V^2$, where we used result (2.50) for the equilibrium value of the order parameter. On the other hand, the volume average of the parallel mean square fluctuations is provided by eq. (2.87): $\bar{\delta m_\parallel}^2 = \int d\mathbf{r}d\mathbf{r}'\langle\delta m_\parallel(\mathbf{r})\delta m_\parallel(\mathbf{r}')\rangle = k_B T\chi V$. The ratio of the two quantities gives

$$\frac{\bar{\delta m_\parallel}^2}{\bar{m}^2} = \frac{k_B T_c b_0}{2a_1^2 t^2}\frac{1}{V} \ , \tag{2.91}$$

where we replaced T by T_c, consistently with the fact that we are close to the transition point, and we used the result $\chi = 1/4a_1|t|$ for the susceptibility. Since fluctuations decay rapidly beyond the correlation length ξ, the relevant volume V should have a linear size on the order of this length scale and we can set $V = \xi^D$, where D is the dimensionality of the system. Using $\xi = (c_0/2a_1|t|)^{1/2}$, we arrive at the Ginzburg criterium for the applicability of the mean-field theory to the phase transition[1]

$$\frac{\bar{\delta m_\parallel}^2}{\bar{m}^2} = \frac{k_B T_c b_0}{2a_1^2}\left(\frac{2a_1}{c_0}\right)^{D/2}|t|^{D/2-2} \ll 1 \ . \tag{2.92}$$

We notice that for $D > 4$ the reduced temperature $|t|$ appears with a positive exponent. In this case the Landau theory is correct close to the critical point and its predictions for the critical exponents are valid. For $D < 4$, instead, fluctuations diverge close to $t = 0$ and the theory is inapplicable. The dimensionality $D = 4$ is special and it is called upper critical dimension.

Nevertheless, also in the case $D < 4$ there might be a window of temperatures where both conditions $|t| \ll 1$ and (2.92) are satisfied. This happens if

$$1 \gg |t| \gg \frac{1}{2a_1}\left(\frac{2k_B T_c b_0}{c_0^{D/2}}\right)^{2/(4-D)} \sim \left(\frac{k_B V}{|\Delta C_V|\xi_0^D}\right)^{2/(4-D)} \ , \tag{2.93}$$

where in the last equation we used the jump in the specific heat $|\Delta C_V|/V = a_1^2/(2T_c b_0)$ and we introduced $\xi_0 = \sqrt{c_0/a_1}$. This two quantities are expected to be on the order of the experimentally

---

[1] The contribution from transverse fluctuations $\bar{\delta\mathbf{m}_\perp}^2/\bar{m}^2$, where $\bar{\delta\mathbf{m}_\perp}^2 = \int d\mathbf{r}\, d\mathbf{r}'\langle\delta\mathbf{m}_\perp(\mathbf{r})\delta\mathbf{m}_\perp(\mathbf{r}')\rangle$, differs from $\bar{\delta m_\parallel}^2/\bar{m}^2$ by a factor $V^{2/D}/\xi^2$ (see eq. (2.88) with $1/q^2 \sim V^{2/D}$). This factor is of order one if $V \sim \xi^D$.

measurable difference in specific heat and correlation length away from the transition region. For the relevant case $D = 3$ the above condition (2.93) requires that $(k_B V/|\Delta C_V|\xi_0^3)^2 \ll 1$. For some phase transitions this condition is actually met and the Landau theory can be applied in a window of temperatures not too close to the critical point. This is for example the case of the BCS transition in superconductors. In other cases, such as the superfluid transition in liquid ^{4}He, the Landau theory is never applicable [2]. The critical region, where mean-field theory does not hold, corresponds to the regime of temperatures

$$|t| \ll \left(\frac{k_B V}{|\Delta C_V|\xi_0^D} \right)^{2/(4-D)} . \tag{2.94}$$

If condition (2.93) is satisfied, entailing the existence of a temperature range where the Landau theory is applicable, the values of the critical exponents change from their mean-field predictions once the critical region is entered.

The Ginzburg criterium shows that fluctuations play an increasingly important role if the dimensionality of the system is reduced, limiting the applicability of the mean-field theory. As a first effect, critical fluctuations change the behavior of the thermodynamic quantities close to the transition by affecting the values of the critical exponent. By reducing further the dimensionality, fluctuations become so strong that they wash out the transition altogether. The dimensionality D at which this happens is called lower critical dimension. For a single component order parameter ($n = 1$) the lower critical dimension corresponds to $D = 1$. An example is provided by the Ising model, for which a phase transition exists in dimension $D = 2$ but not in $D = 1$. In the case of $n \geq 2$ the lower critical dimension is instead $D = 2$, as it was explained in connection with the infrared divergence of transverse fluctuations discussed after eq. (2.88).

Some conclusive remarks concerning the Landau theory are in order here:

- The Landau theory provides a qualitatively correct description of continuous phase transitions. In particular, it provides a physical explanation for the universal behavior exhibited by very different systems close to a phase transition.
- In dimensionality $D > 4$ the Landau theory is also quantitatively correct and it provides exact results for the critical exponents.

---

[2] In general $\Delta C_V \sim N k_B$, where N is the number of particles in the system. The condition thus reads $1/n\xi_0^3 \ll 1$, in terms of the density $n = N/V$. In a BCS superconductor the correlation length, fixed by the size of Cooper pairs, is much larger than the mean interparticle distance. On the contrary, in liquid ^{4}He, $n\xi_0^3 \sim 1$.

- In dimensionality $D \leq 4$ the values of the critical exponents predicted by the theory are incorrect. To improve on the theory one should include fluctuations to all orders. This can be done in a systematic way using the Renormalization Group scheme within the so-called ϵ-expansion, where $\epsilon = 4 - D$ is the deviation from the upper critical dimension.

- These more advanced theoretical methods predict that the value of critical exponents is the same for all systems belonging to the same universality class, defined by the dimensionality D and by the number n of components of the order parameter.

2.4 Supplements

2.4.1 Thermodynamic potentials

- Helmoltz free energy Let us consider a system at a fixed temperature T undergoing a transition from state A to state B. The work produced by the system during the transition is given by

  $$W = -\Delta U + Q = -(U_B - U_A) + \int_A^B \delta Q \leq -(U_B - U_A) + T(S_B - S_A)\ ,$$

  where we used the second law of thermodynamics stating that $\int_A^B \frac{\delta Q}{T} \leq \Delta S$. By introducing the Helmoltz free energy $F = U - TS$ we find that

  $$W \leq F_A - F_B = -\Delta F\ , \tag{2.95}$$

  which is the analog for systems exchanging heat with a thermostat at a fixed temperature T of the relation $W = -\Delta V$ between the mechanical work and the change of potential energy for conservative forces.

  For different systems, where the Hamiltonian $H(a)$ depends on the external parameter a, the infinitesimal amount of work $\delta W = -\langle \frac{\partial H}{\partial a} \rangle da$ is given by the average variation of the Hamiltonian upon a change of the external parameter. The minus sign implies that a decrease of energy results in a positive work done by the system on the surroundings.

  1. Fluid systems

     The external parameter is the volume V and the infinitesimal work is given by $\delta W = pdV$. If the volume is constant Eq. (2.95) implies that $\Delta F \leq 0$ or in words that in a system where $T =$ const and $V =$ const the equilibrium state corresponds to a minimum of F. The differential of F is given by

     $$dF = dU - TdS - SdT = -pdV - SdT\ ,$$

     which implies $S = -\left(\frac{\partial F}{\partial T}\right)_V$ and $p = -\left(\frac{\partial F}{\partial V}\right)_T$.

  2. Magnetic systems

The external parameter is the magnetic field h and the infinitesimal work is given by $\delta W = \langle M\rangle dh$, where $\langle M\rangle = -\langle \frac{\partial H}{\partial h}\rangle$ is the magnetization in the direction of the field. In analogy with fluid systems we can state that if $T = \text{const}$ and $h = \text{const}$ the equilibrium state corresponds to a minimum of F. The differential of F is given by

$$dF = dU - TdS - SdT = -\langle M\rangle dh - SdT \ ,$$

from which $S = -\left(\frac{\partial F}{\partial T}\right)_V$ and $\langle M\rangle = -\left(\frac{\partial F}{\partial h}\right)_T$.

- Gibbs free energy

  1. Fluid systems

     Let us consider that the system is at constant temperature T and constant pressure p. Then Eq. (2.95) reads

     $$p(V_B - V_A) \leq F_A - F_B \ .$$

     By introducing the Gibbs free energy $G = F + pV$ one obtains $\Delta G \leq 0$. Thus, in a system where $T = \text{const}$ and $p = \text{const}$ the equilibrium state corresponds to a minimum of G. The differential of G is given by

     $$dG = dF + pdV + Vdp = -SdT + Vdp \ ,$$

     yielding the relations $S = -\left(\frac{\partial G}{\partial T}\right)_p$ and $V = \left(\frac{\partial F}{\partial p}\right)_T$.

  2. Magnetic systems

     Similarly to fluid systems, if $T = \text{const}$ and $\langle M\rangle = \text{const}$ the corresponding Gibbs free energy $G = F + h\langle M\rangle$ obeys the condition $\Delta G \leq 0$ for any transformation $A \to B$. The equilibrium state is therefore a minimum of G and one has

     $$dG = dF + hd\langle M\rangle + \langle M\rangle dh = -SdT + hd\langle M\rangle$$

     and the following relations $S = -\left(\frac{\partial G}{\partial T}\right)_{\langle M\rangle}$ and $h = \left(\frac{\partial G}{\partial \langle M\rangle}\right)_T$.

- Fluctuations

Given a state A and a state B of an isolated system the probability of a thermodynamic fluctuation $A \to B$ is given by the exponential of the entropy difference between the two states

$$\mathrm{Prob}(B) = \mathrm{Prob}(A) \exp(\Delta S/k_B) \ ,$$

where $\Delta S = S(B) - S(A)$. Let us consider the physical system (system 1) embedded in an environment (system 2) with which system 1 can exchange heat and work at some fixed temperature T. For the total system 1+2 we have $\Delta S = \Delta S_1 + \Delta S_2$. The change of entropy in the environment can be related to the variation of internal energy and the work performed by system 1

$$\Delta S_2 = \frac{W_2 + \Delta U_2}{T} = \frac{-W_1 - \Delta U_1}{T} \ ,$$

since $W_1 + W_2 = 0$ and $\Delta U = 0$. The probability associated with the fluctuation $A \to B$ can thus be written as

$$\mathrm{Prob}(A \to B) \propto \exp\left(\frac{T\Delta S_1 - W_1 - \Delta U_1}{k_B T}\right) = \exp\left(\frac{-\Delta F_1 - W_1}{k_B T}\right) \ , \tag{2.96}$$

in terms of the change in free energy. For fluid systems, where $\delta W = pdV$, one finds that

$$\mathrm{Prob}(A \to B) \propto \exp\left(-\frac{[\Delta G]_p}{k_B T}\right) \ .$$

in terms of the change in the Gibbs free energy at constant pressure. Analogously, for magnetic systems, the elementary work is given by $\delta W = \langle M \rangle dh$ and

$$\mathrm{Prob}(A \to B) \propto \exp\left(-\frac{[\Delta(G - h\langle M \rangle)]_h}{k_B T}\right) \ ,$$

at constant external magnetic field.

2.5 Problems

- 1. Classical theory of paramagnetism (Langevin 1905): Consider a system of N magnetic dipoles with magnetic moment μ in an external field $\mathbf{H}$. The system is described by the Hamiltonian

$H = -\sum_{i=1}^{N} \mu_i \cdot \mathbf{H}$, where each dipole is coupled to the external field. Calculate the partition function and the magnetization. Show that for weak fields the magnetic susceptibility obeys Curie's law $\chi \propto 1/T$.

Solution: The partition function is the product of the partition functions of each independent spin: $Z = (Z_1)^N$, where $Z_1 = \sum_\theta e^{\beta\mu H\cos\theta}$. The average magnetization follows from the derivative of the free energy with respect to the external field H

$$\frac{M}{N} = \frac{\sum_\theta \mu\cos\theta\, e^{\beta\mu H\cos\theta}}{\sum_\theta e^{\beta\mu H\cos\theta}} \; .$$

Since all projections of the magnetic moment on the direction of the external field are equiprobable, we have

$$\begin{aligned}\sum_\theta e^{\beta\mu H\cos\theta} &= \int_{-1}^{+1} dx\; e^{\beta\mu H x} = \frac{2}{\beta\mu H}\sinh(\beta\mu H)\\ \sum_\theta \mu\cos\theta\, e^{\beta\mu H\cos\theta} &= \int_{-1}^{+1} dx\; \mu x e^{\beta\mu H x} = \frac{2\mu}{(\beta\mu H)^2}\left(\beta\mu H\cosh(\beta\mu H) - \sinh(\beta\mu H)\right) \; .\end{aligned}$$

The final result for the magnetization is given by

$$\frac{M}{N} = \mu\left(\coth(\beta\mu H) - \frac{1}{\beta\mu H}\right) \equiv \mu\, L(\beta\mu H) \; ,$$

where we introduced the Langevin function $L(x) = \coth(x) - 1/x$. For weak fields, $\mu H \ll k_B T$, the Langevin function behaves as $L(x) \to x/3$ and the magnetization density is given by $M/V \simeq \mu^2 n H/(3k_B T)$, where $n = N/V$ is the density of dipoles. Then, Curie's law for the susceptibility follows $\chi = \mu^2 n/(3k_B T)$. In the opposite regime of strong fields, $\mu H \gg k_B T$, one has $L(x) \to 1 - 1/x$ and the magnetization reaches the saturation value $M = N\mu$.

- 2. Model of antiferromagnetism: Consider the Ising Hamiltonian with $J < 0$ and solve it within the mean-field approximation by assuming that the system splits into two interpenetrating sublattices and that spins belonging to the same sublattice are parallel while spins belonging to different sublattices are antiparallel. Calculate the Nèel temperature T_N of the antiferromagnet where a spontaneous magnetization starts to develop in each sublattice. Determine the temperature dependence of the order parameter and of the magnetic susceptibility.

Solution: $J < 0$ favors antiferromagnetic correlations between neighboring spins. We can divide the cubic lattice into sublattice A and sublattice B such that each site of one sublattice is surrounded by nearest neighboring sites belonging to the other sublattice. The following mean-field decomposition can be used: $S_i^A S_j^B = S_i^A \langle S^B\rangle +$

$S_j^B\langle S^A\rangle - \langle S^A\rangle\langle S^B\rangle$. The corresponding mean-field Hamiltonian is given by

$$H_{\rm MF} = E_0^{\rm MF} - \sum_a \left(\tilde{J}\langle S^B\rangle + h^A\right) S_a^A - \sum_b \left(\tilde{J}\langle S^A\rangle + h^B\right) S_b^B \ ,$$

where a (b) runs over the $N/2$ sites of sublattice A (B), $\tilde{J} = zJ$ is the coupling constant renormalized by the coordination number z, $E_0^{\rm MF} = (N\tilde{J}/2)\langle S^A\rangle\langle S^B\rangle$ is the ground-state energy and we introduced the magnetic fields $h^A = h^B = h$ acting on the sites of each sublattice. The partition function is easily calculated and one finds $Z_C = e^{-\beta E_0^{\rm MF}}(Z_A)^{N/2}(Z_B)^{N/2}$, where $Z_{A(B)}$ is the single-site partition function of sublattice A (B). We further define the partial spin densities

$$\begin{aligned}
\langle S^A\rangle &= -\frac{2}{N}\left(\frac{\partial F}{\partial h^A}\right)_T = \tanh\left(\frac{\tilde{J}\langle S^B\rangle + h^A}{k_B T}\right) \\
\langle S^B\rangle &= -\frac{2}{N}\left(\frac{\partial F}{\partial h^B}\right)_T = \tanh\left(\frac{\tilde{J}\langle S^A\rangle + h^B}{k_B T}\right) \ ,
\end{aligned}$$

which can be written as $\langle S^A\rangle = m+s$ and $\langle S^B\rangle = m-s$ in tems of the total $m = (\langle S^a\rangle + \langle S^B\rangle)/2$ and staggered $s = (\langle S^A\rangle - \langle S^B\rangle)/2$ magnetization. By inverting the above equations one gets

$$\begin{aligned}
-\frac{T_N}{T}(m-s) + \frac{h}{k_B T} = \operatorname{atanh}(m+s) &\simeq (m+s) + \frac{1}{3}(m+s)^3 \\
-\frac{T_N}{T}(m+s) + \frac{h}{k_B T} = \operatorname{atanh}(m-s) &\simeq (m-s) + \frac{1}{3}(m-s)^3 \ ,
\end{aligned}$$

where we defined $|\tilde{J}|/k_B = T_N$ as the Nèel temperature and we expanded the argument of $\operatorname{atanh}(x)$ in the vicinity of T_N and for small values of the magnetic field h. By summing and subtracting the above two equations one gets

$$\begin{aligned}
m\left(1 + \frac{T_N}{T} + s^2\right) &= -\frac{m^3}{3} + \frac{h}{k_B T} \\
s\left(\frac{T_N}{T} - 1 - m^2\right) &= \frac{s^3}{3} \ .
\end{aligned}$$

If $h = 0$, the solution is $m = 0$, $s = 0$ if $T > T_N$ and $s = \pm\sqrt{3\frac{T_N - T}{T_N}}$ if $T \to T_N^-$. Thus, T_N is the temperature below which a staggered magnetization appears. If h is finite, m is proportional to h with the susceptibility $\chi = 1/(2k_B T_N)$. Notice that if a small h is present the Nèel temperature is shifted $T_N' \simeq T_N(1 - h^2/(4k_B^2 T_N^2))$.

- 3. Weiss model: Consider the following Hamiltonian of N two-level spins ($S_i = \pm 1$)

  $H = -(J/2N)\sum_{i\neq j} S_i S_j - h\sum_i S_i$

  where each spin interacts with every other spin. Show that in the thermodynamic limit $N \to \infty$ the mean-field approach provides the exact solution of the model.

Solution: The Hamiltonian can be conveniently rewritten in the form

$$H = \frac{J}{2} - \frac{JN}{2} m^2 - Nhm \ ,$$

where we introduced the average magnetization $m = (1/N)\sum_i S_i$. The partition function is given by

$$Z = e^{-\beta J/2} \sum_{S1,\ldots,S_N} \exp\left(\beta \frac{JN}{2} m^2 + \beta N h m\right) \ .$$

The term proportional to m^2 in the exponential can be converted into something linear in m by using the Hubbard-Stratonovich transformation

$$e^{a^2} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \ e^{-x^2/2} e^{\sqrt{2}ax} \ .$$

In our case $a = \sqrt{\beta JN/2} m$ and the partition function can be evaluated as for independent spins

$$\begin{aligned} Z &= e^{-\beta J/2} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \ e^{-x^2/2} \left[\sum_{S=\pm 1} \exp\left(\sqrt{\beta \frac{J}{N}} x S + \beta h S\right)\right]^N \ . \\ &= e^{-\beta J/2} 2^N \sqrt{\frac{N}{2\pi}} \int_{-\infty}^{+\infty} dx \ \left[e^{-x^2/2} \cosh\left(\sqrt{\beta J} x + \beta h\right)\right]^N \ . \end{aligned}$$

In the large N limit the free energy per spin is given by

$$\begin{aligned} \frac{F}{N} &= -k_B T \log 2 - k_B T \log \left\{ \int_{-\infty}^{+\infty} dx \ \left[e^{-x^2/2} \cosh\left(\sqrt{\frac{J}{k_B T}} x + \frac{h}{k_B T}\right)\right]^N \right\}^{1/N} \\ &= -k_B T \log 2 - k_B T \log \left[e^{-\bar{x}^2/2} \cosh\left(\sqrt{\frac{J}{k_B T}} \bar{x} + \frac{h}{k_B T}\right)\right] \ , \end{aligned}$$

where $\bar{x}$ is the solution of the equation $\frac{d}{dx}\left[e^{-x^2/2}\cosh\left(\sqrt{\frac{J}{k_BT}}x + \frac{h}{k_BT}\right)\right] = 0$ and we have used the fact that for a non negative continuous function $f(x)$ the expression $\left(\int_{-\infty}^{+\infty} dx \ (f(x))^N\right)^{1/N}$ yields $\max f(x)$ as $N \to \infty$. One finds that $\bar{x}$ is the solution of the equation

$$\sqrt{\frac{k_B T}{J}} \bar{x} = \tanh\left(\sqrt{\frac{J}{k_B T}} \bar{x} + \frac{h}{k_B T}\right) \ ,$$

on the other hand, from the expression of the free energy per particle, the average magnetization is given by

$$m = -\frac{1}{N}\left(\frac{\partial F}{\partial h}\right)_T = \tanh\left(\sqrt{\frac{J}{k_B T}} \bar{x} + \frac{h}{k_B T}\right) \ .$$

Therefore, we see that m satisfies the same self-consistent equation

$$m = \tanh\left(\frac{J}{k_B T} m + \frac{h}{k_B T}\right)$$

of the standard Ising model in the mean-field approximation which predicts a ferromagnetic transition at the temperature $T_c = J/k_B$.

- 4. Model of first-order phase transition: Consider the following expansion of the Gibbs free energy

  $G(m)/V = a_1(T - T_0)m^2 + b_0 m^4 + c_0 m^6$

  in terms of the order parameter m. Here we assume: $a_1 > 0$, $b_0 < 0$ and $c_0 > 0$. Determine the superheating T_{SH} and supercooling T_{SC} temperature below which, respectively, relative minima appear and disappear. Determine the transition temperature T_c, where all minima are degenerate, and the discontinuous jump of the order parameter at T_c.

  Solution: We notice that the Gibbs free energy is an even function of m. Extremal points correspond to $m = 0$ and to the solutions of the equation

$$m^4 - \frac{2|b_0|}{3c_0}m^2 + \frac{a_1}{3c_0}(T - T_0) = 0 \,,$$

yielding

$$(m^2)_{1,2} = \frac{|b_0|}{3c_0} \pm \sqrt{\frac{|b_0|^2}{9c_0^2} - \frac{a_1}{3c_0}(T - T_0)} \,.$$

If the quantity under the square root is negative only the solution $m = 0$ survives corresponding to a global minimum of G. This happens for $T > T_{SH} = T_0 + \frac{|b_0|^2}{3a_1 c_0}$. For smaller temperatures two additional relative minima start to appear at

$$m = \pm\sqrt{\frac{|b_0|}{3c_0} + \sqrt{\frac{|b_0|^2}{9c_0^2} - \frac{a_1}{3c_0}(T - T_0)}} \,.$$

Furthermore, $m = 0$ remains a relative minimum for temperatures above $T_{SC} = T_0$, whereas for $T < T_0$ the value $m = 0$ corresponds to a maximum of G. Notice also that, if $T < T_0$, the solutions for m^2 with the minus sign should be discarded and only three extremal points remain: a maximum at $m = 0$ and the two degenerate minima in the equation above. The temperature T_c at which the three existing minima have the same energy is obtained from the equation

$$\frac{2a_1}{|b_0|}(T_c - T_0) = \frac{|b_0|}{3c_0} + \sqrt{\frac{|b_0|^2}{9c_0^2} - \frac{a_1}{3c_0}(T_c - T_0)} \,,$$

yielding the result $T_c = T_0 + \frac{|b_0|^2}{4a_1 c_0}$. The discontinuous jump at T_c is given by $\delta m = \pm\sqrt{\frac{|b_0|}{2c_0}}$.

- 5. Gaussian approximation to Ginzburg-Landau theory: By including the contribution from fluctuations up to quadratic order calculate the partition function, the free energy and the specific heat for $T > T_c$. Show that in 3D the corrected critical exponent is $\alpha = 1/2$.

  Solution: We start from the expression of the partition function given in Eq. (2.80). For each wave vector $\mathbf{k}$ and each of the n components of the order parameter we separate the real and imaginary parts of $m_{n\mathbf{k}}$

and carry out the gaussian integral obtaining $Z_G = e^{-\beta G(m_0)} \prod_{\mathbf{k}} \left(\frac{\pi k_B T}{a_1 t + c_0 k^2}\right)^{n/2}$. The specific heat is given by $C/V = -T\left(\frac{\partial^2 F/V}{\partial T^2}\right)_V$, where $F/V = F_0/V - \frac{k_B T}{V}\sum_{\mathbf{k}} \frac{n}{2}\log\left(\frac{\pi k_B T}{a_1 t + c_0 k^2}\right)$ being F_0 the free energy in the absence of fluctuations of the order parameter. We stress that the ultraviolet behavior of the integrals is always well behaved because of a high-momentum cut-off Λ. Singularities at the transition point can instead occur from the infrared behavior of the integrals. The most singular term in C/V as $T \to T_c^+$ is given by

$$\frac{C}{V} = k_B a_1^2 \frac{n}{2}\frac{1}{V}\sum_{\mathbf{k}} \frac{1}{(a_1 t + c_0 k^2)^2} = k_B \left(\frac{a_1}{c_0}\right)^2 \frac{n}{2}\int_0^\infty dq \frac{q^2}{2\pi^2}\frac{\xi}{(1+q^2)^2} \ ,$$

where we introduced the correlation length $\xi = \sqrt{\frac{c_0}{a_1 t}}$. Thus, at T_c^+, the specifc heat diverges as the correlation length: $C/V \simeq A_+ \xi$, being $A_+ = \frac{k_B}{8\pi}\left(\frac{a_1}{c_0}\right)^2 \frac{n}{2}$. The corresponding critical exponent is therefore $\alpha = 1/2$.

- 6. Repeat the calculation of Problem 5 in the ordered phase $T < T_c$ and show that the critical exponent of the specific heat coincides with the one obtained in the disordered phase.

Solution: At $T < T_c$, the free energy including fluctuations is given by Eq. (2.86). The corresponding partition function takes the form

$$Z_G = e^{-\beta G(m_0)} \int \left(\prod_{\mathbf{k}} dm_{\parallel\mathbf{k}} d\mathbf{m}_{\perp\mathbf{k}}\right) e^{-\beta\sum_{\mathbf{k}}\left[|m_{\parallel\mathbf{k}}|^2(2a_1|t| + c_0 k^2) + |\mathbf{m}_{\perp\mathbf{k}}|^2 c_0 k^2\right]} \ .$$

By performing the gaussian integral of each $\mathbf{k}$ component of the $\parallel$ fluctuations and of the $n-1$ components of the $\perp$ fluctuations one finds

$$Z_G = e^{-\beta G(m_0)} \prod_{\mathbf{k}} \left(\frac{\pi k_B T}{2a_1|t| + c_0 k^2}\right)^{1/2} \left(\frac{\pi k_B T}{c_0 k^2}\right)^{(n-1)/2} \ .$$

The free energy is then given by

$$\frac{F}{V} = \frac{F_0}{V} - \frac{k_B T}{2V}\sum_{\mathbf{k}} \left(\log\frac{\pi k_B T}{2a_1|t| + c_0 k^2} + (n-1)\log\frac{\pi k_B T}{c_0 k^2}\right) \ ,$$

and the most divergent contribution to C/V is given by

$$\frac{C}{V} = \frac{2k_B a_1^2}{V}\sum_{\mathbf{k}} \frac{1}{(2a_1|t| + c_0 k^2)^2} = A_- \xi \ ,$$

where $\xi = \sqrt{\frac{c_0}{2a_1|t|}}$ is the correlation length in the ordered phase and $A_- = \frac{4}{n}A_+$. The above result shows that the specific heat indeed diverges at T_c, exhibiting the same critical exponent when approaching the transition point both from above and from below.

- 7. Determine the spatial dependence of correlation functions below and above T_c in the case $D = 2$ and $D = 1$. For transverse correlations consider the explicit dependence on the external field h by recalling that $h = 2m_0(a_1 t + 2b_0 m_0^2)$.

Solution: First we consider the behavior of the correlation function above the transition $T > T_c$. From Eq. (2.84) we have

$$G(r) = \frac{1}{V}\sum_{\mathbf{k}} \frac{k_B T}{2(a_1 t + c_0 k^2)} e^{i\mathbf{k}\cdot\mathbf{r}} \ .$$

For $D = 2$ the above integral yields $G(r) = \frac{k_B T}{4\pi c_0} K_0(\frac{r}{\xi})$, where $K_0(x)$ is the modified Bessel function, $\xi = \sqrt{\frac{c_0}{a_1 t}}$ is the correlation length and we used the integrals $\frac{1}{2\pi}\int_0^{2\pi} dx e^{i|a|x} = J_0(|a|)$ and $\int_0^\infty dx \frac{J_0(\sqrt{x})}{1+a^2 x} = \frac{2}{a^2} K_0\left(\frac{1}{|a|}\right)$. For $D = 1$ we find instead $G(r) = \frac{k_B T}{2c_0} r e^{-r/\xi}$, where we used the integral $\int_0^\infty dx \frac{\cos x}{1+a^2x^2} = \frac{\pi e^{-1/|a|}}{2a^2}$.

In the ordered phase, $T < T_c$, one must distinguish between parallel and transverse fluctuations. We obtain

$$G_{\parallel}(r) = \frac{1}{V}\sum_{\mathbf{k}} \frac{k_B T}{2(2a_1|t| + c_0 k^2)} e^{i\mathbf{k}\cdot\mathbf{r}} \ ,$$

for the parallel component yielding the results $G_{\parallel}(r) = \frac{k_B T}{4\pi c_0} K_0(\frac{r}{\xi})$ if $D = 2$ and $G_{\parallel}(r) = \frac{k_B T}{2c_0} r e^{-r/\xi}$ if $D = 1$. In the case of transverse fluctuations, we replace the term $a_1 t + 2b_0 m_0^2$ in Eq. (2.76) with $\frac{h}{2m_0}$ where m_0 and h have the same sign. One then gets for the corresponding correlation function

$$G_{\perp}(r) = \frac{1}{V}\sum_{\mathbf{k}} \frac{k_B T}{2\left(\frac{h}{2m_0} + c_0 k^2\right)} e^{i\mathbf{k}\cdot\mathbf{r}} \ ,$$

yielding the results $G_{\perp}(r) = \frac{k_B T}{4\pi c_0} K_0\left(r\sqrt{\frac{|h|}{2|m_0|c_0}}\right)$ if $D = 2$ and $G_{\perp}(r) = \frac{k_B T}{2c_0} r e^{-r\sqrt{\frac{|h|}{2|m_0|c_0}}}$ if $D = 1$. In the limit $h \to 0$ we find $G_{\perp}(r) = -\frac{k_B T}{4\pi c_0}\log\left(r\sqrt{\frac{|h|}{2|m_0|c_0}}\right)$ and $G_{\perp}(r) = \frac{k_B T}{2c_0} r$ respectively in $D = 2$ and $D = 1$.

Chapter 3

Fermi systems

We deal with fermionic systems. First we consider non-interacting particles, both at $T = 0$ and at finite T. As a second step we treat systems with contact interaction at the level of the Hartree-Fock mean-field theory. The structure of the chapter is as follows:

- Non-interacting gas at $T = 0$:
  - Properties of the Fermi sea.
  - Pauli paramagnetism.
  - Pair correlation function.
  - Excited states and quasi-particle description.
- Non-interacting gas at finite T:
  - Particle distribution function and equation of state.
  - High-temperature thermodynamics and virial expansion.
  - Low-temperature thermodynamics and Sommerfeld expansion.
  - Fluctuations in the particle number.
- Interacting gas:
  - Hartree-Fock theory for contact interatomic potentials.
  - Stoner model and quantum phase transition for itinerant ferromagnetism.

3.1 Non-interacting gas: zero temperature

We consider a two component (spin 1/2) Fermi gas in a cubic box with p.b.c.: $N_\uparrow$ is the number of spin-up particles, $N_\downarrow$ the number of spin-down particles and $N = N_\uparrow + N_\downarrow$ is the total number of particles. The Hamiltonian of the gas has the form

$$H = \sum_{\mathbf{k}} \epsilon_k a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}\uparrow} + \sum_{\mathbf{k}} \epsilon_k a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}\downarrow} \ , \tag{3.1}$$

where $\epsilon_k = \hbar^2 k^2/(2m)$ is the single-particle kinetic energy, independent of spin. We consider the thermodynamic limit where $V \to \infty$ and $N_\sigma \to \infty$ for each spin component $\sigma =\uparrow,\downarrow$. The limit is taken in such a way that both densities $n_\sigma = N_\sigma/V$ remain finite.

We notice that the Hamiltonian (3.1) commutes with the number operator $n_{\mathbf{k}\sigma} = a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}$ in the single-particle state $(\mathbf{k}, \sigma)$. As a consequence, eigenstates of (3.1) are also eigenstates of $n_{\mathbf{k}\sigma}$. In particular, the ground state corresponds to the state $|n_{\mathbf{k}_\alpha\uparrow}..n_{\mathbf{k}_\alpha\downarrow}..\rangle$ for which the sum $\sum_{\mathbf{k}\sigma} \epsilon_k n_{\mathbf{k}\sigma}$ is minimal.

3.1.1 Ground-state properties

The completely antisymmetric ground state of the Hamiltonian (3.1) is provided by the so called Fermi sea

$$|FS\rangle = |\mathbf{k}_{\uparrow 1}...\mathbf{k}_{\uparrow N_\uparrow} \mathbf{k}_{\downarrow 1}...\mathbf{k}_{\downarrow N_\downarrow}\rangle_A \ ,$$

where both $\mathbf{k}_{\uparrow i}$ and $\mathbf{k}_{\downarrow i}$ run over the smallest wave vectors compatible with p.b.c. up to the Fermi wave vector $k_{F\sigma}$ defined as follows

$$\sum_{k<k_{F\sigma}} n_{\mathbf{k}\sigma} = \frac{4\pi V}{(2\pi)^3} \int_0^{k_{F\sigma}} dk k^2 = \frac{1}{6\pi^2} V k^3_{F\sigma} = N_\sigma \ . \tag{3.2}$$

The Fermi wave vector is related to the density of each spin component: $k_{F\sigma} = (6\pi^2 n_\sigma)^{1/3}$. Its inverse $1/k_{F\sigma}$ provides the relevant length scale associated with the average interparticle distance for the two spin species. For balanced mixtures of the two spin species, $N_\uparrow = N_\downarrow = N/2$, one finds $k_F = k_{F\uparrow} = k_{F\downarrow} = (3\pi^2 n)^{1/3}$, where $n = n_\uparrow + n_\downarrow$ is the total density. Similarly to eq. (3.2) one can calculate the ground-state energy

$$E_0 = \sum_{k<k_{F\uparrow}} \epsilon_k n_{\mathbf{k}\uparrow} + \sum_{k<k_{F\downarrow}} \epsilon_k n_{\mathbf{k}\downarrow} = \frac{3}{5} N_\uparrow \epsilon_{F\uparrow} + \frac{3}{5} N_\downarrow \epsilon_{F\downarrow} \, , \tag{3.3}$$

where we introduced the Fermi energies $\epsilon_{F\sigma} = \hbar^2 k_{F\sigma}^2/(2m)$ giving the scale of the average energy per particle in the gas. Pressure and chemical potential for the two spin species can be calculated using standard thermodynamic relations

$$p_\sigma = -\frac{\partial E_\sigma}{\partial V} = \frac{2}{5} n_\sigma \epsilon_{F\sigma} \qquad \mu_\sigma = \frac{\partial E}{\partial N_\sigma} = \epsilon_{F\sigma} \, .$$

If $N_\uparrow \neq N_\downarrow$ the mixture is not in chemical equilibrium ($\mu_\uparrow \neq \mu_\downarrow$). This situation is physically possible only if spin-up particles can not be converted into spin-down particles. The balanced configuration corresponds in fact to a minimum of the ground-state energy (3.3) as one can show by introducing the total number of particles $N = N_\uparrow + N_\downarrow$, the polarization $P = (N_\downarrow - N_\uparrow)/N$ and the Fermi energy $\epsilon_F = \hbar^2 k_F^2/(2m)$ of the balanced case

$$E_0 = \frac{3}{5} N \epsilon_F \frac{1}{2} \Big((1-P)^{5/3} + (1+P)^{5/3} \Big) \underset{P \to 0}{\longrightarrow} \frac{3}{5} N \epsilon_F \Big(1 + \frac{5}{9} P^2 + \frac{5}{243} P^4 ... \Big) \, . \tag{3.4}$$

3.1.2 Magnetic susceptibility

If particles can be converted from spin down to spin up, *e.g.* by adding an external magnetic field, the magnetized state is stable only if the external field is present. In the case of electrons immersed in a homogeneous magnetic field $\mathbf{H} = H\hat{z}$ directed along the z-direction, the Hamiltonian reads

$$H = \sum_{\mathbf{k}} (\epsilon_k + \mu_B H) a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}\uparrow} + \sum_{\mathbf{k}} (\epsilon_k - \mu_B H) a_{\mathbf{k}\downarrow}^\dagger a_{\mathbf{k}\downarrow} \, , \tag{3.5}$$

where the Zeeman splitting proportional to the Bohr magneton $\mu_B = e\hbar/(2mc)$ arises from the coupling term $\delta H = -\vec{\mu} \cdot \mathbf{H} = (e/mc) \mathbf{S} \cdot \mathbf{H}$, $S_{x,y,z}$ being the components of the spin operator. The resulting ground-state energy is given by

$$E_0(H) = \frac{3}{5}N_\uparrow\epsilon_{F\uparrow} + \frac{3}{5}N_\downarrow\epsilon_{F\downarrow} - \mu_B H(N_\downarrow - N_\uparrow) \ .$$

The densities of spin-up and spin-down particles are determined by the chemical equilibrium equation $\mu_\uparrow = \mu_\downarrow$ (see Fig. 3.1), reading

$$\epsilon_{F\uparrow} + \mu_B H = \epsilon_{F\downarrow} - \mu_B H \ .$$

For small fields ($H \ll \epsilon_F/\mu_B$) using the above equation one finds $m = (3\mu_B^2 n/2\epsilon_F)H$ for the magnetization density $m = \mu_B(N_\downarrow - N_\uparrow)/V = \mu_B nP$. This shows that the electron gas is paramagnetic with the magnetic susceptibility given by $\chi_{para} = 3\mu_B^2 n/2\epsilon_F$ (Pauli paramagnetism).

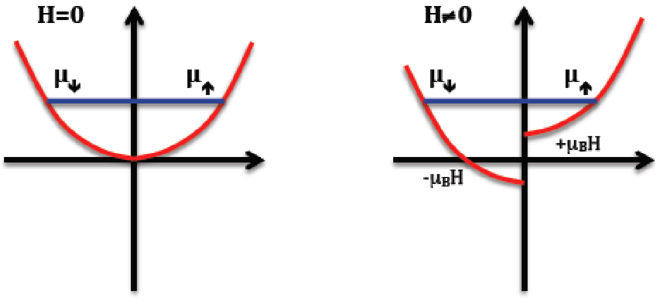

Figure 3.1: Fermi energy of a spin 1/2 ideal Fermi gas at $T = 0$, without and with a magnetic field H. Spin-up particles are on the right and spin-down particles on the left.

The gain in magnetic energy $-\mu_B H\Delta N$ overcomes the energy cost arising from the finite polarization and the ground-state energy density up to order H^2 is given by

$$\frac{E_0(H)}{V} = \frac{3}{5}n\epsilon_F - \frac{1}{2}\chi_{para}H^2 = \frac{3}{5}n\epsilon_F - \frac{1}{2}\frac{m^2}{\chi_{para}} \ ,$$

where the second equation is expressed in terms of the magnetization density m. For strong fields ($H \geq \epsilon_{F\downarrow}/(2\mu_B)$) the system becomes fully polarized ($P = 1$) and the ground-state energy density takes the value $E_0(H)/V = 3n_\downarrow\epsilon_{F\downarrow}/5 - \mu_B H n_\downarrow$ dominated by the Zeeman energy.

It is worth noticing that the magnetic response of an electron gas contains also a diamagnetic contribution arising from the orbital angular momentum not accounted for by eq. (3.5). The total magnetic susceptibility of an electron gas turns out to be positive, corresponding to a paramagnetic behavior, but is reduced by a factor 2/3 compared to χ_{para} giving the result $\chi = \mu_B^2 n/\epsilon_F$ at $T = 0$.

3.1.3 Structure of the ground state - pair-correlation function

An important quantity, containing a wealth of information about the structure of the ground state, is provided by the pair-correlation function describing the density fluctuations in the gas. We consider a balanced system with $N_\uparrow = N_\downarrow$: the parallel pair correlation function is defined as

$$\langle \big(n_\uparrow(\mathbf{r}) - n_\uparrow\big)\big(n_\uparrow(\mathbf{r}') - n_\uparrow\big)\rangle = n_\uparrow \delta(\mathbf{r} - \mathbf{r}') + n_\uparrow^2 \big(g_{\uparrow\uparrow}(|\mathbf{r} - \mathbf{r}'|) - 1\big) \ ,$$

and similarly for $g_{\downarrow\downarrow}$, while the anti-parallel pair-correlation function is given by

$$\langle \big(n_\uparrow(\mathbf{r}) - n_\uparrow\big)\big(n_\downarrow(\mathbf{r}') - n_\downarrow\big)\rangle = n_\uparrow n_\downarrow \big(g_{\uparrow\downarrow}(|\mathbf{r} - \mathbf{r}'|) - 1\big) \ .$$

The notation $\langle ... \rangle$ indicates either expectation value on the system ground state or statistical average at finite T. From the definitions given above the pair-correlation functions can be written directly in terms of averages of two-body hermitian operators. Namely, one has

$$g_{\uparrow\uparrow}(s) = \frac{1}{n_\uparrow^2} \langle \psi_\uparrow^\dagger(\mathbf{r}) \psi_\uparrow^\dagger(\mathbf{r} + \mathbf{s}) \psi_\uparrow(\mathbf{r} + \mathbf{s}) \psi_\uparrow(\mathbf{r}) \rangle \ , \tag{3.6}$$

and analogously for $g_{\downarrow\downarrow(s)}$, while

$$g_{\uparrow\downarrow}(s) = \frac{1}{n_\uparrow n_\downarrow} \langle \psi_\uparrow^\dagger(\mathbf{r}) \psi_\downarrow^\dagger(\mathbf{r} + \mathbf{s}) \psi_\downarrow(\mathbf{r} + \mathbf{s}) \psi_\uparrow(\mathbf{r}) \rangle \ . \tag{3.7}$$

The above correlation functions (3.6)-(3.7) yield the amplitude of the process of removing two particles from positions $\mathbf{r}$ and $\mathbf{r} + \mathbf{s}$, returning back to the same state after replacing the particles in the same positions. Thus, they are proportional to the probability of finding two particles, respectively of parallel and opposite spin, a distance s apart.

By calculating the expectation value on the ground state $|FS\rangle$ one obtains from eq. (3.7)

$$g_{\uparrow\downarrow}(s) = \frac{1}{n_\uparrow n_\downarrow} \frac{1}{V^2} \sum_{\mathbf{k}\mathbf{k}'} \langle FS | a_{\mathbf{k}\uparrow}^\dagger a_{\mathbf{k}'\downarrow}^\dagger a_{\mathbf{k}'\downarrow} a_{\mathbf{k}\uparrow} | FS \rangle = 1 \ ,$$

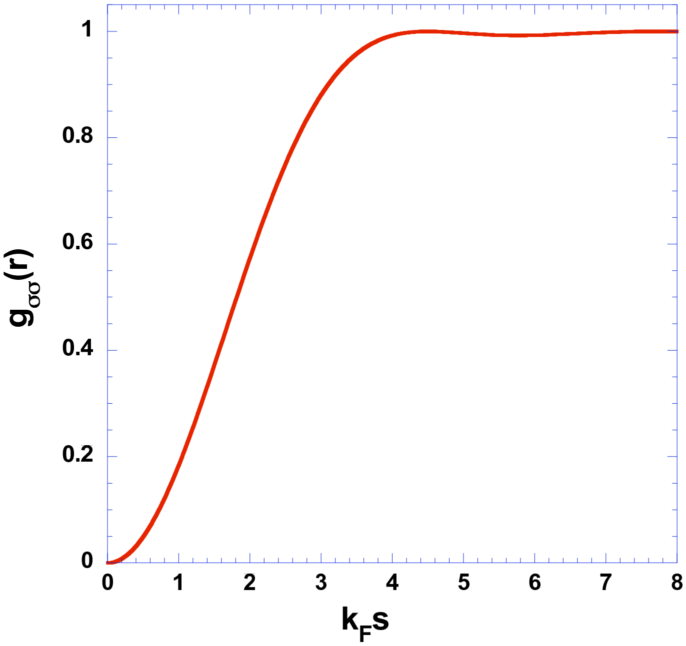

Figure 3.2: Parallel spin pair-correlation function $g_{\sigma\sigma}(s)$.

where we used the fact that the state $|FS\rangle$ is an eigenstate of the operator $a^\dagger_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma}$, corresponding to the number of particles in the single-particle state $(\mathbf{k},\sigma)$, with eigenvalue $n_{\mathbf{k}\sigma}$. The above result for $g_{\uparrow\downarrow}$ entails that there are no correlations between spin-up and spin-down particles. On the contrary, from eq. (3.6), one finds non trivial correlations exhibited by parallel spins

$$\begin{aligned} g_{\uparrow\uparrow}(s) &= \frac{1}{n_\uparrow^2}\frac{1}{V^2}\sum_{\mathbf{k}\mathbf{k}'}\langle FS|a^\dagger_{\mathbf{k}\uparrow}a^\dagger_{\mathbf{k}'\uparrow}a_{\mathbf{k}'\uparrow}a_{\mathbf{k}\uparrow}|FS\rangle\left(1-e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{s}}\right) \\ &= 1-\left|\frac{1}{n_\uparrow}\frac{1}{V}\sum_{\mathbf{k}}n_{\mathbf{k}\uparrow}e^{i\mathbf{k}\cdot\mathbf{s}}\right|^2 \\ &= 1-\frac{1}{n_\uparrow^2}\frac{1}{4\pi^4 s^6}\left(\int_0^{k_F s}dx\,x\sin x\right)^2 = 1-\frac{9}{(k_F s)^4}\left(\frac{\sin k_F s}{k_F s}-\cos k_F s\right)^2 . \end{aligned} \tag{3.8}$$

The plot of $g_{\sigma\sigma}(s)$ given by eq. (3.8) is shown in Fig. 3.2. Notice that $g_{\sigma\sigma}$ reaches the maximum value $g_{\sigma\sigma}=1$ at the points obeying the equation $\tan k_F s = k_F s$. We also notice that correlations rapidly decay as a function of the distance s, but in the short-range region the probability to find two particles with equal spin within a distance on the order of $1/k_F$ or less is greatly suppressed. This effective repulsion experienced by parallel spins has a purely statistical origin (called anti-bunching effect), being a direct consequence of the Pauli exclusion principle.

3.1.4 Excited states

It is convenient to consider the grand-canonical Hamiltonian defined as

$$H - \mu N = \sum_{\mathbf{k}} (\epsilon_k - \mu) a^\dagger_{\mathbf{k}} a_{\mathbf{k}} \ . \tag{3.9}$$

For simplicity we limit the analysis to the case of a single spin component, being the generalization to multiple spin components straightforward. We remind that in the canonical description N is fixed and μ is determined through the thermodynamic relation $\mu(T=0) = dE_0/dN$. Conversely, in the grand-canonical description, μ is fixed and N is obtained from the average of the number of particles operator. The antisymmetric ground state of the Hamiltonian (3.9) is still given by the Fermi see $|FS\rangle$, where all single-particles states are filled up to the level determined by $\mu(T=0) \equiv \epsilon_F$. This state minimizes the quantity $\sum_{\mathbf{k}}(\epsilon_k - \epsilon_F) n_{\mathbf{k}} = E_0 - \epsilon_F N$, as a function of the number N.

The excited states of the system are represented by particle excitations

$$\alpha^\dagger_{\mathbf{k}} |FS\rangle \equiv a^\dagger_{\mathbf{k}, k>k_F} |FS\rangle \ ,$$

corresponding to a system of $N+1$ particles with a particle created outside the Fermi sphere; and by hole excitations

$$\beta^\dagger_{\mathbf{k}} |FS\rangle \equiv a_{\mathbf{k}, k<k_F} |FS\rangle \ ,$$

corresponding to a system of $N-1$ particles with a particle removed from inside the Fermi sphere. We notice that both particle and hole excitations satisfy fermionic anticommutation relations and that the Fermi-see state $|FS\rangle$ acts as a vacuum for both type of excitations

$$\alpha_{\mathbf{k}} |FS\rangle = \beta_{\mathbf{k}} |FS\rangle = 0 \ .$$

The particle and hole excitations are given the name of quasi-particles and the ground state can be defined as the vacuum of quasi-particles. The excitation energy associated to a quasi-particle is defined as the energy difference

$$\langle FS | \alpha_{\mathbf{k}} (H - \mu N) \alpha^\dagger_{\mathbf{k}} | FS\rangle - \langle FS | H - \mu N | FS \rangle = \epsilon_{\mathbf{k}} - \epsilon_F \ ,$$

and

$$\langle FS|\beta_{\mathbf{k}}(H-\mu N)\beta^{\dagger}_{\mathbf{k}}|FS\rangle - \langle FS|H-\mu N|FS\rangle = \epsilon_F - \epsilon_{\mathbf{k}} \ ,$$

where we used the identity $\mu(T=0)=\epsilon_F$ holding at $T=0$. Close to the Fermi surface ($|k-k_F|/k_F \ll 1$), where quasi-particles have their lowest energies, both particle and hole excitations exhibit a spectrum linear in $k-k_F$:

$$|\epsilon_F - \epsilon_{\mathbf{k}}| \simeq \hbar v_F |k-k_F| \ ,$$

where $v_F = \hbar k_F/m$ is the Fermi velocity. We notice that the excitation energies have a minimum around the Fermi level. The quasiparticles around k_F are indeed responsible for the thermodynamic behavior at low temperatures.

For a fixed number of particles N the excited states are particle-hole pairs of the form

$$\alpha^{\dagger}_{\mathbf{k}}\beta^{\dagger}_{\mathbf{q}}|FS\rangle = a^{\dagger}_{\mathbf{k},k>k_F}a_{\mathbf{q},q<k_F}|FS\rangle \ ,$$

corresponding to the excitation energy $\epsilon_k - \epsilon_q = \hbar^2(k^2-q^2)/(2m)$.

In terms of quasiparticle operators the grand-canonical Hamiltonian (3.9) can be written in the form

$$H-\mu N = E_0 - \mu N + \sum_{k>k_F}(\epsilon_k-\mu)\alpha^{\dagger}_{\mathbf{k}}\alpha_{\mathbf{k}} + \sum_{k<k_F}(\epsilon_k-\mu)\beta^{\dagger}_{\mathbf{k}}\beta_{\mathbf{k}} \ , \tag{3.10}$$

where the first sum refers to particles and the second to holes. In this picture the ground state of the system corresponds to the vacuum $|\text{vac}\rangle$ of quasiparticles defined by $\alpha_{\mathbf{k}}|\text{vac}\rangle = \beta_{\mathbf{k}}|\text{vac}\rangle = 0$. Excited states correspond instead to quasiparticles created from the vacuum such as $\alpha^{\dagger}_{\mathbf{k}}|\text{vac}\rangle$ and $\beta^{\dagger}_{\mathbf{k}}|\text{vac}\rangle$ and have a definite number of both particles and holes.

3.2 Non-interacting gas: finite temperature

3.2.1 Fock space and statistical averages

It is convenient to work in the statistical ensemble where the independent thermodynamic variables are temperature T, volume V and chemical potential μ. Such a statistical ensemble is the grand-canonical ensemble characterized by the density matrix operator (see Supplement 3.4.1)

$$\rho_{GC} = \frac{1}{Z_{GC}} e^{-\beta(H-\mu N)} ,$$

where $\beta = 1/k_B T$ is the inverse temperature factor and Z_{GC} is the grand-canonical partition function defined as the trace over a complete set of states in the Fock space $\mathcal{F}$, conveniently provided by the states in the occupation number representation

$$Z_{GC} = \mathrm{Tr}\big(e^{-\beta(H-\mu N)}\big) = \sum_{n_\alpha,\ldots,n_\omega} \langle n_\alpha \ldots n_\omega | e^{-\beta(H-\mu N)} | n_\alpha \ldots n_\omega \rangle .$$

Of course, since the trace is independent of the basis states, the partition function can be calculated using any complete set of states of the space $\mathcal{F}$ with the proper particle symmetry.

The connection with thermodynamics is provided by the relation

$$\Omega(T, V, \mu) = -k_B T \log Z_{GC} ,$$

between grand-canonical potential and partition function. In terms of other thermodynamic functions the thermodynamic potential is written as $\Omega = U - TS - \mu N = -pV$ and its differential is given by $d\Omega = -SdT - pdV - Nd\mu$, so that the following relations are obtained

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V\mu} \qquad p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T\mu} \qquad N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{TV} . \tag{3.11}$$

For a generic operator O the statistical average is obtained using the prescription

$$\langle O \rangle \equiv \mathrm{Tr}\big(\rho_{GC} O\big) = \frac{1}{Z_{GC}} \sum_{n_\alpha,\ldots,n_\omega} \langle n_\alpha \ldots n_\omega | e^{-\beta(H-\mu N)} O | n_\alpha \ldots n_\omega \rangle . \tag{3.12}$$

We notice that:

- At $T = 0$ the grand-canonical potential $\Omega_0 \equiv \Omega(T = 0, V, \mu)$ coincides with the grand-canonical ground-state energy: $\Omega_0 = E_0 - \mu N$.

- Let $|\Psi_{n,s}\rangle$ be the common eigenstates, with the proper symmetry concerning particle exchange, of the commuting operators H and N: $H|\Psi_{n,s}\rangle = E_n|\Psi_{n,s}\rangle$ and $N|\Psi_{n,s}\rangle = N_s|\Psi_{n,s}\rangle$. The grand-canonical partition function and statistical averages can be written in terms of the basis $|\Psi_{n,s}\rangle$ in the following form: $Z_{GC} = \sum_{n,s} e^{-\beta(E_n-\mu N_s)}$ and $\langle O\rangle = \sum_{n,s} e^{-\beta(E_n-\mu N_s)}\langle\Psi_{n,s}|O|\Psi_{n,s}\rangle/Z_{CG}$.

- As $T \to 0$ ($\beta \to \infty$) the partition function reduces to the contribution of the ground state $|GS\rangle$, *i.e.* the state $|\Psi_{\bar{n},\bar{s}}\rangle$ for which $E_{\bar{n}} - \mu N_{\bar{s}}$ is minimal. One has thus $Z_{GC} = \langle GS|e^{-\beta(H-\mu N)}|GS\rangle$, and statistical averages reduce to expectation values on the ground state $\langle O\rangle = \langle GS|O|GS\rangle$.

3.2.2 Fermi distribution function and equation of state

By using the non-interacting Hamiltonian (3.1) the grand-canonical partition function can be readily calculated

$$\begin{aligned} Z_{GC} &= \sum_{n_{\mathbf{k}\sigma}} e^{-\beta\sum_{\mathbf{k}\sigma}(\epsilon_k-\mu)n_{\mathbf{k}\sigma}} = \prod_{\mathbf{k}\sigma}\sum_{n_{\mathbf{k}\sigma}} e^{-\beta(\epsilon_k-\mu)n_{\mathbf{k}\sigma}} \\ &= \prod_{\mathbf{k},\sigma}\left(1 + e^{-\beta(\epsilon_k-\mu)}\right), \end{aligned}$$

where the sum over $n_{\mathbf{k}\sigma}$ contains only two terms $n_{\mathbf{k}\sigma} = 0, 1$ and we assumed equal number of particles for each spin component. The thermodynamic potential then reads

$$\Omega(T, V, \mu) = -k_B T \sum_{\mathbf{k}\sigma} \log\left(1 + e^{-\beta(\epsilon_k-\mu)}\right), \tag{3.13}$$

giving the following result for the pressure

$$p(T, V, \mu) = -\frac{\Omega(T, V, \mu)}{V} = g_s k_B T \frac{1}{2\pi^2}\int_0^\infty dk k^2 \log\left(1 + e^{-\beta(\epsilon_k-\mu)}\right),$$

where $g_s = 2s+1$ is the degeneracy associated with the value s of the spin. By expressing the integral in terms of the energy $\epsilon = \epsilon_k$ and by integrating by parts, one finds

$$\begin{aligned} p(T,V,\mu) &= g_s \frac{(2m)^{3/2}}{6\pi^2\hbar^3} \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)}+1} \\ &= g_s \frac{k_B T}{\lambda_T^3} \frac{4}{3\sqrt{\pi}} \int_0^\infty dx \frac{x^{3/2}}{z^{-1}e^x+1} \ , \end{aligned} \tag{3.14}$$

where we introduced the fugacity $z = e^{\beta\mu}$ and the thermal wave length $\lambda_T = \sqrt{2\pi\hbar^2/mk_BT}$. The equation (3.14) determines the pressure in the grand-canonical ensemble. In order to obtain p in the canonical ensemble (*i.e.* as a function of T, V and N) one should eliminate the chemical potential using the equation for the total number of particles given by the rightmost thermodynamic identity in eq. (3.11)

$$N(T,V,\mu) = \sum_{\mathbf{k}\sigma} \frac{1}{e^{\beta(\epsilon_k-\mu)}+1} = g_s \frac{V}{2\pi^2} \int_0^\infty dk \frac{k^2}{e^{\beta(\epsilon_k-\mu)}+1} \ . \tag{3.15}$$

By transforming the integral similarly to eq. (3.14), one gets

$$\begin{aligned} N(T,V,\mu) &= g_s V \frac{(2m)^{3/2}}{4\pi^2\hbar^3} \int_0^\infty d\epsilon \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)}+1} \\ &= g_s \frac{V}{\lambda_T^3} \frac{2}{\sqrt{\pi}} \int_0^\infty dx \frac{x^{1/2}}{z^{-1}e^x+1} \ , \end{aligned} \tag{3.16}$$

The number of particles in the system can also be obtained from the statistical average $N = \sum_{\mathbf{k},\sigma} \langle n_{\mathbf{k},\sigma} \rangle$, involving the number operators $n_{\mathbf{k},\sigma} = a^\dagger_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma}$, relative to the single-particle state $(\mathbf{k},\sigma)$. A comparison with eq. (3.15) yields the well-known result

$$\langle n_{\mathbf{k},\sigma} \rangle = \frac{1}{e^{\beta(\epsilon_k-\mu)}+1} \ . \tag{3.17}$$

for the fermionic particle distribution. This result can be derived directly using the prescription (3.12) for the statistical average of $n_{\mathbf{k},\sigma}$ in the grand-canonical ensemble.

Another important thermodynamic quantity is the internal energy $U = \Omega + TS + \mu N$. By using eq. (3.13) for the thermodynamic potential, eq. (3.15) for N and the leftmost thermodynamic identity in eq. (3.11) for the entropy S, one finds

$$U(T,V,\mu) = \sum_{\mathbf{k}\sigma} \frac{\epsilon_k}{e^{\beta(\epsilon_k-\mu)}+1} \ , \tag{3.18}$$

which agrees with the direct statistical average $\langle H\rangle$ of the Hamiltonian $H = \sum_{\mathbf{k}\sigma} \epsilon_k a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}$. If one uses integration by parts in the integral (3.13), expressing Ω in terms of the single-particle energy ϵ, one can prove the relevant identity

$$U(T,V,\mu) = -\frac{3}{2}\Omega(T,V,\mu) \ , \tag{3.19}$$

relating the internal energy and the thermodynamic potential in a homogeneous non-interacting gas.

It is customary to introduce the special functions

$$f_\nu(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^x+1} \ ,$$

which can be defined for $z \geq 0$ and $\nu > 0$. Here $\Gamma(x)$ is the Euler Gamma function, whose relevant property for our purposes is $\Gamma(x+1) = x\Gamma(x)$ for any real x and the special value $\Gamma(1/2) = \sqrt{\pi}$. By using the functions $f_\nu(z)$ we can recast eqs. (3.14) and (4.28) in the more compact form

$$\begin{aligned} \frac{p}{k_BT} &= g_s\frac{1}{\lambda_T^3} f_{5/2}(z) \\ \frac{N}{V} &= g_s\frac{1}{\lambda_T^3} f_{3/2}(z) \ . \end{aligned} \tag{3.20}$$

This set of equations, from which one can eliminate the fugacity z, provides the equation of state of the gas in the canonical ensemble.

3.2.3 High temperature behavior: virial expansion

In the high temperature regime particles can access a huge number of single-particle states and the mean occupation of a given state $(\mathbf{k},\sigma)$ becomes very small: $\langle n_{\mathbf{k},\sigma}\rangle \ll 1$. This condition implies from eq. (3.17) that $e^{\beta(\epsilon_k-\mu)} \gg 1$ and, as expected, particles get distributed according to the Maxwell-Boltzmann law $\langle n_{\mathbf{k},\sigma}\rangle \simeq e^{-\beta(\epsilon_k-\mu)}$, independent of statistics. The normalization condition for the total density n reads in this case: $n\lambda_T^3 = g_s z$. The dimensionless parameter $n\lambda_T^3$, giving the average number of particles in a cube of the size of the thermal wave length, is small ($n\lambda_T^3 \ll 1$) in the high temperature regime and, consequently, the fugacity z is also small.

For $z \ll 1$ the function $f_\nu(z)$ admits the following power-law expansion

$$\begin{aligned} f_\nu(z) &= \frac{1}{\Gamma(\nu)}\int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^x}\Big(1 - ze^{-x} + (ze^{-x})^2 + ...\Big) = \int_0^\infty dx \frac{x^{\nu-1}}{\Gamma(\nu)}\sum_{\ell=1}^\infty (-1)^{\ell-1}(ze^{-x})^\ell \\ &= \sum_{\ell=1}^\infty (-1)^{\ell-1}\frac{z^\ell}{\ell^\nu}\int_0^\infty dx \frac{x^{\nu-1}e^{-x}}{\Gamma(\nu)} = \sum_{\ell=1}^\infty (-1)^{\ell-1}\frac{z^\ell}{\ell^\nu} \ , \end{aligned}$$

where we used the integral representation of the Gamma function $\Gamma(\nu) = \int_0^\infty dx x^{\nu-1}e^{-x}$. By expanding the two equations in (3.20) in terms of the fugacity and by eliminating z to the corresponding order, one obtains the following expansion in powers of the small parameter $n\lambda_T^3$

$$pV = Nk_BT\Big(1 + \frac{1}{4\sqrt{2}g_s}n\lambda_T^3 + ...\Big) \ , \tag{3.21}$$

where the coefficient of the $n\lambda_T^3$ term is named second virial coefficient and higher virial coefficients correspond to higher powers of $n\lambda_T^3$. From eq. (3.19) one gets immediately the virial expansion of the internal energy

$$U = \frac{3}{2}Nk_BT\Big(1 + \frac{1}{4\sqrt{2}g_s}n\lambda_T^3 + ...\Big) \ . \tag{3.22}$$

The first term in eqs. (3.21) and (3.22) corresponds to the equation of state of a non-interacting classical gas. The term proportional to the second virial coefficient gives instead the first correction to this equation of state arising from statistical effects. In the case of fermionic statistics this effect shows up as an increase in the average energy per particle, consistently with the role of effective repulsion played by the Pauli exclusion principle.

It is instructive to calculate the parallel spin pair-correlation function $g_{\uparrow\uparrow}(s)$ in the regime $n\lambda_T^3 \ll 1$ (we assume $s = 1/2$ and $n_\uparrow = n_\downarrow$).

First of all we notice that the results obtained in Section A) for the ground state $|FS\rangle$ can be extended to general statistical averages giving the expression

$$g_{\sigma\sigma'}(s) = 1 - \delta_{\sigma,\sigma'}\Big|\frac{1}{n_\sigma}\frac{1}{V}\sum_{\mathbf{k}}\langle n_{\mathbf{k}\sigma}\rangle e^{i\mathbf{k}\cdot\mathbf{s}}\Big|^2 \ ,$$

for the pair correlation function in a non-interacting Fermi gas. In fact, at finite temperature, the statistical average implies the calculation of the trace over states that have a definite number of particles $n_{\mathbf{k}\sigma}$ in each single-particle state $(\mathbf{k}, \sigma)$.

In the highly non degenerate regime one can use the Maxwell-Boltzmann approximation for the particle distribution function finding the following result in the case of parallel spins

$$\begin{aligned} g_{\sigma\sigma}(s) &\simeq 1 - \Big| \frac{\lambda_T^3}{V} \sum_{\mathbf{k}} e^{-\beta\epsilon_k} e^{i\mathbf{k}\cdot\mathbf{s}} \Big|^2 = 1 - \Big| \frac{2\lambda_T}{\pi s} \int_0^\infty dx x e^{-x^2} \sin\left(\frac{\sqrt{4\pi} s x}{\lambda_T} \right) \Big|^2 \\ &= 1 - e^{-2\pi s^2/\lambda_T^2} , \end{aligned}$$

where we used the tabulated integral $\int_0^\infty dx x \sin(2ax) e^{-x^2} = (\sqrt{\pi} a/2) e^{-a^2}$. The above result shows that in the classical regime correlations decay exponentially over a length scale on the order of the thermal wave length, but the effective repulsion arising from the Pauli principle remains active for distances shorter than λ_T. In particular, $g_{\sigma\sigma}(0) = 0$.

3.2.4 Low temperature behavior: Sommerfeld expansion

The high-temperature condition $n\lambda_T^3 \ll 1$ can be reformulated in terms of the temperature scale $T_F = \epsilon_F/k_B$, denoting the Fermi temperature. One has $n\lambda_T^3 = (4g_s/3\sqrt{\pi})(T_F/T)^{3/2}$, implying that $n\lambda_T^3 \ll 1$ is equivalent to $T \gg T_F$.

The opposite regime $T \ll T_F$ is also worth exploring as it addresses the first corrections arising from a finite T to the ground-state properties investigated in Section A). A useful mathematical expansion due to Sommerfeld can be proved in this regime for integrals containing the Fermi distribution. Let us consider the integral

$$I = \int_0^\infty dx \Phi(x) \frac{1}{e^{x-\xi} + 1} ,$$

where $\Phi(x)$ is a continuous function and we assume $\xi \gg 1$. In fact, the fugacity is $z = e^\xi$ and $\xi = \mu/k_B T \simeq T_F/T \gg 1$ at very low temperatures. By performing some formal manipulations one can rewrite I as

$$\begin{aligned} I &= \int_0^\xi dx\Phi(x)\left(1-\frac{1}{e^{\xi-x}+1}\right)+\int_\xi^\infty dx\Phi(x)\frac{1}{e^{x-\xi}+1} \\ &= \int_0^\xi dx\Phi(x)-\int_0^\xi dx\frac{\Phi(\xi-x)}{e^x+1}+\int_0^\infty dx\frac{\Phi(\xi+x)}{e^x+1} \\ &\simeq \int_0^\xi dx\Phi(x)+\int_0^\infty dx\frac{\Phi(\xi+x)-\Phi(\xi-x)}{e^x+1} \\ &= \int_0^\xi dx\Phi(x)+2\Phi'(\xi)\int_0^\infty dx\frac{x}{e^x+1}=\int_0^\xi dx\Phi(x)+\frac{\pi^2}{6}\Phi'(\xi)\ , \end{aligned} \tag{3.23}$$

where we used the value of the tabulated integral $\int_0^\infty dxx/(e^x+1)=\pi^2/12$.

The Sommerfeld expansion (3.23) allows one to obtain the following result for the special Fermi function $f_\nu(z)$

$$f_\nu(e^{\mu/k_BT})=\frac{1}{\nu\Gamma(\nu)}\left(\frac{\mu}{k_BT}\right)^\nu\left(1+\frac{\pi^2\nu(\nu-1)}{6}\left(\frac{k_BT}{\mu}\right)^2+...\right)\ ,$$

holding for $k_BT/\mu \ll 1$. By using the above expansion in the eqs. (3.20) for the equation of state of a Fermi gas, one derives the following results for the low-temperature behavior of the relevant thermodynamic quantities

$$\begin{aligned} \mu &= \epsilon_F\left(1-\frac{\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2+...\right)\ , \\ p &= \frac{2}{5}n\epsilon_F\left(1+\frac{5\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2+...\right)\ , \\ U &= \frac{3}{2}pV=\frac{3}{5}N\epsilon_F\left(1+\frac{5\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2+...\right)\ , \\ c_V &= \left(\frac{\partial U}{\partial T}\right)_{VN}=Nk_B\frac{\pi^2}{2}\frac{T}{T_F}+...\ , \\ F &= N\mu-pV=\frac{3}{5}N\epsilon_F\left(1-\frac{5\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2+...\right)\ , \\ S &= \frac{1}{T}\Big(U-F\Big)=Nk_B\frac{\pi^2}{2}\frac{T}{T_F}+...\ , \end{aligned} \tag{3.24}$$

holding for $T \ll T_F$.

The temperature dependence of some relevant thermodynamic functions is reported in Fig. 3.3.

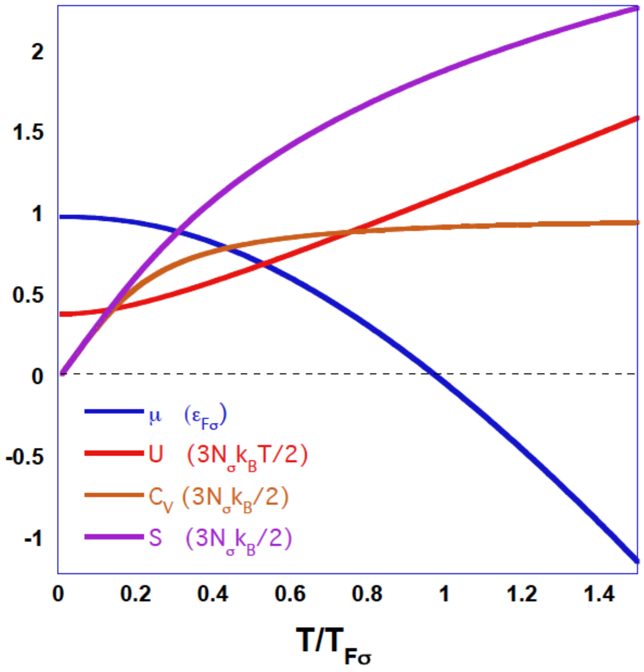

Figure 3.3: Thermodynamic functions of a Fermi gas.

We show the chemical potential $\mu(T)$, the internal energy

$$U(T) = \frac{3}{2} N_\sigma k_B T \frac{f_{5/2}(z)}{f_{3/2}(z)} \ ,$$

the entropy

$$S(T) = N_\sigma k_B \left(\frac{5}{2} \frac{f_{5/2}(z)}{f_{3/2}(z)} - \log z \right) \ ,$$

and the specific heat

$$c_V(T) = N_\sigma k_B \left(\frac{15}{4} \frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4} \frac{f_{3/2}(z)}{f_{1/2}(z)} \right) \ .$$

This last result can be easily derived using the definition $c_V = (\partial U/\partial T)_{VN}$ and the following relations holding for the Fermi special functions: $(d/dT f_\nu(z)) = f_{\nu-1}(z)(d/dT \log z)$ and $(\partial \log z/\partial T)_{VN} = (-3/2T) f_{3/2}(z)/f_{1/2}(z)$.

3.2.5 Fluctuations in the number of particles

Let us consider the fluctuations in the occupation number of the single-particle state ($\mathbf{k}\sigma$). The average value was calculated in eq. (3.17). We are now interested in the mean-square fluctuations around this average value

$$\delta n_{\mathbf{k}\sigma}^2 = \langle \big(n_{\mathbf{k}\sigma} - \langle n_{\mathbf{k}\sigma}\rangle\big)^2 \rangle = \langle n_{\mathbf{k}\sigma}^2\rangle - \langle n_{\mathbf{k}\sigma}\rangle^2 \; .$$

The determination of $\langle n_{\mathbf{k}\sigma}^2\rangle$ can be obtained using eq. (3.12) for the statistical average in the grand-canonical ensemble. One gets

$$\langle n_{\mathbf{k}\sigma}^2\rangle = \frac{1}{1+e^{-\beta(\epsilon_k-\mu)}} \sum_{n_{\mathbf{k}\sigma}} n_{\mathbf{k}\sigma}^2 e^{-\beta(\epsilon_k-\mu)n_{\mathbf{k}\sigma}} = \frac{1}{e^{\beta(\epsilon_k-\mu)}+1} \; ,$$

where we summed over $n_{\mathbf{k}\sigma} = 0, 1$. We find thus the following result

$$\delta n_{\mathbf{k}\sigma}^2 = \langle n_{\mathbf{k}\sigma}\rangle - \langle n_{\mathbf{k}\sigma}\rangle^2 \; . \tag{3.25}$$

At high temperatures $\langle n_{\mathbf{k}\sigma}\rangle \ll 1$ and one can neglect the quadratic term in the above equation. One then finds the "normal" behavior of the relative fluctuations $\sqrt{\delta n_{\mathbf{k}\sigma}^2}/\langle n_{\mathbf{k}\sigma}\rangle \simeq 1/\sqrt{\langle n_{\mathbf{k}\sigma}\rangle}$. When statistical effects start to matter, fluctuations are below the classical value. At $T = 0$, the average occupation of states $(\mathbf{k}, \sigma)$ below the Fermi sphere $k < k_{F\sigma}$ is $\langle n_{\mathbf{k}\sigma}\rangle = 1$ and $\langle n_{\mathbf{k}\sigma}\rangle = 0$ for $k > k_{F\sigma}$. The fluctuations vanish in this limit yielding a completely non-classical behavior.

For the fluctuations in the total number of particles $\delta N_\sigma^2 = \langle (N_\sigma - \langle N_\sigma\rangle)^2\rangle$ one finds the result

$$\delta N_\sigma^2 = \sum_{\mathbf{k}} \delta n_{\mathbf{k}\sigma}^2 = \langle N_\sigma\rangle - \sum_{\mathbf{k}} \langle n_{\mathbf{k}\sigma}\rangle^2 \; , \tag{3.26}$$

where we made use of the fact that fluctuations relative to different states are statistically independent: $\langle n_{\mathbf{k}\sigma} n_{\mathbf{k}'\sigma'}\rangle = \langle n_{\mathbf{k}\sigma}\rangle\langle n_{\mathbf{k}'\sigma'}\rangle$ if $\mathbf{k} \neq \mathbf{k}'$ or $\sigma \neq \sigma'$. The above result shows that the fluctuations in the total number of particles are also anomalously small in a non-interacting Fermi gas and vanish in the zero temperature limit where $\sum_{\mathbf{k}} \langle n_{\mathbf{k}\sigma}\rangle^2 = \sum_{k<k_{F\sigma}} = \langle N_\sigma\rangle$.

From the result $\langle N\rangle = \sum_{n,s} N_s e^{-\beta(E_n-\mu N_s)}/Z_{GC}$, holding for the statistical average of the total number of particles, one finds $(\partial N/\partial\mu)_{TV} = \beta(\langle N^2\rangle - \langle N\rangle^2)$. Furthermore, if one uses the equivalent definitions of the isothermal compressibility giving $\kappa_T = -(1/V)(\partial V/\partial p)_{TN} = (V/N^2)(\partial N/\partial \mu)_{TV}$, one finds the following relevant relation

$$N_\sigma n_\sigma k_B T \kappa_T = \delta N_\sigma^2 = \langle N_\sigma \rangle - \sum_{\mathbf{k}} \langle n_{\mathbf{k}\sigma} \rangle^2 \,, \tag{3.27}$$

valid for an ideal Fermi gas at any temperature. The above equation is an example of the fluctuation-dissipation theorem relating response functions to fluctuations.

3.3 Interacting gas

We consider a gas of fermions interacting via a two-body spherical potential independent of the spin of the particles. In terms of the matrix elements in coordinate space of the two-body operator we require that

$$\langle \mathbf{r}_1\sigma_1\mathbf{r}_2\sigma_2|V_2|\mathbf{r}_1'\sigma_1'\mathbf{r}_2'\sigma_2'\rangle = \delta(\mathbf{r}_1-\mathbf{r}_1')\delta_{\sigma_1,\sigma_1'}\delta(\mathbf{r}_2-\mathbf{r}_2')\delta_{\sigma_2,\sigma_2'}V(|\mathbf{r}_1-\mathbf{r}_2|)\ .$$

The representation in the Fock space of the interaction potential operator is thus given by

$$V = \frac{1}{2}\sum_{\sigma\sigma'}\int d\mathbf{r}\int d\mathbf{r}'\psi_\sigma^\dagger(\mathbf{r})\psi_{\sigma'}^\dagger(\mathbf{r}')V(|\mathbf{r}-\mathbf{r}'|)\psi_{\sigma'}(\mathbf{r}')\psi_\sigma(\mathbf{r})$$

In momentum space the Hamiltonian of the interacting gas is written as

$$H = \sum_{\mathbf{k}\sigma}\epsilon_k a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} + \frac{1}{2V}\sum_{\sigma\sigma'}\sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} V_{\mathbf{q}} a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}'-\mathbf{q}\sigma'}^\dagger a_{\mathbf{k}'\sigma'}a_{\mathbf{k}-\mathbf{q}\sigma}\ , \tag{3.28}$$

involving the Fourier transform $V_{\mathbf{q}} = V_{-\mathbf{q}} = \int d\mathbf{r}V(r)e^{-i\mathbf{q}\cdot\mathbf{r}}$. We notice that the interaction term does not commute with the occupation number operator $a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma}$, implying that eigenstates of H will not have definite single-particle occupation numbers $n_{\mathbf{k}\sigma}$.

Examples of two-body interaction potentials are:

- The repulsive Coulomb potential $V(r) = e^2/r$ between electrons. The Fourier transform of the Coulomb potential gives $V_{\mathbf{q}} = 4\pi e^2/q^2$. This result can be easily obtained using the Fourier transformation formula $\int d\mathbf{r}e^{-i\mathbf{q}\cdot\mathbf{r}}(e^{-\kappa r}/r) = 4\pi/(\kappa^2+q^2)$ holding for positive κ, and letting κ go to zero. A gas of interacting electrons, placed in a uniformly distributed background of positive charge to ensure that the system is neutral, is an important model in many-body theory called *jellium* model.

- The contact potential $V(\mathbf{r}) = g\delta(\mathbf{r})$, where g is the coupling constant that can be conveniently expressed in terms of the s-wave scattering length a as $g = 4\pi\hbar^2 a/m$ (see Supplement 3.4.2). The scattering length can be either positive or negative depending on weather the contact potential is respectively repulsive or attractive. The Fourier transform of the contact potential gives the simple result $V_{\mathbf{q}} = g$ independent of the wave vector $\mathbf{q}$.

In the following we consider a generic interaction potential $V(r)$ for which the Fourier transform $V_{\mathbf{q}}$ exists for any value of $\mathbf{q}$.

3.3.1 Mean-field approach: Hartree-Fock theory

The mean-field approximation consists of replacing the product of four creation/annihilation operators present in the summation in (3.28) with a combination of terms involving a maximum number of two operators. The approximation is valid in the regime of weak interactions. The recipe is as follows:

$$\begin{aligned} a^\dagger_{\mathbf{k}\sigma} a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}'\sigma'} a_{\mathbf{k}-\mathbf{q}\sigma} &= \langle a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}-\mathbf{q}\sigma}\rangle a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}'\sigma'} - \langle a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}'\sigma'}\rangle a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}-\mathbf{q}\sigma} \\ &+ \langle a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}'\sigma'}\rangle a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}-\mathbf{q}\sigma} - \langle a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}-\mathbf{q}\sigma}\rangle a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}'\sigma'} \\ &- \langle a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}-\mathbf{q}\sigma}\rangle \langle a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}'\sigma'}\rangle + \langle a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}'\sigma'}\rangle \langle a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}-\mathbf{q}\sigma}\rangle \ . \end{aligned} \tag{3.29}$$

The last two terms in the above equation avoid double counting when calculating the average value of the operator and the sign accounts for the parity of the permutation bringing the creation/annihilation operators to the original ordering. By replacing the above expression in (3.28) one finds the following simpler Hamiltonian

$$H_{HF} = \sum_{\mathbf{k}\sigma} \epsilon_k a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \frac{1}{2}\sum_{\mathbf{k}\sigma} V_0 n \big(2a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} - \langle n_{\mathbf{k}\sigma}\rangle\big) - \frac{1}{2}\sum_{\mathbf{k}\sigma} \frac{1}{V}\sum_{\mathbf{q}} V_{\mathbf{k}-\mathbf{q}} \langle n_{\mathbf{q}\sigma}\rangle \big(2a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} - \langle n_{\mathbf{k}\sigma}\rangle\big) \ . \tag{3.30}$$

The first term containing the interaction potential is referred to as the Hartree or direct term. It arises from the odd terms in the decomposition (3.29). The second arising instead from the even terms in (3.29) and is referred to as the Fock or exchange term. The complete expression in (3.30) is called Hartree-Fock (HF) Hamiltonian. It is diagonal in the occupation number representation and describes non-interacting particles subject to an effective external field generated by the average interaction with the other particles of the system (mean field). By grouping together constant and operator terms, one can recast eq. (3.30) in the form

$$H_{HF} = E_{HF} + \sum_{\mathbf{k}\sigma} \big(\epsilon_k + V_0 n - \tilde{V}_{\mathbf{k}\sigma}\big) a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} \ , \tag{3.31}$$

where $\tilde{V}$ denotes the effective potential $\tilde{V}_{\mathbf{k}\sigma} = (1/V)\sum_{\mathbf{q}} V_{\mathbf{k}-\mathbf{q}} \langle n_{\mathbf{q}\sigma}\rangle$ and $E_{HF} = (1/2)\sum_{\mathbf{k}\sigma}\langle n_{\mathbf{k}\sigma}\rangle(\tilde{V}_{\mathbf{k}\sigma} - V_0 n)$ is a constant term.

The HF ground state $|HF\rangle$ is obtained by solving for the single-particle energies

$$\tilde{\epsilon}_{\mathbf{k}\sigma} = \epsilon_k + V_0 n - \tilde{V}_{\mathbf{k}\sigma}$$

and by filling the lowest N_σ orbitals with occupation $\langle n_{\mathbf{k}\sigma}\rangle = 1$. However, the occupation numbers enter the definition of the effective potential $\tilde{V}$ and the solution must be obtained self consistently.

A significant reduction in the complexity of the HF equations is obtained in the case of a contact potential $V(\mathbf{r}) = g\delta(\mathbf{r})$. The HF Hamiltonian becomes in this case

$$H_{HF} = -g\frac{N_\uparrow N_\downarrow}{V} + \sum_{\mathbf{k}}\left(\epsilon_k + g n_\downarrow\right) a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}\uparrow} + \sum_{\mathbf{k}}\left(\epsilon_k + g n_\uparrow\right) a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}\downarrow} \;, \tag{3.32}$$

for the two-component gas. The single-particle energies are the same as in the non-interacting case, apart from a constant shift, and the HF ground state $|HF\rangle$ coincides with the Fermi sea $|FS\rangle$. The corresponding energy is given by

$$E_0^{HF} = \frac{3}{5}N_\uparrow \epsilon_{F\uparrow} + \frac{3}{5}N_\downarrow \epsilon_{F\downarrow} + g\frac{N_\uparrow N_\downarrow}{V} \;, \tag{3.33}$$

in terms of the spin-up and spin-down Fermi energies defined in (3.3). From eqs. (3.32) and (3.33) we notice that interactions are present between spin-up and spin-down particles, while they are absent between identical particles. This is a consequence of the Pauli exclusion principle, prohibiting particles with the same spin from occupying the same spatial position (see Fig. 3.2), and of the zero-range nature of the interaction potential.

The independent particle nature of the HF Hamiltonian (3.32) can be exploited to calculate the thermodynamic behavior. In fact, apart from constant terms, the grand-canonical Hamiltonian

$$H_{HF} - \mu N = -g\frac{N^2}{4V} + \sum_{\mathbf{k}}\left(\epsilon_k - \tilde{\mu}\right) a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}\uparrow} + \sum_{\mathbf{k}}\left(\epsilon_k - \tilde{\mu}\right) a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}\downarrow} \;,$$

coincides with the one of a non-interacting gas with the shifted chemical potential $\tilde{\mu} = \mu - gn/2$, where we assumed $n_\uparrow = n_\downarrow = n/2$. The equation of state at finite T can be derived straightforwardly using the method of Sec. B), one gets

$$\begin{aligned} \frac{p}{k_B T} &= \frac{g}{k_B T}\frac{n^2}{4} + \frac{2}{\lambda_T^3} f_{5/2}(\tilde{z}) \\ n\lambda_T^3 &= 2 f_{3/2}(\tilde{z}) \ , \end{aligned} \tag{3.34}$$

where $\tilde{z} = e^{\tilde{\mu}/k_B T}$ is the reduced fugacity. At high temperatures, it is worth calculating the interaction contribution to the virial expansion (3.21). One finds

$$pV = N k_B T \left(1 + \Big(\frac{1}{8\sqrt{2}} + \frac{a}{2\lambda_T} \Big) n\lambda_T^3 + ... \right) \ ,$$

where we used the expression $g = 4\pi\hbar a/m$ of the coupling constant in terms of the scattering length a. Notice that the validity of the above result requires that λ_T is much larger than the range of the interaction potential, as this condition justifies the description in terms of a contact potential.

3.3.2 Itinerant ferromagnetism: Stoner model

The HF energy functional (3.33) was used by Stoner (1933) as a model for itinerant ferromagnetism in a gas of electrons with screened short-range interactions. Itinerant ferromagnetism refers to the ferromagnetic transition in a system of delocalized particles, in contrast to usual ferromagnetism of magnetic moments on a lattice. Whether a gas of electrons displays ferromagnetic behavior is still under debate, but the Stoner model remains as the simplest example of a quantum phase transition in a fermionic gas. Interest in this model was recently revised because of the experimental activity in the field of ultracold gases.

Let us consider a gas with repulsive interactions (the scattering length a is positive) at $T = 0$ treated at the level of HF theory. The energy functional (3.33) can be conveniently rewritten using the total density $n = n_\uparrow + n_\downarrow$ and the polarization $P = (n_\downarrow - n_\uparrow)/n$. One finds

$$\frac{E_0^{HF}(P)}{V} = \frac{3}{5} n\epsilon_F \left(\frac{1}{2}(1+P)^{5/3} + \frac{1}{2}(1-P)^{5/3} + \frac{10}{9\pi} k_F a (1-P^2) \right) \equiv \frac{3}{5} n\epsilon_F \ F(P) \ , \tag{3.35}$$

where $k_F = (3\pi^2 n)^{1/3}$ is the Fermi wave vector fixed by the total density and $\epsilon_F = \hbar^2 k_F^2/(2m)$ is the corresponding Fermi energy. We notice that $E_0^{HF}(P)$ is symmetric with respect to the inversion $P \to -P$.

We first assume that the system is unpolarized $N_\uparrow = N_\downarrow = N/2$. For a given volume V and total number of particles N, the lowest energy state is given by the minimum of the dimensionless function $F(P)$. If the minimum is at $P = 0$, as it is the case for the non-interacting gas of eq. (3.4), then the ground state is paramagnetic with an equal density of spin-up and spin-down particles everywhere. If instead the minimum value corresponds to $P \neq 0$ (degenerate with the value at $-P$), then the ground state is ferromagnetic with a majority of spin-up particles in half of the volume and a symmetric majority of spin-down particles in the other half. The transition can be determined by investigating the behavior of $F(P)$ at small polarization

$$F(P) = 1 + \frac{10}{9\pi}k_F a + \frac{5}{9}\left(1 - \frac{k_F a}{\pi/2}\right)P^2 + \frac{5}{243}P^4 + \ldots\ ,$$

where we used the expansion (3.4) for the first two terms in (3.35). For the interaction parameter $k_F a$ smaller than the critical value $k_F a < \pi/2$, the minimum is indeed at $P = 0$. If instead $k_F a > \pi/2 \simeq 1.57$, the minimum is at

$$P = \pm\sqrt{\frac{27(k_F a - \pi/2)}{\pi}}\ , \tag{3.36}$$

to lowest order in $(k_F a - \pi/2)$. From the equation $dF/dP = 0$, one also finds that the value $P = \pm 1$ corresponds to the lowest energy state if $k_F a > 3\pi/2^{7/3} \simeq 1.87$. This latter state is the fully ferromagnetic ground state, where all spin-up particles occupy half of the volume V and all spin-down particles occupy the other half. The behavior of the function $F(P)$ for four different values of the interaction strength $k_F a$ is shown in Fig. 3.4.

The behavior of $F(P)$ shows a quantum phase transition from a paramagnetic to a ferromagnetic state. The term "quantum" refers to phase transitions that take place at $T = 0$ and that are driven by a parameter in the Hamiltonian instead of by the temperature. In our case the relevant parameter is the interaction strength $k_F a$, that can be changed either by tuning the value of the scattering length a or more simply by varying the density and thus the value of the Fermi wave vector k_F. There are some important aspects of the phase transitions that are worth stressing:

- a) The phase transition is characterized by an order parameter (in our case the polarization P), that is different from zero in the ordered phase and is equal to zero in the disordered one.

- b) The appearance of the order parameter is associated with the spontaneous breaking of a

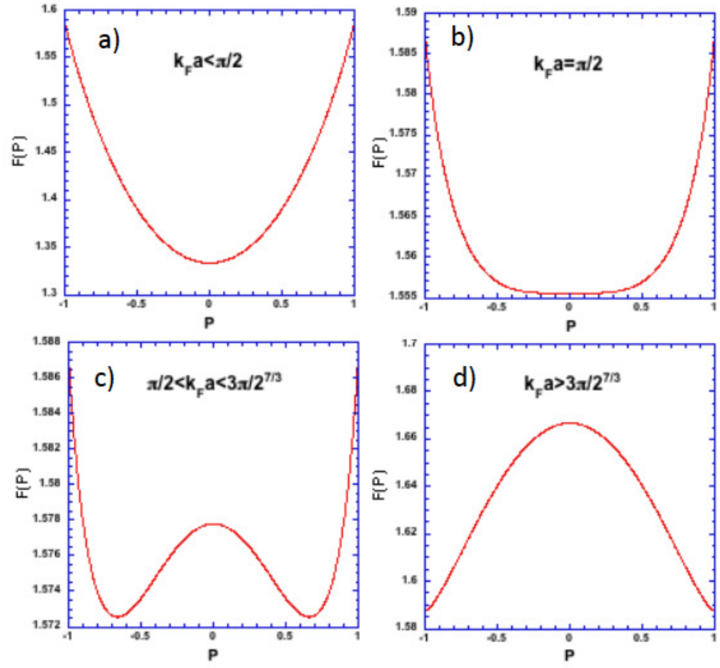

Figure 3.4: Function $F(P)$ for different values of $k_F a$.

symmetry of the Hamiltonian. In our case this is the discrete symmetry $\uparrow\leftrightarrows\downarrow$: in the ordered phase the system spontaneously picks up a finite value of P in half of the volume.

- c) The transition is continuous. The order parameter grows continuously from the value $P = 0$ to the maximum value $P = 1$.

- d) The phase transition is associated with a diverging susceptibility. In our case the susceptibility χ is inversely proportional to the coefficient of the P^2 term in eq. (3.35)

$$\frac{1}{3} n\epsilon_F \left(1 - \frac{k_F a}{\pi/2}\right) P^2 \equiv \frac{1}{2}\frac{1}{\chi} m^2 ,$$

where we introduced the magnetization density $m = nP$ and

$$\chi = \frac{3n}{2\epsilon_F} \frac{\pi/2}{(\pi/2 - k_F a)} ,$$

in analogy with the magnetic susceptibility of Sec. A.

In the paramagnetic phase the value of the susceptibility determines how easy it is to magnetize the system for a given strength of the external field. At the critical point χ diverges, implying that large values of m are possible even for small intensities of the external field. Beyond the critical point a finite value of m is present at equilibrium even in the absence of applied external fields.

The unbalanced configuration where $N_\downarrow > N_\uparrow$ can be dealt with by introducing a fictitious external field H that produces the desired polarization P. In analogy with the electron gas magnetic response we write

$$\frac{E_0^{HF}(P)}{V} - HnP = \frac{3}{5} n \epsilon_F \Big[F(P) - hP \Big] ,$$

where $h = 5H/(3\epsilon_F)$. For a given strength of the effective field h the equilibrium value of P corresponds to the minimum of the function $F(P) - hP$ obtained from the equation

$$\frac{5}{6}(1+P)^{2/3} - \frac{5}{6}(1-P)^{2/3} - \frac{20}{9\pi} k_F a P = h \ . \tag{3.37}$$

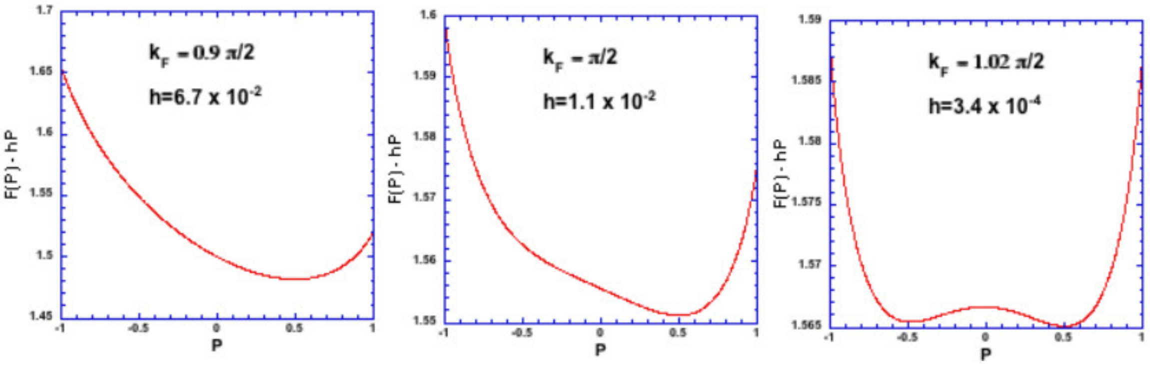

Figure 3.5: Behavior of the functional $F(P) - hP$ around the interaction strength $k_F a = \pi/2$ at a fixed polarization $P = 0.5$. The reported values of h correspond to the solutions of eq. (3.37).

If, for example, one considers the solution of eq. (3.37) corresponding to $P = 0.5$ for different values of the interaction strength $k_F a$, one obtains the curves of $F(P) - hP$ shown in Fig. 3.5. We notice that $P = 0.5$ remains the absolute minimum also for values of $k_F a$ slightly larger than $\pi/2$. However, for increasing values of the interaction strength, a second relative minimum starts to appear and the effective field h becomes vanishingly small. At some $k_F a > \pi/2$, the two minima at $P = 0.5$ and $P = -0.5$ become degenerate and $h = 0$. At this point the system separates into two volumes, one with polarization $P = 0.5$ and the other with polarization $P = -0.5$. The relative proportion of the volumes is such that the overall polarization $P = 0.5$ is preserved. For larger values of $k_F a$, the absolute value of the polarization in the two islands increases similarly to the balanced case until, at $k_F a = 3\pi/2^{7/3}$, the two islands are fully polarized with $P = \pm 1$. The second minimum, which becomes degenerate at $h = 0$, is at some finite negative polarization. The transition in this case is not a continuous one, but of first order.

In the parameter plane $(k_F a, P)$ the first order transition line corresponds to eq. (3.37) with $h = 0$. The phase diagram is depicted in Fig. 3.6.

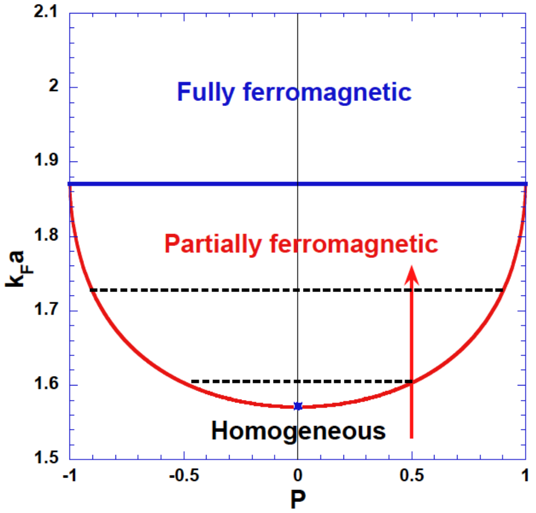

Figure 3.6: Phase diagram of the Stoner model in the $(k_F a, P)$ plane. The blue point at $P = 0$ corresponds to the continuous transition, while the red line marks the first-order transition line. This line separates the region of the homogeneous gas from the region where the system is composed of two islands with opposite polarization (horizontal dashed lines). Above the blue horizontal line at $k_F a = 3\pi/2^{7/3}$ the gas is fully ferromagnetic with two islands at $P = \pm 1$. The red arrow shows the trajectory at $P = 0.5$ described in the text.

3.4 Supplements

3.4.1 Density matrix and statistical ensembles

The density matrix over a certain set of independent states $|\psi_i\rangle$ is an hermitian operator defined as

$$\rho(t) = \sum_i p_i |\psi_i(t)\rangle\langle\psi_i(t)| \ , \tag{3.38}$$

where $|\psi_i(t)\rangle$ is the time evolution of the state $|\psi_i\rangle$. The coefficients p_i should obey the following conditions: $p_i \geq 0$ and $\sum_i p_i = 1$. In particular, this latter condition makes the trace of the density matrix equal to unity: $\mathrm{Tr}\,(\rho(t)) = \sum_i p_i = 1$, where we assumed that the states $|\psi_i(t)\rangle$ are normalized ($\langle\psi_i(t)|\psi_i(t)\rangle = 1$).

The density matrix generalizes the quantum mechanical evolution to the case where the knowledge of the initial state of the system is incomplete and the p_i's are the probabilities providing the occurrence of a given state $|\psi_i\rangle$ in the ensemble. In this respect an important distinction should be underlined:

- Pure states: If in the sum (3.38) there is only one state $|\psi\rangle$ occurring with probability one, then the density matrix $\rho(t) = |\psi(t)\rangle\langle\psi(t)|$ coincides with the projector operator on the state at time t and the following identity holds: $\rho^2 = \rho$. This case corresponds to a full knowledge of the initial state.

- Mixed states: If there are at least two states in the sum (3.38), then the system is prepared in a mixed state. In this general case one finds: $\rho^2 \neq \rho$.

From the time evolution of the states $|\psi_i\rangle$ according to the Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle$, one immediately derives the time-evolution equation for the density matrix (Liouville's equation)

$$i\hbar\frac{\partial}{\partial t}\rho(t) = [H, \rho(t)] \ .$$

Once the above equation is solved for a given initial condition $\rho(0)$ at time $t = 0$, the average value at time t of any observable O on the ensemble can be evaluated using

$$\langle O\rangle(t) \equiv \sum_i p_i \langle\psi_i(t)|O|\psi_i(t)\rangle = \mathrm{Tr}(\rho(t)O) \ .$$

Equilibrium states are such that the corresponding density matrix ρ_{eq} should be independent of time: $\frac{\partial}{\partial t}\rho_{eq} = 0$. On the basis of Liouville's equation this condition implies:

- the Hamiltonian H does not depend on time, *i.e.* $\frac{\partial}{\partial t}H = 0$
- the density matrix commutes with the Hamiltonian, *i.e.* $[H, \rho_{eq}] = 0$.

  This latter condition is satisfied if ρ_{eq} is a function of H (and in general of other operators commuting with H).

At equilibrium, the following chain of identities involving the expectation values of an observable O is verified under very general conditions

$$\langle O \rangle = \overline{\langle O \rangle (t)} = \langle \overline{O(t)} \rangle = \overline{O(t)} \; ,$$

where $\langle O \rangle = \mathrm{Tr}(\rho_{eq} O)$ is the statistical average, $O(t) = \langle \psi(t)|O|\psi(t)\rangle$ is the expectation value of the operator O on the state of the system at time t and $\overline{\cdots}$ stands for time average. The first identity follows from the time independence of ρ_{eq}, the second from the independence of statistical and time averages and the third holds if the system is ergodic, meaning that the state of the system visits all possible states with the proper frequency. The above chain of identities ensures that the time averages of an observable obtained in experiments can be calculated using statistical averages over properly defined ensembles.

Thermodynamic ensembles correspond to equilibrium states defined by density matrices ρ_{eq} which are constructed using the eigenstates $|\varphi_n\rangle$ of the Hamiltonian, *i.e.* states satisfying the Schrödinger equation $H|\varphi_n\rangle = E_n|\varphi_n\rangle$. The specific equilibrium ensembles are:

- Microcanonical ensemble: the density matrix is defined as $\rho_{eq} = \sum_n \rho_{nn} |\varphi_n\rangle\langle\varphi_n|$ and

$$\rho_{nn} = \begin{cases} \frac{1}{g(E)\Delta} & \text{if } E \leq E_n \leq E + \Delta \\ 0 & \text{otherwise} \end{cases} \; , \tag{3.39}$$

  where $g(E)\Delta$ is defined as the number of eigenstates E_n in the energy interval from E to $E + \Delta$ ($\Delta \ll E$) in terms of the density of states $g(E)$. We notice that the above density matrix assigns the same probability p_i to all the eigenstates lying within the energy shell at some given energy

E. The connection with thermodynamics is provided by the following equation for the entropy (k_B is Boltzmann's constant)

$$S \equiv -k_B \langle \log(\rho_{eq}) \rangle = -k_B \mathrm{Tr}\left(\rho_{eq} \log(\rho_{eq})\right) \ . \tag{3.40}$$

From Eq. (3.39) for the matrix elements of ρ_{eq} we obtain in the microcanonical ensemble

$$S(E,V,N) = -k_B \sum_n \rho_{nn} \log(\rho_{nn}) = k_B \log\left(g(E)\Delta\right) \ ,$$

which coincides with the definition of S in classical statistical mechanics as a function of energy, volume V and number of particles N in the system. We remind at this point that, apart from contributions which vanish in the thermodynamic limit of the number of particles $N \to \infty$, one has $\log\left(g(E)\Delta\right) \simeq \log\left(G(E)\right)$, where $G(E)$ is the total number of states having energy $E_n \leq E$.

- Canonical ensemble: the density matrix is written as $\rho_{eq} = \sum_n \rho_{nn} |\varphi_n\rangle\langle\varphi_n|$, where the diagonal matrix elements are given by

  $$\rho_{nn} = \frac{e^{-\beta E_n}}{Z_C} \ .$$

  Here $\beta = \frac{1}{k_B T}$ is the inverse temperature and $Z_C = \sum_n e^{-\beta E_n}$ is the partition function which ensures the normalization condition $\mathrm{Tr}(\rho_{eq}) = 1$ of the density matrix. From expression (3.40) for the thermodynamic entropy one gets

  $$S(T,V,N) = \frac{1}{T} \sum_n \rho_{nn} E_n + k_B \log Z_C = \frac{U}{T} + k_B \log Z_C \ .$$

  where we used the definition of internal energy $U = \mathrm{Tr}(\rho_{eq} H)$. From the equation $F = U - TS$ defining the Helmoltz free energy we get the useful relationship

  $$F(T,V,N) = -k_B T \log Z_C \ .$$

- Grand-canonical ensemble: from the complete set of common eigenstates of the operators H

and N one constructs the following density matrix $\rho_{eq} = \sum_n \rho_{nn} |\varphi_n\rangle\langle\varphi_n|$, where

$$\rho_{nn} = \frac{e^{-\beta(E_n - \mu N_n)}}{Z_{GC}} \ .$$

Here μ is the chemical potential multiplying the eigenvalues N_n of the number of particles operator $N|\varphi_n\rangle = N_n|\varphi_n\rangle$ and $Z_{GC} = \sum_n e^{-\beta(E_n - \mu N_n)}$ is the grand-canonical partition function. For the entropy we get in this case

$$S(T, V, \mu) = \frac{U}{T} - \frac{\mu N}{T} + k_B \log Z_{GC} \ ,$$

where we used the equation $N = \mathrm{Tr}(\rho_{eq} N)$ for the average number of particles. From the thermodynamic relation $\Omega = U - TS - \mu N$ defining the grand-canonical potential Ω one recovers the identity

$$\Omega(T, V, \mu) = -k_B T \log Z_{GC} \ .$$

Notice that from the Gibbs-Duhem relation, $U = TS - pV + \mu N$, one finds the useful relation $\Omega = -pV$ for the grand-canonical potential.

3.4.2 Diffusion amplitude and scattering length

Let us consider the quantum mechanical problem of one particle impinging on a potential $V(r)$ that we assume spherically symmetric. Let the incident particle be described by a plane wave e^{ikz} along the z-direction. In the stationary state and far away from the region of the potential $V(r)$ the particle will be described by the wavefunction

$$\psi(\mathbf{r}) = e^{ikz} + \frac{f(\theta)}{r} e^{ikr} \ , \tag{3.41}$$

obtained from the superposition of the incident and the scattered wave. Here θ is the angle between the direction of the incident wave vector $\mathbf{k}$ (chosen along the z-axis) and the scattered wave vector $\mathbf{k}'$ (conservation of energy implies that $|\mathbf{k}'| = |\mathbf{k}|$). The scattering amplitude $f(\theta)$ can be in general decomposed into the angular momentum components

$$f(\theta) = \sum_{\ell=0}^{\infty} (2\ell+1) P_\ell(\cos\theta) f_\ell \ ,$$

where $P_\ell(x)$ are the Legendre polynomials. Notice that the factors f_ℓ have the dimension of a length. At low energy (*i.e.* for $k \to 0$) only the $\ell = 0$ component in the above expansion is relevant and from Eq. (3.41) one finds in this limit ($P_0(x) = 1$)

$$\psi(\mathbf{r}) = 1 + \frac{f_0}{r} \ . \tag{3.42}$$

The fact that s-wave scattering dominates at low energy can be easily seen from the Schrödinger equation of the relative motion between the two interacting particles

$$\left(-\frac{\hbar^2}{m} \nabla^2 + V(r) \right) \psi(\mathbf{r}) = E \psi(\mathbf{r}) \ .$$

By writing the wavefunction in terms of spherical harmonics: $\psi(\mathbf{r}) = \phi_\ell(r) Y_{\ell,m}(\theta, \varphi)$ one gets the following radial equation

$$-\frac{\hbar^2}{m} \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \frac{\ell(\ell+1)}{r^2} \right) \phi_\ell(r) + V(r)\phi_\ell(r) = E\phi_\ell(r) \ . \tag{3.43}$$

Short-range interactions between atoms are well modeled by a van der Waals potential of the form $V(r) = \epsilon \left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \right]$, which at large distances decays as $1/r^6$. At low energy, the centrifugal barrier in Eq. (3.43) is strong enough to avoid that particles with $\ell > 0$ can approach each other at small distance thereby experiencing the effects of the potential. So, particles in channels with $\ell > 0$ behave as free particles and only the ones in $\ell = 0$ interact through the potential $V(r)$. By choosing $\ell = 0$ in Eq. (3.43) and by considering at the same time the asymptotic region $r \gg r_0$ and the low energy limit, one gets the simplified equation

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} \right) \phi_0(r) = 0 \ .$$

The solution is given by $\phi_0(r) = \text{const} \left(1 - \frac{a}{r}\right)$, where a is by definition the s-wave scattering length.

By comparing this solution with the result in Eq. (3.42), one identifies the $\ell = 0$ component of the scattering amplitude with $-a$.

The pseudopotential $V(\mathbf{r}) = g\delta(\mathbf{r})$ is introduced in order to reproduce the low-energy scattering properties of the true interatomic potential. By writing the energy $E = \frac{\hbar^2 k^2}{m}$ in terms of the scattering wave vector k, one can recast the Schrödinger equation in the form

$$\frac{\hbar^2}{m}\left(\nabla^2 + k^2\right)\psi(\mathbf{r}) = V(\mathbf{r})\psi(\mathbf{r}) \ , \tag{3.44}$$

which admits the formal solution

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \int d\mathbf{r}' G(\mathbf{r}-\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}') \ . \tag{3.45}$$

Here the plane wave solves the homogeneous equation given by the left hand side of Eq. (3.44), while the Green's function $G(\mathbf{r})$ satisfies the equation

$$\frac{\hbar^2}{m}\left(\nabla^2 + k^2\right)G(\mathbf{r}) = -\delta(\mathbf{r}) \ ,$$

with the solution $G(\mathbf{r}) = \frac{m}{4\pi\hbar^2}\frac{e^{ikr}}{r}$. By plugging this result into Eq. (3.45) one finds

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{4\pi\hbar^2}\int d\mathbf{r}' \ \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}V(\mathbf{r}')\psi(\mathbf{r}') \ .$$

If one now substitutes for $V(\mathbf{r}')$ the pseudopotential and, using the Born approximation, replaces the wave function $\psi(\mathbf{r}')$ with the incident plane wave $e^{i\mathbf{k}\cdot\mathbf{r}'}$, the above equation becomes

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{mg}{4\pi\hbar^2}\frac{e^{ikr}}{r} \ .$$

In the low-energy limit this result reproduces the s-wave scattering result (3.42) if the coupling constant g is given by $g = \frac{4\pi\hbar^2 a}{m}$.

3.5 Problems

- 1. Calculate the magnetic susceptibility of an electron gas as a function of temperature and verify that at high temperatures one recovers Curie's law $\chi \propto 1/T$.

  Solution: The effects of a magnetic field $\mathbf{H} = H\hat{z}$ on the single-particle energies $\epsilon_k = \frac{\hbar^2 k^2}{2m}$ is to shift them by the Zeeman splitting: $\epsilon_k \to \epsilon_k \pm \mu_B H$, where $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton and the upper (lower) sign refers to spin-up (down) particles. In the grand-canonical picture of a free gas the effect of $\mathbf{H}$ corresponds to a shift $\mu \to \mu \mp \mu_B H$ of the chemical potential. One can write the following expression for the thermodynamic potential in the presence of the magnetic field $\mathbf{H}$

  $$\Omega(T, V, \mu, \mathbf{H}) = \frac{1}{2}\Omega_0(T, V, \mu - \mu_B H) + \frac{1}{2}\Omega_0(T, V, \mu + \mu_B H) \; ,$$

  where $\Omega_0(T, V, \mu)$ is the grand-canonical potential in the absence of $\mathbf{H}$ and the factor 1/2 reflects the fact that the two contributions refer to systems with spin degeneracy $g_s = 1$ instead of $g_s = 2$. For small fields, $\mu_B H \ll \epsilon_F$, one can write

  $$\Omega(T, V, \mu, \mathbf{H}) \simeq \Omega_0(T, V, \mu) + \frac{1}{2}(\mu_B H)^2 \left(\frac{\partial^2 \Omega_0}{\partial \mu^2}\right)_{T,V} \; ,$$

  yielding the result

  $$M_z = -\left(\frac{\partial \Omega}{\partial H}\right)_{T,V} = -\mu_B^2 \left(\frac{\partial^2 \Omega_0}{\partial \mu^2}\right)_{T,V} H$$

  for the magnetization parallel to the field. By using the thermodynamic relation $N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$, one obtains the following result for the magnetic susceptibility

  $$\chi = \frac{\mu_B^2}{V} \left(\frac{\partial N}{\partial \mu}\right)_{T,V} \; .$$

  At high temperature the fugacity of the two-component free Fermi gas is approximated by $z \simeq \frac{n\lambda_T^3}{2}\left(1 + \frac{n\lambda_T^3}{2^{5/2}}\right)$, or equivalently $\frac{\mu}{k_B T} \simeq \log(n\lambda_T^3/2) + n\lambda_T^3/2^{5/2}$ for the chemical potential. The derivative with respect to the number of particles gives

  $$\frac{\partial \mu}{\partial N} = \frac{k_B T}{N}\left(1 + \frac{n\lambda_T^3}{2^{5/2}}\right) \; .$$

  The susceptibility is then given by

  $$\chi = \frac{\mu_B^2 n}{k_B T}\left(1 - \frac{n\lambda_T^3}{2^{5/2}}\right)$$

  and in the limit $n\lambda_T^3 \ll 1$ one indeed recovers Curie's law: $\chi = \frac{\mu_B^2 n}{k_B T}$.

- 2. The density of states of a non-interacting gas is defined as

  $g(\epsilon) = \sum_\alpha \delta(\epsilon - \epsilon_\alpha)$,

  where ϵ_α is the energy of the single-particle state $|\alpha\rangle$. Determine the density of states of a homogeneous gas in three dimensions and write the expressions for the total number of particles, internal energy and thermodynamic potential of a Fermi gas in terms of the density of states $g(\epsilon)$.

Solution: From the definition one has $g(\epsilon) = \sum_{\mathbf{k}\sigma} \delta(\epsilon - \epsilon_k)$, where the sum runs over the wave vectors $\mathbf{k}$ and the components of the spin σ and $\epsilon_k = \frac{\hbar^2 k^2}{2m}$. By replacing the sum with an integral when the thermodynamic limit is considered, one finds the result

$$g(\epsilon) = \frac{V g_s}{\sqrt{2}\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \int_0^\infty d\epsilon_k \sqrt{\epsilon_k}\, \delta(\epsilon - \epsilon_k) = \frac{V g_s}{\sqrt{2}\pi^2} \left(\frac{m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon}\,,$$

where $g_s = 2s + 1$ is the spin degeneracy. It is immediate to verify the relation

$$N = \sum_{\mathbf{k}\sigma} \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} = \sum_{\mathbf{k}\sigma} \int_0^\infty d\epsilon \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \delta(\epsilon - \epsilon_k) = \int_0^\infty d\epsilon\, g(\epsilon) \frac{1}{e^{\beta(\epsilon - \mu)} + 1}\,,$$

and analogous ones for the internal energy

$$U = \sum_{\mathbf{k}\sigma} \frac{\epsilon_k}{e^{\beta(\epsilon_k - \mu)} + 1} = \int_0^\infty d\epsilon\, g(\epsilon) \frac{\epsilon}{e^{\beta(\epsilon - \mu)} + 1}\,,$$

and for the thermodynamic potential

$$\Omega = -k_B T \sum_{\mathbf{k}\sigma} \log\left(1 + e^{-\beta(\epsilon_k - \mu)}\right) = -k_B T \int_0^\infty d\epsilon\, g(\epsilon) \log\left(1 + e^{-\beta(\epsilon - \mu)}\right)\,.$$

- 3. Show that for a system with density of states $g(\epsilon) = A\epsilon^s$, with $s > 0$ and A a constant with the proper dimensions, the thermodynamic potential and internal energy satisfy the relation $-\Omega = U/(s + 1)$.

Solution: From the previous problem one can write

$$-\Omega = k_B T \int_0^\infty d\epsilon\, A\epsilon^s \log\left(1 + e^{-\beta(\epsilon - \mu)}\right)\,.$$

By using integration by parts one finds

$$-\Omega = k_B T \frac{A}{s+1} \left[\epsilon^{s+1} \log\left(1 + e^{-\beta(\epsilon - \mu)}\right)\right]_0^\infty + \frac{1}{s+1} \int_0^\infty d\epsilon\, A\epsilon^s \frac{\epsilon}{e^{\beta(\epsilon - \mu)} + 1}\,.$$

Since the term in the square bracket vanishes, we are left with the required relation $-\Omega = \frac{U}{s+1}$.

- 4. Determine the density of states $g(\epsilon)$ of a non-interacting gas confined by an isotropic harmonic potential $U(\mathbf{r}) = m\omega^2 r^2/2$ for energies $\epsilon \gg \hbar\omega$, the level spacing of the harmonic oscillator states.

Solution: The eigenenergies are given by $\epsilon_{n_x n_y n_z} = \hbar\omega\,(n_x + n_y + n_z + 3/2)$, where $n_{x,y,z} = 0, 1, 2, \dots$ are non negative integers, and the density of states results in the sum

$$g(\epsilon) = \sum_{n_x n_y n_z} \delta\left[\epsilon - \hbar\omega(n_x + n_y + n_z + 3/2)\right] \ .$$

In the limit $\epsilon \gg \hbar\omega$ the sums can be converted into integrals and by changing variables one writes

$$g(\epsilon) = \int_0^\infty dn \int_0^n dn_1 \int_0^{n-n_1} dn_2 \; \delta\left[\epsilon - \hbar\omega(n + 3/2)\right] = \int_0^\infty dn \; \frac{n^2}{2} \delta\left[\epsilon - \hbar\omega(n + 3/2)\right] = \frac{1}{2}\frac{\epsilon^2}{(\hbar\omega)^3} \ ,$$

where, following the replacement of sums by integrals, we neglect 3/2 compared to $\epsilon/\hbar\omega$.

- 5. Calculate the expression of the Fermi energy of a two-component non-interacting Fermi gas in the harmonic oscillator potential $U(\mathbf{r}) = m\omega^2 r^2/2$. Consider the limit where $N_\sigma \gg 1$.

Solution: The approach to the thermodynamic limit, $N_\sigma \gg 1$, allows one to use the density of states obtained in problem 4. At $T = 0$ the number of particles for each spin component is given by

$$N_\sigma = \int_0^{\epsilon_{F\sigma}} d\epsilon \; \frac{1}{2}\frac{\epsilon^2}{(\hbar\omega)^3} = \frac{1}{6}\frac{\epsilon_{F\sigma}^3}{(\hbar\omega)^3} \ ,$$

which yields for the Fermi energy

$$\epsilon_{F\sigma} = \hbar\omega(6N_\sigma)^{1/3} \ .$$

The above results holds if $\epsilon_{F\sigma} \gg \hbar\omega$, the condition ensuring that the level spacing energy of the harmonic oscillator is safely neglected.

- 6. Show that the entropy of a non-interacting Fermi gas can be written as

  $S = k_B \sum_\alpha [-\langle n_\alpha\rangle \log\langle n_\alpha\rangle - (1 - \langle n_\alpha\rangle)\log(1 - \langle n_\alpha\rangle)]$,

  where $\langle n_\alpha\rangle$ is the mean occupation number of the single-particle state $|\alpha\rangle$ having energy ϵ_α.

  Show that minimization of S with respect to $\langle n_\alpha\rangle$, with the constraints that the total number of particles and the total energy remain fixed, gives the Fermi distribution function.

Solution: We use combinatorial analysis: let $g_{\bar\alpha}$ be the degeneracy of the single-particle level with energy $\epsilon_{\bar\alpha}$ and $N_{\bar\alpha}$ the number of particles occupying the $g_{\bar\alpha}$ levels. The average occupation of the level is defined as $\langle n_{\bar\alpha}\rangle = \frac{N_{\bar\alpha}}{g_{\bar\alpha}}$. The total number of particles reads: $N = \sum_{\bar\alpha} g_{\bar\alpha}\langle n_{\bar\alpha}\rangle = \sum_\alpha \langle n_\alpha\rangle$, where we introduced the sum over the total number of levels $\sum_\alpha = \sum_{\bar\alpha} g_{\bar\alpha}$. Since we are dealing with fermions, the number of ways we can accommodate $N_{\bar\alpha}$ particles into $g_{\bar\alpha}$ is given by the product $g_{\bar\alpha}(g_{\bar\alpha} - 1)\dots(g_{\bar\alpha} - N_{\bar\alpha} + 1)$. This is because for the first particle we have $g_{\bar\alpha}$ possibilities, for the second particle only $g_{\bar\alpha} - 1$ and so forth. Since particles are indistinguishable, the total number of different ways to accommodate the particles is

$$W_{\bar{\alpha}} = \frac{g_{\bar{\alpha}}!}{(g_{\bar{\alpha}} - N_{\bar{\alpha}})! N_{\bar{\alpha}}!} \ .$$

By considering all $\bar{\alpha}$ groups of levels $W = \prod_{\bar{\alpha}} W_{\bar{\alpha}}$. Entropy is given by $S = k_B \log W$ and by using Stirling's expansion $\log n! \simeq n \log n - n$ one finds

$$\begin{aligned} S &= k_B \sum_{\bar{\alpha}} \left[-g_{\bar{\alpha}} \log \left(1 - \frac{N_{\bar{\alpha}}}{g_{\bar{\alpha}}} \right) + N_{\bar{\alpha}} \log \left(\frac{g_{\bar{\alpha}}}{N_{\bar{\alpha}}} - 1 \right) \right] \\ &= k_B \sum_{\bar{\alpha}} g_{\bar{\alpha}} \left[-(1 - \langle n_{\bar{\alpha}} \rangle) \log (1 - \langle n_{\bar{\alpha}} \rangle) - \langle n_{\bar{\alpha}} \rangle \log \langle n_{\bar{\alpha}} \rangle \right] \\ &= k_B \sum_{\alpha} \left[-(1 - \langle n_{\alpha} \rangle) \log (1 - \langle n_{\alpha} \rangle) - \langle n_{\alpha} \rangle \log \langle n_{\alpha} \rangle \right] \ . \end{aligned}$$

- 7. Calculate the third coefficient of the virial expansion of a homogeneous non-interacting Fermi gas.

Solution: From the expansions

$$\begin{aligned} \frac{n\lambda_T^3}{g_s} &\simeq z \left(1 - \frac{z}{2^{3/2}} + \frac{z^2}{3^{3/2}} \right) \\ \frac{p\lambda_T^3}{g_s k_B T} &\simeq z \left(1 - \frac{z}{2^{5/2}} + \frac{z^2}{3^{5/2}} \right) \ , \end{aligned}$$

one gets for the ratio $p/(nk_BT)$

$$\frac{p}{nk_BT} \simeq 1 + \frac{z}{2^{5/2}} + z^2 \left(\frac{1}{2^4} - \frac{2}{3^{5/2}} \right) \ .$$

By solving for z in terms of $n\lambda_T^3$ one finds to order $(n\lambda_T^3)^2$

$$\frac{p}{nk_BT} \simeq 1 + \frac{1}{4\sqrt{2}} \frac{n\lambda_T^3}{g_s} - \frac{16 - 9\sqrt{3}}{72\sqrt{3}} \left(\frac{n\lambda_T^3}{g_s} \right)^2 \ .$$

- 8. Solve numerically the equation of state of a non-interacting Fermi gas and determine the temperature dependence of μ, U and S for a fixed number of particles N_σ (see Fig. 3.3).

Solution: We consider the dimensionless quantities: $\tilde{\mu} = \mu/\epsilon_F$, $\tilde{U} = U/(3N_\sigma k_B T/2)$, $\tilde{S} = S/(N_\sigma k_B)$ and $t = T/T_F$. For a fixed density $n_\sigma = \frac{N_\sigma}{V}$, the function $\tilde{\mu}(t)$ is obtained by inverting the equation

$$\frac{4}{3\sqrt{\pi}} = t^{3/2} f_{3/2}(e^{t\tilde{\mu}}) \ .$$

Once $\tilde{\mu}(t)$ is known, one gets immediately

$$\tilde{U}(t) = \frac{f_{5/2}(e^{t\tilde{\mu}})}{f_{3/2}(e^{t\tilde{\mu}})} \ ,$$

and

$$\tilde{S}(t) = \frac{5}{2}\frac{f_{5/2}(e^{t\tilde{\mu}})}{f_{3/2}(e^{t\tilde{\mu}})} - t\tilde{\mu} \; .$$

- 9. Calculate the isothermal compressibility κ_T of a homogeneous non-interacting Fermi gas in the limit $T \ll T_F$ and verify the fluctuation-dissipation relation given by eq. (3.27).

Solution: For a single-component Fermi gas one has the following result for the pressure at low temperatures

$$p \simeq \frac{2}{5} n\epsilon_F \left(1 + \frac{5\pi^2}{12}\frac{T^2}{T_F^2}\right) \; ,$$

where $\epsilon_F = \frac{\hbar^2}{2m}(6\pi^2 n)^{2/3}$ is the Fermi energy and $T_F = \epsilon_F/k_B$ the Fermi temperature. For the isothermal compressibility one then finds

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{3}{2n\epsilon_F}\left(1 - \frac{\pi^2}{12}\frac{T^2}{T_F^2}\right) \; .$$

Eq. (3.27) then reads

$$\frac{3}{2}\frac{T}{T_F}\left(1 - \frac{\pi^2}{12}\frac{T^2}{T_F^2}\right) = 1 - \frac{1}{N}\sum_{\mathbf{k}} \frac{1}{(e^{\beta(\epsilon_k - \mu)} + 1)^2} \; .$$

The sum on the right hand side can be written as

$$\frac{1}{N}\sum_{\mathbf{k}} \frac{1}{(e^{\beta(\epsilon_k - \mu)} + 1)^2} = \frac{2}{\sqrt{\pi} n\lambda_T^3}\int_0^\infty dx \frac{\sqrt{x}}{(z^{-1}e^x + 1)^2} = \frac{1}{n\lambda_T^3}\left(f_{3/2}(z) - f_{1/2}(z)\right) \; ,$$

where we used the relation $\frac{1}{(z^{-1}e^x+1)^2} = \frac{1}{z^{-1}e^x+1} + \frac{d}{dx}\frac{1}{z^{-1}e^x+1}$ and integration by parts. In the low-temperature limit the right hand side of the above expression gives: $1 - \frac{3}{2}\frac{T}{T_F}\left(1 - \frac{\pi^2}{12}\frac{T^2}{T_F^2}\right)$, where we used the expansion $\mu = \epsilon_F\left(1 - \frac{\pi^2}{12}\frac{T^2}{T_F^2}\right)$ of the chemical potential. Then eq. (3.27) follows directly.

- 10. Show that the HF ground-state energy (3.33) for the contact interaction potential $V(\mathbf{r}) = g\delta(\mathbf{r})$ coincides with the result of first order perturbation theory, where the energy shift is evaluated from the expectation value of the interaction term in the Hamiltonian on the unperturbed Fermi sea state $|FS\rangle$.

Solution: From first-order perturbation theory the ground-state energy is given by

$$E = E_0 + \langle FS|H_{int}|FS\rangle \; ,$$

where $E_0 = \frac{3}{5}N_\uparrow\epsilon_{F\uparrow} + \frac{3}{5}N_\downarrow\epsilon_{F\downarrow}$ is the unperturbed energy and

$$H_{int} = \frac{g}{2V}\sum_{\sigma\sigma'}\sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} a^\dagger_{\mathbf{k}\sigma} a^\dagger_{\mathbf{k}'-\mathbf{q}\sigma'} a_{\mathbf{k}'\sigma'} a_{\mathbf{k}-\mathbf{q}\sigma}$$

is the operator associated to the perturbation. We notice that the contributions coming from $\sigma = \sigma'$ vanish because

$$\sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} a^{\dagger}_{\mathbf{k}\sigma} a^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma} a_{\mathbf{k}'\sigma} a_{\mathbf{k}-\mathbf{q}\sigma} = - \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} a^{\dagger}_{\mathbf{k}\sigma} a^{\dagger}_{\mathbf{k}'-\mathbf{q}\sigma} a_{\mathbf{k}'\sigma} a_{\mathbf{k}-\mathbf{q}\sigma} \ .$$

Thus, only the terms with $\sigma \neq \sigma'$ contribute to H_{int}

$$H_{int} = \frac{g}{2V} \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} a^{\dagger}_{\mathbf{k}\uparrow} a^{\dagger}_{\mathbf{k}'-\mathbf{q}\downarrow} a_{\mathbf{k}'\downarrow} a_{\mathbf{k}-\mathbf{q}\uparrow} + a^{\dagger}_{\mathbf{k}\downarrow} a^{\dagger}_{\mathbf{k}'-\mathbf{q}\uparrow} a_{\mathbf{k}'\uparrow} a_{\mathbf{k}-\mathbf{q}\downarrow} \ .$$

The matrix element of H_{int} of the Fermi sea $|FS\rangle$ yields then

$$\langle FS|H_{int}|FS\rangle = \frac{g}{V} \sum_{\mathbf{k}\mathbf{k}'} \langle FS| a^{\dagger}_{\mathbf{k}\uparrow} a_{\mathbf{k}\uparrow} a^{\dagger}_{\mathbf{k}'\downarrow} a_{\mathbf{k}'\downarrow} |FS\rangle = \frac{g}{V} N_{\uparrow} N_{\downarrow} \ ,$$

which coincides with the HF result (3.33).

Chapter 4

Bose systems

We consider systems of bosonic particles. We study a non-interacting gas at finite temperature and we show that it undergoes a phase transition, named Bose-Einstein condensation (BEC), driven by purely statistical effects. Interactions are introduced at the level of mean-field theory providing a description valid in the regime of weak coupling. For inhomogeneous condensates we derive the Gross-Pitaevskii equation equivalent to Hartree-Fock theory. We develop the formalism of canonical transformation and of Bogolubov quasiparticles, which give a correct description of the system at very low temperatures. We discuss then superfluidity and how it is related to the existence of collective excitations through the Landau criterium. The structure of the chapter is as follows:

- Non-interacting gas and Bose-Einstein condensation.
    - Condensate states and coherent states.
    - Bose distribution and BEC transition temperature.
    - Thermodynamics below and above T_c.
    - High temperature behavior and virial expansion.
    - Fluctuations of the condensate and of the total number of particles.
    - Pair correlation function and off-diagonal long-range order.
- Interacting gas: mean-field theory.
    - Hartree-Fock theory at finite T and corrections to thermodynamics.

- Hartree-Fock theory at $T = 0$ and Gross-Pitaevskii equation for inhomogeneous condensates.
- Bogoliubov theory and quasiparticle picture.
- Superfluidity: Landau criterium and two-fluid model.

4.1 Non-interacting gas and Bose-Einstein condensation

Similarly to the non-interacting Fermi gas discussed in Chapter 3, we consider a Bose gas of N particles in a cubic box of volume V described by the Hamiltonian

$$H = \sum_{\mathbf{k}} \epsilon_k a^\dagger_{\mathbf{k}} a_{\mathbf{k}} \ , \tag{4.1}$$

where $\epsilon_k = \hbar^2 k^2/(2m)$ is the single-particle kinetic energy. Again we consider the thermodynamic limit where $V \to \infty$ and $N \to \infty$ such as $n = N/V$ remains finite. Notice that we are considering spinless bosons ($s = 0$). The extension to integer values of s is straightforward by including the spin degeneracy $g_s = 2s + 1$.

4.1.1 Condensates and coherent states

The lowest single-particle state, corresponding to a vanishing energy ϵ_k, is the state $|\mathbf{k} = 0\rangle$, whose wave function is the constant $\varphi_0(\mathbf{r}) = 1/\sqrt{V}$. The ground state of the Hamiltonian (4.1) is realized by creating all N particles in this lowest orbital

$$|\text{con}(N)\rangle = \frac{(a^\dagger_0)^N}{\sqrt{N!}} |0\rangle \ . \tag{4.2}$$

The corresponding many-body state is called a N-particle condensate. The ground-state wave function is given by $\psi_0(\mathbf{r}_1, ..., \mathbf{r}_N) = (1/V)^{N/2}$ and the ground-state energy is $E_0 = 0$. The condensate state can be straightforwardly extended to other single-particle Hamiltonians characterized by the spectrum ϵ_α. Let $|\alpha_0\rangle$ be the state with the lowest energy ϵ_{α_0}: the condensate corresponds to all N particles sharing the same single-particle wave function, $\psi_0(\mathbf{r}_1, ..., \mathbf{r}_N) = \varphi_{\alpha_0}(\mathbf{r}_1)...\varphi_{\alpha_0}(\mathbf{r}_N)$, with an energy given by the simple product $E_0 = N\epsilon_{\alpha_0}$. The condensate state consists in a macroscopic occupation of a single-particle state, described by a macroscopic wave function.

In the grand-canonical picture the value of μ at $T = 0$ corresponds to the minimum value of $\sum_{\mathbf{k}}(\epsilon_k - \mu)n_{\mathbf{k}}$. Since the chemical potential can not be positive or otherwise the mean occupation of the $\mathbf{k} = 0$ state would become negative, one has $\mu(T = 0) = 0$ consistently with the derivative dE_0/dN obtained in the canonical picture.[1] If the number of particles is not fixed an equivalent

---

[1] Notice that if $\mu < 0$ the quantity $\sum_{\mathbf{k}}(\epsilon_k - \mu)n_{\mathbf{k}}$ is minimized by $n_{\mathbf{k}} = 0 \ \forall\mathbf{k}$, corresponding to the particle vacuum.

ground state of the grand-canonical Hamiltonian $H - \mu N$ is provided by the so-called coherent state defined as

$$|\mathrm{coh}(\Phi)\rangle = e^{(\Phi a_0^\dagger - |\Phi|^2/2)}|0\rangle = e^{-|\Phi|^2/2} \sum_{M=0}^{\infty} \frac{\Phi^M (a_0^\dagger)^M}{M!}|0\rangle \ , \tag{4.3}$$

where $\Phi = |\Phi|e^{i\phi}$ is a complex number. The coherent state represents a superposition of condensate states with a phase difference ϕ between components with M and $M+1$ particles

$$|\mathrm{coh}(\Phi)\rangle = \sum_{M=0}^{\infty} \frac{e^{-|\Phi|^2/2}|\Phi|^M e^{iM\phi}}{\sqrt{M!}}|\mathrm{con}(M)\rangle \ .$$

Furthermore, it is normalized as one can explicitly verify

$$\langle \mathrm{coh}(\Phi)|\mathrm{coh}(\Phi)\rangle = e^{-|\Phi|^2} \sum_{M=0}^{\infty} \frac{|\Phi|^{2M}}{M!} = 1 \ ,$$

and the modulus of Φ is fixed by the normalization condition

$$N = \langle \mathrm{coh}(\Phi)| \sum_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} |\mathrm{coh}(\Phi)\rangle = |\Phi|^2 \ ,$$

giving $|\Phi| = \sqrt{N}$. The projection of $|\mathrm{coh}(\Phi)\rangle$ on the condensate state $|\mathrm{con}(M)\rangle$ is thus proportional to $(N^M/M!)^{1/2}$ which, for large values of N, exhibits a very peaked maximum at $M = N$. In the thermodynamic limit $N \to \infty$, a single condensate with $M = N$ exhausts the superposition defining $|\mathrm{coh}(\Phi)\rangle$ and the two descriptions of the ground state in terms of condensate or coherent states are completely equivalent.

The coherent state possess the remarkable property that

$$a_0|\mathrm{coh}(\Phi)\rangle = \Phi|\mathrm{coh}(\Phi)\rangle \ ,$$

i.e. it is an eigenstate of the annihilation operator a_0 with eigenvalue Φ. This property can be immediately proved by using the simple result $[a_0, (a_0^\dagger)^M] = M(a_0^\dagger)^{M-1}$ for the commutator between annihilation and creation operators. As a consequence, the expectation value $\langle \mathrm{coh}(\Phi)|a_0|\mathrm{coh}(\Phi)\rangle = \Phi$ is finite on a coherent state, while it vanishes when calculated on the condensate state $|\mathrm{con}(N)\rangle$. Some important remarks are in order here:

- In the thermodynamic limit, where coherent- and condensate-state description are equivalent, the ground state of non interacting bosons allows for a finite expectation value $\Phi = \sqrt{N}e^{i\phi}$ of the annihilation operator, characterized by a well-defined value of the phase ϕ.

- States with different phase ϕ are degenerate in energy, but correspond to different states characterized by a different macroscopic variable Φ.

- The original Hamiltonian (4.1) is obviously symmetric under the gauge transformation $a^\dagger_{\mathbf{k}} \to e^{-i\alpha}a^\dagger_{\mathbf{k}}$ of the creation/annihilation operators corresponding to the transformation $|\mathbf{k}\rangle \to e^{-i\alpha}|\mathbf{k}\rangle$ of the single-particle states. However, the ground state of the system breaks the gauge symmetry by choosing a specific phase ϕ. Indeed, the gauge transformation applied to the coherent state: $|\text{coh}(\Phi)\rangle \to e^{-N/2}\sum_{M=0}^{\infty}\frac{N^{M/2}e^{i(\phi-\alpha)M}}{M!}(a^\dagger_0)^M|0\rangle$, results in a state $|\text{coh}(\Phi')\rangle$, where $\Phi' = \sqrt{N}e^{i(\phi-\alpha)}$, different from the original state $|\text{coh}(\Phi)\rangle$.

The phenomenon of broken gauge symmetry associated with the macroscopic occupation of a single-partiecle state persists also at finite temperature and marks the Bose-Einstein phase transition.

4.1.2 Bose distribution and BEC transition temperature

The grand-canonical partition function Z_{GC} can be calculated using the general formulae introduced in Section 3-B for the case of fermions. The crucial difference is that the sum over occupation numbers extends to all integers $n_{\mathbf{k}} \geq 0$ and one uses the sum of geometric series, $\sum_{n_{\mathbf{k}}=0}^{\infty} q^{n_{\mathbf{k}}} = 1/(1-q)$ for $|q| < 1$, to obtain the following result

$$\begin{aligned} Z_{GC} &= \sum_{n_{\mathbf{k}}} e^{-\beta\sum_{\mathbf{k}}(\epsilon_k-\mu)n_{\mathbf{k}}} = \sum_{N_0} e^{\beta\mu N_0}\prod_{\mathbf{k}\neq 0}\sum_{n_{\mathbf{k}}} e^{-\beta(\epsilon_k-\mu)n_{\mathbf{k}}} \\ &= \frac{1}{1-e^{\beta\mu}}\prod_{\mathbf{k}\neq 0}\frac{1}{1-e^{-\beta(\epsilon_k-\mu)}} \ . \end{aligned}$$

This result requires that the fugacity $z = e^{\beta\mu} < 1$, or equivalently $\mu < 0$. In the above equation N_0 denotes the occupation number $n_{\mathbf{k}=0}$ of the $|\mathbf{k}=0\rangle$ state, whose contribution has been separated from the other single-particle states since it requires a special treatment. In fact, if $\mu \to 0$ this contribution to the partition function diverges. We also notice that this pathology is not present in the case of fermions, as the corresponding contribution $1 + e^{\beta\mu}$ to Z_{GC} is well behaved.

The result for the thermodynamic potential then reads

$$\Omega(T, V, \mu) = k_B T \log(1 - e^{\beta\mu}) + k_B T \sum_{\mathbf{k}\neq 0} \log(1 - e^{-\beta(\epsilon_k - \mu)}) \ . \tag{4.4}$$

From the derivative $N = -(\partial\Omega/\partial\mu)_{TV}$ we get the total number of particles

$$N(T, V, \mu) \equiv N_0 + N_{k>0} = \frac{z}{1-z} + \sum_{\mathbf{k}\neq 0} \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} \ , \tag{4.5}$$

where the first term on the right hand side refers to the occupation N_0 of the $\mathbf{k} = 0$ state and the sum gives the occupation of states with $\mathbf{k} \neq 0$ which we refer to as $N_{k>0}$. The average occupation of the state $|\mathbf{k}\rangle$ in general reads

$$\langle n_{\mathbf{k}} \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} \ , \tag{4.6}$$

as it can be proven from the statistical average of $a^\dagger_{\mathbf{k}} a_{\mathbf{k}}$ in the grand-canonical ensemble. The number of particles in states having $\mathbf{k} \neq 0$ can be calculated using the standard transformation of sums into integrals holding in the thermodynamic limit. One gets

$$\begin{aligned} \frac{N_{k>0}}{V} = \frac{1}{V} \sum_{\mathbf{k}\neq 0} \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} &= \frac{4\pi}{(2\pi)^3} \int_0^\infty dk \frac{k^2}{z^{-1} e^{\beta\epsilon_k} - 1} \\ &= \frac{1}{\lambda_T^3} \frac{2}{\sqrt{\pi}} \int_0^\infty dx \frac{\sqrt{x}}{z^{-1} e^x - 1} \ , \end{aligned}$$

where to obtain the last identity we changed the integration variable and we introduced the thermal wave length $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$. The function of the fugacity z expressed as the integral entering the above equation is an example of the special function defined as

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

Here $\Gamma(x)$ is the Euler Gamma function already introduced in Chapter 3 in the definition of the Fermi special functions $f_\nu(z)$. The above function $g_\nu(z)$ is defined in the range $0 \leq z \leq 1$ if $\nu > 1$ and in the range $0 \leq z < 1$ if $0 < \nu \leq 1$. For $z = 1$ the function $g_\nu(z)$ coincides with Riemann's zeta function: $g_\nu(1) = \zeta(\nu)$.

In terms of the special function defined above the number of particles $N_{k>0}$ can be written as

$$\frac{N_{k>0}}{V} = \frac{1}{\lambda_T^3} g_{3/2}(z) \; . \tag{4.7}$$

We should consider that:

- The function $g_{3/2}(z)$ is a monotonous increasing function of z, reaching its maximum at $z = 1$ where it takes the value $\zeta(3/2) \simeq 2.612$.
- The left hand side of the above equation can not be larger than the total density n, while the right hand side can not be larger than $\zeta(3/2)/\lambda_T^3$ for a given temperature T.

If $n > \zeta(3/2)/\lambda_T^3$ then, from eq. (4.5), N_0/V should be finite in the thermodynamic limit accounting for the missing contribution. This implies that:

- The number of particles N_0 in the $\mathbf{k} = 0$ state should diverge as the total number of particles N and the fugacity $z = N_0/(N_0 + 1)$ should approach 1. This phenomenon is called Bose-Einstein condensation and corresponds to a macroscopic occupation of a single-particle state.
- If $z < 1$ in the thermodynamic limit, the condensate contribution N_0/V to the density n vanishes and $n = N_{k>0}/V$. If instead $z = 1$ in the thermodynamic limit, then the condensate fraction N_0/N is finite.
- For a given temperature T the transition between non-condensed and condensed gas takes place at the critical density $n_c = \zeta(3/2)/\lambda_T^3$ for which eq. (4.7) is still verified with a vanishing condensate fraction N_0/N. For smaller values of n ($n < n_c$) the fugacity is $z < 1$. For larger values ($n > n_c$) the condensate fraction is finite ($N_0/N > 0$).
- If one varies the temperature at a fixed density n, the transition takes place at the critical temperature

  $$T_c = \frac{2\pi\hbar^2}{m k_B} \left(\frac{n}{\zeta(3/2)} \right)^{2/3} \; . \tag{4.8}$$

  For temperatures larger than T_c the gas is non-condensed, while it is condensed for $T < T_c$.

- From eq. (4.4) one obtains the pressure $p = -\Omega/V$ which reads

$$p = \frac{k_B T}{V}\log(N_0+1) - \frac{k_B T}{2\pi^2}\int_0^\infty dk k^2 \log(1 - z e^{-\beta\epsilon_k}) \; .$$

We notice that the $\mathbf{k} = 0$ contribution to the pressure always vanishes in the thermodynamic limit. In fact, in the condensed phase it scales only as $\log(N)/V$.

Some remarks are in order here:

- Bose-Einstein condensation (BEC) is a true phase transition associated with the appearance of an order parameter and of discontinuities in thermodynamic functions as we will see in more details later. The order parameter is a complex quantity defined as the average value of the annihilation operator a_0. First, we notice that from the definition of the statistical average $\langle a_0 \rangle = (1/Z_{GC}) \sum_{N_0 n_{\mathbf{k}\neq 0}} \langle N_0 \; n_{\mathbf{k}\neq 0}| a_0 e^{-\beta(H-\mu N)} | N_0 \; n_{\mathbf{k}\neq 0}\rangle$ as being the trace over states with a definite number of particles, strictly speaking the quantity $\langle a_0 \rangle$ vanishes. One can give sense to it only in the thermodynamic limit if a macroscopic condensate is present.There are two ways of understanding this feature:

  a) If a macroscopic condensate with N_0 particles is present, the state $|N_0 \; n_{\mathbf{k}\neq 0}\rangle$ with a definite number of particles can be replaced by the state $e^{-N_0/2} \sum_{M=0}^{\infty} e^{iM\phi} (N_0^M/M!)^{1/2} |M \; n_{\mathbf{k}\neq 0}\rangle$. The result $\langle a_0 \rangle = \sqrt{N_0} e^{i\phi}$ follows then from the properties of coherent states.

  b) In the thermodynamic limit, there is no difference between the states $a_0 a_0^\dagger |N_0 \; n_{\mathbf{k}\neq 0}\rangle = (N_0+1)|N_0 \; n_{\mathbf{k}\neq 0}\rangle$ and $a_0^\dagger a_0 |N_0 \; n_{\mathbf{k}\neq 0}\rangle = N_0 |N_0 \; n_{\mathbf{k}\neq 0}\rangle$, if the condensate occupation N_0 is macroscopically large. As a consequence, the operator nature of a_0 and $a_0^\dagger$ is lost and these operators can be replaced by c-numbers: $a_0 = \sqrt{N_0} e^{i\phi}$ and $a_0^\dagger = \sqrt{N_0} e^{-i\phi}$. Their statistical averages are then trivial.

- The BEC transition is the only phase transition that is mediated by purely statistical effects and not by interaction effects.

- Strictly speaking BEC takes place only in the thermodynamic limit, as is the case for all phase transitions. In fact, for a finite number of particles eq. (4.5) can always be satisfied with $z < 1$.

- For systems with similar density and particle mass the transition temperature $T_c \sim \hbar^2 n^{2/3}/m$

is on the same order as the Fermi temperature T_F introduced in Chapter 3. In both cases the temperature scale corresponds to the degeneracy temperature where quantum effects start to play a role at the many-body level.

- In the non-condensed phase ($z < 1$) the equation of state reads

$$\begin{aligned} n &= \frac{g_{3/2}(z)}{\lambda_T^3} \\ p &= -\frac{k_BT}{\lambda_T^3}\frac{2}{\sqrt{\pi}}\int_0^\infty dx x^{1/2}\log(1-ze^{-x}) \\ &= \frac{k_BT}{\lambda_T^3}\frac{4}{3\sqrt{\pi}}\int_0^\infty dx\frac{x^{3/2}}{z^{-1}e^x-1} = \frac{k_BT}{\lambda_T^3}g_{5/2}(z) \ , \end{aligned} \tag{4.9}$$

  where we used integration by parts to obtain the equation for the pressure. The fugacity z must be eliminated from the first of the above equations to get the equation of state in the canonical ensemble.

- In the condensed phase ($z = 1$) the equation of state is simpler and reads

$$\begin{aligned} n &= n_0 + \frac{\zeta(3/2)}{\lambda_T^3} \\ p &= \frac{k_BT}{\lambda_T^3}\zeta(5/2) \ , \end{aligned} \tag{4.10}$$

  where the contribution $n_0 = N_0/V$ of the condensate density appears explicitly in the equation for the density and in the equation for the pressure $\zeta(5/2) \simeq 1.341$.

4.1.3 Thermodynamics below and above T_c

For temperatures $T < T_c$ the thermodynamic behavior of the gas can be derived from the equation of state (4.10). The condensate fraction, characterizing the condensed phase, exhibits the following temperature dependence

$$\frac{N_0}{N} = 1 - \frac{\zeta(3/2)}{n\lambda_T^3} = 1 - \left(\frac{T}{T_c}\right)^{3/2} \ , \tag{4.11}$$

consistently with the requirement that N_0/N vanishes at T_c and that the condensate exhausts the total number of particles at $T = 0$. Close to the transition point the temperature dependence of the intensive order parameter $\Phi/\sqrt{V}$ can be written as

$$\frac{\Phi}{\sqrt{V}} = \sqrt{n_0}e^{i\phi} \simeq \sqrt{\frac{3}{2}}\sqrt{n}e^{i\phi}\sqrt{\frac{T_c - T}{T_c}} \ ,$$

to lowest order in $T_c - T$. Pressure p, entropy $S = V(\partial p/\partial T)_{V\mu}$, internal energy $U = \mu N + TS - pV$ and specific heat at constant volume $c_V = (\partial U/\partial T)_{VN}$ are readily obtained in terms of the number $N_T \equiv N - N_0 = N(T/T_c)^{3/2}$ of thermally excited atoms. One finds

$$\begin{aligned} p &= \frac{N_T}{V}k_BT\frac{\zeta(5/2)}{\zeta(3/2)} \ , \\ S &= \frac{5}{2}N_Tk_B\frac{\zeta(5/2)}{\zeta(3/2)} \ , \\ U &= \frac{3}{2}N_Tk_BT\frac{\zeta(5/2)}{\zeta(3/2)} \ , \\ c_V &= \frac{15}{4}N_Tk_B\frac{\zeta(5/2)}{\zeta(3/2)} \ . \end{aligned} \tag{4.12}$$

We notice that the thermodynamic properties are solely determined by the non condensed component, being the condensate just a reservoir of particles. Another important remark concerns the pressure $p = \zeta(5/2)k_BT/\lambda_T^3$ that is independent of the volume. As a result the isothermal compressibility $\kappa_T = -(1/V)(\partial V/\partial p)_{TN}$ diverges. This is a pathology of the non interacting Bose gas in the grand-canonical ensemble. Another important quantity, whose behavior is worth investigating, is the average momentum distribution $\langle n_{\mathbf{k}}\rangle$, which from eq. (4.6) in the condensed phase reads

$$\langle n_{\mathbf{k}}\rangle = \frac{1}{e^{\hbar^2k^2/2mk_BT} - 1} \longrightarrow \frac{2mk_BT}{\hbar^2k^2} \ ,$$

where we focus on the $k \to 0$ limit. Besides the macroscopic occupation N_0 of the $\mathbf{k} = 0$ state, also states with finite wave vector $\mathbf{k}$ have a relatively large average occupation that is diverging as $1/k^2$. This peculiar behavior clarifies that BEC in a homogeneous system corresponds to a condensation in momentum space, while in coordinate space the condensate density n_0 remains uniform.

For temperatures $\underline{T > T_c}$ the thermodynamic behavior can be extracted from the equation of state (4.9). It is interesting to investigate the thermodynamic properties in the interval of temperatures immediately above the transition temperature T_c. To carry out this study we make use of the following expansion of the special bosonic functions $g_\nu(z)$ when the fugacity approaches $z = 1$

$$g_\nu(e^{-\alpha}) = \Gamma(1-\nu)\alpha^{\nu-1} + \sum_{m=0}^{\infty}(-1)^m \frac{\zeta(\nu-m)}{m!}\alpha^m \ .$$

This expansion holds for α small and positive and if ν is not an integer. In particular, for the relevant cases of $g_{3/2}$ and $g_{5/2}$ one gets the results

$$\begin{aligned} g_{3/2}(e^{-\beta|\mu|}) &= \zeta(3/2) - 2\sqrt{\pi}\sqrt{\beta|\mu|} - \zeta(1/2)\beta|\mu| + \dots \ , \\ g_{5/2}(e^{-\beta|\mu|}) &= \zeta(5/2) - \zeta(3/2)\beta|\mu| + \dots \ , \end{aligned}$$

to order linear in $|\mu|$ and where we used the result $-(1/2)\Gamma(-1/2) = \Gamma(1-1/2) = \sqrt{\pi}$. From the first of eqs. (4.9) we obtain the behavior of the chemical potential for $T \to T_c^+$

$$\mu \simeq -\frac{9\zeta^2(3/2)}{16\pi} k_B T_c \left(\frac{T-T_c}{T_c}\right)^2 \ .$$

From the second equation one calculates the pressure p and then using $S = V(\partial p/\partial T)_{V\mu}$ one gets the following result for the entropy

$$S \simeq \frac{5Nk_B\zeta(5/2)}{2\zeta(3/2)}\left[\left(\frac{T}{T_c}\right)^{3/2} - \frac{3\zeta(3/2)}{5\zeta(5/2)}\frac{|\mu|}{k_B T_c}\right] \ .$$

We notice that S is continuous at T_c where $N_T = N$, implying that there is no latent heat associated with the BEC transition. By using the thermodynamic relation $c_V = T(\partial S/\partial T)_{NV}$ and the expansion for μ in terms of $T - T_c$, one gets the following result for the specific heat

$$c_V = k_B N \left[\frac{15\zeta(5/2)}{4\zeta(3/2)}\left(\frac{T}{T_c}\right)^{3/2} - \frac{27\zeta^2(3/2)}{16\pi}\frac{T-T_c}{T_c}\right] \ .$$

At T_c the specific heat is continuous and takes the value $c_V(T_c)/N = k_B(15\zeta(5/2)/4\zeta(3/2)) \simeq 1.28\ 3k_B/2$, about a 30% larger than the classical result of a monoatomic gas. From the above equation and from the latter of eqs. (4.12) one immediately verifies that the temperature derivative of c_V exhibits a discontinuity at T_c, signaling that BEC is indeed a phase transition associated with a non analytic behavior of the thermodynamic functions. One finds

$$\left(\frac{dc_V}{dT}\right)_{T_c^+} - \left(\frac{dc_V}{dT}\right)_{T_c^-} = -\frac{27\zeta^2(3/2)}{16\pi}\frac{Nk_B}{T_c} \simeq -3.66\frac{Nk_B}{T_c} \; .$$

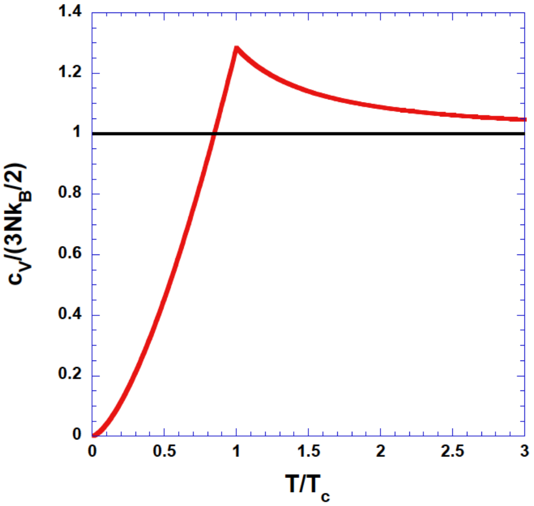

Figure 4.1: Specific heat of a Bose gas as a function of T/T_c. The horizontal line indicates the classical value.

The behavior of c_V as a function of T/T_c is shown in fig. 4.1. The result is obtained by carrying out a calculation similar to the one in Chapter 3 for the specific heat of a non-interacting Fermi gas which yields

$$c_V(T) = Nk_B\left(\frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}\right) \; .$$

Here we used the relation $(dg_\nu(z)/dT) = g_{\nu-1}(z)(d\log z/dT)$, holding for the temperature derivative of Bose special functions, and $(\partial \log z/\partial T)_{VN} = (-3/2T)g_{3/2}(z)/g_{1/2}(z)$ valid for homogeneous Bose gases..

The internal energy U is given by

$$U(T) = \frac{3}{2}Nk_BT\frac{g_{5/2}(z)}{g_{3/2}(z)} \; .$$

It is continuous at T_c where its value $U(T_c)/N = (\zeta(5/2)/\zeta(3/2))\; 3k_BT/2 \simeq 0.51\; 3k_BT/2$ is about half of the classical result. The important identity $U = -3\Omega/2$ relating internal energy and thermodynamic potential can be derived using a similar reasoning as the one applied to Fermi gases in

Chapter 3. Furthermore, it is worth stressing that this relation holds both above and below T_c. In figure 4.2 we show the comparison of the temperature dependence of the internal energy per particle U/N in a Bose and in a single-component Fermi gas, assuming that the mass and the density are the same. The figure clearly shows the emergence of the effects of statistics at low temperatures and the deviations from the classical law $U/N = 3k_BT/2$.

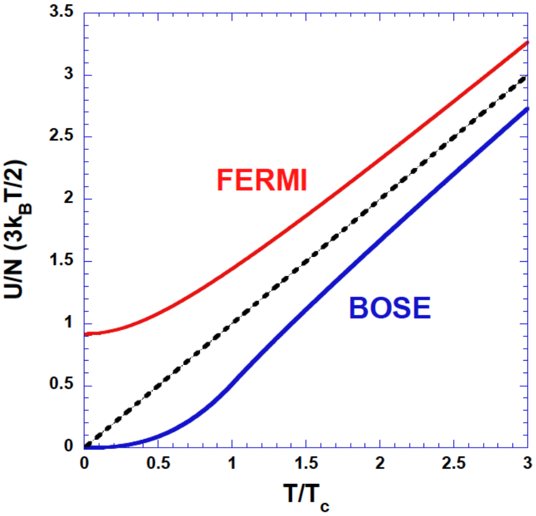

Figure 4.2: Comparison of the internal energies per particle of a Bose and a single-component Fermi gas. Density and mass are the same. Notice that $T_c = (4/3\sqrt{\pi}\zeta(3/2))^{2/3}T_{F\sigma} \simeq 0.44T_{F\sigma}$. The black dashed line shows the result for classical particles.

Finally, it is worth discussing the isothermal transformation in a degenerate Bose gas. These are schematically depicted in Fig. 4.3 in the plane pressure p *vs* volume per particle $v = V/N$. For a fixed temperature T, the pressure increases by reducing the volume in the non-condensed phase ($N_0/N = 0$). When the volume reaches the critical value $v_c = 1/n_c$, the gas enters the condensed phase ($N_0/N \neq 0$) and the pressure remains constant $p = p_c = \zeta(5/2)k_BT/\lambda_T^3$. The critical line corresponds to $p_c v_c^{5/3} = 2\pi\hbar^2\zeta(5/2)/(m\zeta(3/2)^{5/3})$. The horizontal line in the condensed phase is a consequence of the infinite compressibility of the non-interacting gas, a pathological behavior that will be cured by taking into account interaction effects.

4.1.4 High temperature behavior: virial expansion

In the high temperature regime, where the gas is highly non degenerate, one can expand the equation of state in powers of the small parameter $n\lambda_T^3$. This expansion, called virial expansion, is analogous

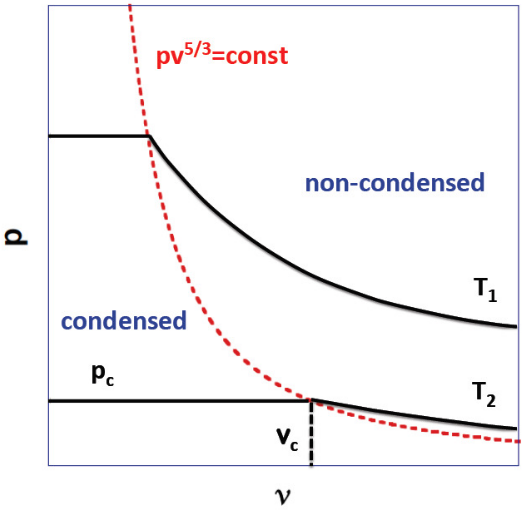

Figure 4.3: Isothermal lines in the $p - v$ plane corresponding to temperatures T_1 and $T_2 < T_1$.

to the one discussed in Chapter 3 for a Fermi gas and allows one for a systematic account of statistical and interaction effects.

We now proceed to calculate the second virial coefficient for a non-interacting Bose gas. Similarly to the corresponding Fermi functions, the Bose special functions admit the following series representation in terms of the fugacity z

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{z^{-1}e^x}\Big(1 + ze^{-x} + (ze^{-x})^2 + ...\Big) = \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^\nu} \ .$$

By eliminating z to second order in $n\lambda_T^3$ from eqs. (4.9) one gets the results

$$pV = Nk_BT\Big(1 - \frac{1}{4\sqrt{2}g_s}n\lambda_T^3 + ...\Big) \ , \tag{4.13}$$

for the pressure and

$$U = \frac{3}{2}Nk_BT\Big(1 - \frac{1}{4\sqrt{2}g_s}n\lambda_T^3 + ...\Big) \ , \tag{4.14}$$

for the internal energy. Thus, the second virial coefficient of Fermi and Bose gases are identical in absolute value, but have opposite sign. As a consequence, to the lowest order, statistical effects give raise to the same effective interaction, repulsive in the case of fermions and attractive in the case of bosons.

4.1.5 Fluctuations in the number of particles

Similarly to what has been carried out in Chapter 3 for fermions, it is worth investigating the fluctuations of the number of particles around the mean value, where effects of quantum degeneracy play a dominant role.

The mean-square fluctuations of the number of particles in the state $\mathbf{k}$ are given by

$$\delta n_{\mathbf{k}}^2 = \langle \big(n_{\mathbf{k}} - \langle n_{\mathbf{k}}\rangle\big)^2\rangle = \langle n_{\mathbf{k}}^2\rangle - \langle n_{\mathbf{k}}\rangle^2 \ .$$

To obtain $\langle n_{\mathbf{k}}^2\rangle$ we calculate the statistical average in the grand-canonical ensemble yielding

$$\begin{aligned} \langle n_{\mathbf{k}}^2\rangle &= \Big(1-e^{-\beta(\epsilon_k-\mu)}\Big)\sum_{n_{\mathbf{k}}=0}^{\infty} n_{\mathbf{k}}^2 e^{-\beta(\epsilon_k-\mu)n_{\mathbf{k}}} = \Big(1-e^{-\beta(\epsilon_k-\mu)}\Big)\sum_{n_{\mathbf{k}}=0}^{\infty}\frac{1}{\beta^2}\frac{\partial^2}{\partial\epsilon_k^2}e^{-\beta(\epsilon_k-\mu)n_{\mathbf{k}}} \\ &= \Big(1-e^{-\beta(\epsilon_k-\mu)}\Big)\frac{1}{\beta^2}\frac{\partial^2}{\partial\epsilon_k^2}\frac{1}{1-e^{-\beta(\epsilon_k-\mu)}} = \langle n_{\mathbf{k}}\rangle + 2\langle n_{\mathbf{k}}\rangle^2 \ . \end{aligned}$$

Thus, we find the following result

$$\delta n_{\mathbf{k}}^2 = \langle n_{\mathbf{k}}\rangle + \langle n_{\mathbf{k}}\rangle^2 \ . \tag{4.15}$$

The normal behavior of fluctuations is recovered at high temperatures, where $\langle n_{\mathbf{k}}\rangle \ll 1$ and one finds $\sqrt{\delta n_{\mathbf{k}}^2}/\langle n_{\mathbf{k}}\rangle \simeq 1/\sqrt{\langle n_{\mathbf{k}}\rangle}$. However, in general, fluctuations in a non interacting Bose gas are larger than normal. This becomes particularly evident in the condensed phase ($T < T_c$) where the occupation $N_0 = \langle n_{\mathbf{k}=0}\rangle$ of the lowest single-particle state is macroscopically large and the relative fluctuations of the condensate are on the order of unity $\sqrt{\delta n_0^2}/N_0 = (1+1/N_0)^{1/2}$.

The fluctuations in the total number of particles $\delta N^2 = \langle (N - \langle N\rangle)^2\rangle$ are also anomalously large. By exploiting the statistical independence of fluctuations relative to different states one finds the result

$$\delta N^2 = \sum_{\mathbf{k}} \delta n_{\mathbf{k}}^2 = \langle N\rangle + \sum_{\mathbf{k}}\langle n_{\mathbf{k}}\rangle^2 \ . \tag{4.16}$$

In particular, at $T = 0$, the occupation of the condensate coincides with the total number of particles and $\langle n_{\mathbf{k}}\rangle = 0$ for $\mathbf{k} \neq 0$. In this case $\delta N^2 = \langle N\rangle + \langle N\rangle^2$, showing that relative fluctuations in the number of particles do not vanish in the thermodynamic limit. This is a pathology of the ideal Bose gas in the condensed phase.

The fluctuation-dissipation equation relating the isothermal compressibility κ_T to particle fluctuations can be derived using the same thermodynamic relations as in the case of free fermions discussed in Chapter 3. The result for a non interacting Bose gas is as follows

$$N n k_B T \kappa_T = \delta N^2 = \langle N \rangle + \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle^2 \, , \tag{4.17}$$

where the second term on the right hand side is responsible for the divergence of κ_T in the condensed phase.

4.1.6 Pair correlation function and off-diagonal long range order

The pair correlation function of a Bose gas is defined through the space correlations of density fluctuations similarly to the corresponding function of a Fermi gas

$$\langle \big(n(\mathbf{r}) - n\big)\big(n(\mathbf{r}') - n\big) \rangle = n\delta(\mathbf{r} - \mathbf{r}') + n^2\big(g(|\mathbf{r} - \mathbf{r}'|) - 1\big) \, .$$

In terms of averages of field operators one finds the expressions

$$g(s) = \frac{1}{n^2} \langle \psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r} + \mathbf{s}) \psi(\mathbf{r} + \mathbf{s}) \psi(\mathbf{r}) \rangle = \frac{1}{n^2} \frac{1}{V^2} \sum_{\mathbf{k}\mathbf{k}'} \langle a^\dagger_{\mathbf{k}} a^\dagger_{\mathbf{k}'} a_{\mathbf{k}'} a_{\mathbf{k}} \rangle \big(1 + e^{i(\mathbf{k} - \mathbf{k}')\cdot\mathbf{s}} - \delta_{\mathbf{k},\mathbf{k}'}\big) \, , \tag{4.18}$$

respectively in coordinate and in momentum space. Apart from terms scaling as $1/V$ and vanishing in the thermodynamic limit, the above pair correlation function can be rewritten in the form

$$g(s) = 1 + \left| \frac{1}{n} \frac{1}{V} \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle e^{i\mathbf{k}\cdot\mathbf{s}} \right|^2 - \frac{1}{n^2} \left(\frac{N_0}{V} \right)^2 \, . \tag{4.19}$$

The last term in the above equation arises from the sum $(1/nV)^2 \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle^2$ where only the contribution from the $\mathbf{k} = 0$ state survives in the thermodynamic limit provided the system is in the condensed phase.

Some limiting cases are worth investigating in more details:

- High temperature regime $n\lambda_T^3 \ll 1$: in this regime the Maxwell-Boltzmann approximation

$\langle n_{\mathbf{k}} \rangle \simeq n\lambda_T^3 e^{-\beta\epsilon_k}$ for the particle distribution holds and eq. (4.19) can be evaluated explicitly

$$g(s) = 1 + \left| \frac{2\lambda_T}{\pi s} \int_0^\infty dx x e^{-x^2} \sin\left(\frac{\sqrt{4\pi} s x}{\lambda_T} \right) \right|^2 = 1 + e^{-2\pi s^2/\lambda_T^2} \ .$$

We notice that at short distance $g(s)$ approaches the value 2 and that it remains significantly larger than unity for distances smaller than the thermal wavelength λ_T.

- Zero temperature: only the $\mathbf{k} = 0$ state is occupied and $N_0 = N$ yielding $g(s) = 1$. This behavior of the pair correlation function resembles what happens in an uncorrelated gas.

- Zero separation distance: non interacting bosons exhibit a bunching effect yielding $g(0) = 2 - (N_0/N)^2 > 1$ for all $T > 0$.

We introduce another important correlation function playing a central role in the theoretical description of Bose-condensed systems. This is the one-body density matrix (OBDM) which is defined as the amplitude of the process where one particle is removed from position $\mathbf{r}$ and the same state is recovered by replacing the particle at position $\mathbf{r} + \mathbf{s}$. In a homogeneous system the OBDM is a function of the distance s and is conveniently normalized to unity at zero distance:

$$n_1(s) = \frac{1}{n} \langle \psi^\dagger(\mathbf{r} + \mathbf{s}) \psi(\mathbf{r}) \rangle \ . \tag{4.20}$$

By replacing the field operators with their k-space representation we get that n_1 is the Fourier transform of the momentum distribution

$$n_1(s) = \frac{1}{nV} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{s}} \langle n_{\mathbf{k}} \rangle \ . \tag{4.21}$$

In the non-degenerate regime, where one can assume a Maxwell-Boltzmann distribution for the particles, the OBDM decays to zero for distances larger that the thermal wavelength λ_T. More precisely, one finds

$$n_1(s) \simeq \frac{\lambda_T^3}{V} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{s}} e^{-\beta\epsilon_k} = \frac{2\lambda_T}{\pi s} \int_0^\infty dx x e^{-x^2} \sin\left(\frac{\sqrt{4\pi} x s}{\lambda_T} \right) = e^{-\pi s^2/\lambda_T^2} \ .$$

For a Fermi gas a similar behavior, *i.e.* the vanishing of $n_1(s)$ at large distances, continues to hold also in the degenerate regime. For example at $T = 0$, where the momentum distribution corresponds to the step function at the Fermi wave vector k_F, one finds the result $n_1(s) = 3/(k_F s)\int_0^1 dx x \sin(k_F s x) = 3/(k_F s)^3(\sin k_F s - k_F s \cos k_F s)$, holding for a single-component gas.

The behavior of a system of bosons is different. Once it enters the condensed phase, there exists a finite probability that the particle is extracted from the condensate and replaced in the condensate returning back to the same state. The amplitude of this process is independent of the distance and the OBDM remains finite even in the limit $s \to \infty$. This corresponds to the existence of off-diagonal long-range order (ODLRO), meaning that very far off-diagonal elements of the OBDM have non-zero values. Indeed, one can show that the contribution coming from $\mathbf{k} \neq 0$ states to $n_1(s)$ in eq. (4.21) vanishes when s gets larger that the thermal wavelength λ_T and one is left with the contribution from the condensate, yielding the result

$$\lim_{s\to\infty} n_1(s) = \frac{N_0}{N} \ ,$$

which involves the condensate fraction N_0/N. In particular, at $T = 0$, the OBDM is constant $n_1(s) = 1$.

4.2 Interacting gas and mean-field theory

In momentum space the grand-canonical Hamiltonian of the gas with pair-wise interactions can be written as

$$H - \mu N = \sum_{\mathbf{k}} (\epsilon_k - \mu) a^\dagger_{\mathbf{k}} a_{\mathbf{k}} + \frac{1}{2V} \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} V_{\mathbf{q}} a^\dagger_{\mathbf{k}} a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}'} a_{\mathbf{k}-\mathbf{q}} \, , \tag{4.22}$$

where, as usual, $V_{\mathbf{q}} = V_{-\mathbf{q}} = \int d\mathbf{r} V(r) e^{-i\mathbf{q}\cdot\mathbf{r}}$ is the Fourier transform of the two-body potential.

4.2.1 Hartree-Fock theory

Similarly to the treatment of interacting fermions in Chapter 3, we replace the product of four creation/annihilation operators in eq. (4.22) with a combination of terms involving at most two operators. The recipe is as follows:

$$\begin{aligned} a^\dagger_{\mathbf{k}} a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}'} a_{\mathbf{k}-\mathbf{q}} &= \langle a^\dagger_{\mathbf{k}} a_{\mathbf{k}-\mathbf{q}} \rangle a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}'} + \langle a^\dagger_{\mathbf{k}} a_{\mathbf{k}'} \rangle a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}-\mathbf{q}} \\ &+ \langle a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}'} \rangle a^\dagger_{\mathbf{k}} a_{\mathbf{k}-\mathbf{q}} + \langle a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}-\mathbf{q}} \rangle a^\dagger_{\mathbf{k}} a_{\mathbf{k}'} \\ &- \langle a^\dagger_{\mathbf{k}} a_{\mathbf{k}-\mathbf{q}} \rangle \langle a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}'} \rangle - \langle a^\dagger_{\mathbf{k}} a_{\mathbf{k}'} \rangle \langle a^\dagger_{\mathbf{k}'-\mathbf{q}} a_{\mathbf{k}-\mathbf{q}} \rangle - N_0^2 \, \delta_{\mathbf{k},0} \delta_{\mathbf{k}',0} \delta_{\mathbf{q},0} \, , \end{aligned} \tag{4.23}$$

where all possible pairings of a creation and an annihilation operator have been considered and the last three terms avoid double counting when considering the statistical average of the interaction Hamiltonian. In particular, the last term avoids double counting when all wave vectors are zero and should be included if the $\mathbf{k} = 0$ state is macroscopically occupied. By inserting the above expansion in eq. (4.22) one gets the Hamiltonian in the Hartree-Fock approximation

$$\begin{aligned} H_{HF} &= \sum_{\mathbf{k}} \epsilon_k a^\dagger_{\mathbf{k}} a_{\mathbf{k}} + \frac{1}{2} \sum_{\mathbf{k}} V_0 n \big(2 a^\dagger_{\mathbf{k}} a_{\mathbf{k}} - \langle n_{\mathbf{k}} \rangle \big) + \frac{1}{2} \sum_{\mathbf{k}} \frac{1}{V} \sum_{\mathbf{q}} V_{\mathbf{k}-\mathbf{q}} \langle n_{\mathbf{q}} \rangle \big(2 a^\dagger_{\mathbf{k}} a_{\mathbf{k}} - \langle n_{\mathbf{k}} \rangle \big) - \frac{V_0}{2} n_0 N_0 \\ &= E_{HF} + \sum_{\mathbf{k}} \big(\epsilon_k + V_0 n + \tilde{V}_{\mathbf{k}} \big) a^\dagger_{\mathbf{k}} a_{\mathbf{k}} \, , \end{aligned} \tag{4.24}$$

where we introduced the effective potential $\tilde{V}_{\mathbf{k}} = (1/V) \sum_{\mathbf{q}} V_{\mathbf{k}-\mathbf{q}} \langle n_{\mathbf{q}} \rangle$ and the constant term $E_{HF} = -(1/2)[\sum_{\mathbf{k}} (\tilde{V}_{\mathbf{k}} + V_0 n) \langle n_{\mathbf{k}} \rangle + V_0 n_0 N_0]$. Here $n_0 = N_0/V$ is the condensate density and the corresponding term in E_{HF} is present only in the condensed phase, where the condensate fraction N_0/N is finite.

In the relevant case of a contact potential for which the Fourier transform of the interaction potential is constant $V_{\mathbf{q}} = g$, the effective potential reads $\tilde{V}_{\mathbf{k}} = gn$ and the Hartree-Fock grand-canonical Hamiltonian takes the simple form

$$H_{HF} - \mu N = -gnN - \frac{gn_0 N_0}{2} + \sum_{\mathbf{k}} \big(\epsilon_k - \mu + 2gn\big) a^{\dagger}_{\mathbf{k}} a_{\mathbf{k}} \ . \tag{4.25}$$

It is worth investigating the implications of the use of the Hartree-Fock approximation at finite temperature.

- Non-condensed phase $T > T_c$:

  The equation of state is provided by

$$\begin{aligned} n\lambda_T^3 &= g_{3/2}(\tilde{z}) \\ \frac{p}{k_B T} &= \frac{gn^2}{k_B T} + \frac{g_{5/2}(\tilde{z})}{\lambda_T^3} \ , \end{aligned}$$

  where $\tilde{z} = e^{\beta(\mu - 2gn)}$ is the effective fugacity. From the above equations one can derive all thermodynamic quantities including the effects of interactions. For example, in the highly non-degenerate regime $n\lambda_T^3 \ll 1$, one obtains the following result for the virial expansion

$$pV = Nk_B T\Big[1 - \Big(\frac{1}{4\sqrt{2}} - \frac{2a}{\lambda_T}\Big) n\lambda_T^3 + ...\Big] \ , \tag{4.26}$$

  where we used $g = 4\pi\hbar^2 a/m$. Notice that, similarly to the fermionic case in Chapter 3, the above result is valid if the thermal wave length is much larger that the range of the interatomic potential.

- Transition temperature T_c:

  As in the non-interacting case the transition corresponds to the lowest temperature satisfying the normalization condition for the density n without resorting to a finite condensate fraction N_0/N. This happens for $\tilde{z} = 1$ and $n\lambda_T^3 = \zeta(3/2)$, yielding the same transition temperature T_c as in the non-interacting gas. At the transition, the critical chemical potential is shifted by interactions taking the value $\mu_c = 2gn$.

- Condensed phase $T < T_c$:

The $\mathbf{k} = 0$ contribution to the Hamiltonian (4.25) should be treated separately and the product $a_0^\dagger a_0$ should be replaced by the average value N_0 (see the discussion in Section 4-A about a_0 and $a_0^\dagger$ replaced by c-numbers). The grand-canonical Hamiltonian (4.25) takes the form

$$H_{HF} - \mu N = -gnN - \frac{gn_0 N_0}{2} + (-\mu + 2gn)N_0 + \sum_{\mathbf{k}\neq 0} (\epsilon_k - \mu + 2gn) a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \; .$$

By calculating the partition function in the usual way including the terms depending on N and N_0, one finds the following result for the thermodynamic potential

$$\Omega(T, V, \mu) = -gnN - \frac{gn_0 N_0}{2} - \mu N_0 + 2gnN_0 + k_B T \sum_{\mathbf{k}\neq 0} \log(1 - e^{-\beta(\epsilon_k - \tilde{\mu})}) \; , \tag{4.27}$$

where $\tilde{\mu} = \mu - 2gn$. From the thermodynamic relation $N = -(\partial\Omega/\partial\mu)_{TV}$ one gets the equation

$$\left(1 - 2g\frac{\partial n}{\partial \mu}\right)\left(N - N_0 - \sum_{\mathbf{k}\neq 0} \frac{1}{e^{\beta(\epsilon_k - \tilde{\mu})} - 1}\right) = (\mu + gn_0 - 2gn)\,\frac{\partial N_0}{\partial \mu} \; ,$$

whose solution gives the following relations for the condensate density n_0 and chemical potential respectively

$$n = n_0 + \frac{1}{\lambda_T^3} g_{3/2}(\tilde{z}) \tag{4.28}$$

$$\mu = gn_0 + 2gn_T \; , \tag{4.29}$$

where $\tilde{z} = e^{\tilde{\mu}/k_B T}$ is the effective fugacity and $n_T = n - n_0$ is the density of thermally excited atoms. The equation for the pressure

$$p = gn^2 - \frac{1}{2} g n_0^2 + \frac{k_B T}{\lambda_T^3} g_{5/2}(\tilde{z}) \; , \tag{4.30}$$

obtained using $pV = -\Omega$ from eq. (4.27), completes the determination of the equation of state in the condensed phase.

We notice that:

  - At $T = 0$, where $n_0 = n$, both the pressure $p = gn^2/2$ and the internal energy $U = \langle H_{HF} \rangle = gn^2 V/2$ are different from zero, in contrast to the non-interacting case.
  - Interactions must be repulsive ($g > 0$) to ensure that the spectrum of H_{HF} is bounded from below in the thermodynamic limit.
  - The chemical potential ranges from $\mu = gn$ at $T = 0$ to $\mu = 2gn$ at $T = T_c$, where it matches the value in the non-condensed phase.
  - The pressure depends on volume and therefore the compressibility is finite, eliminating the pathology of the non-interacting gas.

- Critical region $T \sim T_c$:

From eq. (4.27) we can eliminate the density n in favor of the condensate and non-condensate contributions $n = n_0 + n_T = n_0 + g_{3/2}(\tilde{z})/\lambda_T^3$. One finds

$$\frac{\Omega}{V} = -\mu n_0 + \frac{1}{2} g n_0^2 - g \frac{g_{3/2}^2(\tilde{z})}{\lambda_T^6} - \frac{k_B T}{\lambda_T^3} g_{5/2}(\tilde{z}) \; . \tag{4.31}$$

By considering the effect of interactions to the lowest order and assuming $n_0 \ll n$ one can replace $g_{3/2}^2(\tilde{z}) \simeq \zeta^2(3/2)$ and

$$\begin{aligned} g_{5/2}(\tilde{z}) &\simeq g_{5/2}(e^{\beta(\mu - 2gn_0 - 2g\zeta(3/2)/\lambda_T^3)}) \\ &\simeq \zeta(5/2) + \zeta(3/2)\frac{\mu}{k_B T} - \zeta(3/2)\frac{2gn_0}{k_B T} - \zeta^2(3/2)\frac{2g}{k_B T \lambda_T^3} \; . \end{aligned} \tag{4.32}$$

Eq. (4.31) now reads

$$\begin{aligned} \frac{\Omega}{V} &= -\frac{k_B T}{\lambda_T^3}\left(\zeta(5/2) + \zeta(3/2)\frac{\mu}{k_B T} - \zeta^2(3/2)\frac{g}{k_B T \lambda_T^3}\right) \\ &- \left(\mu - \zeta(3/2)\frac{2g}{\lambda_T^3}\right) n_0 + \frac{1}{2} g n_0^2 \; . \end{aligned} \tag{4.33}$$

This result provides the change of Ω/V for fixed μ and T if the condensate density is changed by the amount n_0. As we see, it has the general structure of the relevant thermodynamic potential close to a second order phase transition:

  - if $\mu < \mu_c = \zeta(3/2) 2g/\lambda_T^3$, the minimum of Ω/V corresponds to $n_0 = 0$,

– if $\mu > \mu_c = \zeta(3/2)2g/\lambda_T^3$, the minimum corresponds to $n_0 = (\mu - \mu_c)/g > 0$.

By eliminating the chemical potential using $\mu = 2gn - gn_0$, we find $n_0 = n[1-(T/T_c)^{3/2}] \simeq (3n/2)(T-T_c)/T_c$. This result is in agreement with the expected behavior from the Landau theory of phase transitions that the order parameter $\sqrt{n_0}$ should vanish at T_c with the critical exponent $\beta = 1/2$.

4.2.2 Gross-Pitaevskii equation for inhomogeneous condensates

In the presence of an external time-dependent potential $U(\mathbf{r}, t)$ the Hamiltonian at time t is written in coordinate representation in the form

$$H(t) = \int d\mathbf{r}\, \psi^\dagger(\mathbf{r}, t) \left(-\frac{\hbar^2 \nabla^2}{2m} + U(\mathbf{r}, t) \right) \psi(\mathbf{r}, t) + \frac{g}{2} \int d\mathbf{r}\, \psi^\dagger(\mathbf{r}, t)\psi^\dagger(\mathbf{r}, t)\psi(\mathbf{r}, t)\psi(\mathbf{r}, t) \;, \tag{4.34}$$

where we assumed a contact interaction described by the coupling constant $g = 4\pi\hbar^2 a/m$ in terms of the s-wave scattering length a and we introduced the time-dependent field operators $\psi(\mathbf{r}, t)$, $\psi^\dagger(\mathbf{r}, t)$ that at time t respectively annihilate and create a particle at position $\mathbf{r}$. The time evolution of the operator $\psi(\mathbf{r}, t)$ is determined by Heisenberg's equation

$$i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \Big[\psi(\mathbf{r}, t), H(t)\Big] = \left(-\frac{\hbar^2 \nabla^2}{2m} + U(\mathbf{r}, t) \right) \psi(\mathbf{r}, t) + g\, \psi^\dagger(\mathbf{r}, t)\psi(\mathbf{r}, t)\psi(\mathbf{r}, t) \;. \tag{4.35}$$

At $T = 0$, according to Hartree-Fock theory, all particles share the same single-particle state whose occupation is thus $N_0 = N$. In the limit of large N, the condensate state, having a well defined number of particles, and the coherent state, where particle normalization is satisfied only on average, are both equivalent description of the system's ground state. Furthermore, if the time variation of the external potential is much slower than the typical time scale of relaxation, at each time t the system can be assumed to occupy the instantaneous ground state of the Hamiltonian $H(t)$ (adiabatic approximation). By analogy with the definition given in Section 4-A, the corresponding coherent state can be written in the following form

$$|\mathrm{coh}(\Phi)\rangle_t = e^{\int d\mathbf{r} [\Phi(\mathbf{r},t)\psi^\dagger(\mathbf{r},t) - |\Phi(\mathbf{r},t)|^2/2]}|0\rangle \;, \tag{4.36}$$

where the complex function $\Phi(\mathbf{r}, t)$ is the macroscopically occupied single-particle state to be determined self consistently. The above state obeys to the eigenvalue equation

$$\psi(\mathbf{r},t)|\mathrm{coh}(\Phi)\rangle_t = \Phi(\mathbf{r},t)|\mathrm{coh}(\Phi)\rangle_t \ ,$$

while particle normalization is enforced by the condition

$$N = {}_t\langle \mathrm{coh}(\Phi)| \int d\mathbf{r}\ \psi^\dagger(\mathbf{r},t)\psi(\mathbf{r},t)|\mathrm{coh}(\Phi)\rangle_t = \int d\mathbf{r}\ |\Phi(\mathbf{r},t)|^2 \ ,$$

holding at any time t. Notice also that the projection of the state (4.36) on the N-particle Hilbert space corresponds to the wave function $\psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_N,t) = \Phi(\mathbf{r}_1,t)/\sqrt{N}...\Phi(\mathbf{r}_N,t)/\sqrt{N}$.

By calculating the expectation value of the left and right hand side of Heisenberg's equation (4.35) on the coherent state (4.36) one derives the Gross-Pitaevskii (GP) equation

$$i\hbar\frac{\partial\Phi(\mathbf{r},t)}{\partial t} = \left(-\frac{\hbar^2\nabla^2}{2m} + U(\mathbf{r},t)\right)\Phi(\mathbf{r},t) + g\ |\Phi(\mathbf{r},t)|^2\Phi(\mathbf{r},t)\ . \tag{4.37}$$

which is a differential equation for the unknown particle orbital $\Phi(\mathbf{r},t)$. The corresponding energy at time t is provided by the functional

$$E_{GP}(t) = \int d\mathbf{r}\left[\frac{\hbar^2}{2m}|\nabla\Phi(\mathbf{r},t)|^2 + U(\mathbf{r},t)|\Phi(\mathbf{r},t)|^2 + \frac{g}{2}|\Phi(\mathbf{r},t)|^4\right]\ , \tag{4.38}$$

obtained from the expectation value of $H(t)$ given in eq. (4.34) on the state $|\mathrm{coh}(\Phi)\rangle_t$. To obtain the kinetic energy term, we used integration by parts under the constraint that $\Phi(\mathbf{r},t)$ should vanish at infinite distances. We notice that the GP equation (4.37) can be written in a compact form in terms of the functional derivative of the GP energy functional

$$i\hbar\frac{\partial\Phi(\mathbf{r},t)}{\partial t} = \frac{\delta E_{GP}}{\delta\Phi^*}\ ,$$

where by δE_{GP} we intend the small variation $\delta E_{GP}(\Phi,\Phi^*) = E_{GP}(\Phi,\Phi^*+\delta\Phi^*) - E_{GP}(\Phi,\Phi^*)$.

If the external potential is independent of time the GP equation admits the stationary solution

$\Phi(\mathbf{r},t) = e^{-i\mu t/\hbar}\Phi_0(\mathbf{r})$, where $\Phi_0(\mathbf{r})$ is the solution of the stationary GP equation

$$\left(-\frac{\hbar^2\nabla^2}{2m} + U(\mathbf{r}) - \mu\right)\Phi_0(\mathbf{r}) + g\,|\Phi_0(\mathbf{r})|^2\Phi_0(\mathbf{r}) = 0\ . \tag{4.39}$$

The real parameter μ corresponds to the chemical potential of the gas. In fact, the following identity holds

$$\frac{\partial E}{\partial N} = \mu \int d\mathbf{r}\Big[\Phi_0(\mathbf{r})\frac{\partial \Phi_0^*(\mathbf{r})}{\partial N} + \Phi_0^*(\mathbf{r})\frac{\partial \Phi_0(\mathbf{r})}{\partial N}\Big] = \mu\frac{\partial}{\partial N}\int d\mathbf{r}\,|\Phi_0(\mathbf{r})|^2 = \mu\ .$$

Here we used the local relation: $i\hbar\frac{\partial\Phi(\mathbf{r},t)}{\partial t} = \frac{\partial\mathcal{E}_{GP}(\Phi^*(\mathbf{r},t),\Phi(\mathbf{r},t))}{\partial\Phi^*(\mathbf{r},t)}$, where $\mathcal{E}_{GP}(\Phi^*(\mathbf{r},t),\Phi(\mathbf{r},t))$ is the GP energy density such that $E_{GP}(t) = \int d\mathbf{r}\ \mathcal{E}_{GP}(\Phi^*(\mathbf{r},t),\Phi(\mathbf{r},t))$.

Some relevant cases are worth discussing in details:

- a) Homogeneous gas: If $U(\mathbf{r}) = 0$, the solution of eq. (4.39) satisfying the normalization condition is given by $\Phi_0(\mathbf{r}) = \sqrt{N/V}$. The chemical potential reads then $\mu = gn$ and the ground-state energy density is $E_{GP}/V = gn^2/2$, in agreement with the HF results discussed in the previous subsection.

- b) Non interacting gas: In the absence of interactions ($g = 0$) eqs. (4.37), (4.39) reduce respectively to the the time-dependent and time-independent Schrödinger equations for the single-particle state $\Phi(\mathbf{r},t)$ in the presence of the external field $U(\mathbf{r},t)$.

- c) Inhomogeneous gas: If an external potential $U(\mathbf{r})$ is present, the solution $\Phi_0(\mathbf{r})$ of eq. (4.39) with and without interactions can be completely different. For example, in the case of the harmonic confinement $U(\mathbf{r}) = m\omega^2r^2/2$, the non-interacting solution for the condensate density is given by the gaussian $|\Phi_0(\mathbf{r})|^2 = N/(a_{ho}^3\pi^{3/2})e^{-r^2/a_{ho}^2}$, where $a_{ho} = \sqrt{\hbar/m\omega}$ is the oscillator length. In the limit of large number of particles N, one can neglect the quantum kinetic energy term proportional to $\hbar^2$ in eq. (4.39) (Thomas-Fermi approximation) and one finds the inverted parabola

  $$|\Phi_0(\mathbf{r})|^2 = \frac{\mu}{g}\left(1 - \frac{m\omega^2r^2}{2\mu}\right)\ ,$$

  for $r < \sqrt{2\mu/m\omega^2}$ and $|\Phi_0(\mathbf{r})| = 0$ for larger values of r. The chemical potential is obtained from the normalization condition and is given by

$$\mu = \frac{\hbar\omega}{2}\left(\frac{15Na}{a_{ho}}\right)^{2/5} \quad .$$

The above results can also be derived within the so-called local density approximation, based on the local equilibrium equation $\mu - U(\mathbf{r}) = \mu_{local}(\mathbf{r})$ and on the local description of the gas in terms of a homogeneous system at the density $n(\mathbf{r})$: $\mu_{local}(\mathbf{r}) = gn(\mathbf{r})$. They have been shown to provide a quantitatively accurate account of harmonically trapped atomic condensates, where the number of particles is typically larger that few thousands.

Another important feature of the gross-Pitaevskii theory of condensates is related to the expectation value of the current operator

$$\begin{aligned} \langle j(\mathbf{r},t)\rangle &= -\frac{i\hbar}{2}\langle\psi^\dagger(\mathbf{r},t)\nabla\psi(\mathbf{r},t) - (\nabla\psi^\dagger(\mathbf{r},t))\psi(\mathbf{r},t)\rangle \\ &= -\frac{i\hbar}{2}\Big(\Phi^*(\mathbf{r},t)\nabla\Phi(\mathbf{r},t) - (\nabla\Phi^*(\mathbf{r},t))\Phi(\mathbf{r},t)\Big) = m\, n(\mathbf{r},t)\frac{\hbar}{m}\nabla S(\mathbf{r},t)\ , \end{aligned}$$

where we used the decomposition of the order parameter $\Phi(\mathbf{r},t) = \sqrt{n(\mathbf{r},t)}e^{iS(\mathbf{r},t)}$ in terms of the density $n = |\Phi|^2$ and the phase S. From the last of the above equalities we identify

$$\mathbf{v}(\mathbf{r},t) = \frac{\hbar}{m}\nabla S(\mathbf{r},t)$$

with the velocity field associated to the motion of the condensate. This velocity field, being the gradient of the scalar function S, is irrotational, $\nabla \times v(\mathbf{r},t) = 0$, and consequently can not be dissipative. The motion of the condensate has thus the property of being a superfluid flow. Notice that the concept of velocity field can be defined for any system, but in general it corresponds to an average over many different single-particle states and thus can not be written as the gradient of a phase. On the other hand the velocity associated to a single particle is indeed the gradient of a phase, but it is subject to huge fluctuations due to interactions and thermal effects. Only in the presence of a condensate the velocity field at the same time has a quantum nature and describes the behavior of a macroscopic number of particles.

Let us consider the stationary solutions of GP equation in a spatial region where there is a hole, namely a region where $n(\mathbf{r}) = 0$ and such that a path around it can not be shrunk to a point. By drawing a continuous path around the hole it must happen that

$$S_{\text{path ends}}(\mathbf{r}) - S_{\text{path starts}}(\mathbf{r}) = 2\pi\ell \ ,$$

where ℓ is an integer, because of the single-valuedness of the order parameter. The phase S should then be of the form $S(\mathbf{r}) = \ell\theta$, where θ is the azimuthal angle around the hole, and the corresponding velocity is given by the azimuthal field

$$\mathbf{v}(\mathbf{r}) = \frac{\hbar}{m}\frac{\ell}{r}\hat{\theta} \ . \tag{4.40}$$

For $\ell = 1$ the above velocity field describes a vortex state centered in the hole. Vortices describe excited states where the condensate rotates around some axis at $r = 0$ and correspond to a total angular momentum given by $\langle L_z \rangle = N\ell\hbar$, where z is the direction of the vortex axis. Notice that the velocity field (4.40), associated with the only possible rotating state of a condensate, is different from the field associated with a rigid-body rotation $\mathbf{v} = \Omega r\hat{\theta}$ having angular frequency Ω. We also notice that the circulation of the velocity field around a vortex is quantized. In fact, one finds

$$\oint_{\text{path}} d\mathbf{r} \cdot \mathbf{v}(\mathbf{r}) = 2\pi\ell\frac{\hbar}{m} \ ,$$

along any closed path encircling the vortex axis.

In a large bucket of volume V having the form of an annulus of radius R one can neglect the space variation of the density and the ground state of the gas is given by $\Phi_0(\mathbf{r}) = \sqrt{N/V}$ with the energy $E_0 = gnN/2$. Excited states corresponding to vortex excitations are described by the wave function $\Phi_\ell(\mathbf{r}) = \sqrt{N/V}e^{i\ell\theta}$ and have energy $E_\ell = E_0 + N\hbar^2\ell^2/(2mR^2)$. States with different ℓ are topologically different and are separated by energy barriers. If one starts rotating the container around the z-axis at some angular frequency Ω, the first vortex ($\ell = 1$) will appear once the corresponding energy increase $\Delta E = E_{\ell=1} - E_0$ becomes smaller than the gain in rotational energy $\Omega N\hbar$, *i.e.* when the energy difference in the rotating frame $\Delta E - \Omega\langle L_z \rangle$ becomes negative. This condition sets a lower bound to the frequency $\Omega_c > \hbar/(2mR^2)$, such that if $\Omega < \Omega_c$ the condensate is not able to rotate.

4.2.3 Bogoliubov theory

The HF grand-canonical Hamiltonian (4.25) in the condensed phase ($T < T_c$) can be rewritten as

$$H_{HF} - \mu N = -gnN + \frac{gn_0 N_0}{2} + \sum_{\mathbf{k} \neq 0} \left(\epsilon_k + gn_0 \right) a^\dagger_{\mathbf{k}} a_{\mathbf{k}} \ ,$$

where we separated the contribution from the condensate and we used the equation $\mu = 2gn - gn_0$ for the chemical potential. Excitations above the ground state are obtained by creating a particle in a state with finite momentum $\mathbf{k} \neq 0$. Such states correspond to an excitation energy $\epsilon_k + gn$, which exhibits a gap for vanishing values of k. The low-lying excitations of a Bose gas should be gapless and the presence of a gap is an artifact of the HF approach, which correctly describes the thermodynamics of the gas only in the range of temperatures $k_B T \gg \mu$. A more accurate account of the low temperature behavior of the gas is provided by the Bogoliubov approach, based on the expansion of the grand-canonical Hamiltonian (4.22) in the small condensate-depletion parameter $(N - N_0)/N \ll 1$.

We start from the grand-canonical Hamiltonian (4.22) in the case of contact interaction ($V_{\mathbf{q}} = g$) and we replace the creation and annihilation operators on the state $\mathbf{k} = 0$ by c-numbers: $a_0 = a^\dagger_0 = \sqrt{N_0}$, where we set to zero the arbitrary phase ϕ. To order N_0 in the interaction term, we get the following truncation of the Hamiltonian

$$H_{BOG} - \mu N = -\mu N_0 + \sum_{\mathbf{k} \neq 0} (\epsilon_k - \mu) a^\dagger_{\mathbf{k}} a_{\mathbf{k}} + \frac{gN_0^2}{2V} + \frac{gN_0}{2V} \sum_{\mathbf{k} \neq 0} \left(4 a^\dagger_{\mathbf{k}} a_{\mathbf{k}} + a^\dagger_{\mathbf{k}} a^\dagger_{-\mathbf{k}} + a_{-\mathbf{k}} a_{\mathbf{k}} \right) \ , \tag{4.41}$$

where higher order terms contain three creation/annihilation operators relative to $\mathbf{k} \neq 0$ states and are proportional to $\sqrt{N_0}$. We notice that the above operator is bilinear in $a_{\mathbf{k}}$ and $a^\dagger_{\mathbf{k}}$ and can be cast in diagonal form using the operator transformation (canonical transformation)

$$\begin{aligned} a_{\mathbf{k}} &= u_k \alpha_{\mathbf{k}} + v^*_k \alpha^\dagger_{-\mathbf{k}} \\ a^\dagger_{\mathbf{k}} &= u^*_k \alpha^\dagger_{\mathbf{k}} + v_k \alpha_{-\mathbf{k}} \ . \end{aligned} \tag{4.42}$$

Here u_k and v_k are complex numbers and $\alpha_{\mathbf{k}}$, $\alpha^\dagger_{\mathbf{k}}$ are new creation/annihilation operators for which we require the same commutation relations as for the particle operators $a_{\mathbf{k}}$, $a^\dagger_{\mathbf{k}}$. Namely we must have: $[\alpha_{\mathbf{k}}, \alpha_{\mathbf{k}'}] = [\alpha^\dagger_{\mathbf{k}}, \alpha^\dagger_{\mathbf{k}'}] = 0$ and $[\alpha_{\mathbf{k}}, \alpha^\dagger_{\mathbf{k}'}] = \delta_{\mathbf{k},\mathbf{k}'}$. As a consequence, the coefficients u_k and v_k satisfy the condition

$$|u_k|^2 - |v_k|^2 = 1 \; . \tag{4.43}$$

The transformation (4.42) can also be inverted giving

$$\begin{aligned} \alpha_{\mathbf{k}} &= u_k^* a_{\mathbf{k}} - v_k a^\dagger_{-\mathbf{k}} \\ \alpha^\dagger_{\mathbf{k}} &= u_k a^\dagger_{\mathbf{k}} - v_k^* a_{-\mathbf{k}} \; . \end{aligned} \tag{4.44}$$

We notice that the operator $\alpha_{\mathbf{k}}$ is associated with amplitude u_k^* to the annihilation of a particle with wavevector $\mathbf{k}$ and with amplitude $-v_k$ to the creation of a particle with wavevector $-\mathbf{k}$. Thus, if v_k is non zero, the operators $\alpha_{\mathbf{k}}$, $\alpha^\dagger_{\mathbf{k}}$ correspond to superpositions of states with different number of particles and are thereby called quasi-particle operators.

After inserting the operator transformation (4.42) into the Hamiltonian (4.41), we require that the term proportional to the products $\alpha^\dagger_{\mathbf{k}}\alpha^\dagger_{-\mathbf{k}}$ and $\alpha_{-\mathbf{k}}\alpha_{\mathbf{k}}$ vanish obtaining the equation

$$(\epsilon_k - \mu + 2gn_0)u_k v_k + \frac{gn_0}{2}(u_k^2 + v_k^2) = 0 \; .$$

The solution of the above equation, consistent with the normalization condition (4.43), yields the real roots

$$u_k v_k = -\frac{gn_0}{2E_k} \qquad u_k^2 = \frac{\epsilon_k - \mu + 2gn_0 + E_k}{2E_k} \qquad v_k^2 = \frac{\epsilon_k - \mu + 2gn_0 - E_k}{2E_k} \; , \tag{4.45}$$

where the energy E_k is given by the result

$$E_k^2 = (\epsilon_k - \mu + 2gn_0)^2 - (gn_0)^2 \; , \tag{4.46}$$

that can be obtained from the relation $1 = (u_k^2 - v_k^2)^2 = (u_k^2 + v_k^2)^2 - 4u_k^2 v_k^2$.

The Hamiltonian (4.41) can be finally rewritten in terms of the quasi-particle operators in the form

$$H_{BOG} - \mu N = \frac{gN_0^2}{2V} - \mu N_0 + \frac{1}{2}\sum_{\mathbf{k}\neq 0}\left[E_k - (\epsilon_k - \mu + 2gn_0)\right] + \sum_{\mathbf{k}\neq 0} E_k \alpha_k^\dagger \alpha_k \; . \tag{4.47}$$

We notice that:

- a) The above Hamiltonian is diagonal in the quasi-particle operators. Eigenstates of $H_{BOG}-\mu N$ have a definite number $\tilde{n}_{\mathbf{k}}$ of quasi-particles in each state $\mathbf{k}$ and, consequently, the grand-canonical partition function can be calculated using the trace over these states:

  $Z_{GC} = \sum_{\tilde{n}_{\mathbf{k}}} \langle \tilde{n}_{\mathbf{k}} | e^{-\beta(H_{BOG}-\mu N)} | \tilde{n}_{\mathbf{k}} \rangle$.

  For the thermodynamic potential Ω one finds then

$$\Omega(T,V,\mu) = \frac{gN_0^2}{2V} - \mu N_0 + \frac{1}{2}\sum_{\mathbf{k}\neq 0}\left[E_k - (\epsilon_k - \mu + 2gn_0)\right] + k_B T \sum_{\mathbf{k}\neq 0} \log(1-e^{-\beta E_k}) \ . \tag{4.48}$$

- b) The distribution of quasi-particles is calculated from the statistical average of the quasi-particle number operator yielding the bosonic law

$$\langle \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} \rangle = \frac{1}{Z_{GC}} Tr(\alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} e^{-\beta(H_{BOG}-\mu N)}) = \frac{1}{e^{\beta E_{\mathbf{k}}}-1} \ ,$$

  where the positive energies E_k correspond to the quasi-particle energies.

- c) The total number of particles is obtained from the normalization condition

$$N = N_0 + \sum_{\mathbf{k}\neq 0} \langle a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \rangle = N_0 + \sum_{\mathbf{k}\neq 0}\left[v_k^2 + (u_k^2 + v_k^2)\langle \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} \rangle\right] \ , \tag{4.49}$$

  considering that only operators that conserve the number of quasi-particles give non-vanishing statistical averages.

- d) The ground state of $H_{BOG} - \mu N$ is provided by the vacuum $|\text{vac}\rangle$ of quasiparticles, *i.e.* the state such that $\alpha_{\mathbf{k}}|\text{vac}\rangle = 0$. Excited states with wave vector $\mathbf{k}$ are obtained by applying the corresponding quasi-particle creation operator on the vacuum state: $\alpha_{\mathbf{k}}^\dagger|\text{vac}\rangle$. These states have energy E_k relative to the energy of the vacuum state and describe the elementary excitations of the gas.

- e) By requiring that at equilibrium the value of N_0 corresponds to a minimum of the thermodynamic potential, *i.e.* $(\partial\Omega/\partial N_0)_{TV\mu} = 0$, one finds the result $\mu = gn_0$ to leading order in $N - N_0$. We notice that this value of μ makes the energies E_k gapless. In fact, the dispersion relation reads

$$E_k = \sqrt{\epsilon_k^2 + 2gn_0\epsilon_k} \; .$$

Al large momenta, where $\epsilon_k \gg \mu$, one finds the free-particle dispersion $E_k \simeq \epsilon_k$. In this regime the amplitude $v_k^2 \to 0$ ($u_k^2 \to 1$) and quasi-particles coincide with particles. On the contrary, at small momenta, the excitations have a linear (phononic) dispersion $E_k \simeq \sqrt{2gn_0\epsilon_k} = \sqrt{gn_0/m}\hbar k$ and correspond to sound waves propagating with the velocity $c = \sqrt{gn_0/m}$. In this case one finds diverging Bogoliubov amplitudes $u_k^2 \sim v_k^2 \simeq gn_0/(2c\hbar k)$ and quasi-particles involve with the same weight the process of creating a particle and of annihilating another particle with opposite momentum.

- f) From eq. (4.49) one can calculate the depletion of the condensate $N - N_0$ produced both by thermal effects and by quantum effects. The latter persist also at $T = 0$, where the thermal population of quasiparticles $\langle \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} \rangle \to 0$, but the intergral $\sum_{\mathbf{k}\neq 0} v_k^2$ still gives a finite contribution. This quantum depletion arising from purely interaction effects can be calculated analytically obtaining the result

$$n_0 = n - \frac{1}{V}\sum_{\mathbf{k}\neq 0}\frac{\epsilon_k + gn_0 - E_k}{2E_k} = n\Big[1 - \frac{8}{3\sqrt{\pi}}(na^3)^{1/2}\Big] \; ,$$

where in the integral n_0 can be replaced by n to leading order. The above result states that, if the gas parameter na^3 is small, $n_0 \simeq n$ at low temperature providing a sound basis for the Bogoliubov approach.

- g) The ground state energy is obtained from the expectation value on the vacuum state $E_0 = \langle \text{vac}|H_{BOG}|\text{vac}\rangle$. To lowest order in the gas parameter na^3 one obtains the result $E_0/V = gn^2/2$, consistently with the HF approach. Notice that higher order corrections to E_0 can also be calculated with the Bogoliubov theory, but they require a renormalization of the coupling constant to deal with divergencies emerging at large momenta.

4.2.4 Superfluidity: Landau criterium and two-fluid model

- Phenomenology

Superfluidity is a striking phenomenon displayed by some quantum fluids and gases consisting in their ability to flow without dissipation. Superfluidity is the analog for neutral matter of superconductivity, *i.e.* absence of resistivity, in the charged fluid of conduction electrons in a metal. The most remarkable example of a superfluid is provided by liquid ^{4}He below the lambda point.

At normal pressure ^{4}He remains a liquid down to $T = 0$. However, at $T_\lambda = 2.17K$ it undergoes a phase transition from He-I to He-II signaled by a sharp feature in the specific heat. Since the experiments by Kapitza and Allen, Misener (1937) it was realized that He-II can flow in narrow capillaries without friction and that it has vanishing viscosity. Later, in 1946, the experiment by Andronikashvili proved the non-classical rotational inertia of He-II and the coexistence in this phase of a super and a normal fluid. By using a torsional oscillator containing a stack of closely packed disks filled with ^{4}He, the experiment measures the oscillation period, proportional to the moment of inertia of the device, as a function of temperature. Above T_λ liquid helium contributes to the moment of inertia by its rigid-body value, showing that it is dragged completely by the oscillation of the disks as in any normal viscous fluid. Below T_λ, however, a drop in the oscillation period is observed indicating that the moment of inertia of the device is smaller than the classical rigid-body value. A part of He-II does not contribute to the moment of inertia of the torsional oscillator and remains at rest while the disks are oscillating. This superfluid component grows as the temperature is decreased and at $T = 0$ corresponds to the total amount of helium. The fraction of normal component, defined as the part of liquid still contributing to the moment of inertia by its rigid-body value, was measured to be proportional to T^4 at very low temperatures.

Another important series of experiments was carried out in 1967 by Hess and Fairbank using helium confined in a bucket of toroidal geometry having radius R and width $d \ll R$. The first experiment establishes the ability of He-II to sustain persistent currents. By rotating the bucket above T_λ at some angular frequency Ω, after a short while helium rotates rigidly with the bucket. If temperature is reduced below T_λ keeping the rotation on, helium continues to rotate in equilibrium with the container. However, if the rotation is stopped, only the normal component of the fluid reaches equilibrium with the bucket now at rest, whereas the superfluid component continues to rotate for a practically indefinitely long time. A second experiment goes under the name of Hess-Fairbank effect. At $T > T_\lambda$ the bucket is set into rotation, but the angular velocity is very small (if $R \sim 1mm$, $\Omega/2\pi < 1Hz$) and is kept constant during the whole experiment. Similarly to the previous experiment helium starts rotating with the bucket, but as T is reduced below T_λ the superfluid component comes at rest in the laboratory frame even if the container is still rotating. Since helium was already in equilibrium in the rotating frame, this phenomenon indicates that the state with zero angular velocity for the superfluid component is the true equilibrium state both for the laboratory and the rotating frame.

- Statistical mechanics in moving frames

From the above discussion it is clear that superfluidity has to do with the nature of equilibrium states in moving reference frames.

Let us first consider how the Hamiltonian changes under a Galilean transformation from a reference frame at rest O to a reference frame O' moving with linear velocity $\mathbf{v}$. The Hamiltonian H in the reference frame O is given by

$$H \equiv T + V = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} V(\mathbf{r}_i - \mathbf{r}_j) \ ,$$

where T and V are respectively the kinetic and the interaction term and the sums are over the particle labels $i, j = 1, ..., N$. In the reference frame O' the momentum of particle i changes to $\mathbf{p}_i' = \mathbf{p}_i - m\mathbf{v}$ and the corresponding kinetic energy is given by

$$T' = \sum_i \frac{(\mathbf{p}_i - m\mathbf{v})^2}{2m} = T - \sum_i \mathbf{p}_i \cdot \mathbf{v} + N\frac{m}{2}v^2 \ ,$$

whereas $V' = V$ since the transformation does not change the relative distance between particles. In the second quantization formalism the grand-canonical Hamiltonian in the reference frame O' thus takes the form

$$H' - \mu N = \frac{Nmv^2}{2} + \sum_{\mathbf{k}} (\epsilon_k - \hbar\mathbf{k}\cdot\mathbf{v} - \mu) a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + V \ ,$$

where the interaction term V is the same as in eq. (4.22). We notice that, compared to the Hamiltonian $H - \mu N$ in the rest frame O, there is the constant term $Nmv^2/2$, corresponding to the total kinetic energy of the system moving with velocity $\mathbf{v}$, and the single-partcle kinetic energy ϵ_k is replaced by the difference $\epsilon_k - \hbar\mathbf{k}\cdot\mathbf{v}$. After performing the Bogoliubov treatment one finds the quasi-particle Hamiltonian

$$H'_{BOG} - \mu N = \frac{Nmv^2}{2} + E_{BOG} + \sum_{\mathbf{k}\neq 0}(E_k - \hbar\mathbf{k}\cdot\mathbf{v})\alpha^\dagger_{\mathbf{k}}\alpha_{\mathbf{k}} \; , \tag{4.50}$$

to be compared with $H_{BOG} - \mu N = E_{BOG} + \sum_{\mathbf{k}} E_k \alpha^\dagger_{\mathbf{k}}\alpha_{\mathbf{k}}$ given by eq. (4.47) in the rest frame O. To obtain the result (4.50) we used the fact that the total momentum $\mathbf{P}$ carried by particles and by quasi-particles coincide

$$\begin{aligned}\mathbf{P} &= \sum_{\mathbf{k}}\hbar\mathbf{k}a^\dagger_{\mathbf{k}}a_{\mathbf{k}} = \sum_{\mathbf{k}\neq 0}\hbar\mathbf{k}(u_k^2\alpha^\dagger_{\mathbf{k}}\alpha_{\mathbf{k}} + v_k^2\alpha^\dagger_{-\mathbf{k}}\alpha_{-\mathbf{k}} + v_k^2 + u_kv_k\alpha^\dagger_{\mathbf{k}}\alpha^\dagger_{-\mathbf{k}} + u_kv_k\alpha_{-\mathbf{k}}\alpha_{\mathbf{k}}) \\ &= \sum_{\mathbf{k}\neq 0}\hbar\mathbf{k}(u_k^2 - v_k^2)\alpha^\dagger_{\mathbf{k}}\alpha_{\mathbf{k}} = \sum_{\mathbf{k}\neq 0}\hbar\mathbf{k}\alpha^\dagger_{\mathbf{k}}\alpha_{\mathbf{k}} \; ,\end{aligned} \tag{4.51}$$

where we used the odd parity of the last three terms in the sum with respect to the transformation $\mathbf{k} \to -\mathbf{k}$.

If $\mathbf{v}$ is the velocity of the walls of a pipe containing the fluid then, at $T = 0$, the ground state of (4.50) describes the state in equilibrium with the moving walls. We notice that if $E_k - \hbar\mathbf{k}\cdot\mathbf{v}$ is positive for any wave vector $\mathbf{k}$, the ground state corresponds to the vacuum of quasi-particles, *i.e.* the equilibrium state with the walls at rest. As seen from the reference frame O' all particles move with velocity $-\mathbf{v}$, giving rise to the kinetic energy $Nmv^2/2$. The peculiar observation is that this state is in equilibrium with the moving walls. The condition $E_k < \hbar kv\cos\theta < \hbar kv$, where θ is the angle between $\mathbf{k}$ and $\mathbf{v}$, provides the following critical velocity

$$v > v_c = \min_k \frac{E_k}{\hbar k} \; , \tag{4.52}$$

for the break down of the stability of the ground state at rest. In fact, if the walls are moving at a velocity $v > v_c$, excitations with wave vector $\mathbf{k}$ parallel to $\mathbf{v}$ will have negative energy as seen from the reference frame moving together with the walls. Consequently, the ground state in equilibrium with the moving walls will contain a large number of these excitations in contrast to the quasi-particle vacuum corresponding to the ground state in equilibrium with the walls at rest. The above argument and eq. (4.52) for the critical velocity is known as Landau criterium for superfluidity and holds in general for any quasi-particle dispersion E_k. Within the Bogoliubov theory the critical velocity corresponds to the speed of sound $c = \sqrt{gn_0/m}$

$$v_c = \min_k \frac{\sqrt{\epsilon_k^2 + 2gn_0\epsilon_k}}{\hbar k} = \min_k \sqrt{c^2 + \frac{\hbar^2 k^2}{4m^2}} = c \ .$$

In the case of an ideal gas the elementary excitations are given by $E_k = \epsilon_k$ and one finds instead $v_c = 0$, showing that a non-interacting gas can not exhibit superfluidity.

- Normal component and two-fluid model

At finite T the averaged momentum density in the moving reference frame O' is given by

$$\frac{\langle \mathbf{P}' \rangle}{V} = \frac{1}{V} \langle \sum_{\mathbf{k}} \big(\hbar\mathbf{k} - m\mathbf{v}\big) a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \rangle = \frac{1}{V} \sum_{\mathbf{k}\neq 0} \hbar\mathbf{k} \langle \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} \rangle - \rho\mathbf{v} \ , \tag{4.53}$$

where we used result (4.51) for the total momentum operator $\mathbf{P}$ and we introduced the notation $\rho = mn$ for the mass density. According to eq. (4.50) for the grand-canonical Hamiltonian in the reference frame O', the average quasi-particle occupation of the state $\mathbf{k}$ reads

$$\langle \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} \rangle = \frac{1}{e^{\beta(E_k - \hbar\mathbf{k}\cdot\mathbf{v})} - 1} \ .$$

The quasi-particle contribution to eq. (4.53) can be calculated explicitly to lowest order in the velocity v, yielding the result

$$\begin{aligned} \frac{1}{V} \sum_{\mathbf{k}\neq 0} \hbar\mathbf{k} \langle \alpha_{\mathbf{k}}^\dagger \alpha_{\mathbf{k}} \rangle &= \frac{1}{V} \sum_{\mathbf{k}\neq 0} \hbar\mathbf{k} \Big(\frac{1}{e^{\beta E_k} - 1} + \frac{\hbar\mathbf{k}\cdot\mathbf{v}}{k_B T} \frac{e^{\beta E_k}}{(e^{\beta E_k} - 1)^2} \Big) \\ &= \frac{\mathbf{v}}{3} \frac{1}{V} \sum_{\mathbf{k}\neq 0} \frac{\hbar^2 k^2}{k_B T} \frac{e^{\beta E_k}}{(e^{\beta E_k} - 1)^2} \equiv \rho_n \mathbf{v} \ . \end{aligned}$$

Here we used the angular average $\mathbf{k}(\mathbf{k}\cdot\mathbf{v}) = \mathbf{v}k^2/3$ and the last equality defines the mass density of the normal component ρ_n. One has in general $\rho_n \geq 0$ and $\rho_n \leq \rho$, so that eq. (4.53) yields the average momentum density

$$\frac{\langle \mathbf{P}' \rangle}{V} = -(\rho - \rho_n)\mathbf{v} \equiv -\rho_s \mathbf{v} \ ,$$

as measured from the moving reference frame O'. The above equation indicates that the gas of quasi-particles moves together with the walls, being therefore at rest in the reference frame O'. The superfluid component, instead, is defined by the difference $\rho - \rho_n$ and moves with velocity $-\mathbf{v}$, being therefore at rest in the laboratory frame. In the reference frame O one finds of course $\langle \mathbf{P} \rangle / V = \rho_n \mathbf{v}$. It is worthwhile calculating the value of ρ_n at very low temperatures, where only phonons contribute to the statistical average and one can replace the dispersion relation of quasi-particles with the linear law $c\hbar k$. One finds the relevant result

$$\rho_n = \frac{1}{V} \sum_{\mathbf{k} \neq 0} \frac{\hbar^2 k^2}{3 k_B T} \frac{e^{c\hbar k / k_B T}}{(e^{c\hbar k / k_B T} - 1)^2} = \frac{(k_B T)^4}{6\pi^2 \hbar^3 c^5} \int dx \frac{x^4 e^x}{(e^x - 1)^2} = \frac{2\pi^2 (k_B T)^4}{45 \hbar^3 c^5} \ ,$$

in agreement with the temperature dependence of the normal moment of inertia measured in the Andronikashvili experiment.

The general equation for the momentum density in a given reference frame

$$\frac{\langle \mathbf{P} \rangle}{V} = \rho_n \mathbf{v}_n + \rho_s \mathbf{v}_s \ , \tag{4.54}$$

in terms of the normal component moving with velocity $\mathbf{v}_n$ and the superfluid component moving with velocity $\mathbf{v}_s$, is the basic equation of the two-fluid model of superfluidity. Using the two-fluid model one can easily understand the non-classical rotational inertia exhibited by the He-II phase. In the annular geometry of the Hess-Fairbank experiment the azimuthal velocity induced by the angular frequency is given by $v = \Omega R$. If $v < v_c$, the equilibrium state in the rotating frame corresponds to a superfluid component at rest, whereas the normal component moves together with the rotating bucket providing a contribution to the moment of inertia equal to $I = R^2 \int d\mathbf{r} \rho_n$ and smaller than the rigid-body value $I_0 = R^2 \int d\mathbf{r} \rho$. Persistent currents are instead explained through the excitation of vortices having a finite number of quanta of circulation by which the condensate is able to rotate. As we discussed at the end of the paragraph concerning the Gross-Piaevskii theory, these vortex states are metastable and can live for quite a long time giving rise to a persistent flow.

4.3 Problems

- 1. Consider a non-interacting Bose gas confined in an isotropic harmonic trap $U(\mathbf{r}) = m\omega^2 r^2/2$. Show that the proper thermodynamic limit for this problem is $N \to \infty$, $\omega \to 0$ with $N\omega^3 =$ const. In this limit calculate the Bose-Einstein transition temperature T_c.

  Solution: From Problem 4 of Chapter 3 on has that the density of states in an isotropic harmonic trap is given by: $g(\epsilon) = \frac{1}{2}\frac{\epsilon^2}{(\hbar\omega)^3}$ in the limit $\epsilon \gg \hbar\omega$. For the total number of particles one finds

$$N = \int_0^\infty d\epsilon \frac{\epsilon^2}{2(\hbar\omega)^3} \frac{1}{z^{-1}e^{\beta\epsilon} - 1} = \frac{(k_B T)^3}{(\hbar\omega)^3} g_3(z) \ ,$$

  showing that indeed the thermodynamic limit implies $N \to \infty$, $\omega \to 0$ and $N\omega^3 =$ const. Since $g_3(z) \leq \zeta(3) \simeq 1.202$, the transition temperature in the thermodynamic limit is given by

$$T_c = \frac{\hbar\omega}{k_B} \left(\frac{N}{\zeta(3)} \right)^{1/3} \ .$$

- 2. For the system in Problem 1 determine the equation of state both below and above the transition temperature T_c.

  Solution: We consider the gas in the thermodynamic limit. From the density of states $g(\epsilon) = \frac{1}{2}\frac{\epsilon^2}{(\hbar\omega)^3}$, a straightforward calculation yields the thermodynamic potential

$$\Omega(T, \omega, \mu) = k_B T \int_0^\infty d\epsilon \frac{\epsilon^2}{2(\hbar\omega)^3} \log\left(1 - ze^{-\beta\epsilon}\right) = -\frac{(k_B T)^4}{(\hbar\omega)^3} g_4(z) \ .$$

  where we used integration by parts. In the condensed phase ($T < T_c$) the fugacity is given by $z = 1$ and one finds

$$\begin{aligned} \Omega &= -\frac{(k_B T)^4}{(\hbar\omega)^3}\zeta(4) \\ N &= N_0 + \frac{(k_B T)^3}{(\hbar\omega)^3}\zeta(3) \ , \end{aligned}$$

  where N_0 is the macroscopic occupation of the single-particle ground state and $\zeta(4) = \frac{\pi^4}{90} \simeq 1.082$. In the non-condensed phase ($T > T_c$) one has instead

$$\begin{aligned} \Omega &= -\frac{(k_B T)^4}{(\hbar\omega)^3} g_4(z) \\ N &= \frac{(k_B T)^3}{(\hbar\omega)^3} g_3(z) \ . \end{aligned}$$

- 3. For the system in Problem 1 calculate the following thermodynamic functions at $T < T_c$: condensate fraction N_0/N, internal energy U and specific heat $c = (\partial U/\partial T)_N$.

  Solution: From the results of Problem 1 and 2:

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^3 .$$

  In a system with density of states $g(\epsilon) \propto \epsilon^2$, internal energy and thermodynamic potential are related by $U = -3\Omega$ (see Problem 3 of Chapter 3). One gets then

$$U = 3\frac{\zeta(4)}{\zeta(3)} N k_B T \left(\frac{T}{T_c}\right)^3 ,$$

  yielding for the specific heat

$$c = 12\frac{\zeta(4)}{\zeta(3)} N k_B \left(\frac{T}{T_c}\right)^3 .$$

- 4. For the system in Problem 1 show that the specific heat has a discontinuity at T_c.

  Solution: From Problem 3 one finds $c(T_c^-) = 12\frac{\zeta(4)}{\zeta(3)} N k_B$ on approaching T_c from below. At $T > T_c$, the internal energy $U = 3Nk_BT\frac{g_4(z)}{g_3(z)}$ can be expanded for $z \to 1$, yielding the result

$$U = 3Nk_BT\frac{\zeta(4)}{\zeta(3)}\left[1 + \left(\frac{\zeta(2)}{\zeta(3)} - \frac{\zeta(3)}{\zeta(4)}\right)\frac{|\mu|}{k_BT}\right] ,$$

  where we used the expansion $g_n(e^{-|\mu|/k_BT}) \simeq \zeta(n) - \zeta(n-1)\frac{|\mu|}{k_BT}$ holding integers $n > 2$. From the equation for the total number of particles one gets in the same limit

$$\frac{|\mu|}{k_BT} \simeq \frac{3\zeta(3)}{\zeta(2)}\frac{T - T_c}{T_c} .$$

  One finds

$$U \simeq 3Nk_BT\left[\frac{\zeta(4)}{\zeta(3)} + 3\frac{T - T_c}{T_c}\left(\frac{\zeta(4)}{\zeta(3)} - \frac{\zeta(3)}{\zeta(2)}\right)\right] ,$$

  yielding the result

$$c(T_c^+) = 12Nk_B\frac{\zeta(4)}{\zeta(3)} - 9Nk_B\frac{\zeta(3)}{\zeta(2)} ,$$

  for the specific heat just above the transition temperature. At T_c we get thus

$$c(T_c^+) - c(T_c^-) = -9Nk_B\frac{\zeta(3)}{\zeta(2)} .$$

- 5. Consider a homogeneous gas of non-interacting bosons in two dimensions. Show that Bose-

Einstein condensation does not occur in this system.

Solution: We show two alternative ways to solve the problem:

a) In two dimensions the total number of particles is given by

$$N = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_k - \mu} - 1} = \frac{V}{2\pi} \int_0^\infty dk \frac{k}{e^{\beta(\epsilon_k - \mu} - 1} \ ,$$

where in the second equality one takes the thermodynamic limit $N \to \infty$, $V \to \infty$ and $n = \frac{N}{V} = \text{const}$. The above equation can be recast in the form

$$n\lambda_T^2 = g_1(z) \ ,$$

where $g_1(z)$ is the usual special Bose function for which the following relation holds: $g_1(z) = -\log(1-z)$. We notice that for any finite value of $n\lambda_T^2$ the above equation can be solved by $z < 1$, making thus the condensate phase with $z = 1$ impossible at $T > 0$.

b) *Per absurdum argumentatio:* Let us suppose that a condensate phase with $z = 1$ exists. Then the occupation number of particles is given by $n_{\mathbf{k}} = \frac{1}{e^{\beta\epsilon_k} - 1}$. We can then write the following inequality

$$\frac{1}{V} \sum_{\mathbf{k} \neq 0} n_{\mathbf{k}} = \frac{N_{k>0}}{V} \leq \frac{N}{V} \ .$$

In the thermodynamic limit the density n is finite, while the sum over single-particle states turns into

$$\frac{1}{V} \sum_{\mathbf{k} \neq 0} n_{\mathbf{k}} = \frac{1}{2\pi} \int_0^\infty dk \frac{k}{e^{\beta\epsilon_k} - 1} \ .$$

This integral diverges at small k because $n_{\mathbf{k}} \sim \frac{k_B T 2m}{\hbar^2 k^2}$ in this limit. The contradiction with the starting hypothesis is evident. It is worth noticing that the present argument continues to hold also in the presence of interactions. In fact, the Bogoliubov inequality states that $n_{\mathbf{k}} \geq \frac{N_0}{N} \frac{m k_B T}{\hbar^2 k^2} - \frac{1}{2}$, where $\frac{N_0}{N}$ is the condensate fraction. This inequality implies the same above contradiction with the hypothesis $\frac{N_0}{N} \neq 0$.

- 6. Consider a non-interacting gas of bosons in a two-dimensional harmonic trap $U(x, y) = m\omega^2(x^2 + y^2)/2$. Show that the proper thermodynamic limit in this case is $N \to \infty$, $\omega \to 0$ with $N\omega^2 = \text{const}$. Show that this system exhibits Bose-Einstein condensation and determine the transition temperature.

Solution: Following Problem 4 of Chapter 3 the density of states in a two-dimensional harmonic trap is given by $g(\epsilon) = \frac{\epsilon}{(\hbar\omega)^2}$ if $\epsilon \gg \hbar\omega$. The relation for the total number of particles then reads

$$N = \int_0^\infty d\epsilon \frac{\epsilon}{(\hbar\omega)^2} \frac{1}{z^{-1} e^{\beta\epsilon} - 1} = \frac{(k_B T)^2}{(\hbar\omega)^2} g_2(z) \ ,$$

in terms of the special Bose function g_2. The proper thermodynamic limit is the one stated above. Furthermore, a macroscopic occupation N_0 of the single-particle ground state starts if $N > \frac{(k_B T)^2}{(\hbar\omega)^2}\zeta(2)$, where $\zeta(2) = \frac{\pi^2}{6} \simeq 1.645$. This sets the transition temperature to the value

$$T_c = \frac{\hbar\omega}{k_B}\left(\frac{N}{\zeta(2)}\right)^2 .$$

- 7. For a homogeneous non-interacting Bose gas at $T < T_c$ determine the large-distance decay law of the OBDM $n_1(s)$.

Solution: From the definition $n_1(s) = \frac{1}{nV}\sum_{\mathbf{k}}\langle n_{\mathbf{k}}\rangle e^{-i\mathbf{k}\cdot\mathbf{s}}$ one obtains for a Bose gas below the transition point

$$n_1(s) = \frac{N_0}{N} + \frac{1}{2\pi^2 ns}\int_0^\infty dk \frac{k\sin(ks)}{e^{\beta\epsilon_k}-1} = \frac{1}{2\pi^2 ns^3}\int_0^\infty dx \frac{x\sin x}{e^{x^2\lambda_T^2/(4\pi s^2)}-1} .$$

In the limit $s \gg \lambda_T$ one can expand the exponential obtaining the required result

$$n_1(s) \simeq \frac{N_0}{N} + \frac{2}{\pi}\frac{1}{n\lambda_T^2 s}\int_0^\infty dx \frac{\sin x}{x} = \frac{N_0}{N} + \frac{1}{n\lambda_T^2 s} .$$

- 8. Use the Bogoliubov theory to describe a weakly repulsive Bose gas and determine at low temperature the law of the thermal depletion of the condensate.

Solution: The average number of particles in states $\mathbf{k} \neq 0$ is given by $\langle a_{\mathbf{k}}^\dagger a_{\mathbf{k}}\rangle = v_k^2 + (u_k^2 + v_k^2)\langle\alpha_{\mathbf{k}}^\dagger\alpha_{\mathbf{k}}\rangle$ in terms of the thermal average of quasiparticles. Here, u_k and v_k are the Bogoliubov amplitudes. Since $\langle\alpha_{\mathbf{k}}^\dagger\alpha_{\mathbf{k}}\rangle = \frac{1}{e^{\beta E_k}-1}$, where E_k are the quasiparticle energies, vanishes at $T = 0$, the thermal depletion of the condensate is given by

$$\frac{N(T)}{N} = \frac{1}{N}\sum_{\mathbf{k}\neq 0}\frac{\epsilon_k + gn_0}{E_k}\frac{1}{e^{\beta E_k}-1} .$$

At low temperature only phonons contribute and one finds

$$\frac{N(T)}{N} = \frac{1}{2\pi^2 n}\int_0^\infty dk \frac{mc^2k^2}{c\hbar k}\frac{1}{e^{\beta c\hbar k}-1} = \frac{m(k_BT)^2}{12n\hbar^3 c} ,$$

where we used the result $\int_0^\infty dx \frac{x}{e^x-1} = \frac{\pi^2}{6}$.

- 9. Within the Bogoliubov approximation of problem 9 calculate at low temperature the contribution of phonons to the internal energy and to the specific heat.

Solution: The internal energy is given by

$$U = \langle H_{BOG}\rangle = E_0 + \sum_{\mathbf{k}\neq 0} E_k\langle\alpha_{\mathbf{k}}^\dagger\alpha_{\mathbf{k}}\rangle ,$$

where E_0 is the ground-state energy. In the limit of low temperatures, only phonons contribute to the integral yielding

$$U = E_0 + \frac{V}{2\pi^2}\frac{(k_BT)^4}{\hbar^3c^3}\int_0^\infty dx \frac{x^3}{e^x-1} = E_0 + \frac{V\pi^2(k_BT)^4}{180\hbar^3c^3} \ .$$

For the specific heat one finds then $c_v = \frac{V\pi^2k_B^4T^3}{45\hbar^3c^3}$.

- 10. Within the Bogoliubov approximation of problem 9 calculate the momentum distribution of particles $\langle n_{\mathbf{k}}\rangle = \langle a_{\mathbf{k}}^\dagger a_{\mathbf{k}}\rangle$ both at $T = 0$ and at $T > 0$. In both cases discuss the behavior of $\langle n_{\mathbf{k}}\rangle$ at small and large k.

  Solution: We use the result

$$n_{\mathbf{k}} = v_k^2 + (u_k^2 + v_k^2)\frac{1}{e^{\beta E_k}-1} \ .$$

  At $T = 0$ only the first term contributes and one finds $n_{\mathbf{k}} \sim \frac{mc}{2\hbar k}$ at small k and $n_{\mathbf{k}} \sim \frac{m^4c^4}{\hbar^4k^4}$ at large k. At $T > 0$ one finds instead: $n_{\mathbf{k}} \sim \frac{mk_BT}{\hbar^2k^2}$ at small k and the same law $n_{\mathbf{k}} \sim \frac{m^4c^4}{\hbar^4k^4}$ at large k.