THERMODYNAMICAL POTENTIALS OF CLASSICAL AND QUANTUM SYSTEMS

RUIKUAN LIU AND TIAN MA

Department of Mathematics
Sichuan University
Chengdu, Sichuan 610064, China

SHOUHONG WANG∗

Department of Mathematics
Indiana University
Bloomington, IN 47405, USA

JIAYAN YANG

School of Medical Informatics and Engineering
Southwest Medical University
Luzhou, Sichuan 646000, China

(Communicated by Jie Shen)

Abstract. The aim of the paper is to systematically introduce thermodynamic potentials for thermodynamic systems and Hamiltonian energies for quantum systems of condensates. The study is based on the rich previous work done by pioneers in the related fields. The main ingredients of the study consist of 1) SO(3) symmetry of thermodynamical potentials, 2) theory of fundamental interaction of particles, 3) the statistical theory of heat developed recently [23], 4) quantum rules for condensates that we postulate in Quantum Rule 4.1, and 5) the dynamical transition theory developed by Ma and Wang [20]. The statistical and quantum systems we study in this paper include conventional thermodynamic systems, thermodynamic systems of condensates, as well as quantum condensate systems. The potentials and Hamiltonian energies that we derive are based on first principles, and no mean-field theoretic expansions are used.

1. Introduction. For a thermodynamic system, there are three levels of variables that are used to fully describe the system: the control parameters \( \lambda \), the order parameters \( u \), and the thermodynamic potential \( F \). In a recent paper [22], two of the authors postulated the potential-descending principle (PDP): for a non-equilibrium state \( u(t; u_0) \) of a thermodynamic system with initial state \( u(0, u_0) = u_0 \),

\[
\text{(1) the potential } F(u(t; u_0); \lambda) \text{ is strictly decreasing as time evolves;}
\]
The order parameters \( u(t; u_0) \), as time evolves to infinity, tend to an equilibrium of the system, which is a minimal point of the potential \( F \).

We have shown that PDP is a more fundamental principle than the first and second laws of thermodynamics, and provides the first principle for describing irreversibility, and leads to all three distributions: the Maxwell-Boltzmann distribution, the Fermi-Dirac distribution and the Bose-Einstein distribution in statistical physics. Consequently, the potential-descending principle is the first principle of statistical physics.

In addition, for the thermodynamic system with thermodynamic potential \( F(u, \lambda) \), order parameters \( u \) and control parameters \( \lambda \), PDP gives rise to the following dynamic equation [22]:

\[
\frac{du}{dt} = -\delta F(u, \lambda).
\] (1.1)

which offers a complete description of associated phase transitions and transformation of the system from non-equilibrium states to equilibrium states. With (1.1), an important issue boils down to find a better and more accurate account of the thermodynamic potentials.

The main objective of this paper is to systematically introduce thermodynamic potentials for thermodynamic systems and Hamiltonian energies for quantum systems of condensates.

This is a classic topic, and of course, the study presented in this paper relies on the rich previous work done by pioneers in the related fields; we refer the interested readers to, among many others, [26, 29, 17, 19, 18, 13, 8, 30, 3, 15, 5, 9, 31, 10, 28, 16] and the references therein for more details.

The paper studies statistical systems in three categories:

1. conventional thermodynamic systems,
2. thermodynamic systems of condensates, and
3. quantum systems of condensates.

The typical conventional thermodynamic systems include the physical-vapor transport (PVT) systems, the \( N \)-component systems, and the magnetic and dielectric systems.

There are two cases of condensates. The first is the case where the system is near the critical temperature \( T_c \), the condensation is in its early stage and the condensed particle density is small. At this stage, the system is treated essentially as a thermodynamic system, and it is crucial then to find its thermodynamic potential. Such thermodynamic condensate systems belong to Category (2) above, and include thermodynamic systems of superconductors, superfluids, and the Bose-Einstein condensates.

The second is the case where away from the critical temperature, the system enters a deeper condensate state. In this case, the system is a quantum system and obeys the principle of Hamiltonian dynamics. We need to derive the related Hamiltonian energy. Such systems are quantum systems of condensates, as classified as Category (3) above, which include superconducting systems, superfluid systems, and the Bose-Einstein condensates.

Our study in this paper is based on 1) SO(3) symmetry of thermodynamical potentials, 2) theory of fundamental interaction of particles, 3) the statistical theory of heat developed recently [23], 4) quantum rules for condensates that we postulate
in Quantum Rule 4.1, and 5) the dynamical transition theory developed by Ma and Wang [20].

Of course, as mentioned earlier, the study presented in this paper certainly relies on the rich previous work done by pioneers in the related fields. It is worth mentioning that the potentials and Hamiltonians we shall introduce are based on first principles, and no mean-field theoretic expansions are used.

Hereafter we describe briefly the main new ingredients for determining thermodynamic potentials and Hamiltonians.

First, symmetry plays a crucial role in determining the mathematical expression of thermodynamical potentials in statistical physics. As demonstrated in [22], the thermodynamical potential functional should be SO(3) invariant, and \(-\delta F(u, \lambda)\) in (1.1) represents the generalized driving force for the thermodynamic system.

Also, based on known physical facts, we postulate that for a non-uniform thermodynamical system, the potential functional \(F = F(u, \lambda)\) depends only on \(u\) and its first-order derivatives. With the SO(3) symmetry and this postulate, we obtain the following general forms of thermodynamical potentials:

\[
F = \int_{\Omega} \left[ \frac{\alpha}{2} |\nabla u|^2 + \frac{\beta}{2} \vec{a} \cdot \nabla u + g(u, \lambda) \right] dx \quad \text{for scalar fields,} \tag{1.2}
\]

\[
F = \int_{\Omega} \left[ \frac{\alpha}{2} |\nabla \vec{u}|^2 + \frac{\beta}{2} (\text{div} \vec{u})^2 + g(\vec{u}, \lambda) \right] dx \quad \text{for vector fields.} \tag{1.3}
\]

Here \(\alpha > 0\) and \(\beta\) are coefficients, and \(g(\vec{u}, \lambda)\) is an SO(3) invariant with respect to \(\vec{u}\).

Second, another important ingredient is the recently developed statistical theory of heat [23], and we have shown that the entropy represents the number of photons between particles in the system.

Consequently by the vibratory mechanism of thermal radiation, the entropy density depends on the molar density \(\rho\). Hence \(|\nabla \rho|^2\) represents the energy for maintaining the non-homogeneity of the particle distribution of the system, and the non-homogeneous distribution of entropy is due to non-homogeneous distribution of particles. Therefore there is no \(|\nabla S|^2\) term in the potential functionals for all thermodynamic systems, which is reflected by the term \(|\nabla \rho|^2\).

Third, when a thermodynamic system forms a condensate, the order parameter is a family of complex-valued wave functions \(\psi : \Omega \to \mathbb{C}^N\) such that \(|\psi|^2\) represents the particle number density of the condensate. The wave functions \(\psi\) are governed by physical laws, and describe the collective behavior of the condensate particles, which possess mutual interactions.

Based on the combination of physical facts and the repulsive-attractive characteristic of the three interactions: the electromagnetic, the weak and the strong interactions; see [21], we introduce a quantum rule for condensates, stated in Quantum Rule 4.1:

Hence for condensates these wave functions obey their own quantum rules as follows:
the (attractive) binding energy between particles is

\[^{\text{binding energy density \( = -g_0|\psi|^2,\)}}\]

where \( g_0 > 0 \) stands for interaction potential;

(2) the repulsive interaction energy between particles is

\[^{\text{repulsive energy density \( = \frac{1}{2}g_1|\psi|^4,\)}}\]

where \( g_1 > 0 \) is the interaction constant.

It is the attraction potential \( -g_0|\psi|^2 \) that ensures a large collection of particles to condensate, and it is also the short-range repulsive characteristic \( \frac{1}{2}g_1|\psi|^4 \) that ensures the finite density of particles.

Fourth, the repulsive energy density term

\[^{\text{\( \frac{1}{2}g_1|\psi|^4 \) (\( g_1 > 0 \))}}\]

also ensures the stability of the system, a requirement from both the mathematics and physics viewpoints.

In fact, the following terms to be introduced later in the paper

\[^{\text{\( BTS\rho^2 \) in the potential for PVT systems,}}\]
\[^{\text{\( TSB_3u_iu_j \) in the potential for N-component systems,}}\]
\[^{\text{\( -\beta TS|M|^2 \) in the potential for magnetic systems,}}\]
\[^{\text{\( -\beta TS|P|^2 \) in the potential for dielectric systems,}}\]
\[^{\text{\( -\beta TS|\Psi|^2 \) in the potential for condensates,}}\]

are crucial for both stabilities and phase transitions of the underlying physical systems.

Finally, we emphasize that Hamiltonians for quantum systems of condensates in Section 5 are based on the work of Gross [11], Pitaevskii [27], Ho [12] and Ohmi and Machida [25].

The paper is organized as follows. In Section 2, we introduce some preliminaries, focusing on SO(n) symmetry and SO(3) spinor representations. Potentials for conventional thermodynamic systems are carried out in Section 3, and potentials for thermodynamic systems of condensates are introduced in Section 4. Section 5 studies the Hamiltonian energies of quantum condensates. Section 6 makes some remarks on the dynamical equations of the systems discussed in this paper.

2. Preliminaries.

2.1. Potential-descending principle of statistical physics. In this section, we recapitulate the potential-descending principle (PDP), introduced in [22].

For a given thermodynamic system, the order parameters (state functions) \( u = (u_1, \cdots, u_N) \), the control parameters \( \lambda \), and the thermodynamic potential functional (or potential in short) \( F \) are well-defined quantities, fully describing the system. The potential is a functional of the order parameters, and is used to represent the thermodynamic state of the system. There are four commonly used thermodynamic potentials: the internal energy, the Helmholtz free energy, the Gibbs free energy, and the enthalpy.
After a thorough examination of thermodynamics, we discovered in [22] that the following Potential-Descending Principle (PDP) is a fundamental principle in statistical physics.

**Principle 2.1 (Potential-Descending Principle).** For each thermodynamic system, there are order parameters $u = (u_1, \cdots, u_N)$, control parameters $\lambda$, and the thermodynamic potential functional $F(u; \lambda)$. For a non-equilibrium state $u(t; u_0)$ of the system with initial state $u(0; u_0) = u_0$, we have the following properties:

1. The potential $F(u(t; u_0); \lambda)$ is decreasing:
   $$\frac{d}{dt} F(u(t; u_0); \lambda) < 0 \quad \forall t > 0;$$

2. The order parameters $u(t; u_0)$ have a limit
   $$\lim_{t \to \infty} u(t; u_0) = \bar{u};$$

3. There is an open and dense set $\mathcal{O}$ of initial data in the space of state functions, such that for any $u_0 \in \mathcal{O}$, the corresponding $\bar{u}$ is a minimum of $F$, which is called an equilibrium of the thermodynamic system:
   $$\delta F(\bar{u}; \lambda) = 0.$$

We have shown that PDP is a more fundamental principle than the first and second laws of thermodynamics, and provides the first principle for describing irreversibility, leads to all three distributions: the Maxwell-Boltzmann distribution, the Fermi-Dirac distribution and the Bose-Einstein distribution in statistical physics. Consequently, the potential-descending principle is the first principle of statistical physics.

Also importantly, based on PDP, the dynamic equation of a thermodynamic system in a non-equilibrium state takes the form

$$\frac{du}{dt} = -A \delta F(u, \lambda) \quad \text{for isolated systems,}$$

$$\left\{ \begin{align*}
\frac{du}{dt} &= -A \delta F(u, \lambda) + B(u, \lambda), \\
\int A \delta F(u, \lambda) \cdot B(u, \lambda) &= 0
\end{align*} \right. \quad \text{for coupled systems},$$

where $\delta$ is the derivative operator, $B$ represents coupling operators, and $A$ is a symmetric and positive definite matrix of coefficients. We refer interested readers to [22] for details.

A few remarks are now in order.

1. **Conditions for Legendre transformation.** By PDP, for each given thermodynamic system, there is a thermodynamic potential functional $F$, fully describing the system. The potential is a functional of the order parameters, and is used to represent the thermodynamic state of the system. Each thermodynamical potential contains the internal energy $U$, and is derived from $U$ through Legendre transformations as follows:

   1. For a thermodynamics system with the order parameter $u$ and control parameter $v$, then at the thermodynamic equilibrium, the potential functional $F = F(u, v)$ satisfies the equilibrium equation
      $$\frac{\partial}{\partial u} F(u, v) = 0.$$ (2.3)
(2) We know that $U$ is part of $F$. Also as an internal system with potential $U$, the order parameter should be $v$, and control parameter should be $u$, reversed from the case for $F$.

(3) Under the conditions of (1) and (2) above, we need to related $F$ with $U$ by the Legendre transformation:

$$F = U(v, u) - uv, \quad (2.4)$$

$$v = \frac{\partial}{\partial u} U(v, u). \quad (2.5)$$

Notice that (2.5) defines an implicit function relation between $u$ and $v$:

$$u = \varphi(v), \quad (2.6)$$

which ensures that at the equilibrium, $F$ is the potential, $u$ is the order parameter and $v$ is the control parameter. The condition to ensure the existence of (2.6) is

$$\frac{\partial^2}{\partial u^2} U(0, 0) \neq 0. \quad (2.7)$$

Consequently, to ensure the validity of the Legendre transformation (2.4)-(2.5), $U$ must contain the square term $u^2$ of $u$. The condition (2.7) is crucial for deriving thermodynamical potentials in this paper.

2). Equation of state. The equation of state is solution equation

$$u = u(\lambda) \quad (2.8)$$

of the variational equation of the potential $F$:

$$\frac{\delta}{\delta u} F(u, \lambda) = 0.$$

This connection can be viewed in two ways. One is to use the potential to derive the equation of state, and the other is to use known equation of state as a guidance to derive thermodynamical potential of the system.

3). Chemical potentials. Gibbs was the first who introduced the chemical potential $\mu$, which has been considered as the conjugate variable of the number of particles $N$, leading to the quantity $Z = \mu N$. Here we demonstrate that $\mu$ is in fact the Lagrangian multiplier of the conservation of number of particles in the system.

Consider a thermodynamic system with fixed number $N$ of particles and with thermodynamic potential

$$F = F(u, \lambda), \quad (2.9)$$

where $u$ is the molar density of particles. By the conservation of total number of particles,

$$G(u) = \int_{\Omega} u dx = \text{constant}. \quad (2.10)$$

The physical definition of $\mu$ shows that at the equilibrium

$$\mu = \frac{\delta}{\delta u} F(u, \lambda). \quad (2.11)$$

Also, the variation of the functional (2.9) under constraint (2.10) is

$$\frac{\delta}{\delta u} F(u, \lambda) = \beta \delta G(u) = \beta, \quad (2.12)$$
where $G$ is the constraint functional in (2.10), $\beta$ is the Lagrangian multiplier, and $\delta G(u) = 1$. In other words,

$$\mu = \text{Lagrangian multiplier } \beta.$$  \hfill (2.13)

Since the Lagrangian multiplier is a constant, and the chemical potential $\mu$ is also a constant. Hence $Z = \mu N$ plays a different role in the thermodynamic potential than the thermal energy $Q = ST$ and mechanical energy $W = fX$.

In addition, if we modify the thermodynamic energy $F$ by

$$H = F(u, \lambda) - \mu G(u),$$  \hfill (2.14)

where $G(u)$ is as in (2.10), and $\mu$ is the chemical potential, then the equilibrium equation is given by

$$\delta \frac{\delta u H(u, \lambda)}{\delta u} = 0,$$  \hfill (2.15)

which is equivalent to (2.11).

In summary, we have the following physical conclusions for chemical potential.

**Physical Conclusion 2.2 (Physical Properties of Chemical Potential).** For a system with conserved particle numbers, the following hold true for the chemical potential $\mu$:

1. $\mu$ is the Lagrangian multiplier of the thermodynamic potential $F$, and is a constant;
2. $\mu$ is neither an order parameter, nor a control parameter;
3. the potential functional takes the form (2.14).

### 2.2. **SO$(n)$ symmetry.**

#### 2.2.1. **SO$(n)$ invariants and basic forms of thermodynamic potentials.** Symmetry plays a fundamental role in physics, and is characterized by three ingredients:

- spaces, transformation groups, and tensors,

which are applicable to different physical fields. The $SO(n)$ symmetry is also called rotational symmetry, and we shall see that $SO(3)$ symmetry plays a crucial role in determining the mathematical expression of thermodynamical potentials in statistical physics.

For $SO(n)$ symmetry, the space is the $n$-dimensional Euclidean space $\mathbb{R}^n$, and the transformation group is $SO(n)$ defined by

$$SO(n) = \{ n \times n \text{ real matrices } A \mid AA^T = I, \ \det A = 1 \}.$$  \hfill (2.16)

More precisely, let $x = (x_1, \cdots, x_n)$ be the coordinates of a vector in $\mathbb{R}^n$ under an orthogonal coordinate system. Consider the following orthogonal transformation

$$\tilde{x} = Ax \quad \text{or} \quad \tilde{x}_i = a_{ij}x_j \quad \text{for } A = (a_{ij}) \in SO(n),$$  \hfill (2.17)

where the summation convention is used for repeated indices. The corresponding tensors are Cartesian tensors with transformations given by (2.17).

For a thermodynamical system, there are three levels of variables: order parameters $u$ (state variables), the control parameters $\lambda$, and the thermodynamic potential functional $F = F(u, \lambda)$, which are functionals of $u$ and $\lambda$. The order parameters and control parameters are given by in their general form by

- order parameters $\quad u = (u_1, \cdots, u_N),$
- control parameters $\quad \lambda = (\lambda_1, \cdots, \lambda_k).$
If \( u = u(x) \) depends on the position \( x \in \Omega \), the general expression of \( F \) is written as
\[
F(u, \lambda) = \int_{\Omega} f(u, \cdots, D^k u, \lambda) \, dx \quad (k \geq 1),
\]
where \( \Omega \subset \mathbb{R}^n \) \((n = 2, 3)\) is the domain that the system occupies, \( D^k u \) is the \( k \)-th derivative of \( u \). As mentioned earlier, the potential functional (2.18) is \( SO(n) \) invariant. Namely, under the coordinate transformation (2.17), the integrand \( f(u, \cdots, D^k u, \lambda) \) in (2.18) is invariant, and hence it is an \( SO(n) \) invariant. This symmetry requirement leads to natural restrictions on the expression of \( f \), which we explore hereafter.

1). An example of invariants. Consider the following gradient square of a scalar function \( u \):
\[
f(u) = |\nabla u|^2 = \sum_{i=1}^{n} \left( \frac{\partial u}{\partial x_i} \right)^2.
\]
Under the transformation (2.17), by
\[
\tilde{\nabla} u^T = A \nabla u^T \quad (\nabla u^T = A^T \tilde{\nabla} u^T),
\]
where \( A \) is an orthogonal matrix as in (2.17). Then we have
\[
f = \nabla u \cdot \nabla u^T = \tilde{\nabla} u A \cdot A^T \tilde{\nabla} u^T = \tilde{\nabla} u \cdot \tilde{\nabla} u^T,
\]
where \( A^T = A^{-1} \). Hence
\[
f = |\tilde{\nabla} u|^2 = \sum_{i=1}^{n} \left( \frac{\partial u}{\partial \tilde{x}_i} \right)^2,
\]
which shows that the expression (2.21) of \( f \) with coordinates \( \tilde{x} \) is the same as the expression (2.19) of \( f \) with coordinates \( x \). This is the meaning of invariants.

2). Basic forms of invariants. For a scalar field \( u \), the following are invariants associated with the first order derivatives of \( u \):
\[
|\nabla u|^2 = \left( \frac{\partial u}{\partial x_1} \right)^2 + \cdots + \left( \frac{\partial u}{\partial x_n} \right)^2,
\]
\[
\tilde{a} \cdot \nabla u = a_1 \frac{\partial u}{\partial x_1} + \cdots + a_n \frac{\partial u}{\partial x_n},
\]
where \( \tilde{a} \) is a given vector field.

For a vector field \( \tilde{u} = (u_1, \cdots, u_n) \), the following are invariants associated with the first order derivatives of \( u \):
\[
|\tilde{u}|^2 = u_1^2 + \cdots + u_n^2,
\]
\[
\tilde{a} \cdot \tilde{u} = a_1 u_1 + \cdots + a_n u_n,
\]
\[
\text{div} \tilde{u} = \frac{\partial u_1}{\partial x_1} + \cdots + \frac{\partial u_n}{\partial x_n},
\]
\[
|\nabla \tilde{u}|^2 = |\nabla u_1|^2 + \cdots + |\nabla u_n|^2.
\]

3). Basic forms of thermodynamic potentials. Known physical facts are showing that thermodynamical potential functionals depend at most on derivatives of \( u \) up to the first-order; and this leads to the following hypothesis:

**Hypothesis 2.3.** For a non-uniform thermodynamical system, the potential functional (2.18) depends only on \( u \) and its first-order derivatives with \( k = 1 \).
With this assumption and the invariants (2.22)–(2.23) involving the first order derivatives of \( u \), we obtain the following general forms of thermodynamical potentials:

\[
F = \int_{\Omega} \left[ \frac{\alpha}{2} \left| \nabla u \right|^2 + \frac{\beta}{2} \vec{a} \cdot \nabla u + g(u, \lambda) \right] \, dx \quad \text{for scalar fields,} \tag{2.24}
\]

\[
F = \int_{\Omega} \left[ \frac{\alpha}{2} \left| \nabla \vec{u} \right|^2 + \frac{\beta}{2} (\text{div} \vec{u})^2 + g(\vec{u}, \lambda) \right] \, dx \quad \text{for vector fields.} \tag{2.25}
\]

Here \( \alpha > 0 \) and \( \beta \) are coefficients, and \( g(\vec{u}, \lambda) \) is an invariant with respect to \( \vec{u} \).

We see from (2.24) and (2.25) that \( SO(n) \) invariance has already determined the main components of the potential, and what it remains is to determine \( g(u, \lambda) \) and \( g(\vec{u}, \lambda) \).

2.2.2. \( SO(3) \) spinors. In quantum thermodynamical systems, we need to deal with quantum fields where the complex-valued wave functions are order parameters. In this case, the invariance is no longer described by tensors, rather by spinors. Now we introduce the concept of spinors, which are crucial for the mathematical foundation of the theory of condensates.

Let \( \psi = (\psi_1, \cdots, \psi_N) \) be a set of complex valued wave functions:

\[
\psi : \mathbb{R}^3 \to \mathbb{C}^N. \tag{2.26}
\]

Under an orthogonal coordinate transformation in \( \mathbb{R}^3 \):

\[
\vec{x} = Ax \quad \text{for } A \in SO(3), \tag{2.27}
\]

the wave functions \( \psi \) in (2.26) obey the spinor transformation defined as follows. For each orthogonal matrix \( A \) as in (2.27), there is a complex unitary matrix \( U(A) \) such that

\[
\vec{\psi} = U(A) \psi, \quad U(A) \in SU(N). \tag{2.28}
\]

Here \( SU(N) \) is defined by

\[
SU(N) = \{ \text{N-th order complex matrices } U \mid U^\dagger = U^{-1}, \det U = 1 \},
\]

where \( U^\dagger = (U^T)^* \) is the transpose of complex conjugate of \( U \). We have then the following definition.

**Definition 2.1.** For the wave functions \( \psi \) given by (2.26), if under the orthogonal transformation (2.27), there is a group homeomorphism

\[
U : SO(3) \to SU(N), \tag{2.29}
\]

such that for each \( A \) in (2.27), \( \psi \) transform according to (2.28), then \( \psi \) is called an \( SO(3) \) spinor. The homomorphism (2.29) is called an \( SO(3) \) spinor representation of \( \psi \).

In (2.29), the \( SU(N) \) is required to ensure the normality of \( \psi \):

\[
|\vec{\psi}|^2 = |\psi|^2.
\]
2.2.3. SO(3) spinor representations. To derive the covariance of quantum field equations and the invariance of the Hamiltonian energy, we now determine the specific expression of the spinor representation \( U(A) \) in (2.29) with respect to \( A \in SO(3) \). We proceed as follows.

1) Euler representation of SO(3). Consider an orthogonal matrix \( A \in SO(3) \), and the corresponding transformation

\[
\begin{pmatrix}
\tilde{x} \\
\tilde{y} \\
\tilde{z}
\end{pmatrix} = A \begin{pmatrix} x \\ y \\ z \end{pmatrix}.
\]

(2.30)

For the Euler representation, we need to express \( A \) in terms of the three Euler angles \( (\phi, \theta, \psi) \). The above transformation is the composition of the following rotations.

First is the counterclockwise rotation with angle \( \phi \) and with respect to the \( z \)-axis of the coordinate system \( (x, y, z) \):

\[
\begin{pmatrix} x_1 \\ y_1 \\ z_1 
\end{pmatrix} = \begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix} \begin{pmatrix} x \\ y \\ z 
\end{pmatrix} = A_1(\phi) \begin{pmatrix} x \\ y \\ z 
\end{pmatrix}.
\]

(2.31)

Then rotate the \( (x_1, y_1, z_1) \) system with respect to the \( x_1 \)-axis and with angle \( \theta \):

\[
\begin{pmatrix} x_2 \\ y_2 \\ z_2 
\end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\
0 & \cos \theta & \sin \theta \\
0 & -\sin \theta & \cos \theta
\end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 
\end{pmatrix} = A_2(\theta) \begin{pmatrix} x_1 \\ y_1 \\ z_1 
\end{pmatrix}.
\]

(2.32)

The final step is to rotate the \( (x_2, y_2, z_2) \) system around \( z_2 \) with angle \( \psi \):

\[
\begin{pmatrix} \tilde{x} \\ \tilde{y} \\ \tilde{z}
\end{pmatrix} = \begin{pmatrix}
\cos \psi & \sin \psi & 0 \\
-\sin \psi & \cos \psi & 0 \\
0 & 0 & 1
\end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 
\end{pmatrix} = A_1(\psi) \begin{pmatrix} x_2 \\ y_2 \\ z_2 
\end{pmatrix}.
\]

(2.33)

The combined transformation (2.31)–(2.33) leads to the equivalent form of the transformation (2.30):

\[
\begin{pmatrix} \tilde{x} \\ \tilde{y} \\ \tilde{z}
\end{pmatrix} = A_1(\psi)A_2(\theta)A_1(\phi) \begin{pmatrix} x \\ y \\ z 
\end{pmatrix},
\]

where \( A = A_1(\psi)A_2(\theta)A_1(\phi) \) is the matrix given in terms of \( (\phi, \theta, \psi) \) as

\[
A = \begin{pmatrix}
\cos \psi & \sin \psi & 0 \\
-\sin \psi & \cos \psi & 0 \\
0 & 0 & 1
\end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\
0 & \cos \theta & \sin \theta \\
0 & -\sin \theta & \cos \theta
\end{pmatrix} \begin{pmatrix} \cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}.
\]

(2.34)

\[
A = \begin{pmatrix}
f_{11}(\phi, \theta, \psi) & f_{12}(\phi, \theta, \psi) & \sin \psi \sin \theta \\
f_{21}(\phi, \theta, \psi) & f_{22}(\phi, \theta, \psi) & \cos \psi \sin \theta \\
\sin \theta \sin \phi & -\sin \theta \cos \phi & \cos \theta
\end{pmatrix},
\]

where

\[
f_{11} = \cos \phi \cos \psi - \cos \theta \sin \phi \sin \psi,
\]

\[
f_{12} = \sin \phi \cos \psi + \cos \theta \cos \phi \sin \psi,
\]

\[
f_{21} = -\cos \phi \sin \psi - \cos \theta \sin \phi \cos \psi,
\]

\[
f_{22} = -\sin \phi \sin \psi + \cos \theta \cos \phi \cos \psi.
\]
The Euler angles \((\phi, \theta, \psi)\) are independent, and determine all the matrices in \(SO(3)\). Hence (2.34) is the Euler angle representation of \(SO(3)\). Also, we have
\[
0 \leq \phi \leq 2\pi, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \psi \leq 2\pi.
\]

2). \(SO(3)\) spinor representation with \(N = 2\). In this case, the spinor representation
\[
U : SO(3) \rightarrow SU(2)
\] (2.35)
is a two-copy representation. Namely, for each \(A \in SO(3)\) given in terms of the Euler angles \((\phi, \theta, \psi)\), the representation \(U(A)\) in (2.35) has two-copies \(U_1, U_2\):
\[
U_1 = \left( e^{i(\psi+\phi)/2} \cos \frac{\theta}{2}, ie^{i(\psi-\phi)/2} \sin \frac{\theta}{2} \right),
\]
(2.36)
\[
U_2 = \left( e^{-i(\psi+\phi)/2} \cos \frac{\theta}{2}, -ie^{-i(\psi-\phi)/2} \sin \frac{\theta}{2} \right).
\]
(2.37)

With these two copies, there are two types of spinors for the two-component wave function \(\psi = (\psi_1, \psi_2)\): Under the coordinate transformation (2.27),
- Type-I spinor : \(\tilde{\psi} = U_1 \psi\) \(U_1\) is as (2.36),
- Type-II spinor : \(\tilde{\psi} = U_2 \psi\) \(U_2\) is as (2.37).

3). \(SO(3)\) spinor representation with \(N = 3\). The spinor representation with \(N = 3\) corresponds to the Bose-Einstein condensation problem with \(J = 1\). For a Bose system with \(J = 1\), there are three quantum states: \(m = 1, 0, -1\), with \(m\) being the magnetic quantum number. The state of the system is described by a three-component wave function:
\[
\psi = (\psi_1, \psi_0, \psi_{-1}),
\]
where the subindices represent the magnetic quantum number \(m = 1, 0, -1\). The corresponding \(SO(3)\) spinor representation with \(N = 3\)
\[
U : SO(3) \rightarrow SU(3)
\] (2.38)
is defined by
\[
U(A) = M^\dagger AM \quad \forall \ A \in SO(3),
\]
(2.39)
where \(M\) is given by
\[
M = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 0 & 1 \\ -i & 0 & -i \\ 0 & \sqrt{2} & 0 \end{pmatrix}.
\]
(2.40)

When \(A \in SO(3)\) is given in terms of the Euler angles by (2.34):
\[
A = A_1(\psi)A_2(\theta)A_1(\phi),
\]
the corresponding \(U(A)\) in (2.39) can be written as
\[
U(A) = U_1(\psi)U_2(\theta)U_1(\phi),
\]
(2.41)
where
\[
U_1(\phi) = M^\dagger A_1(\phi)M = \begin{pmatrix} e^{i\phi} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\phi} \end{pmatrix},
\]

\[
U_2(\theta) = M^\dagger A_2(\phi) M = \frac{1}{2} \begin{pmatrix}
1 + \cos \theta & i\sqrt{2} \sin \theta & -1 + \cos \theta \\
i\sqrt{2} \sin \theta & 2 \cos \theta & i\sqrt{2} \sin \theta \\
-1 + \cos \theta & i\sqrt{2} \sin \theta & 1 + \cos \theta
\end{pmatrix}.
\]

Consequently
\[
U(A) = U(\phi, \theta, \psi) = \begin{pmatrix}
\alpha \chi (\phi + \psi)(1 + \cos \theta) & i\sqrt{2} e^{i\psi} \sin \theta & -\alpha \chi (\psi - \phi)(1 - \cos \theta) \\
i\sqrt{2} \sin \theta e^{i\phi} & 2 \cos \theta & i\sqrt{2} e^{-i\phi} \sin \theta \\
-\alpha \chi (\phi - \psi)(1 - \cos \theta) & i\sqrt{2} e^{-i\psi} \sin \theta & e^{-i(\phi + \psi)}(1 + \cos \theta)
\end{pmatrix}.
\]

(2.42)

3. Conventional thermodynamic systems.

3.1. PVT systems. The main objective of this section is to establish the thermodynamic potential of PVT (physical-vapor transport) systems. First we recall the van der Waals equation, which is the equation of state for gaseous PVT systems:
\[
(bp + RT)\rho - a\rho^2 + ab\rho^3 - p = 0,
\]
where \(a, b\) are van der Waals constants, \(\rho = n/V\) is the mole density, \(R\) is the gas constant, \(T\) is the temperature, \(p\) is the pressure, and \(n\) is the mole number.

The relation between the thermodynamic potential \(F\) and the equation of state is given by
\[
\delta F = 0 \Rightarrow \text{the equation of state}.
\]
Hence the van der Waals equation (3.1) serves as an important reference for the following construction of the potential functional for PVT systems.

1). Basic form of the thermodynamic potential \(F\). Since a PVT system is an isothermal-isopiestic process, and therefore a Gibbs system with order parameters \(= (\rho, S)\), control parameters \(\lambda = (T, p)\), (3.3)
where \(\rho\) is the density, and \(S\) is the entropy density. By (2.24) and the general form of the Gibbs free energy, the potential functional for the PVT system is given by
\[
F = \int_{\Omega} \left[ \alpha \frac{1}{2} |\nabla \rho|^2 + f(\rho, S, \lambda) - \mu \rho - ST - \frac{1}{\rho_0} \rho \right] dx,
\]
where \(\alpha > 0\) is a constant, \(\rho_0\) is the reference value of \(\rho\), \(\mu\) is the chemical potential as in (2.14) due to the conservation of the number of particles, and \(\lambda\) is as in (3.3).

By the statistical theory of heat [23], entropy represents the number of photons, and by the vibratory mechanism of thermal radiation, the entropy density depends on the molar density \(\rho\). Notice that \(|\nabla \rho|^2\) represents the energy for maintaining the non-homogeneity of the particle distribution of the system, and that the non-homogeneous distribution of entropy is due to non-homogeneous distribution of particles. Therefore there is no \(|\nabla S|^2\) term in the potential functionals for all thermodynamic systems, which is reflected by the term \(|\nabla \rho|^2\).

2). Physical meaning of \(\rho^k\). To derive an explicit form of \(f(\rho, S, \lambda)\) in (3.4), we need to examine the physical meaning of \(\rho^k\). In statistical physics, for \(k \geq 2\),
\[
\rho^k(x) = \text{probability density of collisions of } k \text{ particles at } x.
\]
Also, \(\rho^2\), we have the following additional physical meaning:
\[
A\rho^2(x) \text{ represents the interaction potential energy density of particles at } x, \text{ with } A > 0 \text{ for repulsive interaction, and } A < 0 \text{ for attractive interaction.}
\]
Since the probability for more than \( k \geq 3 \) particles collide with each other at the same time and location is negligible, there is no \( \rho^k \) \( (k \geq 3) \) terms in \( f(\rho, S, \lambda) \), excluding the Taylor expansion with respect to \( \rho \).

In the free energy (3.4), \( f \) contains two parts: the energy corresponding to molar density \( \rho \), denoted by \( f_1(\rho, \lambda) \), and the energy corresponding to entropy density \( S \), denoted by \( f_2(S, \rho, \lambda) \):

\[
\begin{align*}
  f &= f_1(\rho, \lambda) + f_2(S, \rho, \lambda), \\
  f_2(0, \rho, \lambda) &= 0.
\end{align*}
\] (3.7)

3). Expression for \( f_1(\rho, \lambda) \). By (3.6), \( f_1 \) contains a \( \rho^2 \) term, so that

\[
  f_1 = \frac{1}{2} A_1(\lambda) \rho^2 + g_1(\rho, \lambda).
\] (3.8)

Also as a particle system, the internal energy of a PVT system contains the following term

\[
\beta \ln W,
\]
where \( W \) is the number of states of particles. Hence \( g_1 \) is proportional to \( \ln W \):

\[
g_1 = a(\lambda) \ln W.
\] (3.9)

Basic thermodynamics shows that

\[
W = (\rho_0 + \rho)! \approx (\rho_0 + \rho)^{(\rho_0 + \rho)}.
\] (3.10)

where \( \rho_0 \) is the reference number density of particles. With the first order terms of \( \rho \) included in the \( \mu \rho \) in (3.4), we infer from (3.9) and (3.10) that

\[
g_1 = A(\lambda)(1 + \rho/\rho_0) \ln(1 + \rho/\rho_0).
\] (3.11)

Then by (3.8) and (3.11), we derive the expression of \( f_1 \) as follows:

\[
f_1 = \frac{1}{2} A_1 \rho^2 + A(1 + \rho/\rho_0) \ln(1 + \rho/\rho_0),
\] (3.12)

where \( A \) and \( A_1 \) are system parameters depending on \( \lambda = (T, p) \).

For van der Waals gas, we can use the van der Waals equation (3.1) and (3.2) to derive the following relation for the parameters \( A \) and \( A_1 \) in (3.12):

\[
A = 2a/b^2, \quad A_1 = b^2 p + A_0 RTb,
\] (3.13)

where \( \rho_0 = 1/b, a, b \) are the van der Waals constants, and \( A_0 \) is a nondimensional parameter.

4). Expression of \( f_2(S, \rho, \lambda) \). By the condition (2.7) for Legendre transformation, we have

\[
\frac{\partial^2}{\partial S^2} f_2(0, \rho, \lambda) \neq 0.
\] (3.14)

Namely, there is an \( S^2 \) in the expression of \( f_2 \). The statistical theory of heat [23] indicates that the energy density of entropy \( S \) is zero when \( T = 0 \). Hence \( f_2 \) takes the form

\[
f_2 = T \left( \frac{\beta}{2} S^2 + S g_2(\rho, \lambda) \right),
\] (3.15)

where \( \beta \) is a parameter with dimension \( 1/kT_0 \), and \( g_2 \) is a to-be-determined function.

By the photon number entropy formula in [23], \( S \) represents the photon number density in the system, and therefore the physical meaning similar to (3.6) for \( S \)
holds true as well. Also, each photon carries two weak charges, and there is a weak interaction between photons. In particular, there is a radius \( r_0 > 0 \) such that

\[
\text{interaction between photons} = \begin{cases} 
\text{attractive} & \text{for } r < r_0, \\
\text{repulsive} & \text{for } r > r_0.
\end{cases}
\] (3.16)

By (3.6), we derive from the above properties of the weak interaction between photons that for \( f_2 \), the term involving \( S^2 \) is given by \( (\beta = -B) \):

\[
-\frac{1}{2} B T S (S - 2S_0),
\] (3.17)

where \( B = B(\lambda) > 0 \) is a parameter depending on \( \lambda \), and \( 2S_0 \) is the reference entropy density. By (3.16), the physical meaning of (3.17) is as follows:

- the interaction between photons is attractive for \( S > 2S_0 \),
- the interaction between photons is repulsive for \( S < 2S_0 \).

Also by (3.5), \( \rho^2 \) represents collision probability density of two particles. By the absorption and radiation mechanism of photons [23], \( S \) is proportional to \( \rho^2 \). Therefore in the internal energy, the coupling between \( S \) and \( \rho \) involves only the product of \( S \) and \( \rho^2 \). Hence only the following appears as the coupling term in (3.15):

\[
B_1 T S \rho^2
\]

which represents thermal energy density due to the collision of particles. Finally by (3.17), the expression (3.15) for \( f_2 \) is

\[
f_2 = B T \left( -\frac{1}{2} S^2 + S_0 S \right) + B_1 T S \rho^2, \] (3.18)

where \( B, B_1 \) are system parameters depending on \( \lambda = (T, p) \).

5). Gibbs free energy for PVT systems. By (3.12) and (3.18), we derive from (3.7) the expression for \( f \):

\[
f = \frac{1}{2} A_1 (T, p) \rho^2 + A(T, p)(1 + \rho/\rho_0) \ln(1 + \rho/\rho_0)
+ B T \left( -\frac{1}{2} S^2 + S_0 S \right) + B_1 T S \rho^2. \] (3.19)

In summary, we derive from (3.4) and (3.19) the general form of thermodynamic potentials for a general (gaseous, or liquid or solid) PVT system:

\[
F = \int_{\Omega} \left[ \alpha \frac{1}{2} |\nabla \rho|^2 + A(1 + \rho/\rho_0) \ln(1 + \rho/\rho_0) + \frac{1}{2} A_1 \rho^2 - \mu \rho - pp/\rho_0 \\
+ B T \left( -\frac{1}{2} S^2 + S_0 S \right) + B_1 T S \rho^2 - ST \right] dx,
\] (3.20)

where \( A, A_1, B, B_1 \) are system parameters depending on the control parameters \( T, p \). These parameters are system dependent.
6). Gibbs free energy for gaseous PVT systems. In this case, (3.20) can be written as

\[
F = \int_{\Omega} \left[ \frac{\alpha}{2} |\nabla \rho|^2 + \frac{ART}{b} (1 + b\rho) \ln(1 + b\rho) \\
+ \frac{1}{2} (b^2 p + A_0 bRT) \rho^2 - \mu \rho - bpp \\
+ BT \left( -\frac{1}{2} S^2 + S_0 S \right) + B_1 TS \rho^2 - ST \right] dx,
\]

where \(A, A_0\) are nondimensional parameters and \(b\) is the van der Waals constant.

7). Relation between entropy density \(S\) and \(\rho, T, p\). By (3.20), we have

\[
S = B_0 \rho^2 + S_0 - \frac{1}{B} \quad (B_0 = B_1/B).
\]

This shows that the entropy density (photon number density) \(S\) is proportional to \(\rho^2\), in agreement with physical facts.

3.2. N-component systems. An N-component system consists of \(N \geq 2\) different types of particles. The thermodynamical potential functional of an N-component system is either the Helmholtz free energy if the pressure is negligible, or the Gibbs free energy if the pressure is not negligible. We consider only the latter case.

The most important property of an N-component system is the phase separation phenomena as the temperature is lower than a critical value, leading to non-uniform distribution of different type of particles. At the phase separation, the total number density of particles can either be non-uniformly distributed in space, or uniformly distributed. We discuss both scenarios in turn below.

1). Non-uniform phase separation systems. In this case, the distribution of the total number density of the particles is non-uniformly distributed in space, so that the number densities of different types of particles are independent.

For an N-component system, let \(A_1, \cdots, A_N \ (N \geq 2)\) be the different types of particles, and \(u_i\) be the number density of \(A_i\) particles. Then the order parameters of the system are entropy density \(S\) and \(u = (u_1, \cdots, u_N)\). The control parameters are \(\lambda = T, p\), the length scale \(L\), and number ratio \(x_i\) of \(A_i\). Here the number ratio of \(A_i\) is defined by

\[
x_i = \frac{1}{N_0} \int_{\Omega} u_i dx,
\]

where \(N_0\) is the total number of particles.

By the Fick Law of diffusion law and the Onsager reciprocal relations, the fluxes \(J = (J_1, \cdots, J_N)\) of the \(N\)-types of particles are given in terms of \((\nabla u_1, \cdots, \nabla u_N)\) as follows:

\[
J_i = -L_{ij} \nabla u_j,
\]

where the summation convention of repeated indices are used, \((L_{ij})\) is a positive definite and symmetric matrix, called the Onsager coefficients. The potential energy induced by the particle flux \(J\) is

\[
\text{potential energy induced by } J = -\frac{1}{2} J \cdot \nabla u = \frac{1}{2} L_{ij} \nabla u_i \nabla u_j.
\]
Hence the general form of the thermodynamic potential functional for an $N$-component system is

$$F = \int_{\Omega} \left[ \frac{1}{2} L_{ij} \nabla u_i \nabla u_j + f(u, S, \lambda) - \mu_i u_i - ST - b \rho \sum_{i=1}^{N} u_i \right] dx,$$  \hspace{1cm} (3.25)

where $b$ is the van der Waals constant, and $\mu_i$ are the chemical potential of $A_i$. Since the number of particles is conserved, we have

$$\int_{\Omega} u_i dx = \text{constant for } 1 \leq i \leq N.$$  \hspace{1cm} (3.26)

We need to derive the expression of $f(S, u, \lambda)$. As for the PVT system, $f$ consists parts involving $u$ and $S$:

$$f = f_1(u, \lambda) + f_2(S, u, \lambda),$$

with

$$f_2(S, u, \lambda)|_{S=0} = 0.$$  \hspace{1cm} (3.27)

By the Flory-Huggins theory \cite{29}, $f_1$ takes the form

$$f_1 = AkTu_j \ln u_j + A_{ij} u_i u_j,$$  \hspace{1cm} (3.28)

where $(A_{ij})$ is a symmetric matrix, depending on $(T, p)$ and the type of particles, $A_{ij}$ represent the interaction strength of particles $A_i$ and $A_j$, $A_{ij} > 0$ stand for repulsive force, $A_{ij} < 0$ stand for attractive force, $A > 0$ is a nondimensional parameter, and $k$ is the Boltzmann constant.

As for the PVT systems, $f_2$ can be expressed as

$$f_2 = -\frac{B_{ij} b T}{2k} S^2 + b^2 T S B_{ij} u_i u_j + \frac{B_0 b T}{k} S_0 S,$$  \hspace{1cm} (3.29)

where $B_{ij}$, $B_0$ are nondimensional parameters, depending on $(p, T)$, $(B_{ij})$ are positive definite, $S_0$ is the physical unit of entropy, and $b^2 T S B_{ij} u_i u_j$ represents the thermal energy due to the collision of particles.

Hence by (3.27)–(3.29), the potential functional (3.25) is written as

$$F = \int_{\Omega} \left[ \frac{1}{2} L_{ij} \nabla u_i \nabla u_j + AkTu_i \ln u_i + A_{ij} u_i u_j \\
- \mu_i u_i - b \rho - \frac{B_0 b T}{2k} (S - 2S_0) S \\
+ b^2 T S B_{ij} u_i u_j - ST \right] dx,$$  \hspace{1cm} (3.30)

where $\rho = \sum_j u_j$ is the total particle number density.

2). Uniform phase separation systems. In this case, when the phase separation occurs, the distributions of different types of parts are in general non-uniform, but the total number density of particles is uniformly distributed. In other words, the number densities of the $N$ types of particles are not independent.

As in the previous case, consider an N-component system, with $A_1, \cdots, A_N$ ($N \geq 2$) being the types of particles, and $u_i$ be the number density of $A_i$ particles. By assumption, the total number density $u_0$ is a constant:

$$u_1 + \cdots + u_N = u_0 \text{ (a constant)}.$$
Hence there are only \( N - 1 \) independent variables among \((u_1, \cdots, u_N)\). Let
\[
\text{order parameters } = \{S, u\}, \quad u = (u_1, \cdots, u_{N-1})
\]
\[
\text{control parameters } \lambda = \{T, p, L, x_i\}, \quad (3.31)
\]
where \( x_i \) is the molar ratio for the \( i \)-th type particles, and \( u_N \) is given by
\[
u_N = u_0 - \sum_{i=1}^{N-1} u_i. \quad (3.32)
\]
With \( u_N \) in (3.30) given by (3.32), we deduce the potential functional for the uniform phase separation of an \( N \)-component system:
\[
\begin{align*}
F &= \int_{\Omega} \left[ l_{ij} \nabla u_i \nabla u_j + AkT u_i \ln u_i + a_{ij} u_i u_j \\
&\quad + AkT \left( 1 - \sum_{i=1}^{N-1} u_i \right) \ln \left( 1 - \sum_{i=1}^{N-1} u_i \right) - \mu_i u_i \\
&\quad - \frac{B_0 bT}{2k} (S - S_0) S + b^2 T S b_{ij} u_i u_j \\
&\quad - bp \sum_{i=1}^{N-1} u_j - ST \right] dx, \quad (3.33)
\end{align*}
\]
where some rearrangements are made: the constant term is ignored, the linear terms of \( u_i \) are combined with \( \mu_i u_i \), and \((l_{ij})\) and \((b_{ij})\) are \((N-1)\)-th order positive definite and symmetric matrices.

Also we note that the parameters \( l_{ij}, a_{ij}, b_{ij} \) in (3.33) can be directly experimentally measured, or determined by physical laws. \((l_{ij})\) are the Onsager coefficients. The Onsager coefficients \( L_{ij} \) are for non-uniform phase separation systems, and \((l_{ij})\) are coefficients for uniform phase separation systems. The positive definiteness of these two matrices is the consequence of the well-posedness and dynamical stability of the systems.

3.3. **Magnetic and dielectric systems.** 1). **Magnetic systems.** There are three types of magnetic systems: paramagnetic, ferromagnetic, anti-ferromagnetic. A paramagnetic material can be magnetized under an external magnetic field, and a ferromagnetic material can form permanent magnetic field below the Curie temperature without the presence of the external magnetic field. An antiferromagnetic material is paramagnetic above the Neel temperature, and diamagnetic below the Neel temperature. Their equation of state is the Curie-Weiss law:
\[
\chi = \frac{\partial M}{\partial H} = \frac{c}{T + T_0}, \quad T_0 \begin{cases} < 0 & \text{for ferromagnetic,} \\ = 0 & \text{for paramagnetic,} \\ > 0 & \text{for antiferromagnetic}, \end{cases} \quad (3.34)
\]
where \( H \) is the external magnetic field, \( M \) is the magnetization (magnetic moment per unit volume), \( \chi \) is the magnetic susceptibility, and \( T_0 \) is the fixed temperature (Weiss constant).

2). **Order parameters.** The physical meaning of the magnetization \( M \) is as follows. In a ferromagnetic body, magnetic moment can be induced by the spin of an electron, or by the orbital rotation of an electron with respect to axis with direction \( n \), as shown in Figure 3.1:
Magnetic moments aligned in parallel induce a magnetization \( \mathbf{M} \) defined by
\[
\mathbf{M} = \frac{1}{V} \sum m_i,
\]
where \( \sum m_i \) is the sum of all magnetic moments \( m_i \) in a region \( D \), \( V \) is the volume of \( D \), i.e. \( \mathbf{M} \) is the magnetic moment per unit volume.

As the coupling between \( \mathbf{M} \) and the number density \( \rho \) of particles in the system is weak, we can take the order parameters \( u \) and control parameters \( \lambda \) as follows:
\[
u = (\mathbf{M}, S), \quad \lambda = (T, \mathbf{H}, L),
\]
where \( \mathbf{H} \) is the applied magnetic field, and \( L \) is the length scale of the magnetic body.

3). *Thermodynamic potential for magnetic systems.* The general form of the Gibbs free energy of a magnetic system is given by
\[
F = F_0 + \int_\Omega \left[ \frac{\mu}{2} |\nabla \mathbf{M}|^2 + f(\mathbf{M}, S, \lambda) - ST - \mathbf{M} \cdot \mathbf{H} \right] dx,
\]
where \( \mu > 0 \) is a coefficient. The density \( f \) in (3.35) can be decomposed into two parts:
\[
f = f_1(M, \lambda) + f_2(S, M, \lambda).
\]
Since the energy density of the magnetic field is a quadratic form of \( M \), \( f_1 \) takes the form:
\[
f_1 = \frac{1}{2} a_{ij} M_i M_j,
\]
where \( a_{ij} \) is a second-order tensor, called magnetization matrix, reflecting the property of the material:
\[
A = (a_{ij}) \text{ is a } 3 \times 3 \text{ symmetric matrix.}
\]
There are three eigenvalues of this matrix: \( \lambda_k \) \( (1 \leq k \leq 3) \). By the equation of state (3.34), we derive the following relations between \( \lambda_k \) and the properties of the
magnetic materials:

\[ \lambda_k < 0 \quad (1 \leq k \leq 3) \quad \text{for ferromagnetic}, \]
\[ \lambda_k = 0 \quad (1 \leq k \leq 3) \quad \text{for paramagnetic}, \]
\[ \lambda_k > 0 \quad (1 \leq k \leq 3) \quad \text{for antiferromagnetic}. \]

Also, \( \lambda_k(1 \leq k \leq 3) \) characterizes of orientation of the materials:

\[ \lambda_1 = \lambda_2 = \lambda_3 \iff \text{isotropic}, \]
\[ \text{otherwise} \iff \text{anisotropic}. \]

For \( f_2 \) in (3.36), notice that the entropy \( S \) coupling with \( M \) is not the total entropy for the system, \( S \) can take negative values. As for PVT systems, in view of (3.34), we derive the expression for \( f_2 \) as

\[ f_2 = -\frac{T}{2\alpha}S^2 - \beta TS|M|^2, \]

where \( \alpha, \beta > 0 \) are parameters. The second term in the right-hand side stands for loss of thermal energy caused by magnetization, indicating that thermal energy prevents magnetization.

By (3.37) and (3.41), the Gibbs free energy (3.35) for a magnetic system can be written as

\[ F = F_0 + \int_\Omega \left[ \frac{\mu}{2} |\nabla M|^2 + \frac{1}{2} a_{ij} M_i M_j - M \cdot H - \frac{T}{2\alpha}S^2 - \beta TS|M|^2 - ST \right] dx. \]

In (3.42), there are 6 parameters in the symmetric matrix \( A = (a_{ij}) \). However, there are only three independent parameters, which are the three eigenvalues \( \lambda_k(1 \leq k \leq 3) \) of \( A \). Take the three eigenvectors \((e_1, e_2, e_3)\), as the basis, \( A \) is given by

\[ A = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}. \]

Then (3.42) is written as

\[ F = F_0 + \int_\Omega \left[ \frac{\mu}{2} |\nabla M|^2 + \frac{1}{2} \lambda_k M_k^2 - M_k H_k - \frac{T}{2\alpha}S^2 - \beta TS|M|^2 - ST \right] dx. \]

4). Dielectric systems. Dielectric systems can also be classified into three types: paraelectric, ferroelectric, and anti-ferroelectric. Paraelectricity is the ability of materials to become polarized under an applied electric field. Ferroelectricity is a characteristic of materials that have a spontaneous electric polarization without an applied electric field. An antiferroelectric state is defined as one in which lines of ions in the crystal are spontaneously polarized, but with neighboring lines polarized in antiparallel directions.

In a dielectric body, for lattice made by charged atoms and molecules, the non-uniform distribution of positive and negative charges induce electric dipoles, leading to polarization phenomena. The polarization dipole moment of a single electric dipole is \( p = qr \), where \( q \) is the charge of the electric dipole, and \( r \) is the distance vector of the pair of electric charges. When the temperature is lower than the Curie point, or under an applied electric field \( E \), the electric dipoles in a dielectric body...
align in parallel in the same direction, leading to polarization. Such small region is called electric domain. Its electric polarization strength is defined by

\[ P = \frac{1}{V} \sum p_i, \]

which stands for electric dipole moment per unit volume. The order parameters \( u \) and control parameters \( \lambda \) are

\[ u = (P, S), \quad \lambda = (T, E, L), \]

where \( E \) is the applied electric field.

As in (3.34), the equation of state for the dielectric system is

\[ \chi = \frac{\partial P}{\partial E} = a + \frac{b}{T + T_0}, \quad (3.44) \]

where \( a, b > 0 \) are constants and

\[ T_0 \begin{cases} < 0 & \text{for ferroelectric}, \\ = 0 & \text{for paraelectric}, \\ > 0 & \text{for anti-ferroelectric}. \end{cases} \quad (3.45) \]

As the thermodynamic potential for the magnetic systems (3.43), by (3.44) and (3.45), the thermodynamic potential functional of a dielectric system takes the form:

\[ F = F_0 + \int_\Omega \left[ \frac{\mu}{2} |\nabla P|^2 + \frac{1}{2} \lambda_k p_k^2 - (1 + \eta T)P \cdot E \\
- \frac{T}{2\alpha} S^2 - \beta TS|P|^2 - ST \right] dx. \quad (3.46) \]

where \( \mu, \eta, \alpha, \beta > 0 \) are coefficients, and

\[ \begin{cases} \lambda_k < 0 \ (1 \leq k \leq 3) & \text{for ferroelectric,} \\ \lambda_k = 0 \ (1 \leq k \leq 3) & \text{for paraelectric,} \\ \lambda_k > 0 \ (1 \leq k \leq 3) & \text{for anti-ferroelectric,} \end{cases} \]

\[ \lambda_1 = \lambda_2 = \lambda_3 \Leftrightarrow \text{isotropic,} \]

\[ \lambda_1 \neq \lambda_j \Leftrightarrow \text{anisotropic.} \quad (3.47) \]

4. Thermodynamic systems of condensates.

4.1. Quantum rules of condensates. When a thermodynamic system forms a condensate, the order parameter is a family of complex-valued wave functions \( \psi : \Omega \to \mathbb{C}^N \) such that

\[ |\psi|^2 \] represents the particle number density of the condensate. (4.1)

The wave functions \( \psi \) are governed by physical laws, and describes the collective behavior of the condensate particles, which possess mutual interactions. Hence for condensates these wave functions obey their own quantum rules as follows:

**Quantum Rule 4.1.** For quantum physics of condensates, the particle interaction is attractive in long-range, and repulsive in short-range. Hence the wave functions \( \psi \) of condensates obey the following quantum rules:

1. The (attractive) binding energy between particles is

\[ \text{binding energy density} = -g_0 |\psi|^2, \quad (4.2) \]

where \( g_0 > 0 \) stands for interaction potential;
The repulsive interaction energy between particles is

\[ \text{repulsive energy density} = \frac{1}{2} g_1 |\psi|^4, \]

where \( g_1 > 0 \) is the interaction constant.

Remark 4.1. Quantum Rule 4.1 is the consequence of the combination of physical facts and the repulsive-attractive characteristic of the three interactions: the electromagnetic, the weak and the strong interactions; see [21]. It is the attractive potential (4.2) that ensures a large collection of particles to condensate, and it is also the short-range repulsive characteristic (4.3) that ensures the finite density of particles. In (4.2) and (4.3), the interaction constants \( g_0 \) and \( g_1 \) are macroscopic statistical average values, and \( g_0 \) depends on the external magnetic field.

In condensed matter physics, \( \psi \) represents the wave function for the collection of particles in the condensate. The differential operator \( -i\hbar \nabla \) stands for the gradient potential, and \( -\frac{i\hbar^2}{2m} \nabla^2 \) stands for the gradient potential energy. In addition, we have the following correspondences of differential operators and their physical meaning.

In the absence of external electromagnetic field, the following are the basic Hermitian differential operators:

\[
\begin{align*}
\text{energy operator} : & \quad \hat{E} = i\hbar \frac{\partial}{\partial t}, \\
\text{gradient potential operator} : & \quad \hat{P} = -i\hbar \nabla, \\
\text{interaction potential operator} : & \quad \hat{V}\psi = V\psi, \\
\text{gradient energy operator} : & \quad \hat{K} = -\frac{\hbar^2}{2m} \nabla^2.
\end{align*}
\]

The energies induced by the operators in (4.4) are

\[
\begin{align*}
\text{potential energy} & \quad V = \int_{\Omega} V|\psi|^2 dx, \\
\text{gradient energy} & \quad K = \int_{\Omega} \hat{K}\psi \cdot \psi^d x = \int_{\Omega} \frac{\hbar^2}{2m} |\nabla \psi|^2 dx.
\end{align*}
\]

We remark that (4.2) in Quantum Rule 4.1 is the consequence of (4.5) and the potentials of the three interactions [21].

In the presence of electromagnetic field, the Hermitian operators are given by

\[
\begin{align*}
\text{energy operator} : & \quad \hat{E} = i\hbar \frac{\partial}{\partial t} + eA_0, \\
\text{gradient potential operator} : & \quad \hat{P} = -\left( i\hbar \nabla + \frac{e}{c}A \right), \\
\text{gradient energy operator} : & \quad \hat{K} = -\frac{\hbar^2}{2m} \left( \nabla - i\frac{e}{\hbar c}A \right)^2.
\end{align*}
\]

The energy induced by the gradient energy operator \( \hat{K} \) is

\[ K = \int_{\Omega} \frac{1}{2m} \left| \left( -i\hbar \nabla - \frac{e}{c}A \right) \psi \right|^2 dx, \]

where \((A_0, A)\) is the 4-dimensional electromagnetic potential, and \( K \) is the energy induced by the non-uniform distribution.
2). *Implications of basic principles.* By the Pauli exclusion principle, only one Fermion is allowed in each quantum state. The particles in a condensate share the same quantum state; this shows that the particles in a condensate must be Bosons.

By the Heisenberg uncertainty relation, for a particle in the system, the position \( x \) and momentum \( P \), time \( t \), energy \( E \) cannot be determined simultaneously determined. Their deviations \( \Delta x, \Delta P, \Delta t \) and \( \Delta E \) satisfy
\[
\Delta x \Delta P \geq \frac{1}{2} \hbar, \quad \Delta t \Delta E \geq \frac{1}{2} \hbar.
\]
These relations imply that there exist quantum fluctuations in a condensate system—spontaneous deviations of the position, momentum and energy from the equilibrium can occur, and are due to the quantum uncertainty, rather that to thermo effect.

### 4.2. Ginzburg-Landau free energy of superconductivity.

The classical Ginzburg-Landau free energy is a phenomenological model. In this section, we derive the potential functionals for superconducting systems based on 1) Quantum Rule 4.1, 2) quantum kinetic energy formula (4.8), 3) theory of electromagnetism, 4) the statistical theory of heat [23], and 5) the classical Ginzburg-Landau theory.

First the order parameters \( u \) and the control parameters \( \lambda \) are
\[
u = (\psi, A, S), \quad \lambda = (T, H_a, L),
\]
where \( \psi : \Omega \rightarrow \mathbb{C} \) is the wave function of superconducting electrons, \( A \) is the magnetic potential, \( H_a \) is the external magnetic field, and \( |\psi|^2 \) represents superconducting electron density.

The Gibbs free energy consists of
\[
F = \text{gradient energy} + \text{binding energy} + \text{repulsive interaction energy} + \text{magnetic energy} + \text{entropy energy} + \int_{\Omega} \left( -ST - \frac{1}{4\pi} \text{curl} A \cdot H_a \right) dx.
\]
As in (4.8), the gradient energy of \( \psi \) under the electromagnetic field is given by
\[
\text{gradient energy} = \int_{\Omega} \frac{1}{2m_s} \left| \psi \right|^2 dx.
\]
By (4.2), the binding energy of superconducting electrons is
\[
\text{binding energy} = \int_{\Omega} -g_0 |\psi|^2 dx.
\]
By (4.3), the superconducting repulsive interaction energy is
\[
\text{repulsive interaction energy} = \int_{\Omega} \frac{g_1}{2} |\psi|^4 dx.
\]
The magnetic field energy is
\[
\text{magnetic field energy} = \int_{\Omega} \frac{1}{8\pi} |\text{curl} A|^2 dx.
\]
Also, as in (3.41) for magnetic and dielectric systems, the entropy energy of condensates has the form
\[
\text{entropy energy} = \int_{\Omega} \left[ -\frac{T}{2\alpha k} S^2 - \beta ST |\psi|^2 \right] dx,
\]
where \( \alpha, \beta > 0 \) are parameters, and \(-\beta ST|\psi|^2\) represents the loss of thermal energy \( ST \) due to condensation.

By (4.12)-(4.16), the Gibbs free energy (4.11) for superconductivity can be written as

\[
F = \int_{\Omega} \left[ \frac{1}{2m_s} \left( -i\hbar \nabla - \frac{e_s}{c} A \right)|\psi|^2 - g_0|\psi|^2 + \frac{g_1}{2}|\psi|^4 
+ \frac{1}{8\pi} |\text{curl}A|^2 - \frac{T}{2k_\alpha} S^2 - \beta TS|\psi|^2 - ST - \frac{1}{4\pi} |\text{curl}A \cdot \mathbf{H}_a| \right] dx. 
\]

(4.17)

**Remark 4.2.** It is worth mentioning that each term in the potential functional (4.17) is derived based on basic physical principles and physical laws, while the classical GL free energy is a phenomenological model. The parameters \( g_0 \) and \( g_1 \) in (4.17) are different from the corresponding coefficients in the classical GL free energy, which are Taylor expansion coefficients. Here \( g_0 \) and \( g_1 \) possess clear physical meaning, and are independent of the temperature.

### 4.3. Thermodynamical potential for liquid \( ^4\text{He} \).

\( ^4\text{He} \) is a non-radioactive isotope of the element helium. Its nucleus is identical to an alpha particle, and consists of two protons and two neutrons, with two orbiting electrons. It has an integer spin and is a boson, and consequently \( ^4\text{He} \) may condensate.

P. L. Kapitza [14] discovered in 1938 that liquid \( ^4\text{He} \) undergoes a transition from the normal state to superfluid state with vanishing viscosity at the critical temperature \( T_c = 2.17K \). As a condensate system, liquid \( ^4\text{He} \) is a binary system with density \( \rho \) decomposed into

\[
\rho = \rho_n + \rho_s, 
\]

(4.18)

where \( \rho_n \) is the density of normal fluid, and \( \rho_s \) is the density of superfluid. As a superfluid, its state function is a complex-valued wave function \( \psi : \Omega \to \mathbb{C} \) such that

\[
\rho_s = |\psi|^2. 
\]

The order parameters \( u \) and the control parameters \( \lambda \) are

\[
u = (\psi, \rho_n, S), \quad \lambda = (T, p). 
\]

\( ^4\text{He} \) can be viewed as a combined system of a PVT system and a condensate phase, and then its thermodynamic potential is their coupling. First, we have the following conservation of total number of particles:

\[
\int_{\Omega} \left[ \rho_n + |\psi|^2 \right] dx = \text{constant}. 
\]

(4.19)

Also, the Gibbs free energy of the superfluid is given by

\[
F = \rho_n \text{ part} + \psi \text{ part} + \text{coupling of } \rho_n \text{ and } \psi + \text{part for entropy } S - \int_{\Omega} (\mu \rho + b p \rho_n + ST) dx, 
\]

(4.20)

where \( \mu \rho \) corresponds to Lagrangian multiplier of the conservation law (4.19), \( b \) is the van der Waals constant, and \( \rho \) is as in (4.18).

In (4.20), the \( \rho_n \) part obeys the PVT system. Hence

\[
\rho_n \text{ term} = \int_{\Omega} \left[ \frac{\alpha}{2} |\nabla \rho_n|^2 + \frac{1}{2} (b^2 p + A_t T) \rho_n^2 \right] dx, 
\]

(4.21)
By Quantum Rule 4.1 and (4.6), \( \psi \) part is written as
\[
\psi \text{ part } = \int_{\Omega} \left[ \frac{\hbar^2}{2m} |\nabla \psi|^2 - g_0 |\psi|^2 + g_1 |\psi|^4 \right] \, dx.
\] (4.22)

By (4.18) and the log term of \( \rho \) for the PVT systems, the coupling part of \( \rho_{n} \) and \( \psi \) is
\[
\text{coupling term of } \rho_{n} \text{ and } \psi \quad = \int_{\Omega} \left[ A_2 T (1 + b\rho_{n} + b|\psi|^2) \ln(1 + b\rho_{n} + b|\psi|^2) + g_2 b\rho_{n} |\psi|^2 \right] \, dx,
\] (4.23)
where the second term in the integrand represents the interaction energy between normal particles and superfluid particles, and
\[
g_2 = \begin{cases} 
> 0 & \text{for attractive interaction,} \\
< 0 & \text{for repulsive interaction.}
\end{cases}
\]

Also, in view of the case for PVT systems and for condensates, the part involving the entropy is given by
\[
\text{entropy part } = \int_{\Omega} \left[ -\frac{T}{2\beta_0 k} S^2 + \beta_1 S T \rho_{n}^2 - \beta_2 S T |\psi|^2 \right] \, dx.
\] (4.24)

By (4.21)–(4.24), the Gibbs free energy of \( ^4 \)He superfluid is written as
\[
F = \int_{\Omega} \left[ \alpha \frac{1}{2} |\nabla \rho_{n}|^2 + \frac{1}{2} (b^2 \rho + A_1 T) \rho_{n}^2 - b \rho_{n} - \mu \rho \\
+ \frac{\hbar^2}{2m} |\nabla \psi|^2 - g_0 |\psi|^2 + g_1 |\psi|^4 + g_2 b \rho_{n} |\psi|^2 \\
+ A_2 T (1 + b\rho_{n} + b|\psi|^2) \ln(1 + b\rho_{n} + b|\psi|^2) \\
- \frac{T}{2\beta_0 k} S^2 + \beta_1 S T \rho_{n}^2 - \beta_2 S T |\psi|^2 - ST \right] \, dx,
\] (4.25)
where \( m \) is the mass of \( ^4 \)He atom, \( A_1, A_2, \beta_0, \beta_1, \beta_2 \) are parameters, \( \mu \) is the chemical potential, \( b \) is the van der Waals constant, and \( \rho = \rho_{n} + |\psi|^2 \).

4.4. **Liquid \( ^3 \)He superfluidity.** \( ^3 \)He is an isotope of \( ^4 \)He, and the superfluidity of liquid \( ^3 \)He was found in 1971 by D. M. Lee, D. D. Osheroff, and R. C. Richardson, and its transition temperature is \( T \approx 10^{-3} \)K under \( p = 1 \) atm (10^5 Pa). \( ^3 \)He is a fermion and obeys the Fermi-Dirac statistics, and its atoms have to be paired (Cooper pair) to form the superfluid phase, leading to the existence of multiple superfluid phases; see Figure 4.1.

Note that there are four possible spin states for the Cooper pairs of \( ^3 \)He atoms:
\[
\uparrow \uparrow, \quad \downarrow \downarrow, \quad \uparrow \downarrow, \quad \downarrow \uparrow,
\] (4.26)
where \( \uparrow \) represents the \( J = 1/2 \)-spin, and \( \downarrow \) stands for the \( J = -1/2 \)-spin. Consequently, all Cooper pairs in (4.26) have integral spins \( J = 1, -1, 0 \):
\[
J = 1 : \{ |\uparrow \uparrow \rangle \}, \quad J = -1 : \{ |\downarrow \downarrow \rangle \}, \quad J = 0 : \{ |\uparrow \downarrow \rangle + |\downarrow \uparrow \rangle \}.
\] (4.27)

For a \( ^3 \)He superfluid system, the three spin states in (4.27) are described by three wave functions:
\[
\psi_+ = |\uparrow \uparrow \rangle \text{ state, } \quad \psi_0 = \frac{1}{\sqrt{2}} (|\uparrow \downarrow \rangle + |\downarrow \uparrow \rangle) \text{ state, } \quad \psi_- = |\downarrow \downarrow \rangle \text{ state.}
\] (4.28)
Hence \( \psi_+ \) stands for \( J = 1 \) state, \( \psi_0 \) for spin \( J = 0 \) state, and \( \psi_- \) for \( J = -1 \) state.
Experimental evidences show that in the absence of external magnetic field, there are two superfluid states of $^3$He, $A$ and $B$ superfluid phases:

- $A$ superfluid phase: $|\uparrow\rangle$ state + $|\downarrow\rangle$ state,
- $B$ superfluid phase: $|\uparrow\rangle$ state + $|\downarrow\rangle$ state + ($|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$) state.

With the presence of an external magnetic field, there are three $^3$He superfluid phases: $A_1$, $A$, $B$ phases as defined above and

- $A_1$ superfluid phase: $|\uparrow\rangle$ state.

Note that $A_1$ superfluid phase consists of only $J = 1$ Cooper pairs. $A$ phase consists of both $J = 1$, $-1$ Cooper pairs, and the $B$ phase consists of $J = 1$, $-1$, 0 Cooper pairs. The corresponding wave functions of these phases are

- $A_1$ superfluid phase: $\psi_+ \neq 0$, $\psi_- = 0$, $\psi_0 = 0$,
- $A$ superfluid phase: $\psi_+ \neq 0$, $\psi_- \neq 0$, $\psi_0 = 0$, $\psi_{\text{external}} = 0$,
- $B$ superfluid phase: $\psi_+ \neq 0$, $\psi_- \neq 0$, $\psi_0 \neq 0$.

Figures 4.1 and 4.2 provide the experimental phase diagrams for liquid $^3$He without or with external magnetic fields, and provide valuable guidance for deriving the thermodynamic functional for liquid $^3$He superfluid systems.

**Figure 4.1.** The coexistence curve of $^3$He without an applied magnetic field.

**Figure 4.2.** $PT$-phase diagram of $^3$He in a magnetic field.
1). Case without external magnetic field ($H_a = 0$). The order parameters $u$ and control parameters $\lambda$ are

$$u = (\psi_+, \psi_0, \psi_-, \rho_n, S), \quad \lambda = (T, p),$$

where $\Psi = (\psi_+, \psi_0, \psi_-)$ is as in (4.28), and $\rho_n$ is the normal fluid density. As in (4.19), for a liquid $^3$He superfluid system, the number of particles is conserved:

$$\int_{\Omega} \left[ \rho_n + |\Psi|^2 \right] dx = \text{constant}.$$

Hence the Gibbs free energy takes the following form

$$F = \int_{\Omega} \left[ \frac{\hbar^2}{2m} |\nabla \Psi|^2 + \frac{\alpha}{2} |\nabla \rho_n|^2 + f(\Psi, \rho_n, S) - \mu \rho - b \rho_n - ST \right] dx, \quad (4.30)$$

where $\mu$ is the chemical potential, $\rho = \rho_n + |\Psi|^2$ is the fluid density, and $f$ consists of the following:

- $f_1 = \text{interaction energy of } \rho_n$,
- $f_2 = \text{interaction energy density of } \Psi$ particles,
- $f_3 = \text{coupling between } \rho_n \text{ and } \Psi$,
- $f_4 = \text{entropy part}$,
- $f_5 = \text{spin interaction energy density}$.

As in (4.21)-(4.24), for liquid $^3$He superfluid system,

$$f_1 = \frac{1}{2} (b^2 p + A_1 T) \rho_n^2, \quad (4.31)$$

$$f_2 = -g_0 |\psi_0|^2 - g_\pm (|\psi_+|^2 + |\psi_-|^2) + \frac{g_1}{2} |\Psi|^4, \quad (4.32)$$

$$f_3 = A_2 T (1 + b \rho) \ln (1 + b \rho) + g_2 b \rho_n |\Psi|^2, \quad (4.33)$$

$$f_4 = -\frac{T}{2 \beta_0 k} S^2 + \beta_1 ST \rho_n^2 - \beta_2 ST |\psi|^2, \quad (4.34)$$

where $\rho = \rho_n + |\Psi|^2$. For the spin interaction energy $f_5$, by the theory of condensates in the next section, we have

$$f_5 = \frac{g_s}{2} |\Psi^\dagger \hat{F} \Psi|^2. \quad (4.35)$$

Here $g_s$ is the spin coupling constant, and $\hat{F}$ is the spin operator

$$\hat{F} = (F_1, F_2, F_3), \quad (4.36)$$

with $F_i (1 \leq i \leq 3)$ being Hermitian matrixes:

$$F_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad F_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad F_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

Hence $|\Psi^\dagger \hat{F} \Psi|^2$ in (4.35) can be written as

$$|\Psi^\dagger \hat{F} \Psi|^2 = |\Psi^\dagger F_1 \Psi|^2 + |\Psi^\dagger F_2 \Psi|^2 + |\Psi^\dagger F_3 \Psi|^2,$$

$$|\Psi^\dagger F_k \Psi|^2 = \left( |\psi_+ \psi_0^* \psi_-^* \rangle F_k \left( \begin{array}{c} \psi_+ \\ \psi_0 \\ \psi_- \end{array} \right) \right)^2 \quad 1 \leq k \leq 3.$$
Hence by (4.31)-(4.35), the Gibbs free energy (4.30) for liquid $^3$He superfluid system takes the form

$$ F = \int_\Omega \left[ \frac{\hbar^2}{2m} |\nabla \Psi|^2 - g_0 |\psi_0|^2 - g_\pm (|\psi_+|^2 + |\psi_-|^2) + \frac{g_1}{2} |\Psi|^4 \right. $$

$$ + \frac{g_2}{2} |\Psi|^2 + g_2 b |\rho_n|^2 - \mu (|\rho_n|^2 + |\Psi|^2) $$

$$ + \frac{\alpha}{2} |\nabla \rho_n|^2 + \frac{1}{2} \left( b^2 \rho + A_1 T \right) \rho_n^2 - b b \rho_n $$

$$ + A_2 T \left( 1 + b \rho_n + b |\Psi|^2 \right) \ln \left( 1 + b \rho_n + b |\Psi|^2 \right) $$

$$ - \frac{T}{2 b_0 k} s^2 + \beta_1 S T \rho_n^2 - \beta_2 S T |\Psi|^2 - ST \right] dx. \quad (4.37) $$

**Remark 4.3.** The coefficients $g_0$ and $g_\pm$ represent the binding energies for $J = 0$ and $J = 1$ superfluid particles. Since there exists spin magnetic moment potential for $J = 1$ particles, $g_\pm \neq g_0$. \hspace{1cm} (4.38)

It is this relation (4.38) that causes the differences between phase diagrams in Figures 4.1 and 4.2. \hspace{1cm} \Box

2). *Case with external magnetic field* ($H_\alpha \neq 0$). With the presence of external magnetic field $H_\alpha \neq 0$, we can see from Figure 4.2 that $H_\alpha$ influences the potential for a $^3$He superfluid system. Since the total electric charge of Cooper atom pairs is zero, the momentum operator of $\Psi$ is still $-i \hbar \nabla$. However, under the magnetic field $H_\alpha$, there is an additional energy density due to the spin magnetic moment of the Cooper pairs:

$$ \text{spin magnetic moment energy density} = -\mu \cdot H (|\psi_+|^2 - |\psi_-|^2), \quad (4.39) $$

where direction of the external magnetic field is the same as the spin direction of $\psi_+$, $\mu_0$ is the magnetic moment of the Cooper atom pair, and $H$ is the induced magnetic field. Also there is a magnetic part in the free energy:

$$ \int_\Omega \left[ \frac{1}{8 \pi} H^2 - \frac{1}{4 \pi} H \cdot H_\alpha \right] dx, \quad (4.40) $$

where the first term is the induced magnetic field energy, and the second term is the factor due to Legendre transformation. Hence under $H_\alpha \neq 0$, the Gibbs free energy $F_1$ for $^3$He superfluid system is the sum of (4.37), (4.39) and (4.40):

$$ F_1 = F + \int_\Omega \left[ \frac{1}{8 \pi} H^2 - \mu_0 \cdot H (|\psi_+|^2 - |\psi_-|^2) - \frac{1}{4 \pi} H \cdot H_\alpha \right] dx, \quad (4.41) $$

where $F$ is as in (4.37).

4.5. **Gibbs free energy for gaseous condensates (BEC).** Gaseous condensate is called Bose-Einstein condensate (BEC). It is the prediction of a matter form by Einstein in 1924 [2, 6, 7] based on the Bose-Einstein (BE) distribution, which is given by

$$ a_n = \frac{g_n}{e^{(\varepsilon_n - \mu)/kT} - 1}. $$

Einstein hypothesized that at $T = 0$K, $\mu = 0$, and all particles are on the energy level $\varepsilon_1$:

$$ a_1 = \infty, \quad a_n = 0 \text{ for } n > 1.$$
Hence with temperature at absolute zero, particles of the Bose gas are all on a quantum state with zero kinetic energy. This is BEC.

By the temperature formula for a Bose gas system [23]:

\[ kT = \sum_n \left( 1 + \frac{a_n}{g_n} \right) \frac{a_n\varepsilon_n}{N(1 + \beta_n \ln \varepsilon_n)}, \]  

(4.42)

BEC can be viewed clearly as follows:

\[ T = 0 \Leftrightarrow \varepsilon_1 = 0, \quad a_1 = N \text{ and } a_n = 0 \quad \forall \ n > 1. \]

The first gaseous condensate was produced by Eric Cornell and Carl Wieman [1] in 1995 in a gas of rubidium atoms cooled to \( T = 1.7 \times 10^{-7} \) K. At the same time, K. B. Davis and W. Ketterle [4] developed a BEC using sodium. For their achievements Cornell, Wieman, and Ketterle received the 2001 Nobel Prize in Physics. Since then, BEC phenomena were also discovered in the following nine elements: Rb, Na, Li, \(^1\text{H}\), \(^4\text{He}\), \(^{41}\text{K}\), \(^{52}\text{Cr}\), \(^{133}\text{Cs}\) and \(^{174}\text{Yb}\).

In 1997, W. Ketterle’s group discovered the first \( J = 1 \) spinor BEC, using optical trapping of condensates, opening a door for the study of spinor condensates.

BEC phenomena refers specifically to condensates of gaseous systems, and has quite different properties than solid condensates (superconductivity) and liquid condensates (superfluidity). The condensation of gaseous systems occurs at zeroth momentum level, corresponding to momentum condensation. BEC occurs for dilute gases at every extra-low temperatures. Systems with higher densities become liquid or solid states. Hence with temperature at absolute zero, a system can rarely be a gaseous state.

1). Thermodynamic potential of scalar BEC systems. In this case, the order parameters \( u \) and control parameters \( \lambda \) are

\[ u = (\psi, \rho_n, S, H), \quad \lambda = (p, T, H_a). \]

The Gibbs free energy for scalar BEC is similar to (4.25) for \(^4\text{He}\) superfluid systems. The \( \psi \) terms for BEC are different from (4.22), and are given by

\[ \psi \text{ terms} = \int_\Omega \left[ \frac{\hbar^2}{2m} \left| \nabla \psi \right|^2 + \frac{g_1}{2} \left| \psi \right|^4 \right] \, dx. \]  

(4.43)

The reason is that due to the relative large distances between particles for dilute gases, the attracting interaction between particles as described by the \( g_0 \) term in (4.2) is negligible. However, the repulsive behavior due to the strong interaction is still present, i.e. \( g_1 \neq 0 \).

Also for a BEC system, the binding energy, which confines the atoms of the gases in a region is due to the applied magnetic field, called magnetic potential well. As in (4.41), the Gibbs free energy for a BEC system contains an additional magnetic potential-well energy:

\[ \text{magnetic potential-well energy} = \int_\Omega \left[ \frac{1}{8\pi} \mathbf{H}^2 - \mathbf{\mu}_0 \cdot \mathbf{H} \left| \psi \right|^2 - \frac{1}{4\pi} \mathbf{H} \cdot \mathbf{H}_a \right] \, dx, \]  

(4.44)

where \( \mathbf{\mu}_0 \) is the magnetization moment of atoms, representing the collective quantum effect of particles.

Besides (4.43) and (4.44), other terms of the free energy are similar to those in (4.21), (4.23) and (4.24) for \(^4\text{He}\). Then we derive the Gibbs free energy for a BEC...
system as follows:

\[
F = \int_{\Omega} \left[ \frac{\alpha}{2} |\nabla \rho_n|^2 + \frac{1}{2} \left( b^2 + A_1 T \right) \rho_n^2 - b \rho_n \mu \right] \, dx \\
+ \frac{\hbar^2}{2m} |\nabla \psi|^2 + \frac{g_1}{2} |\psi|^4 + g_2 b \rho_n |\psi|^2 \\
+ A_2 T \left( 1 + b \rho_n + b |\psi|^2 \right) \ln \left( 1 + b \rho_n + b |\psi|^2 \right) \\
- \frac{1}{2} T S^2 + \beta_1 TS \rho_n^2 - \beta_2 TS |\psi|^2 - ST \\
+ \frac{1}{8\pi} \mathbf{H}^2 - \mu \cdot \mathbf{H} |\psi|^2 - \frac{1}{4\pi} \mathbf{H} \cdot \mathbf{E}_a \right] \, dx. \tag{4.45}
\]

2). Thermodynamic potential for \( J = 1 \) spinor BEC systems. The binding energy for spinor BEC is induced by the applied electric field, and the order and control parameters \( u \) and \( \lambda \) for the system are

\[
u = (\psi_+, \psi_0, \rho_n, S, E), \quad \lambda = (p, T, \mathbf{E}_a),
\]

where \( \mathbf{E}_a \) is the applied electric field, and \( \mathbf{E} \) is the induced electric field.

The Gibbs free energy for the system is similar to (4.41) for \(^3\text{He}\). The differences are two-fold. First there is no attracting interaction energy between particles. Second, the electromagnetic binding energy is the following optical potential well energy (optical trapping energy), rather than the magnetic potential well energy (4.44):

\[
\text{optical trapping energy} = \int_{\Omega} \left[ \frac{1}{8\pi} \mathbf{E}^2 - \varepsilon_0 \cdot \mathbf{E} |\psi|^2 - \frac{1}{4\pi} \mathbf{E} \cdot \mathbf{E}_a \right] \, dx, \tag{4.46}
\]

where \( \varepsilon_0 \) is the polarization, representing the collective quantum effect of particles, and \( \Psi = (\psi_+, \psi_0, \psi_-) \). Hence the Gibbs free energy for a spinor BEC system is

\[
F = \int_{\Omega} \left[ \frac{\alpha}{2} |\nabla \rho_n|^2 + \frac{1}{2} \left( b^2 + A_1 T \right) \rho_n^2 - b \rho_n \mu \right] \, dx \\
+ \frac{\hbar^2}{2m} |\nabla \Psi|^2 + \frac{g_1}{2} |\Psi|^4 + \frac{g_2}{2} |\Psi|^2 + g_2 b \rho_n |\Psi|^2 \\
+ A_2 T \left( 1 + b \rho_n + b |\psi|^2 \right) \ln \left( 1 + b \rho_n + b |\psi|^2 \right) \\
- \frac{T}{2\beta_0 k} S^2 + \beta_1 TS \rho_n^2 - \beta_2 TS |\psi|^2 - ST \\
+ \frac{1}{8\pi} \mathbf{E}^2 - \varepsilon_0 \cdot \mathbf{E} |\Psi|^2 - \frac{1}{4\pi} \mathbf{E} \cdot \mathbf{E}_a \right] \, dx. \tag{4.47}
\]

We remark that the optical potential well spinor BEC system bounds atoms with the electric potential. There are no constraints on the spin of the atoms so that the \( N = 2J + 1 (J \neq 0) \) spin states are independent and \( \Psi \) is a spinor. In fact, this is also the consequence of the \( \text{SO}(3) \) spinor invariance of the functional (4.47).

3). BEC systems with electromagnetic potential well. For a BEC system with spin \( J \geq 1 \) of atoms and with applied magnetic field \( \mathbf{H}_a \) and electric field \( \mathbf{E}_a \) as the binding energy, the order and control parameters \( u \) and \( \lambda \) are

\[
u = (\Psi, \rho_n, \mathbf{H}, \mathbf{E}), \quad \lambda = (p, T, \mathbf{H}_a, S, \mathbf{E}_a),
\]
where $\Psi = (\psi_J, \cdots, \psi_0, \cdots, \psi_{-J})$ has $2J + 1$ components. Then electromagnetic energy is

$$\text{EM energy} = \int_\Omega \left[ \frac{1}{8\pi} H^2 - \Psi^\dagger(\mathbf{H} \cdot \mathbf{\hat{\mu}})\Psi - \frac{1}{4\pi} \mathbf{H} \cdot \mathbf{H}_a \\
+ \frac{1}{8\pi} \mathbf{E}^2 - \varepsilon_0 \cdot \mathbf{E} |\Psi|^2 - \frac{1}{4\pi} \mathbf{E} \cdot \mathbf{E}_a \right] dx,$$

(4.48)

where $\varepsilon_0$ is the polarization, and $\mathbf{\hat{\mu}}$ is the atomic magnetic moment operator:

$$\mathbf{\hat{\mu}} = \mu_0 + \mu_s \mathbf{S}.$$  

(4.49)

Here $\mu_0$ is the orbital magnetic moment of the atom, $\mu_s$ the spin magnetic moment of the atom, and $\mathbf{S}$ is the spin operator; see the next section.

In view of (4.47) and (4.48), the Gibbs free energy for spin $J$ BEC system with electromagnetic potential well is

$$F = \int_\Omega \left[ \frac{\alpha}{2} \nabla \rho_n \right]^2 + \frac{1}{2} (b^2 p + A_1 T)\rho_n^2 - b \rho_n \mu (\rho_n + |\Psi|^2) \\
+ \frac{\hbar^2}{2m} |\nabla \Psi|^2 + \frac{g_1}{2} |\Psi|^4 + \frac{g_2}{2} |\Psi| \mathbf{\hat{S}} \Psi|^2 + g_2 b \rho_n |\Psi|^2 \\
+ \frac{1}{8\pi} \mathbf{H}^2 - \Psi^\dagger(\mathbf{H} \cdot \mathbf{\hat{\mu}})\Psi - \frac{1}{4\pi} \mathbf{H} \cdot \mathbf{H}_a \\
+ \frac{1}{8\pi} \mathbf{E}^2 - \varepsilon_0 \cdot \mathbf{E} |\Psi|^2 - \frac{1}{4\pi} \mathbf{E} \cdot \mathbf{E}_a \\
- \frac{1}{2\beta_0 k} T S^2 + \beta_1 T S \rho_n^2 - \beta_2 T S |\Psi|^2 - ST \right] dx.$$

(4.50)

**Remark 4.4.** The coupling term for the magnetic field $\Psi^\dagger(\mathbf{H} \cdot \mathbf{\hat{\mu}})\Psi$ in (4.50) breaks the symmetry of spinors for the system. When $\mathbf{H}_a = 0$, the symmetry is then restored. This is the magnetic screening phenomena, which can be more clearly viewed in the theory of phase transitions in authors’ forthcoming paper.

5. Quantum systems of condensates.

5.1. Spin operators of spinors. As we mentioned earlier, the study of condensates can be classified into thermodynamic and quantum categories. Thermodynamic systems of condensates study transitions between normal and condensate states, and quantum system of condensates deal with the quantum behavior of fully developed condensates. Form example, in the phase diagrams give by Figures 4.1 and 4.2 for $^3$He superfluid, when $(T, p)$ are in the normal phase and $A, A_1$ phases, the superfluidity is of thermodynamic, and when $(T, p)$ are region B, the system is a quantum system of condensates.

A quantum system of condensates is a conservative system with the Hamiltonian energy as its potential functional. The wave function $\Psi$ is an $N$-component spinor, which depends on the spin $J$ of the particles:

$$\Psi = (\psi_1, \cdots, \psi_N), \quad N = 2J + 1,$$

(5.1)

where $J$ is the spin of particles, which has $2J + 1$ quantum states, called magnetic quantum number $m$, and each component $\psi_i$ in (5.1) represents the wave function
of the \(i\)-th magnetic quantum state:
\[
\begin{align*}
J = 0 &: \quad m = 0, \\
J = \frac{1}{2} &: \quad m = \frac{1}{2}, -\frac{1}{2}, \\
J = 1 &: \quad m = 1, 0, -1, \\
J = \frac{3}{2} &: \quad m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, \\
J = 2 &: \quad m = 2, 1, 0, -1, -2.
\end{align*}
\] (5.2)

Spin \(J = 0\) corresponds to zeroth order spinors, and \(J \neq 0\) represents \(J\)-spinors. For \(J\)-spinors, its Hamiltonian energy includes spin interaction energy. Hence we need to derive explicit expression for spin interaction energy.

1). Spin operators. For \(J \neq 0\) spinors in (5.1), the spin operator \(\hat{J}\) is a vector operator:
\[
\hat{J} = (J_1, J_2, J_3),
\]
where each component \(J_i\) is a Hermitian matrix of \(N = 2J + 1\), and
\[
\vec{J} = \int_{\Omega} \Psi^\dagger \hat{J} \Psi dx \quad \text{represents total spin vector.} \quad (5.3)
\]
The spin operator \(\hat{J}\) enjoys the following properties:

(1) If \(x_3\) is in the direction of the magnetic field, then the third component of \(\hat{J}\) is
\[
J_3 = \begin{pmatrix}
J & 0 \\
& \ddots \\
& & 0
\end{pmatrix} \quad (\text{tr}J_3 = 0), \quad (5.4)
\]
where the entries on the diagonal of \(J_3\) correspond to the magnetic quantum number in (5.2), as the total spin vector \(\vec{J}\) in (5.3) is parallel to the magnetic field \(\mathbf{H}\).

(2) \(\vec{J}\) is \(SO(3)\) invariant. Namely, under
\[
\tilde{x} = Ax, \quad A \in SO(3), \quad (5.5)
\]
the spinor \(\Psi\) transforms as follows:
\[
\tilde{\Psi} = U_A \Psi, \quad U_A \in SU(N) \quad \text{is the } N(= 2J + 1) \text{ spinor representation,}
\]
then \(\hat{J}\) satisfies
\[
U_A^{-1}(a_{jk}J_j)U_A = J_k, \quad (5.6)
\]
where \((a_{jk}) = A\) is the matrix in (5.5).

2). Spin interaction energy. The spin of a particle induces magnetic moment, and in (4.4.1) we have
\[
g_J \hbar \Psi^\dagger \hat{J} \Psi \quad \text{represents spin magnetic moment,} \quad (5.7)
\]
where \(g_J\) is the magnetic moment coefficient, depending on the types of particles, and corresponds to the Bohr magneton. Also the module square of magnetic moment is its energy density, and we have
\[
\text{spin energy} = g_J^2 \hbar^2 \int_{\Omega} |\Psi^\dagger \hat{J} \Psi|^2 dx. \quad (5.8)
\]
The constant \( g_s = 4g_0^2\hbar^2 \) is called spin coupling constant, as in (4.35). The expression (5.8) shows that once the spin operator \( \hat{J} \) is given, the spin interaction energy is determined.

3). Spin operators for \( J = \frac{1}{2} \). They are given by the Pauli matrices:
\[
\hat{\sigma} = (\sigma_1, \sigma_2, \sigma_3),
\]
where \( \sigma_i \) are given by
\[
\sigma_1 = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\]
Pauli matrices (5.9) satisfy the invariance of the SO(3) spinor representation in (2.36) and (2.37).

4). Spin operators for \( J = 1 \). They are given by (4.36).

5.2. Hamiltonian energy of superconductors. For a superconductor or a superfluid system, when \( T \approx 0K \), the system is a quantum system of condensate. The order parameter for the system is the wave function. The temperature \( T \), the pressure \( p \) and entropy \( S \) are no longer the main parameters. The control parameters are the applied electromagnetic field and the geometric length scales of the system, and the potential functional is the Hamiltonian energy, whose expression plays a crucial role in condensed matter physics.

1). Scalar superconductors. In a condensate state, the order parameters of a scalar superconducting system is the scalar wave function \( \psi : \Omega \rightarrow \mathbb{C} \) and the electromagnetic fields \( E \) and \( A \):
\[
\text{order parameters} = (\psi, E, A).
\]
The control parameters are the applied electromagnetic fields \( E_a \) and \( H_a \):
\[
\lambda = (E_a, H_a).
\]
The Hamiltonian energy \( \mathcal{H} \) of the system contains superconducting electron energy and the electromagnetic energy:
\[
\mathcal{H} = \mathcal{H}_\psi + \mathcal{H}_{EM}. \tag{5.10}
\]
By (4.12)-(4.14), the superconducting electron energy is
\[
\mathcal{H}_\psi = \int_\Omega \left[ \frac{1}{2m_s} \left( -\frac{e_s}{c} \nabla + \frac{e_s}{c} A \right) \psi \right]^2 - g_0 |\psi|^2 + \frac{g_1}{2} |\psi|^4 \right] dx. \tag{5.11}
\]
The electromagnetic energy is
\[
\mathcal{H}_{EM} = \int_\Omega \left[ \frac{1}{8\pi} E^2 - \frac{1}{4\pi} E \cdot E_a - \varepsilon \cdot E |\psi|^2 \\
+ \frac{1}{8\pi} H^2 - \frac{1}{4\pi} H \cdot H_a - \mu \cdot H |\psi|^2 \right] dx, \tag{5.12}
\]
where \( (E, H) \) are the electromagnetic fields, \( (E_a, H_a) \) are the applied electromagnetic fields, \( e_s \) is the charge of the Cooper pair, \( \varepsilon \) is the polarization, \( \mu \) is the induction magneton
\[
\mu = \frac{e_s h}{m_s c} \mu_0 \tilde{H}_a, \tag{5.13}
\]
and $\hat{H}_a$ is the unit vector in the direction of $\mathbf{H}_a$, and $\mu_0$ is
\[
\mu_0 = \frac{N^+ - N^-}{N}.
\]
Here $N^+$, $N^-$ represent the numbers of the Cooper pairs with spin $s = 1$ and $s = -1$, $N$ is the total number of superconducting electrons. The control parameter $\lambda$ is
\[
\lambda = (E_a, H_a).
\]
(5.14)

By (5.11)-(5.13), the Hamiltonian energy (5.10) is written as
\[
H = \int_{\Omega} \left[ \frac{1}{2m_s} \left( -i\hbar \nabla - \frac{e_s}{c} \mathbf{A} \right) \psi |^2 - g_0 |\psi|^2 + \frac{g_1}{2} |\psi|^4 
+ \frac{1}{8\pi} \mathbf{E}^2 - \frac{1}{4\pi} \mathbf{E} \cdot \mathbf{E}_a - \mathbf{E} |\psi|^2 
+ \frac{1}{8\pi} \mathbf{H}^2 - \frac{1}{4\pi} \mathbf{H} \cdot \mathbf{H}_a - \mathbf{H} |\psi|^2 \right] dx.
\]
(5.15)

Remark 5.1. In (5.15), if the total spin of $\mathbf{S}$ is in the reversed direction of $\mathbf{H}_a$, i.e. $\mu_0 = (N^+ - N^-)/N < 0$, then the superconducting magnetic moment can negate the applied field:
\[
\mu |\psi|^2 \text{ negates } \frac{1}{4\pi} \mathbf{H}_a.
\]
This is the Meissner effect. In particular, if
\[
\mu |\psi|^2 = -\frac{1}{4\pi} \mathbf{H}_a,
\]
then a superconductor becomes a perfect diamagnetic system. \hfill \Box

2). Spinor superconductors. In general, the superconducting Cooper electron-pairs have spin zero. However, under magnetic field, nonzero spin Cooper electron-pairs may occur, leading to spinor superconducting electron-pairs, whose spin arrangements are given by
\[
J = 1 : |\uparrow\rangle, \quad J = -1 : |\downarrow\rangle, \quad J = 0 : |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle.
\]
The corresponding wave functions are:
\[
\psi_+ = |\uparrow\rangle, \quad \psi_0 = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle), \quad \psi_- = |\downarrow\rangle.
\]
We then have a three-component spinor wave function:
\[
\Psi = (\psi_+, \psi_0, \psi_-).
\]
(5.16)

The Hamiltonian energy $\mathcal{H}$ of the spinor consists of three parts:
\[
\mathcal{H} = \mathcal{H}_\Psi + \mathcal{H}_{\text{spin}} + \mathcal{H}_{\text{EM}}.
\]
They are given respectively as follows:
\[
\mathcal{H}_\Psi = \int_{\Omega} \left[ \frac{1}{2m_s} \left( -i\hbar \nabla - \frac{e_s}{c} \mathbf{A} \right) \psi |^2 - g_0 |\psi_0|^2 
+ g_\pm (|\psi_+|^2 + |\psi_-|^2) + \frac{g_1}{2} |\Psi|^4 \right] dx,
\]
(5.17)
\[
\mathcal{H}_{\text{spin}} = \int_{\Omega} \frac{g_\pm}{2} |\Psi|^4 d^3\mathbf{x},
\]
(5.18)
\[ H_{EM} = \int_{\Omega} \left[ \frac{1}{8\pi}(E^2 + H^2) - \frac{1}{4\pi}E \cdot E_a - \varepsilon \cdot E \psi^2 \right. \\
- \left. \frac{1}{4\pi}H \cdot H_a - \frac{e\hbar}{m_s c} \Psi \dagger \hat{F} \Psi \right] dx. \] (5.19)

Here \( \hat{F} \) in (5.18) is the spin operator defined by (4.36).

By (5.17)-(5.19), the Hamiltonian energy of a spinor superconducting system is

\[ H = \int_{\Omega} \left[ \frac{1}{2m_s} \left( -i\hbar \nabla - \frac{e}{c} A \right) \Psi \right|^2 - g_0 |\psi_0|^2 \\
- g_\pm (|\psi_+|^2 + |\psi_-|^2) + \frac{g_1}{2} |\Psi|^4 + \frac{g_s}{2} |\Psi \dagger \hat{F} \Psi|^2 \\
+ \frac{1}{8\pi}(E^2 + H^2) - \frac{1}{4\pi}E \cdot E_a - \varepsilon \cdot E |\psi|^2 \\
- \frac{1}{4\pi}H \cdot H_a - \frac{e\hbar}{m_s c} \Psi \dagger H \cdot \hat{F} \Psi \right] dx. \] (5.20)

5.3. Superfluid systems. Superfluid systems include liquid \(^4\)He and liquid \(^3\)He systems. \(^4\)He are made up of bosons and can condensate without forming Cooper atoms. Also, the electric dipole moment of induced by \(^4\)He atoms is small, indicating that the total spin of the ground state electrons is zero, and the total spin of the nuclei is also zero. Hence an applied electromagnetic field has negligible effect on \(^4\)He superfluid.

Atoms of \(^3\)He are Fermions, and need to form Cooper pairs to condensate. Also, the spin arrangements of the pairs may lead to magnetic moments strong enough as depicted in (5.17).

In summary, superfluid systems are less sensitive to the applied electric fields, since the two electrons of a helium atom are on an orbital ground state without electric polarization, very different from Alkali metals. In view of these general properties, we now introduce, respectively, the Hamiltonians of liquid \(^4\)He superfluid systems, liquid \(^3\)He without magnetic fields, and liquid \(^3\)He superfluid systems with the presence of magnetic fields.

1. \(^4\)He Superfluidity. This is a scalar system with a single component complex-valued wave function \( \psi : \Omega \to \mathbb{C} \), and without coupling with electromagnetic fields. Its Hamiltonian is as (5.11):

\[ \mathcal{H} = \int_{\Omega} \left[ \frac{\hbar^2}{2m} |\nabla \psi|^2 - g_0 |\psi|^2 + \frac{g_1}{2} |\Psi|^4 \right] dx, \] (5.21)

which is also called the Gross-Pitaevskii energy functional.

2. \(^3\)He superfluid systems without magnetic fields. This is a three-component spinor system with spinor wave function

\[ \Psi = (\psi_+, \psi_0, \psi_0). \] (5.22)

Its Hamiltonian energy is the \( \Psi \) part of the Gibbs free energy (4.37) for \(^3\)He superfluid system:

\[ \mathcal{H} = \int_{\Omega} \left[ \frac{\hbar^2}{2m} |\nabla \Psi|^2 - g_0 |\psi_0|^2 - g_\pm (|\psi_+|^2 + |\psi_-|^2) \\
+ \frac{g_1}{2} |\Psi|^4 + \frac{g_s}{2} |\Psi \dagger \hat{F} \Psi|^2 \right] dx, \] (5.23)
where the spin operator $\hat{F}$ is given by (4.36), and the attracting interaction potentials $g_0$ and $g_\pm$ satisfy

\[ g_0 \neq g_\pm \quad \text{phase A in Figure 4.1}, \]
\[ g_0 = g_\pm \quad \text{phase B region in Figure 4.1}. \]

3). $^3$He superfluid systems coupling magnetic fields. Since the atom of $^3$He is electric neutral, the gradient operator is the usual $\nabla$, which is different from the superconducting systems. The wave function is as in (5.22), and the Hamiltonian energy contains the energy involving $\Psi$ and the magnetic energy:

\[ \mathcal{H} = \mathcal{H}_{\Psi} + \mathcal{H}_M, \tag{5.24} \]

where $\mathcal{H}_{\Psi}$ is the same as (5.23), and $\mathcal{H}_M$ is the magnetic field portion of the electromagnetic energy in (5.19):

\[ \mathcal{H}_M = \int_\Omega \left[ \frac{\hbar^2}{2m} |\nabla \Psi|^2 - \frac{1}{4\pi} \mathbf{H} \cdot \mathbf{H}_a - \mu_0 \Psi^\dagger \mathbf{H} \cdot \hat{F} \Psi \right] dx. \tag{5.25} \]

Hence the Hamiltonian energy is

\[ \mathcal{H} = \int_\Omega \left[ \frac{\hbar^2}{2m} |\nabla \psi|^2 - g_0 |\psi_0|^2 - g_\pm (|\psi_+|^2 + |\psi_-|^2) + \frac{g_1}{2} |\Psi|^4 \right. \\
\left. + \frac{\mu_0}{2} |\Psi^\dagger \hat{F} \Psi|^2 + \frac{1}{8\pi} \mathbf{H}^2 - \frac{1}{4\pi} \mathbf{H} \cdot \mathbf{H}_a - \mu_0 \Psi^\dagger \mathbf{H} \cdot \hat{F} \Psi \right] dx, \tag{5.26} \]

where $\mu_0$ is the magnetic moment of the $^3$He Cooper atom-pairs, and the attracting interaction potentials $g_0$ and $g_\pm$ enjoy

\[ g_0 \neq g_\pm \quad \text{phases A and A_1 regions in Fig. 4.2}, \]
\[ g_0 = g_\pm \quad \text{phase B region in Fig. 4.2}. \]

5.4. Gaseous BEC systems. BEC is a condensate system, different from superconducting and superfluid systems. BEC occurs at the condensate state with zero kinetic energy, and superconductor and superfluid condensate occur at nonzero lowest energy levels.

There are three types of BEC systems: scalar systems, optical potential well spinor systems, and electromagnetic potential well spinor systems with $J \geq 1$.

1). Gross-Pitaevskii energy for scalar systems. For a scalar such system, the atoms of the dilute gases are confined by the magnetic potential well, leading to a condensate state. Its Hamiltonian energy is the Gross-Pitaevskii functional [11, 27]:

\[ \mathcal{H} = \int_\Omega \left[ \frac{\hbar^2}{2m} |\nabla \psi|^2 - V(x)|\psi|^2 + \frac{g_1}{2} |\psi|^4 \right] dx, \tag{5.27} \]

which has the same form as (5.21) for $^4$He, but with different binding potential. In a superfluid system, $g_0$ is the attracting potential between particles, but in (5.27), $V(x)$ is the binding potential induced by the external magnetic field. Also $g_1$ here takes the form

\[ g_1 = \frac{4\pi \hbar^2 a}{m}, \tag{5.28} \]

where $a$ is the length of the s-wave scattering.

2). Ho-Ohmi-Machida energy for optical potential well spinor systems. Atoms of such a dilute gas system are binding together by an electric potential. The
Hamiltonian energy for such a BEC system with \( J = 1 \) is derived by T.-L. Ho [12], T. Ohmi and K. Machida [25] in the following form, which is SO(3) spinor invariant:

\[
\mathcal{H} = \int_\Omega \left[ \frac{\hbar^2}{2m} |\nabla \Psi|^2 - V|\Psi|^2 + \frac{g_1}{2}|\Psi|^4 + \frac{g_s}{2}|\Psi|^4 \hat{F}|\Psi|^2 \right] dx,
\]

where \( \Psi = (\psi_+, \psi_0, \psi_-) \), \( \hat{F} \) is given by (4.36), and

\[
g_1 = \frac{4\pi \hbar^2 a_0 + 2a_1}{m}, \quad g_s = \frac{4\pi \hbar^2 a_1 - a_0}{m}.
\]

Here \( a_0, a_1 \) are the lengths of s-wave scattering for \( J = 0 \) and \( J = 2 \) respectively, and

\[
g_s < 0 \quad \text{for ferromagnetic},
g_s > 0 \quad \text{for anti-ferromagnetic}.
\]

6. Remarks on PDP based dynamical equations. As mentioned earlier, based on PDP, for a thermodynamical system with thermodynamical potential functional \( F(u, \lambda) \), the dynamic equation is given by (2.1) or (2.2). The order parameters \( u \) for conventional thermodynamic systems usually include the entropy density \( S \) as a component:

\[
u = (\varphi, S),
\]

and for thermodynamic systems of condensates, the order parameters \( u \) include also the electromagnetic fields \( (E, H) \):

\[
\nu = (\varphi, S, E, H).
\]

As we shall demonstrate in forthcoming papers on phase transitions and fluctuation theory, together with the dynamic phase transition theory [20], the order parameters \( (S, E, H) \), in a sense, play a passive role for the transformation of the system from non equilibrium states to equilibrium states, as well as for the phase transition behavior. Consequently, by writing

\[
F = F(\varphi, \Phi, \lambda), \quad \text{with} \quad \Phi = (S, E, H),
\]

in view of (2.1) and (2.2), the PDP based dynamical equations are given by

\[
\frac{d\varphi}{dt} = -A \frac{\delta}{\delta \varphi} F(\varphi, \Phi, \lambda),
\]

\[
\frac{\delta}{\delta \Phi} F(\varphi, \Phi, \lambda) = 0,
\]

which obey the PDP.

For a quantum system of condensates, the Hamiltonian energy \( H \) in general takes the form

\[
H = H(\psi, \Phi, \lambda), \quad \Phi = (E, H).
\]

With the same reason as before, based on the principle of Lagrangian dynamics, the dynamical equations for (6.5) are in the form:

\[
\hbar \frac{\partial \psi}{\partial \tau} = \frac{\delta}{\delta \psi} H(\psi, \Phi, \lambda),
\]

\[
\frac{\delta}{\delta \Phi} H(\varphi, \Phi, \lambda) = 0.
\]
Also, based on the principle of Hamiltonian dynamics, the Hamiltonian equations are

\[
\frac{\hbar}{\partial t} \frac{\partial \psi_1}{\partial t} = \frac{\delta}{\delta \psi_2} H(\psi, \Phi, \lambda), \\
\frac{\hbar}{\partial t} \frac{\partial \psi_2}{\partial t} = -\frac{\delta}{\delta \psi_1} H(\psi, \Phi, \lambda), \\
\frac{\delta}{\delta \Phi} H(\varphi, \Phi, \lambda) = 0,
\]

(6.7)

where \( \psi = \psi_1 + i\psi_2 \).

In Ma and Wang [24], both models (6.6) and (6.7) describe faithfully quantum phase transitions in quantum systems of condensates.

Acknowledgments. The work was supported in part by the US National Science Foundation (NSF), the Office of Naval Research (ONR) and by the Chinese National Science Foundation (11771306).

REFERENCES

[1] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman and E. A. Cornell, Observation of Bose-Einstein Condensation in a Dilute Atomic Vapor, Collected Papers of Carl Wieman, (2008), 453–456.
[2] S. N. Bose, Plancks Gesetz und Lichtquantenhypothese, Zeitschrift Für Physik, 26 (1924), 178–181.
[3] P. M. Chaikin and T. C. Lubensky, Principles of Condensed Matter Physics, Cambridge University Press, New York, 2000.
[4] K. B. Davis, M. O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn and W. Ketterle, Bose-einstein condensation in a gas of sodium atoms, Phys. Rev. Lett., 75 (1996), 3969–3973.
[5] P. de Gennes, Superconductivity of Metals and Alloys, W. A. Benjamin, 1966.
[6] A. Einstein, Quantentheorie des einatomigen idealen gases, Sitzungsberichte der Preussischen Akademie der Wissenschaften, Physik-Mathematik, (1924), 261–267.
[7] A. Einstein, Quantentheorie des einatomigen idealen gases. zweite abhandlung., Sitzungsberichte der Preussischen Akademie der Wissenschaften, Physik-Mathematik, (1925), 3–14.
[8] M. E. Fisher, Renormalization group theory: Its basis and formulation in statistical physics, Reviews of Modern Physics, 70 (1998), 653–681.
[9] V. L. Ginzburg, On superconductivity and super uidity (what i have and have not managed to do), as well as on the 'physical minimum' at the beginning of the xxi century, Phys.-Usp., 47 (2004), 1155–1170.
[10] L. Gor'kov, Generalization of the Ginzburg-Landau equations for non-stationary problems in the case of alloys with paramagnetic impurities, Sov.Phys. JETP, 27 (1968), 328–334.
[11] E. P. Gross, Structure of a quantized vortex in boson systems, Il Nuovo Cimento (1955-1965), 20 (1961), 454–477.
[12] T.-L. Ho, Spinor bose condensates in optical traps, Physical Review Letters, 81 (1998), 742.
[13] L. P. Kadanoff, Statistical Physics: Statics, Dynamics and Renormalization, World Scientific Publishing Co Inc, 2000.
[14] P. Kapitza, E7-Viscosity of liquid helium below the -point, Nature, 141 (1938), 74.
[15] M. Kleman and O. D. Lavrentovich, Soft Matter Physics: An Introduction, Springer Science Business Media, 2007.
[16] J. M. Kosterlitz and D. J. Thouless, Ordering, metastability and phase transitions in two-dimensional systems, Journal of Physics C: Solid State Physics, 6 (1973), 1181.
[17] L. D. Landau and E. M. Lifshitz, Statistical Physics: V. 5: Course of Theoretical Physics, Pergamon Press, 1969.
[18] E. M. Lifschitz and L. P. Pitajewski, Lehrbuch Der Theoretischen Physik ("Landau-Lifschitz"). Band X, 2nd edition, Akademie-Verlag, Berlin, 1990. Physikalische Kinetik. [Physical kinetics]. Translated from the Russian by Gerd Röpke and Thomas Frauenheim, Translation edited and with a foreword by Paul Ziesche and Gerhard Diener.
[19] E. Lifshitz and L. Pitaevskii, *Statistical Physics Part 2*, Landau and Lifshitz Course of Theoretical Physics vol. 9, 1980.
[20] T. Ma and S. Wang, *Phase Transition Dynamics*, Springer-Verlag, New York, 2014.
[21] T. Ma and S. Wang, *Mathematical Principles of Theoretical Physics*, Science Press, Beijing, 2015.
[22] T. Ma and S. Wang, Dynamic law of physical motion and potential-descending principle, *J. Math. Study*, 50 (2017), 215–241.
[23] T. Ma and S. Wang, *Statistical Theory of Heat*, Hal preprint: Hal-01578634, 2017.
[24] T. Ma and S. Wang, Topological phase transitions I: Quantum phase transitions, to appear, (2018).
[25] T. Ohmi and K. Machida, Bose-Einstein condensation with internal degrees of freedom in alkali atom gases, *Journal of the Physical Society of Japan*, 67 (1998), 1822–1825.
[26] R. K. Pathria and F. D. Beale, *Statistical Mechanics, 3rd edition*, Elsevier, 2011.
[27] L. Pitaevskii, Vortex lines in an imperfect Bose gas, *Sov. Phys. JETP*, 13 (1961), 451–454.
[28] L. P. Pitaevskii and S. Stringari, *Bose-Einstein Condensation and Super Fluidity*, vol. 164 of Internat. Ser. Mono. Phys., Clarendon Press, Oxford, 2003.
[29] L. E. Reichl, *A modern Course in Statistical Physics*, A Wiley-Interscience Publication, 2nd edition, John Wiley Sons Inc., New York, 1998.
[30] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press, New York and Oxford, 1971.
[31] M. Tinkham, *Introduction to Superconductivity*, McGraw-Hill, Inc, 1996.

Received for publication November 2017.

E-mail address, Liu: liuruikuan2008@163.com
E-mail address, Ma: matian56@sina.com
E-mail address, Wang: showang@indiana.edu
E-mail address, Yang: jiayan1985@163.com