Towards the Authentic *Ab Intio* Thermodynamics

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1. Introduction

A phase diagram is considered as a starting point to design new materials. Let us quote the statements by DeHoff (1993):

> A phase diagram is a map that presents the domains of stability of phases and their combiations. A point in this space, which represents a state of the system that is of interest in a particular application, lies within a specific domain on the map.

In practice, for example to calculate the lattice stability, the construction of the phase diagram is to find the phase equilibria based on the comparison of the Gibbs free energies among the possible phases. Hence, the most important factor is the accuracy and precesion of the given Gibbs free energy values, which are usually acquired by the experimental assessments. Once the required thermodynamic data are obtained, the phase diagram construction becomes rather straightforward with modern computation techniques, so called CALPHAD (CALculation of PHAse Diagrams) (Spencer, 2007). Hence, the required information for constructing a phase diagram is the reliable Gibbs free energy information. The Gibbs free energy G is defined by

$$G = E + PV - TS, \tag{1}$$

where E is the internal energy, P is the pressure, V is the volume of the system, T is the temperature and S is the entropy. The state which provides the minimum of the free energy under given external conditions at constant P and T is the equilibrium state. However, there is a critical issue to apply the conventional CALPHAD method in general materials design. Most thermodynamic information is relied on the experimental assessments, which do not available occasionally to be obtained, but necessary. For example, the direct thermodynamic information of silicon solubility in cementite had not been available for long time (Ghosh & Olson, 2002; Kozeschnik & Bhadeshia, 2008), because the extremely low silicon solubility which requires the information at very high temperature over the melting point of cementite. The direct thermodynamic information was available recently by an *ab initio* method (Jang et al., 2009). However, the current technology of *ab initio* approaches is usually limited to zero temperature, due to the theoretical foundation; the density functional theory (Hohenberg & Kohn, 1964) guarrentees the unique total energy of the ground states only. The example demonstrates the necessity of a systematic assessment method from first principles. In order to obtain the Gibbs free energy from first principles, it is convenient to use the equilibrium statistical mechanics for grand canonical ensemble by introducing the *grand*

partition function

$$\Xi\left(T, V, \{\mu_i\}\right) = \sum_{N_i} \sum_{\zeta} \exp\left(-\beta\left(E_{\zeta}\left(V\right) - \sum_i \mu_i N_i\right)\right), \tag{2}$$

where β is the inverse temperature $(k_{\mathrm{B}}T)^{-1}$ with the Boltzmann's constant k_{B}, μ_i is the chemical potential of the ith component, N_i is the number of atoms. The sum of ζ runs over all accessible microstates of the system; the microstates include the electronic, magnetic, vibrational and configurational degrees of freedom. The corresponding *grand potential* Ω is found by

$$\Omega\left(T, V, \{\mu_i\}\right) = -\beta^{-1}\ln\Xi. \tag{3}$$

The Legendre transformation relates the grand potential Ω and the *Helmholtz free energy F* as

$$\Omega\left(T, V, \{\mu_i\}\right) = F - \sum_i \mu_i N_i = E - TS - \sum_i \mu_i N_i. \tag{4}$$

It is noticeable to find that the Helmholtz free energy F is able to be obtained by the relation

$$F\left(T, V, N\right) = -\beta^{-1}\ln Z, \tag{5}$$

where Z is the *partition function* of the canonical ensemble defined as

$$Z\left(T, V, N\right) = \sum_{\zeta} \exp\left(-\beta E_{\zeta}\left(V, N\right)\right). \tag{6}$$

Finally, there is a further Legendre transformation relationship between the Helmholtz free energy and the Gibbs free energy as

$$G = F + PV. \tag{7}$$

Let us go back to the grand potential in Eq. (4). The total differential of the grand potential is

$$\mathrm{d}\Omega = -S\mathrm{d}T - P\mathrm{d}V - \sum_i N_i\mathrm{d}\mu_i, \tag{8}$$

with the coefficients

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V\mu}, \quad P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T\mu}, \quad N_i = -\left(\frac{\partial\Omega}{\partial\mu_i}\right)_{TV}. \tag{9}$$

The Gibss-Duhem relation,

$$E = TS - PV + \sum_i \mu_i N_i, \tag{10}$$

yields the thermodynamic functions as

$$F = -PV + \sum_i \mu_i N_i, \quad G = \sum_i \mu_i N_i, \quad \Omega = -PV. \tag{11}$$

Since the thermodynamic properties of a system at equilibrium are specified by Ω and derivatives thereof, one of the tasks will be to develop methods to calculate the grand potential Ω.

In principle, we can calculate any macroscopic thermodynamic states if we have the complete knowledge of the (grand) partition function, which is abled to be constructed from first principles. However, it is impractical to calculates the partition function of a given system because the number of all accessible microstates, indexed by ζ, is enormously large.

Struggles have been devoted to calculate the summation of all accessible states. The number of all accessible states is evaluated by the constitutents of the system and the types of interaction among the constituents. The general procedure in statistical mechanics is nothing more than the calculation of the probability of a specific number of dice with the enormous number of repititions of the dice tosses. The fundamental principles of statistical mechanics of a mechanical system of the degrees of freedom s is well summarized by Landau & Lifshitz (1980). The state of a mechanical system is described a point of the *phase space* represented by the generalized coordinates q_i and the corresponding generalized momenta p_i, where the index i runs from 1 to s. The time evolution of the system is represented by the trajectory in the phase space. Let us consider a closed large mechanical system and a part of the entire system, called *subsystem*, which is also large enough, and is interacting with the rest part of the closed system. An exact solution for the behavior of the subsystem can be obtained only by solving the mechanical problem for the entire closed system.

Let us assume that the subsystem is in the small phase volume $\Delta p \Delta q$ for short intervals. The probability w for the subsystem stays in the $\Delta p \Delta q$ during the short interval Δt is

$$w = \lim_{D \to \infty} \frac{\Delta t}{D}, \tag{12}$$

where D is the long time interval in which the short interval Δt is included. Defining the probability dw of states represented in the phase volum,

$$dpdq = dp_1 dp_2 \ldots dp_s dq_1 dq_2 \ldots dq_s,$$

may be written

$$dw = \rho \left(p_1, p_2, \ldots, p_s, q_1, q_2, \ldots, q_s \right) dpdq, \tag{13}$$

where ρ is a function of all coordinates and momenta in writing for brevity $\rho\left(p,q\right)$. This function ρ represents the density of the probability distribution in phase space, called (*statistical*) *distribution function*. Obviously, the distribution function is normalized as

$$\int \rho \left(p, q \right) dpdq = 1. \tag{14}$$

One should note that the statistical distribution of a given subsystem does not depend on the initial state of any other subsystems of the entire system, due to the entirely outweighed effects of the initial state over a sufficiently long time.

A physical quantity $f = f(p,q)$ depending on the states of the subsystem of the solved entire system is able to be evaluated, in the sense of the statistical average, by the distribution function as

$$\bar{f} = \int f(p,q)\rho(p,q)dpdq. \tag{15}$$

By definition Eq. (12) of the probability, the statistical averaging is exactly equivalent to a time averaging, which is established as

$$\bar{f} = \lim_{D \to \infty} \frac{1}{D} \int_0^D f\left(t\right) dt. \tag{16}$$

In addition, the Liouville's theorem

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \sum_{i=1}^{s} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0 \tag{17}$$

tells us that the distribution function is constant along the phase trajectories of the subsystem. Our interesting systems are (quantum) mechanical objects, so that the counting the number of accessible states is equivalent to the estimation of the relevant phase space volume.

2. Phenomenological Landau theory

A ferromagnet in which the magnetization is the order parameter is served for illustrative purpose. Landau & Lifshitz (1980) suggested a phenomenological description of phase transitions by introducing a concept of *order parameter*. Suppose that the interaction Hamiltonian of the magnetic system to be

$$\sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{18}$$

where $\mathbf{S}_i$ is a localized Heisenberg-type spin at an atomic site i and J_{ij} is the interaction parameter between the spins $\mathbf{S}_i$ and $\mathbf{S}_j$.
In the ferromagnet, the total magnetization $\mathbf{M}$ is defined as the thermodynamic average of the spins

$$\mathbf{M} = \left\langle \sum_i \mathbf{S}_i \right\rangle, \tag{19}$$

and the magnetization $\mathbf{m}$ denotes the magnetization per spin

$$\mathbf{m} = \left\langle \frac{1}{N} \sum_i \mathbf{S}_i \right\rangle, \tag{20}$$

where N is the number of atomic sites. The physical order is the alignment of the microscopic spins.
Let us consider a situation that an external magnetic field $\mathbf{H}$ is applied to the system. Landau's idea[1] is to introduce a function, $\mathcal{L}(\mathbf{m}, \mathbf{H}, T)$, known as the Landau function, which describes the "thermodynamics" of the system as function of $\mathbf{m}$, $\mathbf{H}$, and T. The minimum of $\mathcal{L}$ indicates the system phase at the given variable values. To see more details, let us expand the Ladau function with respect to the order parameter $\mathbf{m}$:

$$\mathcal{L}(m, H, T) = \sum_n^4 a_n(H, T) m^n, \tag{21}$$

where we assumed that both the magnetization $\mathbf{m}$ and the external magnetic field $\mathbf{H}$ are aligned in a specific direction, say $\hat{\mathbf{z}}$. When the system undergoes a *first-order phase transition*, the Landau function should have the properties

$$\left. \frac{\partial \mathcal{L}}{\partial m} \right|_{m_A} = \left. \frac{\partial \mathcal{L}}{\partial m} \right|_{m_B} = 0, \qquad \mathcal{L}(m_A) = \mathcal{L}(m_B), \tag{22}$$

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[1] The description in this section is following Negele & Orland (1988) and Goldenfeld (1992).

for the minima points A and B. For the case of the *second-order phase transition*, it is required that

$$\frac{\partial \mathcal{L}}{\partial m} = \frac{\partial^2 \mathcal{L}}{\partial m^2} = \frac{\partial^3 \mathcal{L}}{\partial m^3} = 0, \qquad \frac{\partial^4 \mathcal{L}}{\partial m^4} > 0. \tag{23}$$

The second derivative must vanish because the curve changes from concave to convex and the third derivative must vanish to ensure that the critical point is a minimum. It is convenient to reduce the variables in the vicinity of the critical point $t \equiv T - T_C$ and $h \equiv H - H_c = H$, where T_C is the Curie temperature and H_c is the critical external field, yielding the Landau coefficient

$$a_n(H, T) \mapsto a_n(h, t) = b_n + c_n h + d_n t, \tag{24}$$

and then the Ladau function near the critical point is

$$\mathcal{L}(m, h, t) = c_1 hm + d_2 tm^2 + c_3 hm^3 + b_4 m^4, \quad d_2 > 0, \quad b_4 > 0. \tag{25}$$

Enforcing the inversion symmetry, $\mathcal{L}(m, H, T) = \mathcal{L}(-m, -H, T)$, the Landau function will be

$$\mathcal{L}(m, h, t) = d_2 tm^2 + b_4 m^4.$$

In order to see the dependency to the external field H, we add an arbitrary H field coupling term and change the symbols of the coefficients d_2 to a and b_4 to $\frac{1}{2}b$:

$$\mathcal{L} = atm^2 + \frac{1}{2}bm^4 - Hm. \tag{26}$$

Let us consider the second-order phase transition with $H = 0$. For $T > T_C$, the minimum of $\mathcal{L}$ is at $m = 0$. For $T = T_C$, the Landau function has zero curvature at $m = 0$, where the point is still the global minimum. For $T < T_C$, the Landau function Eq. (26) has two degenerate minima at $m_s = m_s(T)$, which is explicitly

$$m_s(t) = \pm\sqrt{\frac{-at}{b}}, \quad \text{for } t < 0. \tag{27}$$

When $H \neq 0$, the differentiation of $\mathcal{L}$ with respect to m gives the magnetic equation of state for small m as

$$atm + bm^3 = \frac{1}{2}H. \tag{28}$$

The isothermal magnetic susceptibility is obtained by differentiating Eq. (28) with respect to H:

$$\chi_T(H) \equiv \left.\frac{\partial m(H)}{\partial H}\right|_T = \frac{1}{2\left\{at + 3b\left(m(H)\right)^2\right\}}, \tag{29}$$

where $m(H)$ is the solution of Eq. (28). Let us consider the case of $H = 0$. For $t > 0$, $m = 0$ and $\chi_T = 1/(2at)$, while $m^2 = -at/b$ and $\chi_T = -1/(4at)$. As the system is cooled down, the nonmagnetized system, $m = 0$ for $t > 0$, occurs a spontaneous magnetization of $(-at/b)^{\frac{1}{2}}$ below the critical temperature $t < 0$, while the isothermal magnetic susceptibility χ_T diverges as $1/t$ for $t \to 0$ both for the regions of $t > 0$ and $t < 0$.

For the first-order phase transition, we need to consider Eq. (25) with $c_1 = 0$ and changing the coefficient symbols to yield

$$\mathcal{L} = atm^2 + \frac{1}{2}m^4 + Cm^3 - Hm. \tag{30}$$

For $H = 0$, the equilibrium value of m is obtained as

$$m = 0, \quad m = -c \pm \sqrt{c^2 - at/b}, \tag{31}$$

where $c = 3C/4b$. The nonzero solution is valid only for $t < t^*$, by defining $t^* \equiv bc^2/a$. Let T_c is the temperature where the coefficient of the term quadratic in m vanishes. Suppose t_1 is the temperature where the value of $\mathcal{L}$ at the secondary minimum is equal to the value at $m = 0$. Since t^* is positive, this occurs at a temperature greater than T_c. For $t < t^*$, a secondary minimum and maximum have developed, in addition to the minimum at $m = 0$. For $t < t_1$, the secondary minimum is now the global minimum, and the value of the order parameter which minimizes $\mathcal{L}$ jumps *discontinuously* from $m = 0$ to a non-zero value. This is a first-order transition. Note that at the first-order transition, $m(t_1)$ is not arbitrarily small as $t \to t_1^-$. In other words, the Landau theory is *not* valid. Hence, the first-order phase transition is arosen by introducing the cubic term in m.

Since the Landau theory is fully phenomenological, there is no strong limit in selecting order parameter and the corresponding conjugate field. For example, the magnetization is the order parameter of a ferromagnet with the external magnetic field as the conjugate coupling field, the polarization is the order parameter of a ferroelectric with the external electric field as the conjugate coupling field, and the electron pair amplitude is the order parameter of a superconductor with the electron pair source as the conjugate coupling field. When a system undergoes a phase transition, the Landau theory is usually utilized to understand the phase transition.

The Landau theory is motivated by the observation that we could replace the interaction Hamiltonian Eq. (18)

$$\sum_{i,j} J_{ij} S_i S_j = \sum_i S_i \sum_j J_{ij} \left[\langle S_j \rangle + \left\{ S_j - \langle S_j \rangle \right\} \right] \tag{32}$$

by $\sum_{ij} S_i J_{ij} \langle S_j \rangle$. If we can replace $S_i S_j$ by $S_i \langle S_j \rangle$, it is also possible to replace $\langle S_i S_j \rangle$ by $\langle S_i \rangle \langle S_j \rangle$ on average if we assume the translational invariance. The fractional error implicit in this replacement can be evaluated by

$$\varepsilon_{ij} = \frac{\left| \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle \right|}{\langle S_i \rangle \langle S_j \rangle}, \tag{33}$$

where all quantities are measured for $T < T_C$ under the Landau theory. The numerator is just a correlation function C and the interaction range $\left| \mathbf{r}_i - \mathbf{r}_j \right| \sim R$ will allow us to rewrite ε_{ij} as

$$\varepsilon_R = \frac{|C(R)|}{m_s^2}, \tag{34}$$

where we assume the correlation function being written as

$$C(R) = g f\left(\frac{R}{\xi}\right), \tag{35}$$

where f is a function of the correlation length ξ. For $T \ll T_C$, the correlation length $\xi \sim R$, and the order parameter m is saturated at the low temperature value. The error is roughly

estimated as

$$\varepsilon_R \simeq \left(\frac{T}{T_C} \right) \left(\frac{a}{R} \right)^d, \tag{36}$$

where a is the lattice constant and d is the dimensionality of the interaction. In Eq. (36), $(a/R)^{-d}$ is essentially the corrdination number $z > 1$, so that $\varepsilon_R < 1$ and the mean field theory is self-consistent.

On the other hand, the correlation length grows toward infinity near the critical point; $R \ll \xi$ for $t \to 0$. A simple arithematics yields $m \sim |t|^\beta$, where a *critial exponent* β is $\frac{1}{2}$ for a ferromagnet. This result leaves us the error

$$\varepsilon_R \sim \frac{1}{|t|^{2\beta}} \left(\frac{a}{R} \right)^d, \tag{37}$$

which tends to infinity as $t \to 0$. Hence, the Landau theory based on the mean-field approximation has error which diverges as the system approaches to the critical point. Mathematically, the Landau theory expands the Landau function in terms of the order parameter. The landau expansion itself is mathematically non-sense *near* the critical point for dimensions less than four. Therefore, the Landau theory is not a good tool to investigate significantly the phase transitions of the system.

3. Matters as noninteracting gases

Materials are basically made of atoms; an atom is composed of a nucleus and the surrounding electrons. However, it is convenient to distinguish two types of electrons; the *valence electrons* are responsible for chemical reactions and the *core electrons* are tightly bound around the nucleus to form an *ion* for screening the strongly divergent Coulomb potential from the nucleus. It is customary to call valence electrons as electrons.

The decomposition into electrons and ions provides us at least two advantages in treating materials with first-principles. First of all, the motions of electrons can be decoupled adiabatically from the those of ions, since electrons reach their equilibrium almost immediately by their light mass compared to those factors of ions. The decoupling of the motions of electrons from those of ions is accomplished by the Born-Oppenheimer adiabatic approximation (Born & Oppenheimer, 1927), which decouples the motions of electrons approximately begin independent adiabatically from those of ions. In practice, the motions of electrons are computed under the external potential influenced by the ions at their *static* equilibrium positions, before the motions of ions are computed under the external potential influenced by the electronic distribution. Hence, the fundamental information for thermodynamics of a material is its electronic structures. Secondly, the decoupled electrons of spin half are identical particles following the Fermi-Dirac statistics (Dirac, 1926; Fermi, 1926). Hence, the statistical distribution function of electrons is a closed fixed form. This feature reduces the burdens of calculation of the distribution function of electrons.

3.1 Electronic subsystem as Fermi gas

The consequence of the decoupling electrons from ions allows us to treat the distribution functions of distinguishable atoms, for example, an iron atom is distinguished from a carbon atom, can be treated as the source of external potential to the electronic subsystem. Modelling of electronic subsystem was suggested firstly by Drude (1900), before the birth of quantum mechanics. He assumes that a metal is composed of electrons wandering on the positive homogeneous ionic background. The interaction between electrons are cancelled to allow us

for treating the electrons as a noninteracting gas. Albeit the Drude model oversimplifies the real situation, it contains many useful features of the fundamental properties of the electronic subsystem (Aschcroft & Mermin, 1976; Fetter & Walecka, 2003; Giuliani & Vignale, 2005).

As microstates is indexed as i of the electron subsystem, the Fermi-Dirac distribution function is written in terms of occupation number of the state i,

$$n_i^0 = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}, \tag{38}$$

where ϵ_i is the energy of the electronic microstate i and μ is the chemical potential of the electron gas. At zero-temperature, the Fermi-Dirac distribution function becomes

$$\frac{1}{e^{\beta(\epsilon - \mu)} + 1} = \theta(\mu - \epsilon) \tag{39}$$

and the chemical potential becomes the Fermi energy ϵ_F. In the high-temperature limit, the Fermi-Dirac distribution function recudes to

$$n^0 = e^{\beta(\epsilon - \mu)}, \tag{40}$$

the Maxwell-Boltzmann distribution function. With the nonrelativistic energy spectrum

$$\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2 k^2}{2m} = \epsilon_{\mathbf{k}}, \tag{41}$$

where $\mathbf{p}$ is the single-particle momentum, $\mathbf{k}$ is the corresponding wave vector, the grand potential in Eq. (3) is calculated in a continuum limit[2] as

$$-\beta\Omega_0 = \beta PV = \frac{2}{3}\frac{gV}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \mathrm{d}\epsilon \frac{\epsilon^{\frac{3}{2}}}{e^{\beta(\epsilon - \mu)} + 1} \tag{42}$$

and the number density is written as

$$\frac{N}{V} = \frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty \mathrm{d}\epsilon \frac{\epsilon^{\frac{1}{2}}}{e^{\beta(\epsilon - \mu)} + 1}, \tag{43}$$

where g is 2, the degeneracy factor of an electron. After math (Fetter & Walecka, 2003), we can obtain the low-temperature limit $(T \to 0)$ of the grand potential of the noninteractic homogeneous electron gas as

$$PV = \frac{2}{3}\frac{gV}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{\frac{3}{2}}\left[\frac{2}{5}\mu^{\frac{5}{2}} + \beta^{-2}\frac{\pi^2}{4}\mu^{\frac{1}{2}} + \cdots\right] \tag{44}$$

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[2] It is convenient to convert a summation over single-particle spectra to an integral over wavenumbers according to $\sum_i \to g\int \mathrm{d}^3 n = gV(2\pi)^{-3}\int \mathrm{d}^3 k$ for a very large periodic system, hence a continuum case. If we have knowledge of the single-particle energy dispersion relation, the wavenumber integral is also replaced by an integral over energy as $gV(2\pi)^{-3}\int \mathrm{d}^3 k F(\epsilon_{\mathbf{k}}) \to g\int_{-\infty}^\infty \mathrm{d}\epsilon \mathcal{D}(\epsilon) F(\epsilon)$, where $\mathcal{D}(\epsilon)$ is the density of states.

and the chemical potential from the relation $N = (\partial (PV)/\partial \mu)_{TV}$ as

$$\mu = \epsilon_{\mathrm{F}} \left[1 - \frac{\pi^2}{12} \left(\frac{1}{\beta \epsilon_{\mathrm{F}}} \right)^2 + \cdots \right]. \tag{45}$$

The low temperature limit entropy S is calculated as

$$S(\beta, V, \mu) = \left(\frac{\partial (PV)}{\partial T} \right)_{V\mu} = \frac{gV}{4\pi^2} \left(\frac{2m}{\hbar} \right)^{\frac{3}{2}} \frac{2}{3} \left[\frac{2\pi^2}{4} \frac{k_{\mathrm{B}}}{\beta} + \cdots \right]. \tag{46}$$

It is thus the heat capacity of the noninteracting homogeneous electron gas to be

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{VN} = \frac{\pi^2}{2} N k_{\mathrm{B}} \frac{1}{\epsilon_{\mathrm{F}} \beta}. \tag{47}$$

The internal energy is simply calculated by a summation of the microstate energy of all the occupied states to yield

$$\frac{E}{V} = \frac{g}{4\pi^2} \int_0^\mu \epsilon^{\frac{3}{2}} \mathrm{d}\epsilon = \frac{g}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{2}{5} \mu^{\frac{5}{2}}. \tag{48}$$

All the necessary thermodynamic information of the homogeneous noninteracting electron subsystem is acquired.

3.2 Elementary excitation as massive boson gas

For the case of ions, the treatment is rather complex. One can immediately raise the same treatment of the homogeneous noninteracting ionic gas model as we did for the electronic subsystem. Ignoring the nuclear spins, any kinds of ions are composed of fully occupied electronic shells to yield the effective zero spin; ions are massive bosons. It seems, if the system has single elemental atoms, that the ionic subsystem can be treated as an indistinguishable homogeneous noninteracting bosonic gas, following the Bose-Einstein statistics (Bose, 1926; Einstein, 1924; 1925). However, the ionic subsystem is hardly treated as a boson gas. Real materials are not elemental ones, but they are composed of many different kinds of elements; it is possible to distinguish the atoms. They are partially distinguishable each other, so that a combinatorial analysis is required for calculating thermodynamic properties (Ruban & Abrikosov, 2008; Turchi et al., 2007). It is obvious that the ions in a material are approximately distributed in the space isotropically and homogeneously. Such phases are usually called *fluids*. As temperature goes down, the material in our interests usually crystalizes where the homogeneous and isotropic symmetries are broken spontaneously and individual atoms all occupy nearly fixed positions.

In quantum field theoretical language, there is a massless boson, called Goldstone boson, if the Lagrangian of the system possesses a continuous symmetry group under which the the ground or vacuum state is not invariant (Goldstone, 1961; Goldstone et al., 1962). For example, phonons are emerged by the violation of translational and rotational symmetry of the solid crystal; a longitudinal phonon is emerged by the violation of the gauge invariance in liquid helium; spin waves, or magnons, are emerged by the violation of spin rotation symmetry (Anderson, 1963). These quasi-particles, or elementary excitations, have known in many-body theory for solids (Madelung, 1978; Pines, 1962; 1999). One has to note two facts: (i) the elementary excitations are not necessarily to be a Goldstone boson and (ii) they are not

necessarily limited to the ionic subsystem, but also electronic one. If the elementary excitations are fermionic, thermodynamics are basically calculable as we did for the non-interacting electrons gas model, in the beginning of this section. If the elementary excitations are (Goldstone) bosonic, such as phonons or magnons, a thermodynamics calculation requires special care. In order to illustrative purpose, let us see the thermodynamic information of a system of homogeneous noninteracting massive bosons.

The Bose-Einstein distribution function gives the mean occupation number in the ith state as

$$n_i^0 = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}. \tag{49}$$

Since the chemical potential of a bosonic system vanishes at a certain temperature T_0, a special care is necessary during the thermodynamic property calculations (Cornell & Wieman, 2002; Einstein, 1925; Fetter & Walecka, 2003). The grand potential of an ideal massive boson gas, where the energy spectrum is also calculated as in Eq. (41), is

$$-\beta\Omega_0 = \beta PV = -\frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty d\epsilon\, \epsilon^{\frac{1}{2}}\ln\left(1 - e^{\beta(\mu-\epsilon)}\right). \tag{50}$$

The integration by part yields

$$PV = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\frac{2}{3}\int_0^\infty d\epsilon\frac{\epsilon^{\frac{3}{2}}}{e^{\beta(\epsilon-\mu)} - 1}. \tag{51}$$

The internal energy is calculated to be

$$E = \sum_i n_i^0 \epsilon_i = \frac{3}{2}PV = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty d\epsilon\frac{\epsilon^{\frac{3}{2}}}{e^{\beta(\epsilon-\mu)} - 1}, \tag{52}$$

and the number density is calculated to be

$$\frac{N}{V} = \frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\int_0^\infty d\epsilon\frac{\epsilon^{\frac{1}{2}}}{e^{\beta(\mu-\epsilon)} - 1}. \tag{53}$$

A care is necessary in treating Eq. (53), because it is meaningful only if $\epsilon - \mu \geq 0$, or

$$\mu \leq 0 \tag{54}$$

with the consideration of the fact $\epsilon \geq 0$.

In the classical limit $T \to \infty$, or $\beta \to 0$, for fixed N, we have

$$\beta\mu \to -\infty. \tag{55}$$

Recall that the classical limit yields the Maxwell-Boltzmann distribution

$$n_i^0 = e^{-\beta(\epsilon_i - \mu)} \tag{56}$$

for both fermions and bosons, and the corresponding grand potential becomes

$$\Omega_0 = -PV = -\frac{1}{\beta}\sum_i e^{\beta(\mu-\epsilon_i)}. \tag{57}$$

The classical chemical potential μ_c is now calculated as

$$\beta\mu_c = \ln\left[\frac{N}{gV}\left(\frac{2\pi\hbar^2}{m}\right)^{\frac{3}{2}}\beta^{\frac{3}{2}}\right]. \tag{58}$$

As β increases at fixed density, $\beta\mu_c$ passes through zero and becomes positive, diverging to infinity at $\beta \to \infty$. This contradicts to the requirement Eq. (54). The critical temperature β_0, where the chemical potential of an ideal boson gas vanishes, is calculated by using Eq. (53) with $\mu = 0$ to be

$$\frac{1}{\beta_0} = \frac{\hbar^2}{2m}\left(\frac{4\pi^2}{g\Gamma\left(\frac{3}{2}\right)\zeta\left(\frac{3}{2}\right)}\right)^{\frac{2}{3}}\left(\frac{N}{V}\right)^{\frac{2}{3}}, \tag{59}$$

where Γ and ζ are Gamma function and zeta function, respectively. For $\mu = 0$ and $\beta > \beta_0$, the integral in Eq. (53) is less than N/V because these conditions increase the denominator of the integrand relative to its value at β_0.

The breakdown of the theory was noticed by Einstein (1925) and was traced origin of the breakdown was the converting the conversion of the summation to the integral of the occupation number counting in Eq. (53). The total number of the ideal massive Bose gas is counted, using the Bose-Einstein distribution function Eq. (49), by

$$N = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}. \tag{60}$$

It is obvious that the bosons tends to occupy the ground state for the low temperature range $\beta > \beta_0$, due to the lack of the limitation of the occupation number of bosons. As temperature goes down, the contribution of the ground state occupation to the number summation increases. However, the first term of Eq. (60) is omitted, in the Bose-Einstein distribution, during the conversion to the integral Eq. (53) as $\mu \to 0^-$ for $\beta > \beta_0$, because the fact that $\epsilon_i = 0$ vanishes the denominator $\epsilon^{\frac{1}{2}}$ of the integrand in Eq. (53). The number density of the Bose particles with energies $\epsilon > 0$ is computed by Eq. (53) to be

$$\frac{N_{\epsilon>0}}{V} = \frac{N}{V}\left(\frac{\beta}{\beta_0}\right)^{-\frac{3}{2}}, \tag{61}$$

while the number density at the ground state is evaluated to be

$$\frac{N_{\epsilon=0}}{V} = \frac{N}{V}\left[1 - \left(\frac{\beta}{\beta_0}\right)^{-\frac{3}{2}}\right], \tag{62}$$

with the chemical potential $\mu = 0^-$ for $\beta > \beta_0$. The internal energy density of the degenerate massive boson gas for $\beta > \beta_0$ is then computed (Fowler & Jones, 1938) as

$$\frac{E}{V} = \frac{g}{4\pi^2}\left(\frac{2m}{\beta\hbar^2}\right)^{\frac{3}{2}}\frac{1}{\beta}\Gamma\left(\frac{5}{2}\right)\zeta\left(\frac{5}{2}\right). \tag{63}$$

The constant-volume heat capacity for $\beta > \beta_0$ becomes

$$C_V = \frac{5}{2} \left[\frac{\Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right)}{\Gamma\left(\frac{3}{2}\right) \zeta\left(\frac{3}{2}\right)} N k_B \left(\frac{\beta}{\beta_0}\right)^{-\frac{3}{2}} \right], \tag{64}$$

and the pressure for $\beta > \beta_0$ becomes

$$P = \frac{2}{3} \frac{2\sqrt{2}}{4\pi^2} \Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right) \frac{m^{\frac{3}{2}} g}{\hbar^3} \beta^{-\frac{5}{2}}. \tag{65}$$

It is interesting to find that the pressure approaches to zero as temperature goes to zero, *i.e.* $\beta \to \infty$. In other words, the Bose gas exerts no force on the walls of the container at $T = 0$, because all of the particles condensate in the zero-momentum state. The pressure is independent of the number density N/V, depending only on temperature β. The two different summations above and below the temperature β_0 lead us that the heat capacity as a function of temperature has discontinuity in its slope (Landau & Lifshitz, 1980) as

$$\Delta \left(\frac{\partial C_V}{\partial V}\right)_{\beta_0} = -\frac{27}{4} \left[\frac{\Gamma\left(\frac{3}{2}\right) \zeta\left(\frac{3}{2}\right)}{\pi} \right]^2 N k_B^2 \beta_0^{-1}. \tag{66}$$

This implies that a homogeneous massive ideal Bose gas system exhibits a *phase transition* at β_0 *without* interaction. This phenomenon is known as the *Bose-Einstein condensation*. A good review for the realization of the Bose-Einstein condensation is provided by Cornell & Wieman (2002).

3.3 Elementary excitations as massless boson gas

As we stated previously, some elementary excitations emerged by the spontaneous symmetry breaking are *massless* bosons (Goldstone, 1961; Goldstone et al., 1962) as well as gauge bosons, which are elemental particles, *e.g.* photons, arosen from the fundamental interactions, *electromagnetic fields* for photons, with gauge degrees of freedom. Whether a boson is a Goldstone boson or a gauge one, the procedure described above is not appliable to the massless character of the boson, because its energy spectrum is not in the form of Eq. (41).

One has to remind that a masselss boson does not carry mass, but it carries momentum and energy. The energy spectrum of a massless boson is given by

$$\epsilon = \hbar \omega \tag{67}$$

and the frequency ω is obtained by the corresponding momentum $\mathbf{p} = \hbar \mathbf{k}$ through a dispersion relation

$$\omega = \omega\left(\mathbf{k}\right). \tag{68}$$

The number of bosons N in the massless boson gas is a variable, and not a given constants as in an ordinary gas. Therefore, N itself must be determined from the thermal equilibrium condition, the (Helmholtz) free energy minimum $(\partial F/\partial N)_{T,V} = 0$. Since $(\partial F/\partial N)_{T,V} = \mu$, this gives

$$\mu = 0. \tag{69}$$

In these conditions, the mean occupation number is following the Planck distribution function (Planck, 1901)

$$n_{\mathbf{k}}^0 = \frac{1}{e^{\beta\hbar\omega_{\mathbf{k}}} - 1}, \tag{70}$$

which was originally suggested for describing the distribution function problem of black-body radiations. Note that the Planck distribution function is a special case of the Bose-Einstein distribution function with zero chemical potential.

Considering the relation Eq. (4) and the condition Eq. (69), the grand potential of a massless Bose gas subsystem becomes the same as the Helmholtz free energy. The details of the thermodynamic properties are depending on the dispersion relation of the bosons. Photons are quantized radiations based on the fact of the *linearity* of electrodynamics,[3] so that photons do not interact with one another. The photon dispersion relation is linear,

$$\omega = ck, \tag{71}$$

where k includes the definite polarizations. The photon Helmholtz free energy is calculated as

$$F_0 = T\frac{V}{\pi^2 c^3} \int_0^\infty d\omega\, \omega^2 \ln\left(1 - e^{-\beta\hbar\omega}\right). \tag{72}$$

The standard integration method yields

$$F = -\frac{4}{3}\frac{\sigma V}{c}T^4, \tag{73}$$

where σ is called the *Stefan-Boltzmann constant* defined as

$$\sigma = \frac{\pi^2}{60}\frac{k_{\mathrm{B}}^4}{\hbar^3 c^2}. \tag{74}$$

The entropy is

$$S = -\frac{\partial F}{\partial T} = \frac{16}{3}\frac{\sigma V}{c}T^3. \tag{75}$$

The total radiation energy $E = F + TS$ is

$$E = \frac{4\sigma V}{c}T^4 = -3F, \tag{76}$$

which propotional to the fourth power of the temperature; *Boltzmann's law*. The constant volume heat capacity of the radiation is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{16\sigma V}{c}T^3, \tag{77}$$

and the pressure is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{4\sigma}{3c}T^4. \tag{78}$$

Hence, the equation of states of the photon gas is

$$PV = \frac{1}{3}E. \tag{79}$$

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[3] The nonlinear character appeared in the qunatum electrodynamics will not be discussed here.

The procedure for the photonic subsystem is quite useful in computing thermodynamics for many kinds of elementary exciations, which are usually massless (Goldstone) bosons in a condensed matter system. It is predicted that any crystal must be completely ordered, and the atoms of each kind must occupy entirely definite positions, in a state of complete thermodynamic equilibrium (Andreev & Lifshitz, 1969; Leggett, 1970). It is well known that the ions vibrate even in the zero temperature with several vibration modes (Aschcroft & Mermin, 1976; Callaway, 1974; Jones & March, 1973a; Kittel, 2005; Landau & Lifshitz, 1980; Madelung, 1978; Pines, 1999). The energy spectrum of a phonon in a mode j and a wavevector $\mathbf{q}$ contains the zero vibration term

$$\epsilon_{i\mathbf{q}} = \left(n_{j\mathbf{q}} + \frac{1}{2} \right) \hbar \omega_j \left(\mathbf{q} \right), \tag{80}$$

where $n_{j\mathbf{q}}$ is the occupation number of the single-particle modes of j and $\mathbf{q}$. The corresponding partition function is then written as

$$\begin{aligned}
Z &= \sum_{n_j,\mathbf{q}} \exp \left[-\beta \epsilon_j \left(\mathbf{q} \right) \right] \\
&= \prod_{j,\mathbf{q}} \frac{\exp \left[-\beta \hbar \omega_j \left(\mathbf{q} \right) \right]}{1 - \exp \left[-\beta \hbar \omega_j \left(\mathbf{q} \right) \right]}.
\end{aligned} \tag{81}$$

The Helmholtz free energy of the phonon subsystem is

$$F = -\beta \ln Z = \beta \sum_{j,\mathbf{q}} \ln \left\{ 2 \sinh \left[\frac{\beta \hbar \omega_j \left(\mathbf{q} \right)}{2} \right] \right\}. \tag{82}$$

In the noninteracting phonon gas condition, the entropy S, internal energy E, and the volume constant specific heat C becomes

$$\begin{aligned}
S &= - \left(\frac{\partial F}{\partial T} \right)_V \\
&= k_{\mathrm{B}} \sum_{j,\mathbf{q}} \left[\frac{\beta}{2} \hbar \omega_j \left(\mathbf{q} \right) \coth \left(\frac{\beta}{2} \hbar \omega_j \left(\mathbf{q} \right) \right) - \ln \left\{ 2 \sinh \left(\frac{\beta}{2} \hbar \omega_j \left(\mathbf{q} \right) \right) \right\} \right].
\end{aligned} \tag{83}$$

$$\begin{aligned}
E &= F - TS - \left(\frac{\partial F}{\partial T} \right)_V \\
&= \sum_{j,\mathbf{q}} \left\{ \frac{\hbar \omega_j \left(\mathbf{q} \right)}{2} + \frac{\hbar \omega_j \left(\mathbf{q} \right)}{e^{\beta \hbar \omega_j(\mathbf{q})} - 1} \right\},
\end{aligned} \tag{84}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = k_{\mathrm{B}} \frac{\sum_{j,\mathbf{q}} \left[\frac{\hbar \omega_j(\mathbf{q})}{2} \right]^2}{\sinh \left[\frac{\hbar \omega_j(\mathbf{q})}{2} \right]}. \tag{85}$$

Although the realistic phonon dispersion relations are complicated (Aschcroft & Mermin, 1976; Kittel, 2005), there are two useful model dispersion relations of phonons. Einstein (1907; 1911) modelled the density of states as constant frequences in each vibrational mode as $\mathcal{D} \left(\omega \right) = N \delta \left(\omega - \omega_0 \right)$, where delta function is centered at ω_0. This model is, in turn, useful

to treat high temperature phonon thermodynamics. The thermal energy of the noninteracting phonon system is

$$E = Nn^0\hbar\omega = \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}, \tag{86}$$

and so the heat capacity of the system is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = Nk_B\,(\beta\hbar\omega)^2\,\frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}. \tag{87}$$

On the other hand, Debye (1912) approximated that the velocity of sound is taken as constant for each phonon mode with the dispersion relation $\omega \sim q$. In this case, the method used for the photon gas is directly applied. At low temperature limit, the Debye extracted the T^3 law of the heat capacity as

$$C_V \simeq \frac{12\pi^4}{5}nk_B\left(\frac{T}{\Theta_D}\right)^3, \tag{88}$$

where Θ_D is known as the Debye temperature.

4. Matters as interacting liquids

The discussions in Sec. 3 has succeed to describe the thermodynamic properties of materials in many aspects, and hence such descriptions were treated in many textbooks. However, the oversimplified model fails the many important features on the material properties. One of the important origin of such failures is due to the ignorance of the *electromagnetic* interaction among the constituent particles; electrons and ions, which carry electric charges. However, the inclusion of interactions among the particles is enormously difficult to treat. To date the quantum field theory (QFT) is known as the standard method in dealing with the interacting particles. There are many good textbooks on the QFT (Berestetskii et al., 1994; Bjorken & Drell, 1965; Doniach & Sondheimer, 1982; Fetter & Walecka, 2003; Fradkin, 1991; Gross, 1999; Itzykson & Zuber, 1980; Mahan, 2000; Negele & Orland, 1988; Parisi, 1988; Peskin & Schroeder, 1995; Zinn-Justin, 1997) in treating the interacting particles systematically in various aspects. In this article, the idea of the treatments will be reviewed briefly, instead of dealing with the full details.

The idea of noninteracting particles inspires an idea to deal with the electronic subsystem as a sum of independent particles under a given potential field (Hartree, 1928), with the consideration of the effect of Pauli exclusion principle (Fock, 1930), which it is known as the exchange effect. This idea, known as the Hartree-Fock method, was mathematically formulated by introducing the Slater determinant (Slater, 1951) for the many-body electronic wave function. The individual wave function of an electron can be obtained by solving either Schrödinger equation (Schrödinger, 1926a;b;c;d) for the nonrelativistic cases or Dirac equation (Dirac, 1928a;b) for the relativistic ones.[4]

Since an electron carries a fundamental electric charge *e* in its motion, it is necessary to deal with electromagnetic waves or their quanta photons. Immediate necessity was arosen in order to deal with both electrons and photons in a single quantum theoretical framework in consideration of the Einstein's special theory of relativity (Einstein, 1905). Jordan & Pauli (1928) and Heisenberg & Pauli (1929) suggested that a new formalism to treat both the

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[4] The immediate relativistic version of the Schrödinger equation was derived by Gordon (1926) and Klein (1927), known as the Klein-Gordon equation. The Klein-Gordon equation is valid for the Bose-Einstein particles, while the Dirac equation is valid for the Fermi-Dirac particles.

electrons and the radiations as quantized objects in such a way of a canonical transformation to the normal modes of their fields; this method is called the *second quantization* or the *field quantization*. The canonical transformation technique to the normal mode is a well established classical method for continuous media (Goldstein, 1980). The idea treats both the electrons and radiations as continuous fields and quantized them for their own normal modes (Heisenberg & Pauli, 1929; Jordan & Pauli, 1928). The practically available solutions was suggested for the nonrelativistic case by Bethe (1947) followed by the fully relativistic case by Dyson (1949a;b); Feynman (1949a;b); Schwinger (1948; 1949a;b); Tomonaga (1946), so called the *renormalization* for cancelling the unavoidable divergencies appeared in the quantum field theory. This kind of theory on the electrons and radiations is called as the quantum electrodynamics (QED), which is known to be the most precise theory ever achieved (Peskin & Schroeder, 1995) with the error between the theory and experiment to be less than a part per billion (ppb) (Gabrielse et al., 2006; 2007; Odom et al., 2006).

4.1 The concepts of quantum field theory

Feynman (1949b) visulized the underlying concept of the quantum field theory by reinterpreting the nonrelativistic Schrödinger equation with the Green's function concept. As in classical mechanics, a Hamiltonian operator $\hat{H}$ contains all the mechanical interactions of the system. The necessary physical information of the system is contained in the wave function ψ. The Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi, \tag{89}$$

describes the change in the wave function ψ in an infinitesimally time interval Δt as due to the operation if an operator is $e^{-i\frac{\hat{H}}{\hbar}\Delta t}$. This description is equivalent to the description that the wave function $\psi(\mathbf{x}_2, t_2)$ at $\mathbf{x}_2$ and t_2 is evolved one from the wave function $\psi(\mathbf{x}_1, t_1)$ at $\mathbf{x}_1$ and t_1 through the equation

$$\psi(\mathbf{x}_2, t_2) = \int K(\mathbf{x}_2, t_2; \mathbf{x}_1, t_1)\, \psi(\mathbf{x}_1, t_1)\, d^3\mathbf{x}_1, \tag{90}$$

where K is the kernel of the evolution and $t_2 > t_1$. If $\psi(\mathbf{x}_1, t_1)$ is expanded in terms of the eigen function ϕ_n with the eigenvalue E_n of the constant Hamiltonian operator $\hat{H}$ as $\sum_n c_n \phi_n(\mathbf{x})$, one can find for $t_2 > t_1$

$$K(2, 1) = \sum_n \phi_n(\mathbf{x}_2)\, \phi_n^*(\mathbf{x}_1)\, e^{-i\frac{E_n}{\hbar}(t_2 - t_1)}, \tag{91}$$

where we abbreviated 1 for $\mathbf{x}_1$, t_1 and 2 for $\mathbf{x}_2$, t_2 and define $K(2, 1) = 0$ for $t_2 < t_1$. It is straightforward to show that K can be defined by that solution of

$$\left(i\hbar \frac{\partial}{\partial t_2} - \hat{H}_2\right) K(2, 1) = i\hbar\delta(2, 1), \tag{92}$$

where $\delta(2, 1) = \delta(t_2 - t_1)\,\delta(x_2 - x_1)\,\delta(y_2 - y_1)\,\delta(z_2 - z_1)$ and the subscript 2 on $\hat{H}_2$ means that the operator acts on the variables of 2 of $K(2, 1)$. The kernel K is now called as the *Green's function* and it is the total amplitude for arrival at $\mathbf{x}_2$, t_2 starting from $\mathbf{x}_1$, t_1. The transition amplitude for finding a particle in state $\chi(2)$, if it was in $\psi(1)$, is

$$\int \chi^*(2)\, K(2, 1)\, \psi(1)\, d^3\mathbf{x}_1 d^3\mathbf{x}_2. \tag{93}$$

A quantum mechanical system is described equally well by specifying the function K, or by specifying the Hamiltonian operator $\hat{H}$ from which it results.

Let us consider a situation that a particle propagates from 1 to 2 through 3 in a weak potential operator $\hat{U}(3)$, which differs from zero only for t between t_1 and t_2. The kernel is expanded in powers of $\hat{U}$ that

$$K(2,1) = K_0(2,1) + K^{(1)}(2,1) + K^{(2)}(2,1) + \cdots. \tag{94}$$

To zeroth order in $\hat{U}$, K is that for a free particle, $K_0(2,1)$. Let us consider the situation if U differs from zero only for the infinitesimal time interval Δt_3 between some time t_3 and $t_3 + \Delta t_3$ for $t_1 < t_3 < t_2$. The particle will propagate from 1 to 3 as a *free* particle,

$$\psi(3) = \int K_0(3,1)\,\psi(1)\,\mathrm{d}^3\mathbf{x}_1. \tag{95}$$

For the short time interval Δt_3, the wave function will change to

$$\psi(\mathbf{x}, t_3 + \Delta t_3) = e^{-i\frac{\hat{H}}{\hbar}\Delta t_3}\psi(\mathbf{x}, t_3), \tag{96}$$

after solving the Schrödinger equation in Eq. (89). The particle at 2 then propagates *freely* from $\mathbf{x}_3, t_3 + \Delta t_3$ as

$$\psi(\mathbf{x}_2, t_2) = \int K_0(\mathbf{x}_2, t_2; \mathbf{x}_3, t_3 + \Delta t_3)\,\psi(\mathbf{x}_3, t_3 + \Delta t_3). \tag{97}$$

We can decompose the Hamiltonian operator $\hat{H}$ by $\hat{H}_0 + \hat{U}$, where $\hat{H}_0$ is the Hamiltonian operator of the free particle. The change in wave function by $\hat{U}$ will be

$$\Delta\psi = -\frac{i}{\hbar}\hat{U}(3)\,\psi(3)\,\Delta t_3. \tag{98}$$

The wave function at 2 is that of the propagated particle from $t_3 + \Delta t_3$ to be

$$\psi(2) = \int K_0(2, 3')\,\psi(3')\,\mathrm{d}^3\mathbf{x}_3, \tag{99}$$

where $3'$ abbreviates $\mathbf{x}_3, t_3 + \Delta t_3$, by a free propagation. The difference of the wave function at 2 is obtained by

$$\Delta\psi(2) = -\Delta t_3\frac{i}{\hbar}\int K_0(2,3)\,\hat{U}(3)\,K_0(3,1)\,\psi(1)\,\mathrm{d}^3\mathbf{x}_3\mathrm{d}^3\mathbf{x}_1. \tag{100}$$

Therefore, the first order expansion of the kernel K is then

$$K^{(1)}(2,1) = -\frac{i}{\hbar}\int K_0(2,3)\,\hat{U}(3)\,K_0(3,1)\,\mathrm{d}3, \tag{101}$$

where $\mathrm{d}3 = \mathrm{d}^3\mathbf{x}_3\mathrm{d}t_3$. We can imagine that a particle travels as a free particle from point to point, but is scattered by the potential operator $\hat{U}$ at 3. The higher order terms are also analyzed in a similar way.

The analysis for the charged free Dirac particle gives a new interpretation of the antiparticle, which has the reversed charge of the particle; for example, a positron is the antiparticle of an electron. The Dirac equation (Dirac, 1928a;b) has negative energy states of an electron. Dirac interpreted himself that the negative energy states are fully occupied in vacuum, and an

elimination of one electron from the vacuum will carry a positive charge; the unoccupied state was interpreted as a *hole*. Feynman (1949b) reinterpreted that the *hole* is a positron, which is an electron propagting backward in time. The interpretation has the corresponding classical electrodynamic picture. If we record the trajectory of an electron moving in a magnetic field, the trajectory of the electron will be bent by the Lorentz force exerting on the electron. When we reverse the record in time of the electron in the magnetic field, the bending direction of the trajectory is that of the positively charged particle with the same mass to the electron. Therefore, we understand that a particle is propagting forward in time, while the corresponding antiparticle or the hole is propagating backward in time. Due to the negative energy nature of the hole or antiparticle, a particle-hole pair will be annihilated when the particle meet the hole at a position during their propagations in space-time coincidently. Reversely, vacuum can create the particle-hole pair from the vacuum fluctuations.

Now consider a system of two particles a and b propagate from 1 to 3 interacting at 5 for the particle a and from 2 to 4 interacting at 6 for the particle b. In the case of free particles, the kernel K_0 is a simple multiple of two free particle kernels K_{0a} and K_{0b} as

$$K_0 (3, 4; 1, 2) = K_{0a} (3, 1) K_{0b} (4, 2).$$ (102)

When two particles are interacting through a two particle potential $\hat{U}$, the first-order expansion term of K may be written (Feynman, 1949a) as

$$K^{(1)} (3, 4; 1, 2) = -\frac{i}{\hbar} \iint K_{0a} (3, 5) K_{0b} (4, 6) \hat{U} (5, 6) K_{0a} (5, 1) K_{0b} (6, 2) \, d5 \, d6.$$ (103)

One important difference from Eq. (101) is that the interaction $\hat{U}$ at a specific space-time position 3 is replaced by the interaction field $\hat{U} (5, 6)$. The interaction field is also able to be quantized and the interaction field $\hat{U} (5, 6)$ is interpreted as an interaction field quantum propagating *freely* between 5 and 6. For the case of two-electron interaction, the particles are electrons interacting through the electromagnetic interaction. One electron a propagates from 1 to 3 and the other b propagates from 2 to 4. During their propagations, the electron a emits (aborbs) a photon at point 5, while the electron b absorbs (emits) the photon at 6. The wave function of each electron differs by the emission of the photon at 5 or 6 from its wave function at the origin of the propagation. The process of emission and absorption of the photons during the electrons propagations change the energy of the electronic subsystem. The process to compute the energy of the Fermi liquid in the perturbative treatment of the interaction requires the consideration of the essential many-body treatment available by the procedures suggested by Dyson (1949a;b); Feynman (1949a;b); Schwinger (1948; 1949a;b); Tomonaga (1946).

For the future reasons, it is useful to see the consequence of the step function behavior of the kernel K. As described above, $K (2, 1)$ has its meaning as the solution of the Green's function Eq. (92) only if $t_2 > t_1$. It is convenient to use multiply the step function $\theta (t_2 - t_1)$ to the kernel K for implying the physical meaning. The step function has an integral representation

$$\theta (t - t') = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega(t-t')}}{\omega + i\eta},$$ (104)

where η is an positive real number. If $t > t'$, then the contour must be closed in the lower-half ω plane, including the simple pole at $\omega = -i\eta$ with residue -1. If $t < t'$, then the contour must be closed in the upper-half ω plane and gives zero, because the integrand has no singularity for $\Im \omega > 0$.

For a noninteracting particle, the eigen function will be a plane wave

$$\phi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{x}}, \tag{105}$$

and the eigenvalue will be $\epsilon_{\mathbf{k}}^0 = \hbar\omega_{\mathbf{k}}^0$. In the limit of an infinite volume, the summation over n, to be over $\mathbf{k}$, in Eq. (91) becomes an integration and then the consideration of the identities given in Eqs. (104) and (105) yields

$$K_0\left(\mathbf{x},t;\mathbf{x}',t'\right) = \frac{1}{2\pi^4}\int d^3\mathbf{k}\int_{-\infty}^{\infty}d\omega e^{i\mathbf{k}\cdot\mathbf{x}}e^{-i\omega(t-t')}\left[\frac{\theta\left(k-k_{\mathrm{F}}\right)}{\omega-\omega_{\mathbf{k}}^0+i\eta}+\frac{\theta\left(k_{\mathrm{F}}-k\right)}{\omega-\omega_{\mathbf{k}}^0-i\eta}\right],$$

which immediately yields

$$K_0\left(\mathbf{k},\omega\right) = \left[\frac{\theta\left(k-k_{\mathrm{F}}\right)}{\omega-\omega_{\mathbf{k}}^0+i\eta}+\frac{\theta\left(k_{\mathrm{F}}-k\right)}{\omega-\omega_{\mathbf{k}}^0-i\eta}\right], \tag{106}$$

where k_{F} is the Fermi wave vector. Since the $\pm i\eta$ were introduced to render the time integral in Eq. (104) convergent, it is convenient to take the limit $\eta \to 0^+$. Eq. (106) diverges at $\omega = \omega_{\mathbf{k}}^0 \pm i\eta$. If we compute the transition amplitude in Eq. (93) from the state $\psi(1)$ to the state $\psi(2)$ in the Fourier transformed space, the kernel function form of Eq. (106) implies that the transition amplitude will be maximum around $\omega = \omega_{\mathbf{k}}^0 \pm i\eta$. In the limit $\eta \to 0^+$, the *free* particle remains in the state $\mathbf{k}$: the particle will keep its momentum and hence its (kinetic) energy. This is nothing more than the celebrating statement of *inertial motion* by Galileo.

4.2 Self-energy

This idea that a particle propagates freely until it faced with the a scattering center, where the particles emit or absorb the interacting quanta, is nothing more than an extension of the model introduced by Drude (1900) for electrons in metals. We already obtained the thermodynamic information of noninteracting gases in Sec. 3. Hence, the remaining task is to see the effects of the interaction from the noninteracting gas.

Let us come back to the case of a particle propagating from 1 to 2 in the way given in Eq. (101) by considering the interaction process demonstrated in Eq. (103). The perturbation procedure for the interacting fermions includes, in its first-order expansion, two fundamental processes (Fetter & Walecka, 2003), which are the prototypes of the interactions of all order perturbation expansion. For the first case, the particle *a* propagates from 1 to 3, emits (absorbs) a boson propagating to 4, where the other particle *b* absorbs (emits) the boson. The particle *b* propagates after the absoption (emission) at 4 to the position 4 again, just before it absorbing (emitting) the boson. This process is known as the *vacuum polarization* and it is equivalent, for an electronic system, to the method of Hartree (1928). In terms of the classical electrodynamics, the process is nothing more than that an electron moves in a Coulomb potential generated by the neighboring charge density. Secondly, the particle propagates firstly from 1 to 3 and it emits (absorbs) a boson at 3 to change its state. The particle in the new state then propagates from 3 to 4, where the new state particle absorbs (emits) the boson propagated from 3, and change its states to the original one in propagating to 2. This process is known as the *exchange* and it is equivalent, for the electronic system, to the Fock (1930) consideration of the Pauli's exclusion principle.

The energy spectrum of the particle itself will change during both the processes. Dyson (1949a;b) discussed that the changing the particle energy itself by the perturbative treatment of

the fermion interaction when we consider single particle propagation from 1 to 2. The energy of the particle differs from the noninteracting particle propagation, and it can be systematically included to the particle propagation kernel as

$$K(2,1) = K_0(2,1) + \iint K(2,4) \Sigma(4,3) K(3,1) \, \mathrm{d}3\mathrm{d}4, \tag{107}$$

where Σ is known as the *self-energy*. When we consider the all order perturbation, the exact single-particle propagation can be obtained by using the successive self-energy inclusion as

$$K(2,1) = K_0(2,1) + \iint K(2,4) \Sigma(4,3) K(3,1) \, \mathrm{d}3\mathrm{d}4$$
$$+ \iiiint K(2,6) \Sigma(6,5) K(5,4) \Sigma(4,3) K(3,1) \, \mathrm{d}3\mathrm{d}4\mathrm{d}5\mathrm{d}6 + \cdots, \tag{108}$$

with the special care of the self-energy to be proper.[5] This equation is known as the *Dyson equation*.

The consequence of the Dyson equation can be seen easily if we perform a four dimensional Fourier transform on Eq. (108) with respect to the difference $\mathbf{y} - \mathbf{x}$, $t_2 - t_1$ into the momentum space to an algebraic form

$$K(k) = K_0(k) + K_0(k) \Sigma(k) K(k), \tag{109}$$

where k abbreviates $(\mathbf{k}, \omega)$. We can solve Eq. (109) as

$$K(k) = \frac{1}{K_0^{-1}(k) - \Sigma(k)}. \tag{110}$$

Considering the self-energy Σ is complex, the $i\eta$ in the free particle kernel Eq. (106) is no more relevant. Therefore, we obtain the solution of the Dyson equation as

$$K(k) = K(\mathbf{k}, \omega) = \frac{1}{\omega - \hbar^{-1}\epsilon_{\mathbf{k}}^0 - \Sigma(\mathbf{k}, \omega)}. \tag{111}$$

The physical meaning of Eq. (111) is straightforward: an interacting particle propagates as the free particle does, but its excitation energy differs by a *dressing* term $\Sigma(\mathbf{k}, \omega)$.

Lehmann (1954) and Galitskii & Migdal (1958) discussed the usefulness of Eq. (111) in the applications for many-body systems. In the Lehmann representation, the frequency ω is a complex number to be

$$\hbar\omega = \epsilon_{\mathbf{k}} - i\gamma_{\mathbf{k}}, \tag{112}$$

where $\gamma_{\mathbf{k}}$ is the damping of the particle. The singularity of the exact Green's function $K(\mathbf{k}, \omega)$, considered as a function of ω, determine both the excitation energy $\epsilon_{\mathbf{k}}$ of the system and its damping $\gamma_{\mathbf{k}}$. Furthermore, the chemical potential can be determined as the point where $\Im\Sigma(\mathbf{k}, \omega)$ changes the sign, because

$$\Im\Sigma(\mathbf{k}, \omega) \geq 0, \ \omega < \mu/\hbar$$
$$\Im\Sigma(\mathbf{k}, \omega) \leq 0, \ \omega > \mu/\hbar. \tag{113}$$

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[5] The proper implies the terms that cannot be disintegrated into the lower order expansion terms during the perturbation expansion.

A similar analysis can be carried out for the interaction between two particles, which always consists of the lowest-order interaction plus a series of proper expansion. The four dimensional Fourier transformation to the q coordinates yields

$$U(q) = \frac{U_0(q)}{1 - \Pi(q) U_0(q)}. \tag{114}$$

Introducing a generalized dielectric function

$$\kappa(q) = 1 - U_0(q) \Pi(q), \tag{115}$$

the *screening* of the lowest-order interaction by the polarization of the medium is obtained as

$$U(q) = \frac{U_0(q)}{\kappa(q)}. \tag{116}$$

4.3 Goldstone's theorem: the many-body formalism

Goldstone (1957) provided a new picture of the many-body systems with the quantum field theoretic point of view, presented above. Let us the free particle Hamiltonian $\hat{H}$ has a many-body eigenstate Φ, which is a determinant formed from N particles of the ψ_n, and which is able to be described by enumerating these N one-particle states. Suppose that $\hat{H}_0$ has a non-degenerate ground state Φ_0 formed from the lowest N of the ψ_n. The states ψ_n occupied in Φ_0 will be called unexcited states, and all the higher states ψ_n will be called excited states. An eigenstate Φ of $\hat{H}_0$ can be described by enumerating all the excited states which are occupied, and all the unexcited states which are not occupied. An unoccupied unexcited state is regarded as a *hole*, and the theory will deal with particles in excited states and holes in the unexcited states. In this treatment, the ground state Φ_0 is considered as a new *vacuum*, a particle is considered as an occupied states in the excited states, and the hole is essentially different from the positrons, in which are the symmetric counterpart of the electrons.

Goldstone (1957) derived the energy difference between the system with and without interactions, $\hat{H}_1$, in the Dirac notation,[6] as

$$E - E_0 = \langle \Phi_0 | \hat{H}_1 \sum_n \left(\frac{1}{E_0 - \hat{H}_0} \hat{H}_1 \right)^n | \Phi_0 \rangle, \tag{117}$$

where the summation should do on the linked[7] terms of the perturbation. The noninteracting Hamiltonian $\hat{H}_0$ in the denominator can be replaced by the corresponding eigenvalues, because Eq. (117) is interpreted by inserting a complete set of eigenstates of $\hat{H}_0$ between each interaction $\hat{H}_1$. The physical situation can be visualized as follows: (1) The interaction Hamiltonian $\hat{H}_1$ operate on $|\Phi_0\rangle$ creates a state with two particles and two holes. This state propagates with $(E_0 - \hat{H}_0)^{-1}$. (2) The next $\hat{H}_1$ can create more particle-hole pairs or scatter the existing particle-hole pair and so on. (3) The final $\hat{H}_1$ must then return the system to the ground state $|\Phi_0\rangle$. This process gives the difference in energy of the interacting many-body system from the noninteracting one. By choosing the first-order perturbation in

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[6] In the Dirac notation, a quantum state n is written in the Hilbert space of form $|n\rangle$ and the corresponding conjugate state is written as $\langle n|$. The wave function is the projection to the position space, such that $\psi_n(\mathbf{x}) = \langle \mathbf{x} | n \rangle$. For an operator $\hat{A}$, $\langle m | \hat{A} | n \rangle$ is called as a *matrix element* to represent the probability for transtion from the state $|n\rangle$ by the operation $\hat{A}$ to the state $\langle m|$. Readers can see the details in Dirac (1998); Sakurai (1994).

[7] During the expansion, there are terms describing pair creation and annihilations corresponding to the free particle Green's function.

the Goldstone scheme, it is successfully reproduced the Hartree-Fock equation. The method for the perturbation expansion in the Goldstone scheme is usually called as coupled cluster expansion.

4.4 Matsubara method for finite temperatures

For simplicity, consider a system with one kind of particles in dealing with the grand partition function defined in Eq. (2), *i.e.*,

$$\Xi = \sum_i e^{-\beta(\epsilon_i - \mu N)}. \tag{118}$$

It is convenient to introduce a *grand canonical Hamiltonian* operator

$$\hat{\mathcal{K}} = \hat{H} - \mu\hat{N}. \tag{119}$$

The operator form forces the equivalent form of Eq. (118) to be a trace

$$\Xi = e^{-\beta\Omega} = \mathrm{Tr} e^{-\beta\hat{\mathcal{K}}}, \tag{120}$$

and its corresponding statistical density matrix in the form

$$\hat{\rho} = \frac{e^{-\beta\hat{\mathcal{K}}}}{\Xi} = e^{\beta(\Omega - \hat{\mathcal{K}})}. \tag{121}$$

Armed with Eqs. (120) and (121), all the thermodynamic information are calculable. However, difficulty is in its thermally evolving nature of those equations, instead of their time evolving nature of the Schrödinger equation.

In order to compute thermodynamic properties of ferromagnetic materials, Bloch (1932) suggested a statistical equation, resembling the ordinary Schrödinger equation, by treating the evolution of the statistical density with respect to temperature as

$$-\frac{\partial\rho}{\partial\beta} = \hat{H}\rho. \tag{122}$$

Matsubara (1955) and Gaudin (1960) proved that the Green's function formalism in quantum field theory also satisfies the Wick's theorem (Wick, 1950), hence the perturbation expansion in all order satisfies, when the "single-particle" field operator follows the Bloch equation by switching the real-time t to the *imaginary-time*, $\tau = it$. Note that the term "single-particle" does not mean a real single-particle.

The procedure in Sec. 4.1 is applied also. The single-particle temperature Green's function $\mathcal{G}$ may follow the Green's function equation

$$\left[\hbar\frac{\partial}{\partial\tau_2} - \hat{\mathcal{K}}\right]\mathcal{G}\left(\mathbf{x}_1\tau_1; \mathbf{x}_2\tau_2\right) = \pm\hbar\delta(\mathbf{x}_2 - \mathbf{x}_1)\delta\left(\tau_2 - \tau_1\right), \tag{123}$$

where $\pm$ indicates the temperature Green's function for fermions and bosons, respectively. However, the temperature Green's function does not depend on τ_1 and τ_2 separately, but it depends on the difference $\tau \equiv \tau_1 - \tau_2$. Each imaginary time τ has $\beta\hbar$ periodicity. The temperature Green's function is then in the form

$$\mathcal{G}\left(\mathbf{x}_1, \tau_1; \mathbf{x}_2, \tau_2\right) = \mathcal{G}\left(\mathbf{x}_1, \mathbf{x}_2; \tau\right). \tag{124}$$

For both fermionic and bosonic *statistics*, $\mathcal{G}$ is *periodic* over the range $2\beta\hbar$ and may expanded in a Fourier seriese

$$\mathcal{G}\left(\mathbf{x}_1,\mathbf{x}_2,\tau\right) = \frac{1}{\beta\hbar}\sum_n e^{i\omega_n\tau}\mathcal{G}\left(\mathbf{x}_1,\mathbf{x}_2,\omega_n\right), \tag{125}$$

where

$$\omega_n = \frac{n\pi}{\beta\hbar}. \tag{126}$$

This shows that $e^{-i\omega_n\beta\hbar}$ is equal to $e^{-in\pi} = (-1)^n$, and the factor $\frac{1}{2}\left(1 \pm e^{-i\omega_n\beta\hbar}\right)$ reduces to $\frac{1}{2}\left[1 \pm (-1)^n\right]$. The Fourier coefficient in Eq. (125) is then

$$\mathcal{G}\left(\mathbf{x}_1,\mathbf{x}_2,\omega_n\right) = \int_0^{\beta\hbar} d\tau e^{i\omega_n\tau}\mathcal{G}\left(\mathbf{x}_1,\mathbf{x}_2,\tau\right), \tag{127}$$

where

$$\omega_n = \begin{cases} \frac{2n\pi}{\beta\hbar}, & \text{boson} \\ \frac{(2n+1)\pi}{\beta\hbar}, & \text{fermion} \end{cases}. \tag{128}$$

This is known as the *Matsubara frequency*.

The coordinates in $\mathbf{x}$ can be transformed to the momentum space $\mathbf{k}$. There is a corresponding solution of the Dyson equation in Eq. (110) for the temperature Green's function as

$$\mathcal{G}\left(\mathbf{k},\omega_n\right) = \frac{1}{\mathcal{G}_0^{-1} - \Sigma\left(\mathbf{k},\omega_n\right)}, \tag{129}$$

with the noninteracting temperature Green's function of the form

$$\mathcal{G}_0\left(\mathbf{k},\omega_n\right) = \frac{1}{i\omega_n - \hbar^{-1}\left(\epsilon_{\mathbf{k}}^0 - \mu\right)}. \tag{130}$$

The thermodynamic variables N, E, and Ω can by obtained by the Eq. (129):

The grand potential is

$$\Omega\left(T,V,\mu\right) = \Omega_0\left(T,V,\mu\right)$$
$$\mp V(2s+1)\int_0^1 \frac{d\lambda}{\lambda}\int\frac{d^3k}{(2\pi)^2}\frac{1}{\beta\hbar}\sum_n e^{i\omega_n\eta}$$
$$\times\left[\frac{1}{2}\hbar + \frac{\frac{1}{2}\Sigma^\lambda\left(\mathbf{k},\omega_n\right)}{i\omega_n - \hbar^{-1}\left(\epsilon_{\mathbf{k}}^0 - \mu\right) - \Sigma^\lambda\left(\mathbf{k},\omega_n\right)}\right], \tag{131}$$

where s is the spin of the particles, η is the infinitesimally small positive number, and λ is the interaction strength control parameter.[8] The internal energy is

$$E\left(T,V,\mu\right) = \mp V(2s+1)\int\frac{d^3k}{(2\pi)^2}\frac{1}{\beta\hbar}\sum_n e^{i\omega_n\eta}$$
$$\times\left[\frac{1}{2}\hbar + \frac{\epsilon_{\mathbf{k}}^0 + \frac{1}{2}\Sigma^\lambda\left(\mathbf{k},\omega_n\right)}{i\omega_n - \hbar^{-1}\left(\epsilon_{\mathbf{k}}^0 - \mu\right) - \Sigma^\lambda\left(\mathbf{k},\omega_n\right)}\right], \tag{132}$$

---

[8] When an interacting Hamiltonian $\hat{H}_I$ is applied to the noninteracting system with the Hamiltonian $\hat{H}_0$, the interaction strength is controlled by the parameter λ to yield Hamiltonian $\hat{H} = \hat{H}_0 + \lambda\hat{H}_I$ with its λ parameterized eigenstate $|\Psi_0(\lambda)\rangle$. The energy difference $E - E_0$ is calculated by $\int_0^1 \frac{d\lambda}{\lambda}\langle\Psi_0(\lambda)|\lambda\hat{H}_I|\Psi_0(\lambda)\rangle$.

and the number of particles is

$$N(T,V,\mu) = \mp V(2s+1) \int \frac{\mathrm{d}^3 k}{(2\pi)^2} \frac{1}{\beta\hbar} \sum_n \frac{e^{i\omega_n \eta}}{i\omega_n - \hbar^{-1}(\epsilon_{\mathbf{k}}^0 - \mu) - \Sigma^\lambda(\mathbf{k}, \omega_n)}. \tag{133}$$

The temperature Green's function in Eq. (129) is very similar to Eq. (110), which includes the real single-particle energy spectrum. However, there is one important difference that the frequency is not a real frequency or energy, because ω_n is a *discrete* variable. The computation of the energy spectra is available by using the temperature Green's function.

It is convenient to introduce a real-time Green's function corresponding to the real-time trace in Eq. (120) multiplied by the statistical grand distribution Eq. (121). The real-time Green's function is then written (Fetter & Walecka, 2003) in the momentum space representation as

$$\bar{G}(\mathbf{k}, \omega) = \frac{1}{1 \mp e^{-\beta\hbar\omega}} \bar{G}^R(\mathbf{k}, \omega) + \frac{1}{1 \mp e^{\beta\hbar\omega}} \bar{G}^A(\mathbf{k}, \omega). \tag{134}$$

Let us introduce a generic real-time Green's function of a complex variable z which satisfies

$$\bar{\Gamma}(\mathbf{k}, z) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi} \frac{A(\mathbf{k}, \omega')}{z - \omega'}, \tag{135}$$

where $A(\mathbf{k}, \omega')$ is the spectral weight function (Galitskii & Migdal, 1958), which yields the integral representations of the *retarded* Green's function

$$\bar{G}^R(\mathbf{k}, \omega) = \bar{\Gamma}(\mathbf{k}, \omega + i\eta) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi} \frac{A(\mathbf{k}, \omega')}{\omega - \omega' + i\eta}, \tag{136}$$

and the *advanced* Green's function

$$\bar{G}^A(\mathbf{k}, \omega) = \bar{\Gamma}(\mathbf{k}, \omega - i\eta) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi} \frac{A(\mathbf{k}, \omega')}{\omega - \omega' - i\eta}. \tag{137}$$

The spectral weight function should satisfy the sum rule

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi} A(\mathbf{k}, \omega') = 1 \tag{138}$$

for both bosons and fermions. With this sum rule, we have an asymptoctic behavior of the Green's function

$$\bar{\Gamma}(\mathbf{k}, \omega) \sim \frac{1}{\omega} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi} A(\mathbf{k}, \omega') \sim \frac{1}{\omega} \quad \text{for} \quad |\omega| \to \infty. \tag{139}$$

The spectral function constructs also the temperature Green's function

$$\mathcal{G}(\mathbf{k}, \omega_n) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{2\pi} \frac{A(\mathbf{k}, \omega')}{i\omega_n - \omega'}. \tag{140}$$

In other words, the function $\bar{\Gamma}(\mathbf{k}, z)$ in Eq. (135) determines the temperature Green's function $\mathcal{G}$ as well as the real-time Green's funcitons $\bar{G}^R$ and $\bar{G}^A$ by analytic continuation technique in the complex ω plane. The sum rule ensures the uniqueness of the analytic continuation (Baym & Mermin, 1947). Once we evaluate the temperature Green's function $\mathcal{G}$ only at the

discrete set of points $\{i\omega_n\}$, the thermodynamic variables Ω, E, and N are obtained. The spectral weight function is able to be derived from the temperature Green's function $\mathcal{G}$. Then we can have the real-time Green's functions $\bar{G}^R$ and $\bar{G}^A$, which give us the quasiparticle energy spectrum.

Hence, we complete the equilibrium thermodynamics; information on macroscopic thermodynamic variables as well as microstates.

5. Irreversible processes

The Green's function method reviewed above describes the equilibrium thermodynamics of a matter composed of fermions with the interactions mediated by the corresponding bosons. The power of the Green's function method does not limited to the equilibrium thermodynamics, but does solve many irreversible thermodynamic problems for the situation not far from the equilbrium states. The information from the irreversible processes of not-so-far from the equilibrium is extremely important for building an equilibrium phase diagram.

The procedure for acquiring the thermodynamic information includes a certain perturbation to the system for equilibrium process. For example, one should apply the external pressure to the system for changing its volume, one should apply a magnetic field **H** to the system for measuring its magnetization, one should should add heat to the system for increasing its temperature, etc. Such realistic experimental procedure should be considered for comparing the theoretical and experimental thermodynamic data assessments. However, a certain kind of phases in the system does not stable under the given condition. Even the Gibbs free energies for some metastable/unstable structures are undefinable because they are dynamically unstatble. This kind of problems has been studies extensively in the CALPHAD society, see Kaufman (2001) for example.

Many difficulties in practical CALPHAD computations arise when the system has magnetic instabilities. The inclusion of magnetism in the CALPHAD method has been devoted for long time (Hillert & Jarl, 1978; Midownik, 1977). However, the current methods to build any phase diagram with magnetism are hardly thought to be completed, in terms of both the first-principles and the empirical one. The apparent reason for this failure is due to the nature of magnetism, which we have not understood its underlying physics yet.

Once magnetism involves, we are facing Invar effects (Kim, 1988; 1999), magnetostrictions (Lines, 1979), and magnetocaloric effects (de Oliveira & von Ranke, 2010). As stated in Sec. 3.2, there are spontaneous symmetry breaking related with elementary excitations, for example magnons or spin waves emerge when the spin rotation symmetry is broken. In a ferromagnetic system, the magnetic *susceptibility* which is defined by the magnetization with respect to the external magnetic field diverges below the Curie temperature T_C without external magnetic fields. In general, the computation of the magnetic susceptibility should consider the correct underlying physical mechanism. The experimental procedure for measuring any susceptibilities is the irreversible processes. This is also in great importance to understand the phase transitions.

5.1 Linear response theory

A theory for phase transition should be developed; the theory leaves the non-diverging error near the critical region, where a set of physical observables diverges. Kubo (1957) and Kubo et al. (1957) developed such a theory, called as the *linear reponse theory*, for the case of not-so-far from equilibrium, by the quantum mechanical interpretations on the Liouville' theorem in Eq. (17) and the Bloch equation in Eq. (122).

Let the Hamiltonian of the *natural motion* of a many-body system to be $\hat{H}$. We would like to apply an external perturbation $\hat{H}'$ to the system, which yields now the total Hamiltonian

$$\hat{H}_{\text{total}} = \hat{H} + \hat{H}'. \tag{141}$$

We consider the external perturbation being a time dependent driving force

$$\hat{H}'(t) \sim -F(t). \tag{142}$$

When the system is in its natural motion, the statistical distribution function, or the *density matrix*, $\hat{\rho}$, is calculated by Eq. (121). With the external perturbation $\hat{H}'$, the *total* density matrix will be differ from its natural density matrix as

$$\hat{\rho}_{\text{total}} = \hat{\rho} + \hat{\rho}'. \tag{143}$$

For any physical observables $\hat{A}$, the thermal expectation value of $\hat{A}$ is given by

$$\langle \hat{A} \rangle = \text{Tr}\left(\hat{\rho}'(t)\,\hat{A}\right) \equiv \langle A(t) \rangle. \tag{144}$$

The initial ensemble which represents statistically the initial state of the system is specified by the density matrix $\hat{\rho}$ satisfying

$$\left[\hat{H},\hat{\rho}\right]_{\mp} = \left[\hat{\mathcal{K}},\hat{\rho}\right]_{\mp} = 0, \tag{145}$$

where $\left[\hat{A},\hat{B}\right]_{\mp}$ is the Poisson bracket to be $\hat{A}\hat{B} \mp \hat{B}\hat{A}$, for any quantum operators $\hat{A}$ and $\hat{B}$. The symbol $\mp$ indicates the Poisson bracket for bosons and fermions, respectively. On the other hand, the motion of the ensemble under the perturbation Eq. (142) is represented by $\hat{\rho}'(t)$, which obeys the equation

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}\left(\hat{\rho} + \hat{\rho}'\right) &= \left[\hat{H} + \hat{H}', \hat{\rho} + \hat{\rho}'\right]_{\mp} \\
&= \left[\hat{\mathcal{K}} + \hat{H}', \hat{\rho} + \hat{\rho}'\right]_{\mp}.
\end{aligned} \tag{146}
$$

By assuming that the external perturbation is sufficiently weak, we have a *linear* equation

$$i\hbar\frac{\partial}{\partial t}\hat{\rho}' = \left[\hat{\mathcal{K}},\hat{\rho}\right]_{\mp} + \left[\hat{H}',\hat{\rho}\right]_{\mp}, \tag{147}$$

with Eq. (145) and the neglecting the second order term, $\left[\hat{H}',\hat{\rho}'\right]_{\mp}$.
Let us solve Eq. (147) by introducing the interaction representation of the density matrix as

$$\hat{\rho}'_I(t) = e^{i\hat{\mathcal{K}}t/\hbar}\hat{\rho}'e^{-i\hat{\mathcal{K}}t/\hbar}. \tag{148}$$

Differntiation both sides of Eq. (148) with respect to t yields

$$i\hbar\frac{\partial}{\partial t}\hat{\rho}'_I(t) = -\left[\hat{\mathcal{K}},\hat{\rho}'(t)\right]_{\mp} + e^{i\hat{\mathcal{K}}t/\hbar}\left(i\hbar\frac{\partial}{\partial t}\hat{\rho}'\right)e^{-i\hat{\mathcal{K}}t/\hbar},$$

where the second term on the right hand side is replaced by Eq. (148) to obtain

$$i\hbar\frac{\partial}{\partial t}\hat{\rho}'_I(t) = e^{i\hat{\mathcal{K}}t/\hbar}\left[\hat{H}',\hat{\rho}\right]_{\mp}e^{-i\hat{\mathcal{K}}t/\hbar} \equiv k(t).$$

This differential equation is readily solved as

$$\hat{\rho}'_I(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} k(t')\, \mathrm{d}t' + c,$$

(149)

where c is a constant. Let us assume that the system is in its equilibrium at $t = -\infty$, i.e., $\hat{H}'(t = -\infty) = 0$, and consequently $\hat{\rho} = \hat{\rho}' = 0$ for $t = -\infty$. In this case, the constant $c = 0$. Considering the interaction representation in Eq. (148), we arrive at the solution

$$\hat{\rho}'(t) = \frac{1}{i\hbar} e^{-i\hat{\mathcal{K}}t/\hbar} \int_{-\infty}^{t} \mathrm{d}t' k(t')\, e^{i\hat{\mathcal{K}}t/\hbar}$$

$$= \frac{1}{i\hbar} \int_{-\infty}^{t} \mathrm{d}t' e^{-i\hat{\mathcal{K}}(t-t')/\hbar} \left[\hat{H}'(t'), \hat{\rho} \right]_{\mp} e^{i\hat{\mathcal{K}}(t-t')/\hbar}.$$

(150)

Therefore, the linear response $\hat{A}(t)$ by the external perturbation $\hat{H}'$ is able to be computed by using Eqs. (144) and (150) to be

$$\langle \hat{A}(t) \rangle = \frac{1}{i\hbar} \int_{-\infty}^{t} \mathrm{d}t' \mathrm{Tr} \left(e^{-i\hat{\mathcal{K}}(t-t')/\hbar} \left[\hat{H}'(t'), \hat{\rho} \right]_{\mp} e^{i\hat{\mathcal{K}}(t-t')/\hbar} \hat{A} \right).$$

(151)

When the external perturbation Hamiltonian in Eq. (142) can be written in an oscillatory form

$$\hat{H}' = -\hat{B} e^{i\omega t},$$

(152)

we have the linear response as

$$\langle \hat{A}(\omega) \rangle = \pm \frac{i}{\hbar} \int_{0}^{\infty} e^{i\omega(t-t')} \mathrm{Tr} \left(\hat{\rho} \left[\hat{A}_I((t-t')), \hat{B} \right]_{\mp} \right) \mathrm{d}(t-t'),$$

(153)

where $A_I(t-t')$ is in the interaction representation as in Eq. (148) and we use the cyclic property of trace.

Since the external perturbation $\hat{H}'$ does not appear in Eq. (153) at all, we can treat $\hat{A}_I$ as the Heisenberg representation with respect to the natural motion described by $\hat{\mathcal{K}}$. Consequently, the linear response is determined from a correlation function of the *fluctuations* of the relevant quantities in the absence of the external perturbation.

Computation of the dynamic magnetic susceptibility illustrates the usefulness of the linear response theory. When the oscillatory external field in Eq. (152) is applied in the ν-direction, the thermal expectation value of the magnetization in the μ-direction is obtained as

$$\langle \hat{M}_\mu(\omega) \rangle = \frac{i}{\hbar} \int_{0}^{\infty} e^{i\omega\tau} \mathrm{Tr} \left(\hat{\rho} \left[\hat{M}_\mu(\tau), \hat{M}_\nu \right]_{-} \right) H_\nu \mathrm{d}\tau,$$

(154)

where we use the abbreviation $\tau = t - t'$ and replaces $\hat{B}$ by $\hat{M}_\nu H_\nu$, where H_ν is the ν-the component of the external magnetic field **H**. Dynamic magnetic susceptibility, defined as

$$\chi_{\mu\nu}(\omega) \equiv \frac{\langle \hat{M}_\mu(\omega) \rangle}{H_\nu},$$

(155)

is then calculated as

$$\chi_{\mu\nu}(\omega) = \frac{i}{\hbar} \int_{0}^{\infty} e^{i\omega\tau} \mathrm{Tr} \left(\hat{\rho} \left[\hat{M}_\mu(\tau), \hat{M}_\nu \right]_{-} \right) \mathrm{d}\tau.$$

(156)

The extension to the case of the response to an magnetic field oscillating in space with the wave vector $\mathbf{q}$ is straightforward to be

$$\chi_{\mu\nu}(\mathbf{q},\omega) = \frac{i}{\hbar} \int_0^\infty e^{i\omega\tau} \mathrm{Tr}\left(\hat{\rho}\left[\hat{M}_\mu(\mathbf{q},\tau),\hat{M}_\nu(-\mathbf{q})\right]_-\right) d\tau. \tag{157}$$

In general, a linear response function is given in the form

$$\chi_{AB}(\mathbf{q},\omega) = \pm\frac{i}{\hbar} \int_0^\infty e^{i\omega\tau} \mathrm{Tr}\left(\hat{\rho}\left[\hat{A}(\mathbf{q},\tau),\hat{B}(-\mathbf{q})\right]_\mp\right) d\tau. \tag{158}$$

This is the virtue of the linear response theory.

5.2 Fluctuation-dissipation theorem

The Kubo formula of the linear response function, or the generalized susceptibilty, is given in Eq. (158). By extending the interval of integration to $(-\infty,\infty)$ in Eq. (158), we define a function f as

$$f_{AB}(\mathbf{q},\omega) = \pm\frac{i}{\hbar} \int_{-\infty}^\infty e^{i\omega\tau} \mathrm{Tr}\left(\hat{\rho}\left[\hat{A}(\mathbf{q},\tau),\hat{B}(-\mathbf{q})\right]_\mp\right) d\tau. \tag{159}$$

The integration is now devided into the negative and positive ranges as

$$\begin{aligned} f_{AB}(\mathbf{q},\omega) = &\pm\frac{i}{\hbar} \int_0^\infty e^{i\omega\tau} \mathrm{Tr}\left(\hat{\rho}\left[\hat{A}(\mathbf{q},\tau),\hat{B}(-\mathbf{q})\right]_\mp\right) d\tau \\ &\mp\frac{i}{\hbar} \int_0^\infty e^{i\omega\tau} \mathrm{Tr}\left(\hat{\rho}\left[\hat{A}(\mathbf{q}),\hat{B}(-\mathbf{q},-\tau)\right]_\mp\right) d\tau, \end{aligned} \tag{160}$$

where we changed τ to $-\tau$ in the second term of the right hand side, and moved the factors $\exp(\pm i\mathcal{K}\tau/\hbar)$ around $A(\mathbf{q})$ to aound $B(-\mathbf{q})$ using the cyclic property of trace. Since Eq. (158) has a symmetry

$$\chi_{AB}^*(\mathbf{q},\omega) = \chi_{AB}(-\mathbf{q},-\omega), \tag{161}$$

it is able to denote f_{AB} as

$$f_{AB} = \chi_{AB}(\mathbf{q},\omega) \mp \chi_{BA}^*(\mathbf{q},\omega). \tag{162}$$

Eq. (159) is written as

$$f_{AB}(\mathbf{q},\omega) = \left(1 \mp e^{-\beta\hbar\omega}\right)\frac{i}{\hbar} \int_{-\infty}^\infty e^{i\omega\tau} \mathrm{Tr}\left(\hat{\rho}\left[\hat{A}(\mathbf{q},\tau),\hat{B}(-\mathbf{q})\right]_\mp\right) d\tau, \tag{163}$$

because of the identity

$$\int_{-\infty}^\infty e^{i\omega\tau} \mathrm{Tr}\left(\hat{\rho}\left[\hat{A}(\tau),\hat{B}\right]_\mp\right) d\tau = \pm e^{\beta\hbar\omega} \int_{-\infty}^\infty e^{i\omega\tau} \mathrm{Tr}\left(\hat{\rho}\left[\hat{B},\hat{A}(\tau)\right]_\mp\right) d\tau. \tag{164}$$

The two representations of f_{AB} in Eqs. (162) and (163) lead us a result

$$\int_{-\infty}^\infty e^{i\omega t} \mathrm{Tr}\left(\hat{\rho}\left[\hat{A}(\mathbf{q},t),\hat{B}(-\mathbf{q})\right]_\mp\right) dt = \frac{i\hbar}{e^{-\beta\hbar\omega} \mp 1}\left\{\chi_{AB}(\mathbf{q},\omega) \mp \chi_{BA}^*(\mathbf{q},\omega)\right\}, \tag{165}$$

where we changed the variable τ by t. Eq. (165) relates the linear response function and the ordinary correlation function. For a special case of $A = B$, Eq. (165) is reduced to

$$\int_{-\infty}^\infty e^{i\omega t} \mathrm{Tr}\left(\hat{\rho}\left[\hat{A}(\mathbf{q},t),\hat{A}(-\mathbf{q})\right]_\mp\right) dt = -\frac{\hbar}{e^{-\beta\hbar\omega} \mp 1} 2\Im\chi_{AA}(\mathbf{q},\omega). \tag{166}$$

The physical meaning of Eq. (166) is now clear: the correlation function of the thermal fluctuation determines the imaginary part of the linear response function, *i.e.*, the dissipation of the system. Therefore, we call Eqs. (165) and (166) as the *fluctuation-dissipation theorem*.

One can easily find a similarity between the fluctuation-dissipation theorem in Eqs. (165)–(166) and Eq. (134). The spectral representation of the retarded real-time Green's function Eq. (136) is the momentum space Lehmann representation of the two-time retarded Green's function defined by

$$i\bar{G}^R_{\alpha\beta}\left(\mathbf{x}t, \mathbf{x}'t'\right) = \theta\left(t - t'\right) \text{Tr}\left(\hat{\rho}\left[\hat{\psi}_\alpha\left(\mathbf{x}t\right), \hat{\psi}^\dagger_\beta\left(\mathbf{x}'t'\right)\right]_\mp\right). \tag{167}$$

The corresponding advanced Green's function is defined by

$$i\bar{G}^A_{\alpha\beta}\left(\mathbf{x}t, \mathbf{x}'t'\right) = -\theta\left(t - t'\right) \text{Tr}\left(\hat{\rho}\left[\hat{\psi}_\alpha\left(\mathbf{x}t\right), \hat{\psi}^\dagger_\beta\left(\mathbf{x}'t'\right)\right]_\mp\right). \tag{168}$$

In these definitions of the two-time Green's functions, $\hat{\psi}$ and $\hat{\psi}^\dagger$ are respectively the field annihilation and creation operators in the Heisenberg representation

$$\hat{A}\left(\mathbf{x}t\right) \equiv e^{i\hat{\mathcal{K}}t/\hbar}\hat{A}e^{-i\hat{\mathcal{K}}t/\hbar}. \tag{169}$$

A two-time Green's function represents the correlation of thermal fluctuation of the process that a particle created at $\mathbf{x}'t'$ and it annihilated at $\mathbf{x}t$. In other words, the two-time Green's functions are nothing more than the correlation functions of two operators $\hat{\psi}_\alpha$ and $\hat{\psi}^\dagger_\beta$. Note that all the quantum operators are composed of the field operators $\hat{\psi}_\alpha$ and $\hat{\psi}^\dagger_\beta$, so that the two-time Green's function can be used to describe all the physical correlations of the system. In the linear response theory, the interaction representation of an operator is not different from the Heisenberg representation in the two-time Green's functions. Therefore, the linear response is nothing more than the retarded two-time Green's function. Note that the *causality* of any physical process stresses that the dissipation χ should be the imaginary part of the retarded Green's function.

Now, we have completed the formal theory for computing thermodynamic properties in terms of the quantum field theory. An experimental observation is indeed a measurement of a response of the system by a corresponding external perturbation. The response function is related to the retarded two-time Green's function in terms of the fluctuation-dissipation theory. The two-time Green's function provides the quasiparticle energy spectra. The two-time Green's function can be transformed to a temperature Green's function by introducing the spectral weight function. Once we have the temperature Green's function, we can calculate the thermodynamic information, such as the number of particles N, the internal energy E, and the grand potential Ω, directly. By performing derivatives on the grand potential, the remaining thermodynamic functions can be evaluated. When there is a phase transition, the response function diverges near the critical region, but the grand potential does not, because the grand potential is a integrated value of the temperature Green's function in the complex ω plane.

Kubo (1966) himself demonstrated the applications of the fluctuation-dissipation theorem to compute the density response, conduction and diffusion. The fluctuation-dissipation theorem (Kubo, 1957) is able to explain the irreversible processes related with fluctuations (Callen & Welton, 1951; Casimir, 1945; Nyquist, 1928; Onsager, 1931a;b). Further applications are well summarized by Gammaitoni et al. (1998).

The remained work is mainly on the applications to the realistic matter.

6. Inhomogeneity is reality

We have a brief review on the formalism of the quantum field theoretic approach for thermodynamics properties of the system in homogeneous (and isotropic) distributions. The homogeneous approximation of a matter has served as a model system of matter for investigating the nature of the complex phenomena occuring in the matter. The study on electron liquid is an example (Fetter & Walecka, 2003; Giuliani & Vignale, 2005; Kim, 1999; Pines, 1962; 1999). Phonon-mediated superconductivity can be solvable under the method after performing a suitable transformation for treating Cooper pairs (Schrieffer, 1988). A relativistic version of the method has been applied to plasmas (Melrose, 2008).

However, the realistic materials has internal (micro-)structures and even pure elemental materials are not fully homogeneous. Steels as representative structural materials have large variety of microstructures, which influences on the properties, *e.g.*, strength and elongations (Bhadeshia & Honeycombe, 2006). In metals and alloys, the internal structures of materials are governed by the equilibrium thermodynamics and the irreversible processes (Christian, 2002). It is necessary to deal with the inhomogeneity when we are dealing with thermodynamics and irreversible processes for materials sciences.

6.1 Density functional theory

The applications of the formal quantum theories, developed in a homogeneous model system, to the realistic inhomogeneous systems have long time history (Fermi, 1927; Slater, 1951; Thomas, 1938). An innovative formalism to treat the inhomogeneous electronic system was suggested by Hohenberg & Kohn (1964). They firstly proved that the ground state energy is a *unique* functional of density, $E[n(\mathbf{x})]$. Due to the uniqueness of the ground state energy, the discussions in the previous sections can be reformulated with density. This is the reason why the Hohenberg-Kohn theory is called the density functional theory (DFT). For a slowly vaying density profile, the density functional theory is a generalization of the Thomas-Fermi theory. They proved also that the essential density gradient in the inhomogeneous electron gas can be used for describing the energy functional.

An immediate extension of the Hohenberg-Kohn theory to the finite temperature was done by Mermin (1965). At a given temperature and chemical potential, no two local potential $v(\mathbf{x})$ lead to the same equilibrium density. In other words, one can define a density functional $F[n(\mathbf{x})]$ independent of $v(\mathbf{x})$, such that the quantity

$$\Omega \equiv \int v(\mathbf{x}) n(\mathbf{x}) \, \mathrm{d}^3\mathbf{x} + F[n(\mathbf{x})], \tag{170}$$

is at a minimum and equal to the grand potential when $n(\mathbf{x})$ is the equilibrium density in the grand canonical ensemble in the presence of $v(\mathbf{x})$. Kohn & Sham (1965) themselves were able to derive the forms for the grand potential, specific heat, and spin susceptibility.

Schneider (1971) provided a general theory of the liquid-solid phase transition by employing the finite temperature density functional theory by virtue of the fluctuation-dissipation theorem on the density response. During the construction of the functional $F[n]$, the external perturbation potential is assumed to be of form

$$v^{\mathrm{ext}}(\mathbf{x}) = \frac{1}{2} \sum_{\mathbf{q} \neq 0} \left(v^{\mathrm{ext}}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{x}} + c.c. \right). \tag{171}$$

The density of the system will contain a linear response to be

$$n(\mathbf{x}) = \bar{n} + \frac{1}{2} \sum_{\mathbf{q} \neq 0} \left(n(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{x}} + c.c. \right), \tag{172}$$

where $\bar{n}$ is the mean density and $n(\mathbf{q})$ is the density fluctuations. The Mermin condition (Mermin, 1965) yields

$$\frac{n(\mathbf{q})}{\bar{n}} = \chi(q, [\bar{n}]) \, v^{\text{ext}}(\mathbf{q}), \tag{173}$$

where the density response function is

$$-\chi(q, [\bar{n}]) = \frac{1}{\beta^{-1} + v^{\text{eff}}(q, [\bar{n}])}, \tag{174}$$

and v^{eff} is the corresponding effective potential. For free energy minimum, the density response function should satisfy the condition

$$-\frac{1}{\chi(q, [\bar{n}])} > 0 \tag{175}$$

for the system is in an equilibrium state either absolutely stable or metastable. Therfore, $-\chi^{-1}(q, [\bar{n}]) = 0$ determines the stability limit of the fluid (q_L, P_L, T_L). The static stability condition can be written as

$$-\frac{1}{\chi^{-1}(q, [\bar{n}])} = \frac{1}{\beta S(q)} = \frac{1}{\beta} + v^{\text{eff}}(q, [\bar{n}]) = 0, \tag{176}$$

where $S(q)$ is the static mean density fluctuation. The condition Eq. (176) impiles that the mean density fluctuation $S(q)$ with the particular wave number q_L increases as this limit is approached. Near the stability limit only the region $q \simeq q_L$ is important. We may set the effective potential dependence on T and q as

$$\beta v^{\text{eff}}(q) = -1 + A(T - T_L) + B(q - q_L)^2. \tag{177}$$

Then, the density fluctuation for constant $\bar{n}$ is wrtten as

$$S(q) = \frac{1}{A(T - T_L)} \frac{1/\xi^2}{1/\xi^2 + (q - q_L)^2}, \tag{178}$$

where $\xi^2 = B/A(T - T_L)$. As q approaches to q_L, $S(q)$ increases and the peak becomes sharper. The same effect is also seen in the dynamic mean density fluctuation $S(q, \omega)$ at the static case $\omega = 0$.

This result is consistent with our everyday experiences. In a fluid state, there are random density fluctuations, which can be seen if there is an interface; a random wave distribution on a smooth lake surface is an example. Such density fluctuation is represented in the Fourier terms, by a linear combination of the wave vectors and frequencies. When the temperature is cooled down with a constant pressure, the fluid transforms to crystals, *e.g.*, ice. A crystal is by definition a regular arrangement of density, with a spatial period of a corresponding wave vector. Eq. (178) tells us that the static mean density fluctuation at the critical wave vector q_L with the corresponding regularity will be sustained, even if there is no external

density perturbation, at the given pressure and temperature. In the mean time, the remained fluctuation modes will be suppressed. This state with the density distribution of a specific spatial regularity, represented by q_L, is the *crystal*. Hence, the denominator of Eq. (178) explains the critical properties of the solidification.

Once the liquid transformed to a solid, the description of the system state should be switched to a new language for solid states. Every crystalline solid is categorized by its three dimensional translation and rotation symmetries to be the one of the 230 space groups (Bravais, 1845). Bloch (1928) proved, by using the periodic boundary condition (Born & von Kármán, 1912; 1913) and the group representation theory (Wigner, 1927), that the electronic wave function in a crystalline solid should be in the form

$$\psi_{n\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{R}} u_{n\mathbf{k}}(\mathbf{x}), \tag{179}$$

where n is the band index and $\mathbf{R}$ is the Bravais lattice vector. The Bloch function has three consequencies (Aschcroft & Mermin, 1976): (1) The momentum eigenvalue $\hbar\mathbf{k}$ of the momenum operator $\mathbf{p} = (\hbar/i)\nabla$ does not conserve, instead the crystal momentum $\hbar\mathbf{k} + e^{i\mathbf{k}\cdot\mathbf{x}}\frac{\hbar}{i}\nabla$ conserves. (2) The wave vector $\mathbf{k}$ is confined to the first Brillouin zone, so that the index n appear in Eq. (179) represent the multiplicity of the $\mathbf{k}$ confinements. (3) The nonvanishing velocity of a particle in a level specified by band index n and wave vector $\mathbf{k}$ is given by

$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}\epsilon_n(\mathbf{k}), \tag{180}$$

where $\nabla_{\mathbf{k}}$ is a gradient operator with respect to the wave vector $\mathbf{k}$. Further consequencies can be found in many solid-state physics text books (Altmann, 1995; Aschcroft & Mermin, 1976; Callaway, 1974; Jones & March, 1973a;b; Kittel, 2005; Madelung, 1978).

On the other hand, the numerator, $1/\xi^2$ in Eq. (178) explains another aspect of the solidificaiton. The numerator describes the width in the wave vector space of the divergying static mean density fluctuation $S(q)$. As $q \to q_L$, the wave vectors in a narow range around q_L also contributes to $S(q)$. When two waves of near wave vector (or frequency) superposes in the same position, we observe a very well known phenomenon, *beats* (Landau & Lifshitz, 1978). The broadening in $S(q)$ implies that there are many wave vectors around superposing in the space to exhibits a complex pattern of spatial beats during the crystallization process. In other words, the crystallization will not happen in whole the liquid simultaneously, but the crystal nucleates.

Note that the numerator $1/\xi^2$ contains the details of the interaction of the liquid. As we seen in Sec. 5.2, the dissipation of the external perturbation or the system response is determined by the interal fluctuation of the system. The internal fluctuation is determined by the details of the interaction of the system. Hence, we need to have the detailed interaction information of the system also for understanding phase transition phenomena completely.

6.2 Kohn-Sham equations

Kohn & Sham (1965) suggested two approximation methods for treating an inhomogeneous system of interacting electrons. Let us describe the first approximation first. The ground-state energy of the system in a static potential $v(\mathbf{x})$ can be written in the form, in Hartree atomic unit $\hbar = e^2 = m_e = 1$,

$$E = T_0[n] + \int v(\mathbf{x})n(\mathbf{x})\,\mathrm{d}^3\mathbf{x} + \frac{1}{2}\iint \frac{n(\mathbf{x})n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}\mathrm{d}^3\mathbf{x}\mathrm{d}^3\mathbf{x}' + E_{\mathrm{xc}}[n], \tag{181}$$

where T_0 is the kinetic energy functional of a system of noninteracting electrons and $E_{xc}[n]$ is the exchange and correlation energy functional of an interacting system with density $n(\mathbf{x})$. By assuming

$$E_{xc}[n] = \int n(\mathbf{x})\,\epsilon_{xc}(n(\mathbf{x}))\,d^3\mathbf{x}, \tag{182}$$

the stationary condition of the energy functional Eq. (181) with respect to the density variation δn leads us to have an equation

$$\frac{\delta T_0[n]}{\delta n(\mathbf{x})} + v(\mathbf{x}) + \mu_{xc}(n(\mathbf{x})) = 0, \tag{183}$$

where $v(\mathbf{x})$ is the result of the functional derivatives of the static integration terms of Eq. (181) and μ_{xc} is the result of the functional derivatives of the exchange-correlation functional $E_{xc}[n]$. By assuming $\mu_{xc}(n(\mathbf{x}))$ to be local, we can imagine a "ficticious" particle that moves by the single-particle Schrödinger-like first *Kohn-Sham* equation

$$\left(-\frac{1}{2}\nabla^2 + \varphi(\mathbf{x}) + \mu_{xc}(n(\mathbf{x}))\right)\psi_i^{KS}(\mathbf{x}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{x}), \tag{184}$$

and setting

$$n(\mathbf{x}) = \sum_{i=1}^{N}\left|\psi_i^{KS}(\mathbf{x})\right|^2, \tag{185}$$

where N is the number of electrons. Since we have no knowledge on the density $n(\mathbf{x})$, it should be obtained self-consistently starting from a guessed density profile $n(\mathbf{x})$. We compute the Kohn-Sham orbitals ψ^{KS} under the static potential $\varphi(\mathbf{x})$ as well as the exchange-correlation potential $\mu_{xc}(n(\mathbf{x}))$ and then evaluate the density from Eq. (185). Once we obtain the self-consistent density profile $n(\mathbf{x})$, the energy of the system is obtained by Eq. (181), if we have an *explicit* functional form of $E_{xc}[n]$. Indeed the knowledge of the exchange-correlation functional form is important to obtain the exchange-correlation potential during solving Eq. (184). The cost of computation Eq. (184) is only that of the Hartree equation times the number of self-consistent iterations. The cheap Kohn-Sham equation have get superiority in solving many-body problems as developing computer technology (Argaman & Makov, 2000).
The second approximation by Kohn & Sham (1965) is based on the assumption that

$$E_{xc}[n] = E_x[n] + \int n(\mathbf{x})\,\epsilon_c(n(\mathbf{x}))\,d^3\mathbf{x}. \tag{186}$$

This assumption yields the Hartree-Fock-like second Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + \varphi(\mathbf{x}) + \mu_c(n(\mathbf{x}))\right)\psi_i^{KS}(\mathbf{x}) - \int \frac{n_1(\mathbf{x},\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}\psi_i^{KS}(\mathbf{x}')\,d^3\mathbf{x}' = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{x}), \tag{187}$$

where $\mu_c(\mathbf{x})$ is the correlation potential and

$$n_1(\mathbf{x},\mathbf{x}') = \sum_{j=1}^{N}\psi_j^{KS}(\mathbf{x})\,\psi_j^{*KS}(\mathbf{x}'). \tag{188}$$

This procedure is similar to the Hartree-Fock method with the local correlation effect, and its cost of computation is comparable to the computational labor intensive Hartree-Fock method due to its nonlocal density matrix operation on the Kohn-Sham orbitals $\psi_i(\mathbf{x})$ appeared in

Eq. (187). Hence, the application of the Kohn-Sham equation of the type in Eq. (187) has been hesitated. Although the practical success of the first Kohn-Sham equation in Eq. (184), the approximations are remained uncontrollable, because there is no known explicit exchange-correlation functional. Recent developments of computer technology, many approaches has been tried to utilize the second type Kohn-Sham equation (Kümmel & Kronik, 2008). This kind of approaches has solved many problems in the first-type Kohn-Sham equation.

However, there is a critical issue on the solutions of the Kohn-Sham equations. Koopmans (1934) proved that the ith occupied eigenvalues of the Hartree-Fock equation is identified as the energy required to remove an electron from that orbital without perturbing the rest of the system. This theorem is not valid in the density functional theory, in general. Only the highest occupied eigenvalue of the Kohn-Sham equations has a rigorous physical meaning that the partial derivative is exactly the chemical potential of the system (Almbladh & von Barth, 1985; Levy et al., 1984). In other words, the Kohn-Sham orbitals $\psi_i^{KS}(\mathbf{x})$ except the highest occupied orbital are physically meaningless, but they are useful only for building the density in Eq. (185). Indeed, the Kohn-Sham charge density generated by Eq. (185) differs hardly to that of the Hartree-Fock charge density (Stowasser & Hoffmann, 1999). A quantitative linear scailing interpretation of Kohn-Sham eigenvalues with respect to corresponding Hartree-Fock eigenvalues was suggested (Stowasser & Hoffmann, 1999).

6.3 Spectral weight function and quasiparticle spectra

As seen in Sec. 6.1, the detailed interaction information of the system is equally important to understand the phase transition as well as the equilibrium properties of the system. In the density functional theoretical framework, the Kohn-Sham equations have a critial problem of the unknown physical meanings of their eigenvalues. The resultant Kohn-Sham orbitals ensure the ground state energy, the density $n(\mathbf{x})$, and the chemical potential. The other information obtained by using the Kohn-Sham orbitals are *fictitious*. It is fortunate or unfortunate that the Kohn-Sham orbitals are close to the quasiparticle orbitals, which have the concrete physical meaning through the Koopmans' theorem (Koopmans, 1934). Since there is no further proof on the physical meaning of the Kohn-Sham orbitals, a promising way to build the physically seamless theoretical framework for phase diagrams is starting from the quantum field theory described in Sec. 4, armed with the Kubo's framework in Sec. 5.1–5.2.

The Hamiltonian operator $\hat{H}$, the momentum operator $\hat{\mathbf{P}}$, and the number opertator $\hat{N}$ commute each other. By symmetry, those operators have a set of eigenstates $\{|m\rangle\}$ simultaneously (Tinkam, 1964), such that

$$\hat{\mathbf{P}}|m\rangle = \mathbf{P}_m|m\rangle, \tag{189}$$

$$(\hat{H} - \mu\hat{N})|m\rangle = (E_m - \mu N_m)|m\rangle. \tag{190}$$

Note that Eq. (190) is understood as

$$\hat{\mathcal{K}}|m\rangle = K_m|m\rangle. \tag{191}$$

With the aid of the Sokhotsky-Weierstrass theorem (Byron & Fuller, 1992),

$$\frac{1}{\omega \pm i\eta} = \wp\frac{1}{\omega} \mp i\pi\delta(\omega), \tag{192}$$

we will have a Lehmann representation of the real-time Green's function for real ω such as

$$
\bar{G}\left(\mathbf{k},\omega\right) = \frac{e^{\beta\Omega}}{2s+1} \sum_{m,n} e^{-\beta K_m} \left(2\pi\right)^3 \delta \left[\mathbf{k} - \hbar^{-1} \left(\mathbf{P}_n - \mathbf{P}_m\right)\right] \left|\langle m|\,\hat{\psi}_\alpha\,|n\rangle\right|^2
$$
$$
\times \left\{ \wp \frac{1}{\omega - \hbar^{-1}\left(K_n - K_m\right)} \left(1 \mp e^{-\beta\left(K_n - K_m\right)}\right) \right.
$$
$$
\left. -i\pi\delta\left[\omega - \hbar^{-1}\left(K_n - K_m\right)\right] \left(1 \pm e^{-\beta\left(K_n - K_m\right)}\right) \right\}, \tag{193}
$$

where s is the spin degeneracy and $\wp$ denotes a principal value. The imaginary part of Eq. (193) is written as

$$
\Im\bar{G}\left(\mathbf{k},\omega\right) = -\frac{\pi e^{\beta\Omega}}{2s+1} \sum_{m,n} e^{-\beta K_m} \left(2\pi\right)^3 \delta \left[\mathbf{k} - \hbar^{-1} \left(\mathbf{P}_n - \mathbf{P}_m\right)\right] \left|\langle m|\,\hat{\psi}_\alpha\,|n\rangle\right|^2
$$
$$
\times \delta\left[\omega - \hbar^{-1}\left(K_n - K_m\right)\right] \left(1 \pm e^{-\beta\left(K_n - K_m\right)}\right). \tag{194}
$$

Landau (1958) proved a relation

$$
\Re\bar{G}\left(\mathbf{k},\omega\right) = -\wp \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\Im\bar{G}\left(\mathbf{k},\omega'\right)}{\omega - \omega'} \frac{1 \mp e^{-\beta\omega'}}{1 \pm e^{-\beta\omega'}}. \tag{195}
$$

Considering the spectral representation form in Eq. (135) we have the detailed spectral weight function of form

$$
A\left(\mathbf{k},\omega\right) = \frac{e^{\beta\Omega}}{2s+1} \sum_{m,n} e^{-\beta K_m} \left(2\pi\right)^3 \delta \left[\mathbf{k} - \hbar^{-1} \left(\mathbf{P}_n - \mathbf{P}_m\right)\right]
$$
$$
\times 2\pi\delta\left[\omega - \hbar^{-1}\left(K_n - K_m\right)\right] \left(1 \mp e^{-\beta\left(K_n - K_m\right)}\right) \left|\langle m|\,\hat{\psi}_\alpha\,|n\rangle\right|^2. \tag{196}
$$

Since the spectral weight function $A\left(\mathbf{k},\omega\right)$ relates the real-time Green's function and the temperature Green's function, we can, in principle, solve all the thermodynamic problems with detailed interaction information of the system: The thermal Green's function describes the equation of states, while the imaginary part of the retarded Green's function from the real-time Green's funciton yields the fluctuations to describe the phase transtion, including the transport properties. The remained difficulty is to calculate the eigenvalues K_m and $\mathbf{P}_m$ in Eqs. (189)–(190) in the case of interacting systems.

Is it able to calculate the eigenvalues of the interacting system at a finite temperature?

Let us come back to the idea of Born & Oppenheimer (1927) adiabatic separation of the motions of electrons and ions. In the Born-Oppenheimer scheme, we first calculate the motions of electrons in a given ionic background and then calculate the motions of ions at the given electronic one. It is well konw that the given symmetry and many-body effects will emerges as elementary excitations (Pines, 1999), which can be extended even to a *macroscopic* levels (Anderson, 1997). Some of the elementary excitations may originated from either electrons or ions. For example, plasoms are the elementary excitations of collective motions of electrons, while phonons are the elementary excitation of the collective motions of ions. One can also interesting to more complex excitations, which are composites of those elementary excitations. Anyhow, all such properties are computed from the electronic structures of the system.

It is instructive to consider the formal form in Eq. (129) of the Dyson's equation. Since the Dyson's equation expresses the difference between the noninteracting and interacting temperature Green's functions in terms of the self-energy, $\Sigma\left(\mathbf{k}, \omega_n\right)$; all the many-body effects are contained in the self-energy. Considering the real space Dyson's equation form in Eq. (107), we may have a Hartree-Fock-like self-consistent equation (Fetter & Walecka, 2003)

$$\left[-\frac{\hbar}{2m}\nabla_1^2 + v\left(\mathbf{x}_1\right)\right]\psi_j\left(\mathbf{x}_1\right) + \hbar\int d^3\mathbf{x}_2 \Sigma\left(\mathbf{x}_1, \mathbf{x}_2\right)\psi_j\left(\mathbf{x}_2\right) = \epsilon_j\psi_j\left(\mathbf{x}_1\right), \tag{197}$$

where $v\left(\mathbf{x}_1\right)$ is the static one-body potential to describe the *inhomogeneity* as in the density functional theory, ∇_1^2 is the Laplacian operator with respect to the coordinate $\mathbf{x}_1$, and μ is the chemical potential obtained by

$$N\left(T, V, \mu\right) = (2s+1)\sum_j n_j, \tag{198}$$

with the number distribution function

$$n_j = \frac{1}{e^{\beta\left(\epsilon_j - \mu\right)} \mp 1}. \tag{199}$$

The chemical potential $\mu\left(T, V, N\right)$ is, in principle, able to be inverted from Eq. (198) if N is fixed. In this derivation, we assumed that all the necessary frequency summed are already done for making Σ being depending explicitly on T and μ, but being independent to the frequency ω_n of the Hartree-Fock form and the temperature Green's function

$$\mathcal{G}\left(\mathbf{x}_1, \mathbf{x}_2, \omega_n\right) = \sum_j \frac{\psi_j\left(\mathbf{x}_1\right)\psi_j^*\left(\mathbf{x}_2\right)}{i\omega_n - \hbar^{-1}\left(\epsilon_j - \mu\right)}, \tag{200}$$

where ψ_j is a single-particle wave function with energy ϵ_j for forming a complete orthonormal set, forms the same form of the noninteracting temperature Green's function $\mathcal{G}^0\left(\mathbf{x}_1, \mathbf{x}_2, \omega_n\right)$ with ψ_j^0, the solution of a differential equation

$$\left[i\hbar\omega_n + \frac{\hbar}{2m}\nabla_1^2 + \mu - v\left(\mathbf{x}_1\right)\right]\psi_j^0\left(\mathbf{x}_1\right) = \epsilon_i^0\psi_j^0\left(\mathbf{x}_1\right). \tag{201}$$

In this self-consistent formalism, the quasiparticle energy spectrum becomes

$$\epsilon_{\mathbf{k}} = \epsilon_{\mathbf{k}}^0 + \hbar\Sigma\left(\mathbf{k}\right), \tag{202}$$

where we recover the momentum space representation.
This equation tells us that the noninteracting quasiparticle moving with the energy spectrum $\epsilon_{\mathbf{k}}^0$ *is dressed* by the self-energy $\Sigma\left(\mathbf{k}\right)$ by the sophisticated many-body interactions. The energy dispersion of a free particle of mass m^* will have a dispersion

$$\nabla_{\mathbf{k}}\epsilon_{\mathbf{k}} = \frac{\mathbf{k}}{m^*}.$$

Equating this relation to result of the operation of the gradient operator on Eq. (202) yields

$$\frac{m}{m^*} = 1 + \frac{\hbar \nabla_{\mathbf{k}} \Sigma (\mathbf{k})}{\epsilon_{\mathbf{k}}^0}. \tag{203}$$

This means that the motion of the quasiparticle of mass m may be thought as that of a free particle of mass m^*, of which all the many-body effects are corrected. Now we can call m^* as the *effective mass* of the quasiparticle. The noninteracting quasiparticle Green's function may be in the form

$$\bar{G} (\mathbf{k}, \omega) = \frac{Z}{\omega - \hbar^{-1} (\epsilon_{\mathbf{k}} - \mu)}, \tag{204}$$

where Z is called the *renormalization factor*, which contains the effective mass effect in Eq. (203). Considering the spectral function relation with the Green's function, we have

$$A (\mathbf{k}, \omega) = Z \delta (\omega + \mu - \hbar \mathbf{k}). \tag{205}$$

In other words, the results of a photoemission spectroscopy are just the renormalization factor of the system. The photoemission experiments gives the quasiparticle spectra.

The idea of renormalization was utilized by Landau (1957a;b; 1959), known as the phenomenological *Landau Fermi-liquid theory*. Landau classified the quasiparticles as the levels of a Fermi liquid corresponding to the classification of the levels of noninteracting particles. The interaction is slowly *turned on* to the particles gradually become quasiparticles. The methods described above can be directly applied for the quasiparticles. Using this concept, Landau (1957a;b; 1959) was able to calculate the macroscopic quantities, such as specific heat, entroy, magnetic susceptibility, kinetic motions, thermal conductivity, viscocity, dispersion and absorption of sound, and fluctuations in the distribution function. The relation with the quantum field theory of the Landau Fermi liquid theory was investigated by Nozières & Luttinger (1962) and Luttinger & Nozières (1962), but it is not clear yet. Good introductory reviews on the Ladau Fermi-liquid theory are given by Abrikosov & Khalatnikov (1959); Giuliani & Vignale (2005); v. Löhneysen et al. (2006).

Bohm & Pines (1952) suggested a different point of view with a canonical transformation to treat a particle and its consequent collective excitations simultaneously. In this formalism, the canonical transformation stresses the elementary ingredients of the Hamiltonian are the particle-hole pairs, instead of individual particles. Bohm & Pines (1952) approximated the coupling between the excitations corresponding to different momentum transfers q and q'. This ignorance is originated from an intuition that the momentum transfer phase $q - q'$ will be random to be enough for cancelling themselves. Hence, the method is known as the *random phase approximation (RPA)*. The RPA was applied to the electronic system with plasmons and refined (Sawada, 1957; Sawada et al., 1957). The RPA picture as the similarity with that of (Goldstone, 1957) and it deals with the correlation function corresponding to the collective excitations.

These features of the RPA have been utilized in susceptibility investigations. For instance, Kim et al. (1973) calculated a spin polarized susceptibility[9] based on the fluctuation-dissipation theorem and the free energy by considering higher order self-energy correction (Kim, 1974) withn the RPA. Kim (1982; 1989; 1999) used the RPA technique to demonstrate, within the homogeneous jeullium model, that all the thermodynamic properties, including the ferromagnetic phase transition, of the metallic ferromagnetism can be obtained by considering the spin-polarized electrons with the collective excitations of phonons and

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[9] A practical self-consistent version was given by Lee et al. (1989).

magnons. All those quasiparticles should interact each other, in contrast to the typical considerations that quasiparticles hardly interacts each other. Lee et al. (2006) confirmed that there are interactions between phonon and magnetism, and Bodraykov (2007) in his phenomenological model reproduced the invar effect of the temperature dependent thermal expansion coeffient by considering the results of the interacting phonon-magnon (Kim, 1982).

7. Defects

Although there is criticism on the validaties of the Landau Fermi-liquid concept (v. Löhneysen et al., 2006), a new insight for dealing macroscopic physical observables, *e.g.*, even domain (grain) boundaries and dislocations, combined with the concept of symmetry breaking (Anderson, 1997). Since the semi-phenomenological construction of the Ladau Fermi-liquid theory, it is possible to switch our intersts from the quasiparticle space to the order parameter space. This transformation to the order parameter space is familiar with that of Landau theory of phase transition. Toulouse & Kléman (1976) suggested an innovative idea that the defects in ordered media can be classified in terms of the *topological defects* of the corresponding order parameter. This topological concept was immediately applied to the vortex textures in superfluid ^{3}He for showing that the textures with vorticity without vortex core can be constructed (Anderson & Toulouse, 1977). One of the most striking application of the topological defects theory may be the explanation of the entanglement free dislocation crossings (Poénaru & Toulouse, 1977); dislocations can be entangled if and only if they are members of separate class of $\pi_1(R)$. We will see the meaning of $\pi_1(R)$ later. A pedagogical review on the topological defects was given by Mermin (1979). Recenlty, Kleman & Friedel (2008) reviewed the practical interpretations of the homotopy group theory of the topological disclination, dislocations, and continuous defects.

7.1 Topological defects

In a periodic solid, the elastic variable is the vector displacement field $\mathbf{u}(\mathbf{x})$. Changes of $\mathbf{u}$ by a Bravais lattice vector $\mathbf{R}$ leave the lattice unchanged. Thus the order parameter space for the solid is the three-dimensional space of displacements $\mathbf{u}$ with lattice points. A dislocation with a core along $\mathbf{l}$ is characterized by[10]

$$\oint d\mathbf{u} = \oint_C \frac{d\mathbf{u}}{ds} ds = \mathbf{R} \equiv \mathbf{b}, \tag{206}$$

where C is a curve enclosing the core and $\mathbf{b}$ is called the *Burgers vector*. The construction of the Burgers vector is fully topological, but there are two nontopological descriptions; screw dislocations if $\mathbf{b} \parallel \mathbf{l}$ and edge dislocations if $\mathbf{b} \perp \mathbf{l}$. Since the Bravais lattice vector, which leaves after a single winding curve C passed to enclose the core, is discrete, the dislocation is, from homotopy group theory, *line*.

Let us look at the characters of dislocations with little rigor (Mermin, 1979). Suppose that R is an order-parameter space. There is a map $f(z)$ of interval $0 \leq z \leq 1$ into R defining the real-space loop or circles into order-parameter space to give closed curves in order-parameter space itself. A continuous directed curve described by maps f passing through a base point x in R. The close curve is decribed by $f(0) = f(1) = x$. Two loops f and g are *homotopic at x*, if there is a continous family of loops, all passing through x. The classes of homotopic loops at x form a group, called $\pi_1(R, x)$, and is known as the *fundamental group* of R at x. There are other groups associated with the mappings of the surface of an n sphere S_n in Euclidean $n + 1$ space

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[10] Here, we follow the definition by Chaikin & Lubensky (1995).

called $\pi_n(R, x)$. The fundamental group is called the *first homotopy group* and π_n is then called the nth homotopy group. For example, $\pi_2(S_2, x)$ is called when the maps f at the base point x is on the sphere S, *i.e.*, say, u and v into R, of three dimensional order-parameter space. For an integer Z, if $\pi_1(S_1) = Z$, the group structure does not depend on the choice of base point x and the map is topologically the same as the circle. Any mapping of a loop into a sphere can be shrunk to a point, so that the fundamental group of the surface of a sphere consists only of the identity, $\pi_1(S_1) = 0$. Trivial point defects are associated with mappings that can be deformed to the constant map.

Let us say the group G containing translations as well as proper rotations, *i.e.* the proper part of the full Euclidean group. Let H be the subgroup of G containing those rigid body rotations that leave the reference system invariant. Naively the order-parameter space R is the coset space G/H. If we ignore of the rotational symmetries of crystals, the full proper Euclidean group can be replaced by the subgroup $T(3)$ of translations. On the other hand the isotropy subgroup H becomes the subgroup of $T(3)$ consisting of translations through Bravais lattice vectors. Since $T(3)$ is parameterized by all of Euclidean three-space, it is connected and simply connected. Since H is discrete, we identifies $\pi_1(G/H)$ with H itself. Thus the line defects, in our case dislocations, are characterized by Bravais lattice vectors. The vector is usually known as the Burgers vectors. Because H is discrete $\pi_2(G/H) = 0$. In this case, the homotopy theory says notopologically stable *point* defects. However, we know thermodynamically stable point defects, *e.g.*, vacancies or voids. The physical means of removing a void are reminiscent of the nonlocal means available for the elimination of topologically stable defects.

Now let us recover the operations of the rigid body rotations. The fundamental group is identified with the double group. The three dimensional rotational parts of the group operations are lifted from SO(3) rotation to SU(2). Discrete operations in the space group with no translational part correspond to line defects, in which the local crystal structure rotates through an angle associated with a point group operation as the line is encircled. Such defects are known as disclinations. Although the $\pi_3(R)$ has the classification problem (Mermin, 1979), the domain walls (grain boundaries) are thought as the string bounded topological defects by the broken discrete symmetry (Vilenkin, 1985), hence so that textures evolve.

7.2 Renormalization group and gauge theory

Once the order parameter class is identified, the partition functions are divided by the corresponding topologically invariant number. Indeed, Burakovski et al. (2000) rederived the free energy density as a function of dislocation density depending on temperature, starting from the partition function computation for the indistinguishable dislocation loops. The resultant free energy density function is very similar to that out of the constitutional approach (Cotterill, 1980). The free-energy is in the form of the two-dimensional xy model, which should undergoes a two-dimensional Kosterlitz-Thouless phase transtion (Kosterlitz & Thouless, 1973). The theory break down point, *i.e.*, the melting temperature is also derived. They also showed that the dislocation density ρ cannot be a continuous function of temperature, but it is a gap function

$$\rho(T) = \begin{cases} 0, & T < T_m, \\ \rho(T_m) \sim b^{-2}, & T = T_m, \end{cases} \tag{207}$$

where T_m is the melting temperature. The dislocation-mediated melting mechanism was observed in a bulk colloidal crystals (Alsayed et al., 2005). A good review on two-dimensional melting phenomena is given by Strandburg (1986; 1989).

Since the inclusion of the symmetry classfication, the *renormalization group* approach is appropriate to order parameters, or phase fields. The renormalization group theory has been served as the most appropriate tool for investigating phase transitions and critical phenomena (Anderson, 1997; Fradkin, 1991; Goldenfeld, 1992; Zinn-Justin, 1997). The idea of the renormalization group approach is a sucessive scaling transformation of the system interaction in real space, known as coarse-graining, or cutoff the high momentum fluctuations larger than arbitrary value Λ to eliminate the ultraviolet catastrophe of the perturbation expansion (Wilson, 1975; 1983). During the successive scaling, the interaction Hamiltonian of the phase field should keep its symmetry. The resultant Hamiltonian is arrived at a *fixed point* independent on the scale of the system, so it gives the *universal* behavior of the critical phenomena. The singlularity in the order parameter equation gives the dissipation of the order parameter. The good examples of the RG procedure with the topological defects were given by Fradkin (1991).

Elegance is in the renormalization group theory, because it does not depend on the system scale but on the symmetry. For example, the dislocation-mediated melting transition is categorized as the problems of the vortex formation in superfluid ^{3}He (Anderson & Toulouse, 1977). In this sense, transition phenomena in the world can be categorized by *universality class* defined by the critical exponents.

However, is it enough?

Teichler (1981) criticised the above approach, because it is unsolved how we see the deviation of the equations of motion of elementary excitations in an ordinary medium with topological defects to the corresponding equations in the ideal configuration. He also showed that the transformed single electron Hamiltonian for describing the distorted crystal by dislocation (Brown, 1845) is described in terms of *gauge fields* in addition to the well-known deformation potentials. Gauge means the redundant degrees of freedom in Hamiltonian or Lagrangian, but its transformation behavior characterizes the interaction. The quantization of gauge field is gauge boson; *e.g.*, photons are a kind of gauge bosons out of the gauge degree of freedom of electromagnetic fields.

The quantum motions of electrons in a gauge field due to the topological dislocation defects have been investigated (Bausch, Schmitz & Truski, 1999; Bausch, Schmitz & Turski, 1999; Turski & Mińkowski, 2009). The main conclusions of the gauge field theory (Bausch et al., 1998) are that the motion of a quantum particle is described in a curved-twisted space, as in gravitational field, called Rieman-Cartan manifold and that the Hamiltonian is separated in two parts that the covariant part and noncovariant parts (Larzar, 2010). The gauge field method has been applied to the elastic properties of solids (Dietel & Kleinert, 2006; Kleinert & Jiang, 2003; Turski et al., 2007) by modelling the elastic energy of the lattices by harmonic displacement fields. The computed melting temperatures of selected bcc and fcc elemental crystals agrees acceptably with the experimental values (Kleinert & Jiang, 2003). The most striking result of the defect gauge theory is the Aharonov & Bohm (1949) type interferences near the dislocation. This fact indicates that the dislocations are not be classical objects anymore, but are qunatum mechanical ones.

8. Outlook and proposal

We have arrived at the stage to consider the applications of the theoretical framework in materials science.

Given a problem, we have to identify the order paramers governed by a certain set of symmetries. Based on the symmetry we need to classify the possible topological defects. The problem is separated into two parts: the scale independent universal properties and the elementary excitations. The tools for the universal properties are the homotopy theory and the

renormalization group, while those for elementary excitations are conventional perturbative renormalization technique with the finite temperature Green's function. The effects of the identified topological defects on the elementary excitations can be dealt with the gauge field theory. The phase transition mechanism of each object can be understood by utilizing the fluctuation-dissipation theorem. Note that all the methods are based on the computation of partition functions by quantum field theoretic manner.

A reversed approach, seems more practical, is also possible. One can firstly identify the ideal structure and compute the equilibrium thermodynamics using the Green's function technique. The fundamental irreversible processes are also available from this technique. When one is faced a problem related with (topological) defects, the renormalization group and the defect gauge theory should be considered.

They usually raise a question on the practicality of the quantum field theoretic approach. Theories introduced here are nothing new, but tried to describe them in a unified way. Those theories have been developed and published from individual schools. This fact implies that the methods can be applied to materials engineering with a suitable software package and computers. There are the other approach for materials design. For example, Olson (2000) viewed a material as a system rather than a set of matters. Once an engineering target is given, one has to identifies the required properties in terms of materials properties and the corresponding structure with a suitable set of processes. The basic assumption is that the necessary theoretical and experimental tools are already prepared in a database and identified for the purpose. The length and time scales are covered from electronic scale to devices. A well organized spin-off company indeed does this business. The practicality awareness can be solved if we have a unified theoretical tool. This approach is an *ad hoc* combination of the current methods. The quantum field theoretic approach proposed in this article removes such *ad hoc* awareness.

In view point of computer resources, the required computer performance of Olson's multiscase approach may be of order from peta-floating point operations per second (peta-FLOPS) to exa-FLOPS. The individual sectors of the theories introduced here utilize from a desktop personal computer to one of order tera-FLOPS. If there is a computer software package in a unified theoretical framework, the required computer performance may sit on the performance of order peta-FLOPS. Hence, the practicality will not be a major problem.

In order to utilize a theoretical framework in engineering, a unified software package development is necessary. Unfortunately, such unified theoretical scheme has not been established yet. The reason can be thought in two-folds. Firstly, the theoretical maturity may not been achieved satisfactory by means of both theory itself and its implementation into a computer software package. When the author (hereafter referred as I) experienced first density functional calculation in 1994, I could remember the names of most researchers working in the density functional world. Now the number of citation of Kohn & Sham (1965) paper is approaching to 20,000 at the time of writing this manuscript. Most of them are using the software package as a black-box, due to the maturity of the software packages and the developments of computer technology. This example demonstrates the power of the matured theory and the corresponding computer softwares.

Secondly, the quantum field theory itself is too difficult to understand for beginners. Cardy (2000) explained, at the preface of his book, this situation as

> . . . and the the student, if he or she is lucky, has just about time to learn how to calculate the critical exponents of the Ising model in $4 - \epsilon$ dimensions before the course comes to an end.

The Ising model is considered as one of the simplest solvable "toy" model. In addition, many researchers in quantum field theory are working with their own "toys." The maturity of such

toys seems enough to evolve to as tools. Covering many topics in the renormalization group and quantum field theory is not so practical to learn in depth for typical material scientists. Such study will be done by the experts. The pedagogy for understanding the quantum field theory is also equally important.

To date there is no further fundamental theoretical tool in describing our physical world rather than the quantum field theory. It is hardly necessary to go beyond the quantum field theory for materials scientists. I would like to emphasize that we are standing at the starting point for a long journey to utilize the unified method with the reinterpreted terminology, *ab initio* thermodynamics authentically.

9. Acknowledgements

List of Symbols

- A: spectral weight function
- $C(R)$: correlation function of interaction range R
- C_V: volume constant heat capacity
- D: long time interval
- $\mathcal{D}$: density of states
- E: internal energy
- $E_{xc}[n]$: exchange-correlation energy functional of density n
- F: Helmholtz free energy
- $F(t)$: time dependent driving force
- $F[n(\mathbf{x})]$: energy functional of density $n(\mathbf{x})$
- G: Gibbs free energy; full group in the order-parameter space R (depending on context)
- G/H: coset space
- $\bar{G}$: real-time Green's function
- $\bar{G}^A$: advanced Green's function
- $\bar{G}^R$: retarded Green's function
- $\mathcal{G}$: temperature Green's function
- H: subgroup of G
- $\hat{H}$: Hamiltonian operator
- $\hat{H}'$: external perturbation Hamiltonian operator

- **H**: external magnetic field
- $\Im$: imaginary part extraction operator
- J_{ij}: interaction of spins between ith and jth sites
- K: propagtor, Green's function
- $\hat{\mathcal{K}}$: grand canonical Hamiltonian operator
- $\mathcal{L}$: Landau function
- **M**: total magnetization
- $\hat{M}_\mu$: magnetization in μ-direction
- N: number of particles of the system
- N_i: number of particles of ith component
- P: pressure
- $\wp$: Cauchy principal value
- $\hat{\mathbf{P}}$: momentum operator
- $\mathbf{P}_m$: eigenvalue of the momentum operator
- R: interaction range; order-parameter space (depending on context)
- **R**: Bravais lattice vector
- $\Re$: real part extraction operator
- S: entropy
- $S\,(q)$: mean density fluctuation as function of wavevector q
- $\mathbf{S}_i$: localized atomic spin at the site i
- $SO\,(3)$: special orthogonal rotation group at three dimension
- $SU\,(2)$: special unitary rotation group at two dimension
- T: temperature
- T_0: Bose-Einstein condensation temperature
- $T_0\,[n]$: kinetic energy functional of the noninteracting system of density n
- T_C: Curie temperature
- T_L: liquifying temperature
- T_m: melting temperature
- $T\,(3)$: Euler translational subgroup
- $\hat{U}$: unary external potential operator
- V: volume of the system
- Z: partition function; renormalization factor; an integer (depending on context)
- a: lattice constant
- $a_n\,(H,T)$: expansion coefficient of the Landau function as function of H and T
- b: norm of Burgers vector
- **b**: Burgers vector
- $b_n,\ c_n,\ d_n$: expansion coefficients of the Landau function

- $c.c.$: complex conjugate
- d: dimensionality of the interaction
- d1: differential operator for $\mathbf{x}_1, t_1$
- dw: propability of states represented in the phase volume
- f_{AB}: generalized response function
- $f(p, q)$: any physical quantity as a function of p and q
- $\bar{f}$: average of $f(p, q)$
- $f(z)$: order parameter map
- g: spin degeneracy factor
- h: reduced external magnetic field $(H - H_c)$
- $\hbar$: Planck's constant
- i: index for the microstates
- $\mathbf{k}$: wavevector
- k_B: Boltzmann's constant
- k_F: norm of the Fermi wavevector
- $k(t)$: solution of the equation of motion
- $\mathbf{l}$: dislocation core axis vector
- m: mass of the particle
- m^*: effective mass
- m_s: magnetization of the Landau function at the global minimum
- $\mathbf{m}$: magnetization per spin
- n: band index
- $n(\mathbf{x})$: number density as function of $\mathbf{x}$
- n_i^0: occupation number of the state i of the noninteracting system
- p: norm of the momentum $\mathbf{p}$
- $\mathbf{p}$: single-particle momentum
- p_i: generalized momentum of the ith degree of freedom
- q: norm of wavevector $\mathbf{q}$
- q_L: liquifying wavevector
- $\mathbf{q}$: wavevector
- q_i: generalized coordinate of the ith degree of freedom
- s: degree of freedom of the system; number of spins (depending on context)
- t: time; reduced temperature $T - T_C$ (depending on context)
- t^*: critical temperature
- $\mathbf{u}(\mathbf{x})$: vector displacement field at position $\mathbf{x}$
- $u_{n\mathbf{k}}(\mathbf{k})$: Bloch function of band n and wavevector $\mathbf{k}$ at position $\mathbf{x}$
- v: static potential

- v^{ext}: static external potential
- $\mathbf{v}_n(\mathbf{k})$: nonvanishing velocity of a Bloch wavefunction of the band n and the wavevector $\mathbf{k}$
- x: base point of order parameter space R
- $\mathbf{x}$: position
- $\Delta p \Delta q$: small phase interval
- z: coordinate of the order parameter space R
- Γ: gamma function
- $\bar{\Gamma}$: generic real-time Green's function in Lehmann representation
- Π: generalized polarization
- Σ: self-energy
- Σ^λ: self-energy for the interaction strength of λ
- Θ_{D}: Debye temperature
- $|\Phi_0\rangle$: ground state of the system
- Ξ: grand partition function
- Ω: grand (thermodynamic) potential
- Ω_0: grand potential of the noninteracting system
- β: inverse temperature $1/k_{\text{B}}T$
- $\gamma_{\mathbf{k}}$: damping of the quasiparticle of wavevector $\mathbf{k}$
- δ: Dirac delta function
- ϵ: single-particle energy
- ϵ_{F}: Fermi energy
- $\epsilon_{\mathbf{k}}$: energy spectrum of the particle at the wavevector $\mathbf{k}$
- $\epsilon_{\mathbf{p}}$: energy spectrum of the particle at the momentum $\mathbf{p}$
- $\epsilon_{\mathbf{k}}^0$: energy spectrum of the noninteracting single-particle at wavevector $\mathbf{k}$
- ϵ_{c}: correlation energy density
- ϵ_{xc}: exchange-correlation energy density
- ε_{ij}: fractional error of the Landau theory as function of the ith and jth sites
- ε_R: fractional error of the Landau theory as function of R
- η: infinitesimal real positive convergence factor
- κ: generalized dielectric function
- λ: interaction control parameter
- μ: chemical potential
- μ_i: chemical potential of ith component
- μ_c: correlation energy potential
- μ_{xc}: exchange-correlation potential
- ψ: wavefunction

- $\hat{\psi}_\alpha$: field annihilation operator at the state α
- $\hat{\psi}_\alpha^\dagger$: field creation operator at the state α
- ψ_i^{KS}: ith Kohn-Sham orbital
- ϕ_n: nth eigenfunction of $\hat{H}$
- ρ: statistical distribution function
- $\hat{\rho}$: statistical distribution function operator of unperturbed system
- $\hat{\rho}'$: statistical distribution function operator by perturbation
- θ: step function
- $\chi_T(H)$: isothermal magnetic susceptibility as function of H
- $\chi_{\mu\nu}$: μ-direction magnetic susceptibility with respect to ν-direction external field
- χ^*: final state wavefunction
- σ: Stefan-Boltzmann constant
- τ: imaginary time; time difference (depending on context)
- $\pi_n(R, x)$: nth homotopy group of R at base point x
- ξ: correlation length
- ζ: index for microstates of the system; zeta function (depending on context)
- ω: frequency of a single-particle
- ω_n: Matsubara frequency
- $[\hat{A}, \hat{B}]$: Poisson bracket of operators $\hat{A}$ and $\hat{B}$
- $4 - \epsilon$: near four dimension

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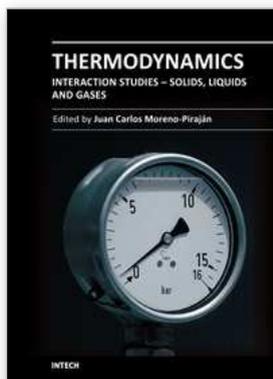Cornell, E. A. & Wieman, C. E. (2002). On the theory of quantum mechanics, *Rev. Mod. Phys.* 74(3): 875–893.

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