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Introduction

Classical thermodynamics is a well-established discipline of physics. In application to crystals, however, the irreversible processes of collective order variables below transition temperatures are essentially nonlinear, responding to the hosting lattice, so the traditional approach should be revised, using the soliton theory to deal with mesoscopic phenomena. Signified by entropy production with varying volume and temperature, the intrinsic correlations among constituent molecules are responsible for the irreversible processes in crystalline states. By revising traditional statistical and field-theoretical approaches, in this introduction basic concepts are redefined for a modulated crystal of finite size in a thermal environment. Here the nonlinear dynamics constitutes the basic objective to be discussed in extending the irreversible processes of crystals from traditional thermodynamics in isotropic systems [1].

0.1 The internal energy of equilibrium crystals

When in equilibrium with the surroundings, the crystalline states of chemically pure materials are characterized by a uniform lattice structure, as determined by crystallographic analysis. However, in the absence of reliable knowledge on molecular cohesion in today’s physics, the equilibrium lattice structure defined by symmetry groups is assumed to be a fact of nature. In this view, the modulated lattice is not always in equilibrium with its surroundings, where the elastic strain energy in the lattice is distributed within the structure, hence the non-equilibrium crystalline state at a given pressure is generally temperature-dependent. On the other hand, the internal dynamics in equilibrium with the lattice should be conservative as determined by canonical equations for steady states, but dispersive and dissipative in non-equilibrium processes.

Referring to space and point groups, the equilibrium structure of crystals is invariant under symmetry operations of the lattice. The point group specifies that all identical constituents remain static at fixed lattice sites, whereas the space group confirms the internal structural invariance of crystals against spatial translations.
Denoting the internal energy of an equilibrium crystal by a constant energy $U_o$ of the lattice structure, the conservation law for the internal energy $U$ determined by external pressure $p$ and temperature $T$ can be expressed in general as

$$U - U_o = \Delta U = Q - p\Delta V,$$

(0.1)

where $Q$ and $-p\Delta V$ represent, respectively, the heat change with the lattice at $T$ and the energy transfer for a volume change $\Delta V$ at constant $p$ of the surroundings; here (0.1) represents the first law of thermodynamics. Invariant geometrical symmetry itself does not represent properties of crystals in a thermodynamic environment, however it can be violated during irreversible processes, and is therefore considered responsible for modulated structure. Moreover, for crystals specified by finite volume, the volume change $\Delta V$ cannot be ignored in principle, while the condition $\Delta V = 0$ is technically difficult to maintain in practical crystals.

Heat transfer processes are always irreversible, where the transferred heat quantity $Q'$ is in fact always less than a given $Q$, so that (0.1) should be replaced by an inequality

$$\Delta U \geq Q' - p\Delta V,$$

as described by the second law of thermodynamics. Mathematically, finding a temperature $T$ such as to keep $Q'/T = \Delta S$ a total differential of entropy $S$, and the above inequality can be expressed by $\Delta U \geq T\Delta S - p\Delta V$; hence we write

$$\Delta F \geq -p\Delta V,$$

(0.2)

where the Helmholtz function $F = U - TS$ defined from (0.2) can be used for equilibrium conditions at constant volume with a given pressure $p$; the free energy $F$ should take a minimum value at $\Delta V = 0$, which can be achieved in constant-volume conditions.

Related to the entropy $S$, the temperature $T$ is associated with the heat $Q$ that can be attributed microscopically to random collisions of air particles in the surroundings. Thereby, the thermodynamic probability $g(T)$ can be defined statistically by the equation $S = k_B \ln g(T)$, where $k_B$ is the Boltzmann constant.

### 0.2 Microscopic order variables and their fluctuations

Spontaneous structural changes are significant phenomena in crystals, which can be attributed to internal order variables $\sigma_n$ associated with constituents at all lattice sites $n$, characterized by the point symmetry or internal degrees of freedom of the constituent. Thermodynamically, $\sigma_n$ should be regarded as continuous variables of space–time average at low energies, as defined by Kirkwood [2] for internal variables in chemical thermodynamics. However, such internal variables $\sigma_n$, called order variables in crystals, are mutually correlated among lattice sites. Assuming binary correlations that are predominant at short distances, the correlation energy can be written as $-\sum_{m} J_{mn} \sigma_m \sigma_n = -\sigma_n \sum_{m} J_{nm} \sigma_m$, where the quantity $X_n = \sum_{m} J_{nm} \sigma_m$ can be defined as a field acting on $\sigma_n$ by analogy of Weiss' molecular field in magnetic crystals. Referring to it as the Weiss field in general, such local fields $X_n$ can be
defined as a continuous field at low energies in crystals. Assuming \( \sigma_n \) and \( X_n \) as continuous variables, (0.1) can be generalized as \( \Delta U = T \Delta S - p \Delta V - \sum_n \sigma_n \Delta X_n \), including an inevitable volume change \( \Delta V \), thereby expressing the equilibrium condition as

\[
\Delta G = 0, \quad (0.3)
\]

where \( G = U - TS + pV + \sum \sigma_n X_n \) is called the Gibbs free energy, indicating that the equilibrium at given \( T \) and \( p \) can be obtained by minimizing \( G \) with respect to \( \sigma_n \). Born and Huang [3] showed in their theory of lattice dynamics that the Weiss field is a valid concept in the adiabatic approximation. It is noted that in the presence of internal \( \sigma_n X_n \) or correlations \( J_{mn} \sigma_m \sigma_n \), the volume is not usually constant, i.e. \( \Delta V \neq 0 \), hence the Gibbs function should be minimized to determine equilibrium conditions. In fact, in order for (0.2) to express the thermodynamic equilibrium, we must consider

\[
\Delta V = \sum_n \sigma_n \Delta X_n, \quad (0.2)
\]

attributing all internal variations to a volume change \( \Delta V \). However, it is more convenient to use the Gibbs function rather than the Helmholtz function, if we consider the internal variable \( \sigma_n \).

Microscopic order variables in crystals are considered to fluctuate among lattice points, which are in fact unavoidable during transitions between different crystalline phases in particular. Crystalline states in transition are inhomogeneous in density, so we consider mean-field averages \( g_1 = G_1/V_1 \) and \( g_2 = G_2/V_2 \) for the phases 1 and 2, respectively. Their equilibrium can then be determined by minimizing the difference \( g_1 - g_2 = \Delta g \), namely

\[
\Delta g = \frac{1}{2} \left[ \frac{\partial^2 \Delta g}{\partial \sigma_1 \partial \sigma_2} \right]_{p,T} \langle \Delta \sigma_1 \Delta \sigma_2 \rangle_{p,T} + \cdots, \quad (0.4)
\]

where the brackets \( \langle \ldots \rangle_{p,T} \) indicate the mean-field average of fluctuations. In deriving (0.4), we consider that the averages of order variables themselves should vanish, so that \( \langle \sigma_1 \rangle_{p,T} = \langle \sigma_2 \rangle_{p,T} = 0 \) are utilized. In this case, from (0.4) the average of binary correlations should be nonzero, as expressed by the inequality \( \langle \Delta \sigma_1 \Delta \sigma_2 \rangle_{p,T} \neq 0 \), which is necessary for the transition to be second-order in the Ehrenfest classification of phase transitions. Nonetheless, observed critical anomalies indicate evidence for such binary correlations to describe thermodynamically adiabatic fluctuations in crystals.

The transition from uncorrelated to correlated variables is associated with a dynamical bifurcation for the nonlinear process; on the other hand, observed anomalies can be attributed to unavoidable quantum-mechanical space–time uncertainties during the transition.

### 0.3 Collective order variables in propagation

Most order variables \( \sigma_n \) at lattice sites \( n \) are related to partial displacements inside constituents, representing relative displacement with respect to the lattice. In crystals, such \( \sigma_n \) are in collective fluctuations in a mesoscopic phase that should be
accompanied by \textit{counter-fluctuations} in the periodic structure, resulting in collective displacements of lattice sites. Mathematically, such collective fluctuations in a \textit{uniformly periodic structure in finite size} can be described by a \textit{Fourier series} \cite{4} as expressed by

\[
\sigma_n = \sum_k \sigma_k \exp i(k \cdot r_n - \omega t_n),
\]

which is convenient to use in crystals as characterized by the \textit{Bloch theorem}, where \( \omega = v|k| \) and \( v \) are the frequency and speed of propagation along a specified direction in a periodic structure.

In sufficiently large crystals, where surfaces are neglected, the local phase \( \phi_n = k \cdot r_n - \omega t_n \) at a site \( n \) varies in the range \( -\pi \leq \phi_n \leq \pi \), but can effectively be redefined by a continuous phase \( \phi = k \cdot r - \omega t \), if \( |k| \) is sufficiently small in crystals of large size. Accordingly, the continuous phase \( \phi \) in the range \( -\pi \leq \phi \leq \pi \) can be employed, instead of \( \phi_n \), to express the collective \( \sigma(r, t) \) as a thermodynamic variable.

Expressing the collective order variable by \( \sigma(r, t) = \sigma_0 \exp i\phi \) for small values of \( |k| \), we can use the Fourier transform

\[
\sigma_k = \frac{1}{\sqrt{N}} \sum_n \sigma_n \exp \{-i(k \cdot r_n - \omega t_n)\},
\]

which can be simplified for a single \( k \)-vector as

\[
\sigma_k(\phi) = \sigma_0 \exp(-i\phi) \quad \text{where} \quad \phi = k \cdot r - \omega t,
\]

and inversion symmetry in finite crystals can thus be signified by the \textit{phase inversion} \( \phi \rightarrow -\phi \).

For thermodynamics, we consider spatial inversion \( r \rightarrow -r \) only, disregarding the time inversion. This is the basic field-theoretical approach to the thermodynamics of crystals, where the surface can be ignored by considering volumes of sufficiently large size, although it is important for the thermodynamics of heat exchange with the surroundings.

We therefore define renormalized phase variables as \( -\pi/2 \leq \pm \phi \leq +\pi/2 \) for order variables, which are employed to express \textit{collective order variables} in crystals. On the other hand, phases \( \phi_n \) are referred to microscopic space–time \( (r_n, t_n) \). In fact, it is particularly convenient to define a range such as \( -\pi/2 \leq \pm \phi \leq +\pi/2 \) to cover phase inversion in the whole crystal from one side to the other of the \textit{finite periodic structure}. Assuming that the one-dimensional length of a crystal is composed of integral multiples of a short renormalized unit, the \textit{terminal surfaces} on the right and left can be determined by boundary conditions

\[
-\pi/2 \leq \pm \phi \quad \text{and} \quad \pm \phi \leq +\pi/2,
\]

respectively, offering a simple but realistic \textit{theoretical model for crystal surfaces to interact with thermodynamic surroundings}.

In the field-theoretical approximation valid for small values of \( |k| \), the motion of \( \sigma_k(\phi) \) is internally driven by a \textit{force} \( -\partial \Delta U_k / \partial \phi \), where \( U_k \) is a function of \( \phi \), and \( \Delta U_k \)
should be responsible for the wave motion of $\sigma_k(\phi)$. For the dynamics of $\sigma_k(\phi)$ in general, we should consider the corresponding kinetic energy $K(\sigma_k)$ as well, where $\sigma_k$ is a momentum variable conjugate to $\sigma_k$. By the least-action principle, the integral of the Lagrangian $L(\dot{\sigma}_k, \sigma_k) = K(\dot{\sigma}_k) - U(\sigma_k)$, namely the action variable $\int_{\mathcal{V}} L(\dot{\sigma}_k, \sigma_k)d\mathcal{V}$, should be minimized for a conservative system to determine the Hamiltonian $\mathcal{H} = K(\dot{\sigma}_k) + U(\sigma_k)$ to be a constant of time, characterizing the equilibrium system by its eigenvalue. Experimentally, the potential $\Delta U_k$, or $\Delta U_k$, has been confirmed to exist in equilibrium crystals.

### 0.4 Crystal surfaces and entropy production

In thermodynamics, crystal surfaces play a significant role in heat exchange with the surroundings. However, we consider idealized crystals of sufficiently large volume, whose properties are determined by the whole crystal, thereby dynamically ignoring the surfaces of the bulk crystal. The surfaces cannot be ignored thermodynamically, because order variables need to be specified by a finite value on surfaces; nevertheless, we minimize surface contributions to the properties of periodic structure for mathematical convenience, assuming a crystal to consist of a large number of unit structures in repetition. Disregarding surfaces, we can consider that surfaces are represented by crystal planes, which actually are convenient for discussing domain structure as well. Nonetheless, for heat exchange with surroundings, we do not have to specify real surfaces, but mathematically require nodal planes for $\sigma_k(\phi)$ at $\phi = (\pi/2) \times \text{integer}$.

*Singularities* of the function $\sigma_k(\phi)$ can be responsible for energy transfer to the crystalline media and to surroundings, where the process is naturally irreversible, as manifested by the second law of thermodynamics. In soliton theory, the energy transfer can be described conveniently by quantized soliton particles\footnote{Here, the word ‘quantized’ refers to discrete soliton numbers in crystals, rather than quantum-mechanical quantization with respect to the Planck’s constant. Nevertheless, solitons can be regarded as quantized particles in crystalline media, regarding discrete lattice energies.} for the thermodynamic description of entropy production. As defined in chemical thermodynamics [1], a continuous parameter for reacting species is a convenient measure for isotropic reactions to be described as an irreversible energy transfer process from $\sigma_k(\phi)$ to the correlation energy $U_k(\phi)$, which is usually expressed in terms of a chemical potential and number $n$ of soliton particles. However, it is important to realize that such a dynamical argument as above should be limited to macroscopically uniform crystals. In order to analyze observed results, sample crystals should be of ellipsoidal shape, in principle.

At this point, we propose considering another quantity called solitons with regard to crystals, thereby making the structure inhomogeneous, as in flowing reactions in chemical systems as will be discussed in later chapters. Writing the soliton density $n$ in the Gibbs function as $G(p, T; n)$ for inhomogeneous crystals, we have

$$G(p, T; n) = \Delta U - T\Delta S + p\Delta V + \mu\Delta n,$$  \hspace{1cm} (0.8)
where $\Delta n$ is a variation of the soliton number that is a function of $T$ and $p$ of the surroundings, and $\mu$ is the chemical potential. Such $\Delta n$ can be written as $\Delta n(T)$ and $\Delta n(p)$ for isothermal and isobaric processes, respectively. Combining the second and fourth terms on the right of (0.7), entropy production can be expressed as

$$T \left( \Delta S - \frac{\mu \Delta n(T, p)}{T} \right),$$

where the second term $\Delta S' = -\frac{\mu \Delta n(T, p)}{T}$ represents effectively the additional entropy production to the conventional heat $Q = T \Delta S$. In this case, as in chemical systems, $Q' = T \Delta S'$ represents effectively either $-\mu \Delta n(T)$ or $-\mu \Delta n(p)$ for entropy production $\Delta S'$ in isothermal or isobaric processes, respectively. While valid in chemical systems in the liquid phase, it is also significant in crystals that such entropy exchanges $\Delta S$ and $\Delta S'$ take place, not only between the system and surroundings, but also between order variables and lattice internally, as theoretically described by Onsager’s reciprocity theorem.

Quantized lattice vibrations represented by phonons are also signified for their energies to be determined by the equipartition theorem as proportional to thermal energy $k_B T$, so that $\Delta n \propto T$, hence $\Delta S' = 0$ for phonons. On the other hand, in crystals such a quantization should be applied to the modulated structure, for which $\Delta n(T)$ is not simply proportional to $T$, to make adiabatic entropy production $\Delta S' \neq 0$, but accompanied by finite temperature change $\Delta T \neq 0$. Furthermore, in modulated crystalline states $\mu \Delta n$ expresses internal work equivalent to mechanical work $-p_{\text{int}} \Delta V'$ at a temperature $T$, where $\Delta V'$ is an adiabatic volume change and $p_{\text{int}}$ is an effective internal pressure, which is more appropriately expressed as external work $+\gamma \Delta p_{\text{ext}}$, if the crystal is under external pressure $p_{\text{ext}}$. In this case, $\mu \Delta n$ can be observed with varying external work on degrading lattice symmetry against the surroundings. The soliton theory is primarily established for isotropic media at constant $V'$, however, in crystalline states $\Delta V' \neq 0$ occurs normally as determined by changing lattice symmetry.

0.5 Timescales for sampling modulated structure and thermodynamic measurements

In the thermodynamics of an irreversible process the collective motion of order variables is vital in the modulated structure at the mesoscopic scale. The timescale for modulation is not determined entirely from the quantization process, unless the minimum modulation energy is specified. Paying attention to the discreteness of the modulated lattice, however, we need to consider observing frequencies under equilibrium conditions. To sample modulated lattices with a known frequency, the timescale of the measurement is significant for correct analysis of experimental results.

---

note2 This relation is consequent on the soliton gas that obey the law of ideal gas, i.e. $pV' = RT$ at constant $T$, applied to the equilibrium condition $\Delta G_{\text{int}} + \Delta G_{\text{ext}} = 0$. 0-6
Structural changes in crystals are detected from observed anomalies due to fluctuations of \( \sigma_k(\phi) \), where phase variations \( \Delta \phi \) dominate the critical region. Such fluctuations, observed as a mesoscopic modulation of \( \sigma_k(\phi) \), can be visualized by an appropriate sampling experiment in the timescale \( t_o \) [5]; in contrast, conventional thermal measurements are macroscopic and are performed on very long timescales. Although theoretically insignificant, it is important for practical observations if the timescale \( t_o \) of the experiments is comparable with the timescale \( t \) of fluctuating \( \sigma_k(\phi) \). In the mesoscopic observation, measured quantities are determined by the time average between \( +t_o \) and \( -t_o \). Accordingly, normal sampling results are related to the thermodynamic average

\[
\langle G(\phi) \rangle_{p,T} = \frac{1}{2t_o} \int_{-t_o}^{+t_o} \langle G(r, t) \rangle_{\text{space av.}} \cos \omega t \, dt = \langle G(r) \rangle_{\text{space av.}} \frac{\sin \omega t_o}{\omega t_o},
\]

which is approximately equal to \( \langle G(r) \rangle_{\text{space av.}} \) if \( \omega t_o \approx 1 \), otherwise (0.8) is averaged out. Nevertheless, \( \langle G(r) \rangle_{\text{space av.}} \) is measurable in timescale \( t_o \), provided that \( t_o < t = 2\pi/\omega \).

We discuss sampling practices in detail in part 2 of this book.

In contrast to sampling experiments, thermodynamic quantities such as \( G(\phi) \) are determined by the surrounding in equilibrium at \( p \) and \( T \), for which the timescale of observations is regarded as infinity. For example, the specific heat of a crystal or any other thermodynamic quantity is measured as a function of \( T \) under \( p = \text{const.} \), where a temperature-dependent frequency \( \omega = \omega(T) \) is detected, referred to as the soft mode.

### 0.6 Statistical theories and the mean-field approximation

The traditional statistical theory of solids is based on the fact that the lattice vibration is random in character, permitting statistical averages of dynamical variables in crystals determined by the temperature of the surroundings. Ordering processes in crystalline media are therefore discussed with statistical theories, considering the lattice as the heat reservoir. The Weiss field was defined originally in the mean-field approximation, dominating thermodynamic discussions of solid-state phenomena. In mean-field accuracy, however, lattice symmetry is only an implicit variable for the thermodynamic analysis of equilibrium crystals at constant volume. As emerged in statistical arguments, the important concepts of order parameter and adiabatic potential should, however, be redefined for mesoscopic collective variables in the soliton theory. In this section, these statistical concepts are reviewed as important prerequisites for revising existing theories.

Although somewhat specific, we consider binary order as fundamental for structural changes of crystals, while it is mathematically simple among other transitions. Binary processes are the subject of detailed discussion in parts 1 and 2, based on which we proceed to nonlinear soliton theories in crystals in parts 3 and 4.
0.6.1 Probabilities and the domain structure

In the order–disorder phenomena of binary alloys of two atoms A and B, we consider probabilities \( p_n(A) \) and \( p_n(B) \) at lattice sites \( n \) that are occupied by either A or B atoms. We assume that there are no vacant lattice sites; each site must be occupied by either one of these atoms. Denoting the number of sites by \( N_A \) and \( N_B \), we have then \( N_A = N_B = N/2 \), where \( N = N_A + N_B \).

The physical properties of alloys, such as \( \beta \)-brass CuZn, are well documented, exhibiting order–disorder transitions at critical temperatures \( T_c \). In their original statistical theory, Bragg and Williams [4, 6, 7] considered probabilities for pairs of like atoms, A–A and B–B, and for unlike pairs, A–B and B–A, at nearest-neighbor sites, thereby introducing the concept of short-range order. Judging from the order of the transition temperature \( T_c \approx 450 \, ^\circ\text{C} \), \( \beta \)-brass cannot be so rigid that the constituent atoms should be in diffusive motion, and the lattice may be unsteady in the timescale of observation; nevertheless, these aspects were ignored in early physics.

By definition, we have the relation

\[
p_n(A) + p_n(B) = 1, \quad 0 \leq p_n(A), \quad p_n(B) \leq 1,
\]

from which we can define the order variable as

\[
\sigma_n = p_n(A) - p_n(B), \quad -1 \leq \sigma_n \leq +1.
\]

The complete order can be specified by \( \sigma_n = \pm 1 \), whereas \( \sigma_n = 0 \) signifies complete disorder, attributing signs of \( \sigma_n \) to opposite domains. In addition, the former corresponds to two domains related by inversion \( \sigma_n \rightarrow -\sigma_n \), and the latter signifies the relations

\[
p_n(A) = p_n(B) = 1/2
\]

Thus, domains are independent of each other in existing theories, which however must be revised for their correlations if collective motion is considered.

0.6.2 Short-range correlations and the mean-field approximation

The idea of mean-field averages can be applied to order-disorder phenomena to deal with long-range correlations. We simply use mathematical averages \( \langle \ldots \rangle = \frac{1}{N} \sum_{n=1}^{N} \ldots \) to obtain averages \( \langle p_n(A) \rangle = p(A) \) and \( \langle p_n(B) \rangle = p(B) \), and \( \langle \sigma_n \rangle = \eta \) is defined as the order parameter.

It is logical to consider the correlations between adjacent atoms in crystals, as the first approximation. We calculate such short-range interactions between nearest-neighbors, which primarily do not violate space symmetry. Denoting interatomic energies by \( \epsilon_{nm}^{AB} \) etc to indicate the interaction between the A and B at sites \( m \) and \( n \), respectively, the short-range interaction energy \( E_n \) at site \( n \) can be expressed as

\[
E_n = \sum_{m} \left\{ \epsilon_{nm}^{AA} p_m(A)p_n(A) + \epsilon_{nm}^{BB} p_m(B)p_n(B) + \epsilon_{nm}^{AB} p_m(A)p_n(B) + \epsilon_{nm}^{BA} p_m(B)p_n(A) \right\}.
\]
Substituting probabilities with the order variables defined in (0.2),

\[ E_n = \sum_m E_{mn}, \]

where

\[
E_{mn} = \frac{1}{2} \left( 2\varepsilon_{mn}^{AB} + \varepsilon_{mn}^{AA} + \varepsilon_{mn}^{BB} \right) + \frac{\varepsilon_{mn}^{AA} - \varepsilon_{mn}^{BB}}{4}(\sigma_m + \sigma_n) \\
+ \frac{2\varepsilon_{mn}^{AB} - \varepsilon_{mn}^{AA} - \varepsilon_{mn}^{BB}}{4}\sigma_m\sigma_n = \text{const.} - K_{mn}(\sigma_m + \sigma_n) - J_{mn}\sigma_m\sigma_n,
\]

where \( K_{mn} = -(\varepsilon_{mn}^{AA} - \varepsilon_{mn}^{BB})/4 \) and \( J_{mn} = -(2\varepsilon_{mn}^{AB} - \varepsilon_{mn}^{AA} - \varepsilon_{mn}^{BB})/4 \). For like-pairs A–A and B–B, we assume that \( \varepsilon_{mn}^{AA} \approx \varepsilon_{mn}^{BB} \) in a binary system, hence \( K_{nn} \approx 0 \) in this case, and we have

\[ E_{nn} = \text{const.} - J_{nn}\sigma_n\sigma_n. \]

If \( \sigma_n \) are uncorrelated, we consider that \( \langle \sigma_m\sigma_n \rangle = 0 \), hence \( \langle \text{const.} \rangle = 0 \) should be held for the average \( \langle E_{nn} \rangle = 0 \). Accordingly, for a correlated case, the correlation energy can be expressed as

\[ \langle E_{nn} \rangle = -J\langle \sigma_n\sigma_n \rangle \quad \text{where} \quad J = \langle J_{nn} \rangle, \quad \text{(0.11)} \]

which is the binary correlation energy in general form, consistent with the average \( \langle \sigma_m\sigma_n \rangle \neq 0 \).

### 0.6.3 The Bragg–Williams theory

Bragg and Williams [6] assumed that the number of unlike pairs A–B determines an ordered arrangement specified by the order parameter \( \eta \). Using \( p(A) = \frac{1}{2}(1 + \eta) \) and \( p(B) = \frac{1}{2}(1 - \eta) \) for a crystal where the number of nearest-neighbors is \( z \), the total number of such pairs can be expressed by

\[ N_{AB} = 2Nzp(A)p(B) = \frac{1}{2}Nz(1 - \eta^2). \]

Hence the ordering energy can be written as

\[ E(\eta) = \frac{1}{2}NzJ(1 - \eta^2) \quad \text{and} \quad E(0) = \frac{1}{2}NzJ, \]

so that

\[ \Delta E(\eta) = E(\eta) - E(0) = \frac{1}{2}NzJ\eta^2 \quad \text{(0.12)} \]

is the energy decrease from the disordered state.

The energy \( \Delta E(\eta) \) is highly degenerate, since there are a large number of combinations for choosing an A–B pair in the crystal, which need to be calculated
as thermodynamic quantities. The statistical weight of the ordering energy $\Delta E(\eta)$ is given by

$$g(\eta) = \left( \frac{N}{N_p(A)} \right) \left( \frac{N}{N_p(B)} \right) = N^2 \left( \frac{1 + \eta}{2} \right) \left( \frac{1}{2} \right),$$

with which the partition function $Z = Z_L g(\eta) \exp\{-\frac{\Delta E(\eta)}{k_B T}\}$ is calculated, where $Z_L$ is the partition function of the lattice. Then, the equilibrium can be obtained by minimizing Helmholtz’ free energy $F = -k_B T \ln Z$. Namely, setting the equation $(\partial F/\partial \eta)_\nu = 0$, we obtain

$$\frac{\partial}{\partial \eta} \left\{ \ln Z_L + \ln g(\eta) + \frac{NzJ\eta^2}{k_B T} \right\} = 0,$$

which is to be solved for $\eta$. We evaluate the second term in the brackets by Stirling’s formula for a large $N$, i.e. $\frac{\partial \ln n}{\partial \eta} = -N \frac{1 + \eta}{1 - \eta}$, resulting in $\frac{zJ}{k_B T} = \ln \frac{1 + \eta}{1 - \eta}$. Consequently, we arrive at the expression

$$\eta = \tanh \frac{zJ\eta}{2k_B T}. \quad (0.13)$$

To solve (0.13) graphically, we set $zJ\eta/2k_B T = y$ and $\eta = \tanh y$ to find the crossing point of the line and curve in the $y$–$\eta$-plane, as illustrated in figure 0.1. It is noted that the tangent at the origin $\eta = y = 0$ corresponds to a critical temperature $T = T_c$; there is one crossing point P if $T < T_c$, but no crossing for all temperature $T > T_c$. The critical point is determined by $T_c$.

For $T < T_c$, if $T_c - T$ is small, we can derive an approximate expression

$$\eta^2 \approx 3(T_c - T)/T_c,$$

yielding a parabolic temperature dependence of the order parameter, $\eta \propto \sqrt{T_c - T}$, in the vicinity of $T_c$, as shown in figure 0.2(a). In addition, the specific heat $C_V = (\partial \Delta E/\partial T)_\nu$ calculated with (0.4), shows a discontinuity

$$\Delta C_V = \frac{NzJ}{2} \left( \frac{\partial \eta^2}{\partial T} \right)_{T_c} = \frac{1}{2} Nk_B$$

at $T = T_c$, as illustrated in figure 0.2(b), which is a consequence of the mean-field approximation.

![Figure 0.1](image_url)

**Figure 0.1.** The $\eta$–$y$ curve of Bragg–Williams’ theory. There is one solution at $P(\eta)$ for $T < T_c$, where as $\eta = 0$ is the solution for $T > T_c$. $T = T_c$ is the critical temperature.
It is notable that (0.13) should be consistent with the definition of probabilities (0.9) and order parameter (0.10). To confirm this, we write

\[ p(A) = \frac{1}{Z} \exp \left( \frac{-zJ\eta}{2k_B T} \right) \quad \text{and} \quad p(B) = \frac{1}{Z} \exp \left( \frac{zJ\eta}{2k_B T} \right), \]

where \( Z = \exp \left( \frac{-zJ\eta}{2k_B T} \right) + \exp \left( \frac{zJ\eta}{2k_B T} \right) \) for the energy gap \( 2zJ\eta = \Delta E(\eta) - \Delta E(-\eta) \), we obtain

\[ \eta_+ = p(A) - p(B) \quad \text{and} \quad \eta_- = p(B) - p(A), \quad (0.14) \]

which are order parameters in domains + and −, respectively. That is an obvious consequence of the Boltzmann statistics, although the basic result (0.13) is quoted in the literature following the original article. Needless to say, it is important to realize that the Boltzmann statistics is a valid concept, as supported by the randomness of phonon collisions in an equilibrium lattice, as will be confirmed in chapter 1.

However, it is a notable conflict that the Bragg–Williams theory is not compatible with the lattice dynamics in finite crystals, as will be discussed in chapter 8; traditional statistical results should thus be re-evaluated for finite crystals.

### 0.6.4 Ferromagnetic order and the Weiss field

Composed of magnetic ions, a ferromagnetic crystal is magnetized along a specific crystallographic axis. In the case of iron metals, we can consider a chain of Fe\(^{3+}\) ions in a periodic arrangement, for which Heisenberg (1929) proposed a model of spin–spin exchange interaction \( -2J_{mn}s_m \cdot s_n \), where \( J_{mn} \) is the exchange integral. Writing \( 2J_{mn} = J_{nn} \) and considering spins as order variables, the exchange interaction is in the same form as \( -J_{mn}\sigma_m \cdot \sigma_n \), which is convenient to use in this section.

For a chain of magnetic spins \( \sigma_n \) arranged in the direction of magnetization, we apply a uniform magnetic field \( B_o \) in parallel, and write the Hamiltonian for the spin \( \sigma_n \) at site \( n \) as

\[ \mathcal{H}_n = -\sigma_n \cdot B_o - \sum_m J_{mn}\sigma_m \cdot \sigma_n. \]
Here, we can consider that the quantity $\langle \sum m J_{mn} \sigma_m \rangle = B_n$ represents a local magnetic field acting on $\sigma_n$, expressed in the mean-field approximation. Accordingly, in the mean-field approximation we write

$$\langle H_n \rangle = -\langle \sigma_n \rangle \cdot (B_o + \langle B_n \rangle)$$

for discussing magnetic ordering. The average $\langle \sigma_n \rangle$ represents the macroscopic magnetization $M$ of a crystal, for which Weiss postulated the relation $\langle B_n \rangle = \lambda M$ with the proportionality constant $\lambda$, writing a susceptibility formula for $M$ in the effective field $B_o + \lambda M$, i.e.

$$M = \chi_o (B_o + \lambda M), \quad (0.15)$$

where $\chi_o = C/T$ is Curie’s law for paramagnetic susceptibility; $C$ is Curie’s constant. Solving (0.15) for $M$, a ferromagnetic susceptibility formula can be derived as

$$\chi = \frac{M}{B_o} = \frac{C}{T - C\lambda} = \frac{C}{T - T_c} \quad \text{for} \quad T > T_c, \quad (0.16)$$

where $T_c = C\lambda$ is the critical temperature. Equation (0.16) is known as the Curie–Weiss law, applicable for $T > T_c$.

At temperatures below $T_c$, on the other hand, the spin order should be discussed with respect to the order parameter $\eta = (N_+ - N_-)/N$, and the domains $\pm$ are separated by the ordering energy in the mean-field approximation. In this case, the ordering energies of two domains can be expressed as

$$\Delta E_\pm = \pm MB_o + \lambda M^2 = \pm N_\pm \beta B_o + \frac{1}{2} N\beta^2 \eta^2,$$

where $\beta$ is Bohr’s magneton. Similar to the Bragg–Williams theory, the partition function can be written as

$$Z = Z_+ Z_- = \left( \frac{N}{N_+} \right)\left( \frac{N}{N_-} \right) \exp \frac{-(\Delta E_+ + \Delta E_-)}{k_B T},$$

thereby minimizing the free energy $F = -k_B T \ln Z$ to obtain $N_+$ and $N_-$ in equilibrium.

Using the relation $\frac{d}{dN_\pm} \ln \left( \frac{N}{N_\pm} \right) = \frac{d}{dN_\pm} (\mp N_\pm \ln N_+ \pm N_\pm \ln N_-) = \frac{1}{k_B T} \frac{d\Delta E_\pm}{dN}$, we drive

$$\ln \frac{N_-}{N_+} = -\frac{2}{N k_B T} \frac{d\Delta E_\pm}{d\eta}, \quad \text{hence} \quad \ln \frac{1 - \eta}{1 + \eta} = -\frac{2}{k_B T} (\lambda \beta^2 \eta \pm \beta B_o).$$

This equation can be solved for the two domains $\pm$ separately and

$$\eta_\pm = \tanh \left( \frac{\lambda \beta^2 \eta_\pm}{2 k_B T} \mp \frac{\beta B_o}{k_B T} \right) \quad (0.17)$$
Nevertheless, as in the case of $B_0 = 0$, (0.17) can be solved graphically in the same way, as illustrated for $B_0 \neq 0$ in figure 0.3(a). Defining $y' = \frac{2\beta}{k_B T}(\eta_\pm \mp \frac{2B_0}{\beta})$ and $\eta_\pm = \tanh y'$, we discuss the crossing point between these. As seen from the figure, the horizontal coordinate shifts as $\beta' \to \pm \frac{\beta}{k_B T}(B_0)$ by increasing $B_0$. Hence the critical temperature changes as $T_c' \to T_c - (\beta B_0/k_B)$ in both domains, which is however very small in a practical field of $\sim 10^4$ gauss, i.e. $\beta B_0/k_B \sim 1K$.

Assuming $\Delta T_c \sim 0$, we can write $y' = \frac{T_c}{T} \eta'_\pm \mp \frac{\beta B_0}{k_B T}$ to describe the volume variation of domains, which is shown in figure 0.3(b). Here, the difference $y'_+ - y'_- = 2\beta B_0/k_B T$ represents the volume change signified by

$$V'_+ - V'_- \propto \frac{B_0}{T} \quad \text{(0.18)}$$

Domains are thus convertible; it is possible to fabricate a single-domain crystal by applying $B_0$ externally.

The probability and Weiss’s adiabatic field defined above are basic concepts in the statistical theory applied to crystalline transitions, which however need to be re-evaluated for phenomena on a mesoscopic timescale. Further, a remark can be made at this point that is about the homogeneity of the internal field, which is important for practical experiments.

In the foregoing ferromagnetic crystals, we considered one-dimensional magnet to simplify complex interactions in three-dimensional structure. This assumption can be justified in a macroscopic crystal of ellipsoidal shape that can be magnetized uniformly by a constant applied field [7].

Thermodynamically, applying $B_0$ is regarded for an external adiabatic potential energy $-M \cdot B_0$ as adequate for dielectric crystals as well. However, isotropic $-p\Delta V$ must always be considered for all materials including polarizable crystals. A single crystal in a particular symmetry at a given temperature is characterized as macroscopically uniaxial, so that $p\Delta V = -pA\Delta x$ is the adiabatic potential, where $A$ and $\Delta x$ are the surface area and its displacement, respectively, equivalent geometrically.

Figure 0.3. (a) A $\eta$--$y'$ plot of magnetic order in the presence of an applied magnetic field $B_0 \propto \eta_0$ to be compared with figure 0.1. (b) Domain-volumes $V'_+$ and $V'_-$, varying with an applied field $B_0$. 

Solitons in Crystalline Processes

0-13
to an ellipsoidal crystal. Nevertheless, adiabatic work such as \(-p\Delta V\) for an isothermal process is not necessary to consider, if holding the relation \(\Delta V = 0\). In contrast, the condition \(\Delta V \neq 0\) is unavoidable or technically difficult to maintain, but significant under external pressure. Accordingly, statistical quantities of the probability and Weiss field need to be redefined to be valid in finite crystals.

### Exercises

1. Discuss the Ehrenfest classification of phase transitions with respect to microscopic order variables, and show that their fluctuations should exist during transition.
2. Argue that the dynamical system representing crystals in equilibrium with the surroundings must be conservative in nature.
3. Discuss the Weiss field. Is Weiss’ mean-field definition an acceptable idea? If not, why?
4. Why do we have to use the Gibbs function if order variables are active? Can we not assume a constant volume in this case? In fact, the Bragg–William theory assumed \(dV = 0\), which seems to be conflicting. Discuss.
5. Why do we need the field-theoretical approximation for the thermodynamics of solid states?

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