

## Order Variables, Their Correlations and Statistics: the Mean-Field Theory

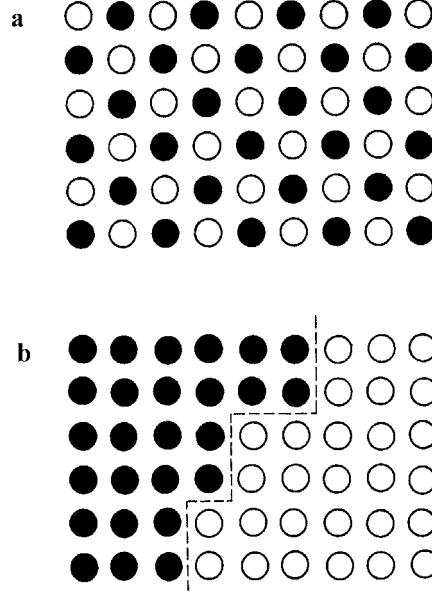
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### 2.1 Order Variables

In Chapter 1, we defined the order parameter as a macroscopic variable that signifies phase transitions. Originating from microscopic variables  $\sigma_m$  attached to ions or molecules *active* at lattice sites  $m$ , their *ensemble average* can be considered to represent the macroscopic order parameter  $\eta$ . Needless to say, such an average is meaningful only if the system is regarded as sufficiently uniform. In addition, if varying as functions of space-time coordinates at a long wavelength, such variables  $\sigma_m$  may not be subjected to statistical averaging in an inhomogeneous state of crystals.

In a disordered phase above  $T_c$ , these  $\sigma_m$  are generally in fast random motion, so that the time average  $\langle \sigma_m \rangle_t$  vanishes at each lattice site. In contrast, below  $T_c$ , these variables are in slow correlated motion, where  $\langle \sigma_m \rangle_t$  averaged over the timescale of observation may take a variety of values distributed over the crystal. Furthermore, at temperatures close to  $T_c$ , the crystal is not fully ordered and topologically inhomogeneous, as illustrated in Fig. 2.1, leading to either domains or a sublattice structure with decreasing temperature. Therefore, the ensemble average is valid only if calculated at least for such a subsystem, instead of the whole crystal. Needless to say, observed results should be so interpreted as related to the observing condition.

Although the active group should be identified in a given system, the variable  $\sigma_m$  is not always evident from the chemical formula or unit-cell structure, except for a few simple cases. Pending identification of  $\sigma_m$ , as is often the case, one has to investigate their dynamical behavior in the critical region. For structural phase transitions, these variables  $\sigma_m$  in collective motion play a significant role, constituting a main objective in our studies. We shall hereafter call microscopic  $\sigma_m$  the *order variable* to distinguish it from the corresponding macroscopic order parameter  $\eta$ .



**Fig. 2.1.** Schematic ordered phases of a binary system in two dimensions, where states of constituents are shown by open and filled circles: (a) ordered phase consisting of intermingling sublattices, and (b) ordered phase of two “opposite” domains. Domain boundaries are shown by broken lines.

In the statistical approach, the relation between  $\eta$  and  $\sigma_m$  may be written in the spatial average

$$\eta = \sum_m \langle \sigma_m \rangle_t / N \quad (2.1a)$$

of  $\langle \sigma_m \rangle_t$  in a subsystem of  $N$  lattice sites, provided that  $\sigma_m$  are uncorrelated or only weakly correlated. On the other hand, when locally correlated, the time average should be first calculated for a cluster of correlated  $\sigma_m$ , which is then averaged over the lattice space in the subsystem; namely,

$$\eta = \langle \eta_i \rangle_s = \sum_i \eta_i / N' \quad \text{where} \quad \eta_i = \left\langle \sum_{\text{cluster}} \sigma_m \right\rangle_t, \quad (2.1b)$$

and  $N'$  the number of clusters. Although unspecified, if such correlated clusters are predominant, the state of the subsystem is regarded as thermodynamically uniform, as postulated in the renormalization group theory. Nevertheless, the crystal is generally inhomogeneous during the ordering process, for which we need precise knowledge of correlated  $\sigma_m$  in collective motion.

Ordering processes in crystals are considerably more complex than in isotropic media, since the strained lattice plays a hidden role [15]. The collective mode of  $\sigma_m$  varies at a slow rate, as inferred from critical anomalies observed in experiments with different timescales. Processes in solid states are generally slow, but timescales of observation are not as seriously considered as

in the critical region. In this chapter, we review existing statistical theories on binary systems, which are discussed in light of a slow variation. In solid-states, values of  $\langle \sigma_m \rangle_t$  are usually calculated by using probabilities at sites  $m$ , which are in fact a valid concept in fast processes, where the timescale is assumed as *infinity* with the ergodic hypothesis that is the basis for statistical theories of random processes.

## 2.2 Probabilities, Short- and Long-Range Correlations, and the Mean-Field Approximation

### 2.2.1 Probabilities

In a binary alloy AB such as Cu-Zn ( $\beta$ -brass), spontaneous atomic ordering takes place as the temperature is lowered through  $T_c$ , due to diffusive atomic rearrangement among lattice sites. If such a rearrangement rate is sufficiently fast, as compared with the timescale of observation, we can interpret  $\sigma_m$  as defined by the relation

$$\sigma_m = p_m(A) - p_m(B) \quad (2.2)$$

and

$$p_m(A) + p_m(B) = 1, \quad (2.3)$$

where  $p_m(A)$  and  $p_m(B)$  represent *probabilities* for the site  $m$  to be occupied by an atom A and by B, respectively. Subject to realistic observations, we are, in fact, uncertain whether the rearrangement process occurs at a sufficiently fast rate. Considering thermal rearrangements of individual atoms, the process can be sufficiently fast, but very slow if they are in collective motion. Nevertheless, sufficiently fast rearrangements and a long timescale of observation are assumed for traditional statistical theories to support the probably concept.

In a disordered phase where atoms are uncorrelated, these probabilities can take only two values, either 1 or 0: for example, if the site  $m$  is occupied by an atom A,  $p_m(A) = 1$ , otherwise = 0. In this case, we can also write  $p_m(B) = 0$  or 1, referring to an atom B at a site  $m$ . These probabilities in a disordered state are independent of  $m$  if all lattice sites are occupied by either A or B, and no vacant sites in the crystal. Below  $T_c$ , on the other hand, due to atomic correlations, different sites  $m$  and  $n$  are not independently occupied, for which the probabilities  $p_m(A)$  and  $p_m(B)$  related by (2.2) and (2.3) can take virtually any continuous values between 1 and 0, because of various atomic arrangements in the neighboring sites around the site  $m$ . Accordingly, these probabilities and variable  $\sigma_m$  can be considered as continuous functions of space-time coordinates, which are called *classical variables* to distinguish them from quantum-mechanical variables such as *spins*. It is noted that quantum-mechanical variables are characterized by discrete values

if uncorrelated, although behaving like classical variables if they are heavily correlated.

Signified by such probabilities, order variables  $\sigma_m$  in slow motion are virtually quasi-static, being distributed over lattice sites, although varying at a sufficiently fast rate for time averaging. The order parameter  $\eta$  can then be calculated by (2.1a) as a spatial average called the *mean-field average*. Needless to say, such a mean-field average is meaningful only if the spatial *variance* for distribution is sufficiently small. The validity of such an order parameter is evaluated by the *correlation function* defined by

$$\Gamma(r_{mn}) = \langle (\sigma_m - \eta)(\sigma_n - \eta) \rangle = \langle \sigma_m \sigma_n \rangle - \eta^2 \delta_{mn}, \quad (2.4)$$

where  $r_{mn}$  is the distance between  $\sigma_m$  and  $\sigma_n$ , and for the last expression we have used the relations  $\langle \sigma_m \rangle = \langle \sigma_n \rangle = \eta$ . Here,  $\delta_{mn}$  is the Kronecker delta, whose value is 1 for  $m = n$ , and otherwise it is 0 for  $m \neq n$ . For complete disorder,  $\Gamma(r_{mn}) = 0$  for all pairs for  $m \neq n$ , meaning that  $\sigma_m \sigma_n = 0$  for no correlations.

On the other hand, the correlation function  $\Gamma(r_{mn})$  is nonzero for all pairs in an ordering process, where the product  $\sigma_m \sigma_n$  should be significant. Therefore, the correlation energy can be expressed as proportional to  $\sigma_m \sigma_n$ ; that is

$$E_{mn} = -J_{mn} \sigma_m \sigma_n, \quad (2.5)$$

where the coefficient  $J_{mn}$  is a function of the distance  $r_{mn}$ , representing the magnitude of correlation between  $\sigma_m$  and  $\sigma_n$ . For convenience, the negative sign attached to (2.5) expresses the stable arrangement of  $\sigma_m$  and  $\sigma_n$ , which are correlated at a lower energy. Although assumed for a correlated pair, (2.5) can also be derived directly for a simple system with short-range energies, as shown next.

Writing interaction energies between two atoms at sites  $m$  and  $n$  as  $\epsilon_{AB}(m, n)$ ,  $\epsilon_{AA}(m, n)$  and so forth, the short-range interaction energy  $E_m$  for  $\sigma_m$  can be expressed in terms of probabilities defined by (2.2) and (2.3), namely

$$E_m = \sum_n E_{mn} = \sum_n [p_m(A)\epsilon_{AA}(m, n)p_n(A) + p_m(B)\epsilon_{BB}(m, n)p_n(B) + p_m(A)\epsilon_{AB}(m, n)p_n(B) + p_m(B)\epsilon_{BA}(m, n)p_n(A)], \quad (2.6)$$

Considering that only interactions between nearest neighbors are essential, (2.6) can be simplified, particularly for a cubic lattice where  $r_{mn}$  are all equal, and hence the site specification  $(m, n)$  can be omitted from  $\epsilon_{AB}$ ,  $\epsilon_{AA}$  and  $\epsilon_{BB}$  in (2.6). Further, using (2.2) and (2.3), these probabilities can be replaced by order variables  $\sigma_m$  and  $\sigma_n$ ; namely

$$p_m(A) = \frac{1}{2}(1 + \sigma_m), \quad p_m(B) = \frac{1}{2}(1 - \sigma_m)$$

and

$$p_n(B) = \frac{1}{2}(1 + \sigma_n), \quad p_n(A) = \frac{1}{2}(1 - \sigma_n).$$

Substituting these relations in  $E_{mn}$ , we have

$$\begin{aligned}
 E_{mn} &= \frac{1}{2}(2\varepsilon_{AB} + \varepsilon_A + \varepsilon_B) \\
 &\quad + \frac{1}{4}(\varepsilon_{AA} - \varepsilon_{BB})(\sigma_m + \sigma_n) \\
 &\quad + \frac{1}{4}(2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB})\sigma_m\sigma_n \\
 &= \text{const.} - K(\sigma_m + \sigma_n) - J\sigma_m\sigma_n,
 \end{aligned} \tag{2.7}$$

where

$$K = \frac{1}{4}(\varepsilon_{AA} - \varepsilon_{BB}) \quad \text{and} \quad J = \frac{1}{4}(\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB}).$$

Here, the parameter  $J$  represents the magnitude of binary correlations with the nearest neighbors, corresponding to  $J_{mn}$  in (2.5). On the other hand, the factor  $K$  can be zero, if  $\varepsilon_{AA} = \varepsilon_{BB}$ , as in most binary systems, while  $K \approx 0$  for alloys of similar atoms for which  $\varepsilon_{AA} \approx \varepsilon_{BB}$ , and hence the term of  $K$  is generally insignificant. The first constant term in (2.7) is independent of order variables, and hence insignificant. In this way, the equation (2.7) has been confirmed as essentially the same as (2.5).

### 2.2.2 The Concept of a Mean Field

Order variables  $\sigma_m$  in crystals were defined as statistical variables, using occupation probabilities at lattice sites, as given by (2.2). Correlations among these variables at lattice sites are basically molecular interactions in short-ranges, which can be interpreted in terms of probabilities for *like* or *unlike* arrangements of atoms, although their ranges are not specified in (2.7). Nevertheless, writing

$$E_m = -\sigma_m \left( \sum_n J_{mn} \sigma_n \right),$$

the quantity  $\sum_n J_{mn} \sigma_n = F_m$  can be considered as the internal field acting on  $\sigma_m$  when summed over effective ranges of  $r_{mn}$ , i.e.  $E_m = -\sigma_m F_m$ . Taking distances  $r_{mn}$  for the nearest and next-nearest neighbors, the correlation energy  $E_m$  is called the *short-range interaction energy* at  $m$ . Statistically, we may proceed to calculate the time average  $\langle F_m \rangle_t$  as the effective local field at site  $m$  below  $T_c$ . Then, the spatial average of these  $\langle F_m \rangle_t$  can be calculated over the whole subsystem to obtain the effective macroscopic field. In the mean-field approximation, such a *long-range average* can be considered as a meaningful quantity for a system that obeys thermodynamic principles. An ordered system can therefore be characterized by the presence of such a macroscopic internal field  $F = \langle F_m \rangle_s = \sum_m \langle F_m \rangle_t / \mathbf{N}$  in mean-field approximation.

We can also express such probabilities by long-range averages, that is

$$p(A) = \langle p_m(A) \rangle_s \quad \text{and} \quad p(B) = \langle p_m(B) \rangle_s,$$

for which the relation  $p(A) + p(B) = 1$  holds at all sites. For a binary system, the order parameter can be defined for the two subsystems as

$$\eta_1 = \eta = p(A) - p(B)$$

and

$$\eta_2 = -\eta = p(B) - p(A).$$

It is noted in general that  $1 \geq \eta_1 \geq 0$  and  $0 \geq \eta_2 \geq -1$ , where  $1 \geq p(A)$ ,  $p(B) \geq 0$ . For complete disorder,  $\eta_1 = \eta_2 = 0$ , and so  $p(A) = p(B) = \frac{1}{2}$ . On the other hand, for complete order,  $\eta_1 = 1$  and  $\eta_2 = -1$ , which correspond to  $p(A) = 1$ ,  $p(B) = 0$  and  $p(B) = 1$ ,  $p(A) = 0$ , respectively.

If long-range correlations are significant, the binary ordering in an alloy AB can simply be interpreted in terms of average probabilities  $p(A)$  and  $p(B)$  in the mean-field accuracy. If  $J > 0$ , two attracting *unlike* atoms at shortest distances lower the interaction energy by  $-J$ , whereas repelling *like* pairs are unstable by the amount  $+J$  in the same domain. On the other hand, two intermingling sublattices can be stabilized in anti-ordered crystal. In the former case, considering only nearest neighbors, the average number of interacting A-B and B-A pairs can be expressed by  $2\mathbf{N}zp(A)p(B)$ , where  $z$  is the number of lattice sites in the shortest distance and  $\mathbf{N} = \frac{1}{2}N$  is the total number of sites in each domain. Therefore, the number of unlike pairs and the corresponding interaction energy are given by

$$N_{AB} = 2\mathbf{N}p(A)p(B) = \frac{1}{2}Nz(1 - \eta^2)$$

and the total ordering energy is

$$E = E_1 + E_2 = \text{const.} + 2J\{\frac{1}{2}Nz(1 - \eta^2)\} = \text{const.} + \frac{1}{2}NzJ(1 - \eta^2), \quad (2.8)$$

which are consistent with  $N_{AB} = \frac{1}{2}Nz$  and  $E = \text{const.} + \frac{1}{2}NzJ$  in the disordered state for  $\eta = 0$ . It is interesting to note that in complete order,  $\eta = \pm 1$  determined from  $N_{AB} = 0$ ,  $E = \text{const.}$ , and the energy difference between ordered and disordered states, i.e.  $-\frac{1}{2}NzJ$ , represents the amount of macroscopic energy lowered from the disordered state. During the ordering process, the energy resulted from partial order is therefore given by the  $\eta$ -dependent term in (2.8), i.e.

$$\Delta E = -\frac{1}{2}NzJ\eta^2, \quad (2.9)$$

which is negative in both domains, representing the correlation energy averaged in the mean-field approximation. Bragg and Williams used (2.9) for their statistical theory of binary alloys, as outlined in Section 2.3.

In the mean-field approximation, mutual interaction energies are averaged in space of the entire system, which is represented by a single internal variable  $\eta$ . Although inadequate for the critical region, the dynamical response to an applied field or stress  $F$  can be estimated as due to the energy  $-\alpha\eta F$ , where  $\alpha$  is a constant. By analogy with the Weiss field in a ferromagnet, we rewrite (2.9) by using the effective internal field  $F_{\text{int}}$  as

$$\Delta E = -\alpha\eta F_{\text{int}},$$

where

$$F_{\text{int}} = \left( \frac{NzJ}{2\alpha} \right) \eta \quad (2.10)$$

with the factor  $\alpha$  used for adjusting units. Like the magnetic Weiss field  $\mathbf{B}_{\text{int}} = \lambda \mathbf{M}$ , the field  $F_{\text{int}}$  is not directly measurable under normal circumstances. However, it is significant that such  $F_{\text{int}}$  can be combined with an external field  $F$ , when dealing with the response of order variables to  $F$ . In this context, the Weiss field is not a mere theoretical concept, but representing a real internal field in an ordered phase. In fact, as will be discussed in Chapter 9, the internal electric field  $F_{\text{int}}$  in some ferroelectric crystals was detected by dipolar paramagnetic probes in magnetic resonance experiments.

## 2.3 Statistical Mechanics of an Order-Disorder Transition

The long-range order is a concept first introduced by Bragg and Williams in their statistical theory of binary alloys. They considered that thermal properties of a partially ordered alloy can be specified by the order parameter  $\eta$  and the macroscopic correlation energy  $-E(\eta)$ , postulating that the ordering system is a *canonical ensemble* governed by statistical principles. Statistically, correlated A-B pairs at the nearest-neighbor sites are responsible for such an ordered state, which occurs in a large number of combinations  $g(\eta)$ . Such a large “degeneracy” of the energy  $-E(\eta)$  corresponds to the entropy  $S(\eta) = k_B \ln g(\eta)$  under a constant-volume condition, and we minimize the Helmholtz free energy  $F(\eta) = E(\eta) - TS(\eta)$  to obtain the equilibrium value of  $\eta$  at a given temperature  $T$ .

In a single-domain crystal, in order for  $N$  lattice sites to be occupied by either A or B atoms with no vacancies, the combination number is given by

$$g(\eta) = \binom{N}{Np(A)} \binom{N}{Np(B)} = \binom{1}{\frac{1}{2}(1+\eta)} \binom{1}{\frac{1}{2}(1-\eta)}.$$

The free energy can be expressed with the partition function

$$Z(\eta) = Z(0)g(\eta) \exp(\tfrac{1}{2}NzJ\eta^2/k_B T),$$

as

$$F(\eta) = -k_B T \ln Z(\eta) = E(\eta) - k_B T \ln g(\eta).$$

From the condition  $(\partial F/\partial \eta)_V = 0$ , we obtain

$$\frac{\partial}{\partial \eta} \left\{ \ln Z(0) + \ln g(\eta) + \tfrac{1}{2} \frac{NzJ\eta^2}{k_B T} \right\} = 0.$$

Using the Stirling formula for a large  $N$ , the term  $\ln g(\eta)$  can be evaluated approximately using

$$\frac{\partial \ln g(\eta)}{\partial \eta} = -\frac{N}{2} \ln \frac{1+\eta}{1-\eta}.$$

Hence, the equilibrium order parameter at  $T$  can be determined from the equation

$$\frac{zJ}{k_B T} \eta = \ln \frac{1 + \eta}{1 - \eta},$$

or

$$\eta = \tanh \frac{zJ\eta}{2k_B T}. \quad (2.11)$$

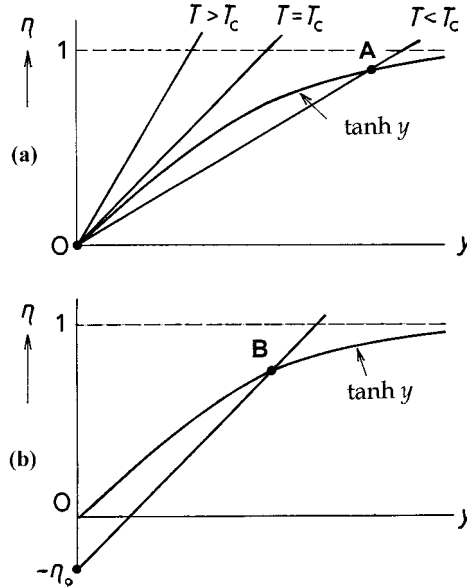
Equation (2.11) can be solved graphically by finding the intersection between the straight line

$$y = \frac{zJ}{2k_B T} \eta$$

and the curve

$$\eta = \tanh y$$

in the  $\eta$ - $y$  plane, as illustrated in Fig. 2.2a. Here, we note that if  $2k_B T/zJ \geq 1$ , only the origin  $\eta = 0$  is the intersection, whereas for  $2k_B T/zJ < 1$ , another intersection is found at  $\eta$  in the range  $0 < \eta \leq 1$ , representing partial order with the limit of  $\eta \rightarrow 1$  as complete order. In this diagram, the transition



**Fig. 2.2.** (a) Graphical solutions for the spontaneous order parameter. The straight line  $y = (zJ/2k_B T)\eta$  intersects the curve  $\eta = \tanh y$  at a point A to give a real solution  $\eta \neq 0$  if  $T > T_c$ , whereas the only intersection is  $\eta = 0$ , if  $T < T_c$ . (b) Graphical solutions for ferromagnetic order. The intersection B is always present between the straight line  $y = (T/T_c)\eta - \eta_0$  and the curve  $\eta = \tanh y$  below  $T_c$ , but no solution above  $T_c$ .



between disordered to ordered states can be specified as  $2k_B T_c / zJ = 1$ , where the unit slope at the origin gives the transition temperature  $T_c$ , namely

$$T_c = zJ/2k_B. \quad (2.12a)$$

Writing  $y = (T/T_c)\eta$ , from (2.11) we have

$$\frac{T}{T_c} \eta = \tanh^{-1} \eta \approx \eta + \eta^3/3$$

for a small  $\eta$ , from which an approximate relation

$$\eta^2 \approx \frac{3(T_c - T)}{T_c} \quad \text{for } T < T_c \quad (2.12b)$$

can be derived. Hence for a small  $\eta$ , the order parameter shows a parabolic temperature-dependence, which is a consequence of the mean-field approximation.

The heat capacity for ordering can be calculated easily with the above results; that is

$$C_V = \frac{\partial E(\eta)}{\partial T} = \frac{dE}{d\eta} \cdot \frac{d\eta}{dT} = (-NzJ\eta) \left( -\frac{3}{2T_c\eta} \right) = 3Nk_B,$$

when  $T_c$  is approached closely from below. In the disordered phase,  $C_V = 0$  as  $\eta = 0$ , and, hence, the discontinuity at  $T_c$  is  $\Delta C_V = 3Nk_B$ .

## 2.4 The Ising Model for Spin-Spin Correlations

In ferromagnetic crystals, internal magnetic interactions are quantum mechanical, and expressed by the Heisenberg exchange energy between spins  $\mathbf{s}_m$  and  $\mathbf{s}_n$ , i.e.

$$\mathbf{H}_{mn} = -2J_{mn} \mathbf{s}_m \cdot \mathbf{s}_n, \quad (2.13)$$

where  $J_{mn}$  is the exchange integral between unpaired electrons of magnetic ions (3d electrons in iron-group ions) at lattice sites  $m$  and  $n$ . In a *uniaxial* magnetic crystal characterized by the unique  $z$  axis, the spin vectors are primarily in *precession* at a constant frequency  $\omega_m$  around the axis  $z$ , keeping the components  $s_{mz}$  constant all the time, provided that the spin-spin interactions due to the terms  $s_{mx}s_{nx} + s_{my}s_{ny}$  in (2.13) are treated as perturbations. In this case, known as the *random phase approximation*, the spin-spin correlations are described by the time average  $\langle \mathbf{H}_{mn} \rangle_t$  calculated over the timescale  $t_o$  of observation. Namely,

$$\langle \mathbf{H}_{mn} \rangle_t = -2J_{mn} [s_{mz}s_{nz} + \langle s_{mx}s_{nx} + s_{my}s_{ny} \rangle_t],$$

where the second term vanishes if  $2\pi/\omega_m$  and  $2\pi/\omega_n$  are both shorter than  $t_o$ . It is noted that if these *precessions* can be assumed at random in phase, we can write in the zero order

$$\langle \mathbf{H}_{mn} \rangle_t = -2J_{mn}s_{mz}s_{nz}, \quad (2.14)$$

where only  $z$  components of spin vectors are significant. Known as the *Ising* model [16], (2.14) is essentially due to random phases in spin precessions, where  $s_{mz}$  can be related to probabilities for two quantum states  $\pm \frac{1}{2}$  of a spin at site  $m$ , analogous to the classical binary variable for ordering. Representing occupation probabilities of the spin states, such an interpretation of spin components  $s_{mz}$  provides a useful classification of magnetic ordering in various types, antiferro-, ferri-, spiral- and other kinds of order. Although unspecified in the above, we have considered that the origin for a unique  $z$ -axis is generally attributed to the significant magnetic anisotropy in a given crystal.

Here, we have discussed the Ising model for a simplified ferromagnetic system, but the idea for such an Ising spin can be applied to other binary systems as well. For example, in binary alloys where diffusive atomic rearrangements are responsible for ordering, Ising's spins can be used for the statistical description. At a site  $m$ , the classical spin variable  $s_{mz}$  can be specified by the state

$$|m\rangle = a_m|+\frac{1}{2}\rangle + b_m|-\frac{1}{2}\rangle, \quad (2.15a)$$

where  $|\pm \frac{1}{2}\rangle$  are the wavefunctions for an uncorrelated spin  $\mathbf{s}_m$ , and the coefficients  $a_m$  and  $b_m$  are normalized as

$$a_m^2 + b_m^2 = 1. \quad (2.15b)$$

In this case,  $a_m^2$  and  $b_m^2$  are interpreted as the probabilities for the site  $m$  to be occupied by  $+\frac{1}{2}$  and  $-\frac{1}{2}$  spins, i.e.  $p(+\frac{1}{2})$  and  $p(-\frac{1}{2})$ , respectively. We can therefore define the order variable by

$$\sigma_m = a_m^2 - b_m^2. \quad (2.15c)$$

Assuming nearest-neighbor interactions, the short-range interaction energy is expressed as

$$\begin{aligned} E_m &= \sum_n \langle m, n | \mathbf{H}_{mn} | m, n \rangle \\ &= -2J \sum_n [a_m^2 a_n^2 \langle ++ | s_{mz}s_{nz} | ++ \rangle + b_m^2 b_n^2 \langle -- | s_{mz}s_{nz} | -- \rangle \\ &\quad + a_m^2 b_n^2 \langle +- | s_{mz}s_{nz} | +- \rangle + b_m^2 a_n^2 \langle -+ | s_{mz}s_{nz} | -+ \rangle], \end{aligned}$$

where we have considered  $z = 8$  and  $J_{mn} = J$  for a cubic lattice. For spins  $\frac{1}{2}$ , these matrix elements are

$$\langle ++ | s_{mz}s_{nz} | ++ \rangle = \langle -- | s_{mz}s_{nz} | -- \rangle = \frac{1}{4}$$

and

$$\langle + - | s_{\text{mz}} s_{\text{nz}} | + - \rangle = \langle - + | s_{\text{mz}} s_{\text{nz}} | - + \rangle = -\frac{1}{4},$$

hence

$$\begin{aligned} E_{\text{m}} &= -2J \sum_{\text{n}} \left[ \frac{1}{4} (a_{\text{m}}^2 a_{\text{n}}^2 + b_{\text{m}}^2 b_{\text{n}}^2) - \frac{1}{4} (a_{\text{m}}^2 b_{\text{n}}^2 + b_{\text{m}}^2 a_{\text{n}}^2) \right] \\ &= -2J \sum_{\text{n}} \left[ \frac{1}{4} (a_{\text{m}}^2 - b_{\text{m}}^2) (a_{\text{n}}^2 - b_{\text{n}}^2) \right] = -\frac{1}{2} \sigma_{\text{m}} \sum_{\text{n}} J \sigma_{\text{n}}. \end{aligned}$$

Replacing the factor  $\frac{1}{2}J$  by  $2J_{\text{mn}}$ , we can write  $E_{\text{mn}} = -J_{\text{mn}} \sigma_{\text{m}} \sigma_{\text{n}}$ , which is identical to (2.5). In contrast to the spin  $s_{\text{mz}}$  with two states  $|\pm \frac{1}{2}\rangle$ , the binary order variable  $\sigma_{\text{m}}$  is characterized by two values of probabilities  $\pm 1$ , and called the *pseudospin*.

Considering the sum  $F_{\text{m}} = \sum_{\text{n}} J \sigma_{\text{n}}$  for the local field at a site m, and the spatial average  $F_{\text{int}} = \langle F_{\text{m}} \rangle$  represents the the internal field at all sites in the crystal in the mean-field approximation. Therefore,

$$\langle E_{\text{m}} \rangle = -\frac{1}{2} \mathbf{N} F_{\text{int}} \left\langle \sum_{\text{m}} \sigma_{\text{m}} \right\rangle = -\frac{1}{2} \mathbf{N} F_{\text{int}} \eta,$$

where

$$F_{\text{int}} = \left\langle J \sum_{\text{n}} \sigma_{\text{n}} \right\rangle = J \eta. \quad (2.16)$$

The internal ordering energy in each of two domains can then be expressed by the identical formula, that is

$$E_1(\eta) = E_2(-\eta) = \langle E_{\text{m}} \rangle = -\frac{1}{2} \mathbf{N} J \eta^2 = -\frac{1}{4} N J \eta^2.$$

Accordingly, the internal energy of the whole crystal is

$$E = E_1(\eta) + E_2(-\eta) = -\frac{1}{2} N J \eta^2.$$

In conventional notations,  $s_{\text{mz}} = \frac{1}{2} \sigma_{\text{m}}$ , the magnetic moment and the internal magnetic field are expressed as  $\mu_{\text{m}} = g\beta s_{\text{mz}}$  and  $B_{\text{mz}} = (2/g\beta) \langle F_{\text{m}} \rangle$ , thereby writing  $E = -M B_{\text{int}}$ , where  $B_{\text{int}}$  is the Weiss field and  $M$  is the macroscopic magnetization. Although derived from magnetic spins with random phase approximation, the Ising spin  $\sigma_{\text{m}}$  defined by (2.15c) can be conveniently used to describe any binary correlations, whenever probabilities matter.

## 2.5 The Role of the Weiss Field in an Ordering Process

In the mean-field approximation, spontaneous ordering signified by  $\eta$  can be considered as induced by the Weiss internal field  $F_{\text{int}}$ , both  $\eta$  and  $F_{\text{int}}$  emerging at  $T_{\text{o}}$ , whose magnitudes increase with decreasing temperature. Although derived specifically for binary alloys, (2.11) can be modified with binary probabilities  $p(\pm 1)$  for Ising's spin states  $\pm 1$  that can be expressed by the Boltzmann statistics, as shown below. Considering the internal field  $F_{\text{int}}$  of (2.10)

where  $\alpha$  is set equal to 1 for simplicity, (2.11) is written as

$$\begin{aligned}\eta &= \tanh \left[ \frac{zJ}{2k_B T} \eta \right] = \tanh \left( \frac{F_{\text{int}}}{k_B T} \right) \\ &= \left[ \exp \left( + \frac{F_{\text{int}}}{k_B T} \right) - \exp \left( - \frac{F_{\text{int}}}{k_B T} \right) \right] / Z,\end{aligned}$$

where

$$Z = \exp \left( + \frac{F_{\text{int}}}{k_B T} \right) + \exp \left( - \frac{F_{\text{int}}}{k_B T} \right)$$

is the partition function for energies  $\pm F_{\text{int}}$  of the Ising spin  $\sigma = \pm 1$  in the field  $F_{\text{int}}$ . Hence, in the mean-field theory, the order parameter  $\eta$  is determined by the difference of the Boltzmann probabilities  $p(+1) = Z^{-1} \exp(+F_{\text{int}}/k_B T)$  and  $p(-1) = Z^{-1} \exp(-F_{\text{int}}/k_B T)$  for these states, i.e.  $\eta = p(+1) - p(-1) = \langle \sigma_m \rangle_s$ . It is notable that in the mean-field approximation the spatial average is determined by the thermal average of pseudospin energy in the internal field  $F_{\text{int}}$ , although  $F_{\text{int}}$  may remain as a conjecture unless supported by experimental evidence.

In a uniaxial ferromagnet, the order parameter is given by the average of pseudospins, i.e.  $\eta = \langle \sigma_m \rangle_s$ , and the internal energy is  $-\frac{1}{2} \mathbf{N} z J \eta^2$ . Applying a magnetic field  $B_o$ , the internal energy in each domain can be written as

$$E_1(+\eta) = -\frac{1}{2} \mathbf{N}_1 z J \eta^2 - \mathbf{N}_1 (g\beta\eta) B_o$$

and

$$E_2(-\eta) = -\frac{1}{2} \mathbf{N}_2 z J \eta^2 + \mathbf{N}_2 (g\beta\eta) B_o,$$

where  $\mathbf{N}_1$  and  $\mathbf{N}_2$  are not equal to  $\frac{1}{2}N$ . Therefore, we can write the internal energies per order variable as  $\epsilon_+ = E_1(+\eta)/\mathbf{N}_1$  and  $\epsilon_- = E_2(-\eta)/\mathbf{N}_2$ ; that is,

$$\epsilon_+ = -\frac{1}{2} z J - g\beta B_o \quad \text{and} \quad \epsilon_- = -\frac{1}{2} z J + g\beta B_o.$$

We may consider the probabilities for these states as given by the Boltzmann statistics, i.e.

$$p(+1) = Z^{-1} \exp \left( - \frac{\epsilon_+}{k_B T} \right) \quad \text{and} \quad p(-1) = Z^{-1} \exp \left( - \frac{\epsilon_-}{k_B T} \right),$$

where

$$Z = \exp \left( - \frac{\epsilon_+}{k_B T} \right) + \exp \left( - \frac{\epsilon_-}{k_B T} \right).$$

Accordingly,

$$\frac{p(+1)}{p(-1)} = \exp \frac{zJ\eta + 2g\beta B_o}{k_B T} = \frac{1+\eta}{1-\eta},$$

where the last expression was derived from the definition of  $p(\pm 1)$  in Section 2.2. From this relation, we obtain

$$\eta = \tanh \frac{\frac{1}{2} z J \eta + g\beta B_o}{k_B T}, \quad (2.17)$$

which is the equation to be solved for  $\eta$  in the field  $B_o$ . Equation (2.17) can be solved for  $\eta$  in exactly the same manner as (2.11), by finding graphically the intersection between the straight line

$$y = \left( \frac{zJ}{2k_B T} \right) \eta + \frac{g\beta B_o}{k_B T}$$

and the curve  $y = \tanh^{-1} \eta$ . Writing  $zJ/2k_B = T_c$  as defined in (2.12a), these are reexpressed as

$$\eta = \left( \frac{T}{T_c} \right) y - \frac{g\beta B_o}{k_B T} \quad \text{and} \quad \eta = \tanh y. \quad (2.18)$$

Figure 2.2b illustrates these intersecting lines in the  $\eta$ - $y$  plane, where the straight one at  $T = T_c$  intersects the  $\eta$  axis at  $\eta_o = -g\beta B_o/k_B T_c$ , which is numerically very small in practical cases. For example, for  $\beta = 1$  Bohr's magneton, assuming  $B_o = 3$  weber/m<sup>2</sup> at  $T_c \sim 10^3$  K in a typical ferromagnet,  $\eta_o$  is only of the order of  $10^{-2}$ . It is noted that in the presence of  $B_o$  (2.18) has always a real solution at all temperatures, and hence there is no critical temperature, although  $\eta$  is singular at  $T_c$  if  $B_o = 0$ .

Above  $T_c$ , when the temperature is close to  $T_c$ , we can set  $y \approx \eta$  and  $T = T_c$  in (2.18), and obtain

$$\eta = \frac{T}{T_c} \eta - \frac{g\beta B_o}{k_B T_c},$$

which is the Curie-Weiss formula as written in the form

$$\chi = \frac{Ng\beta}{2B_o} \cdot \eta = \frac{C}{T - T_c}, \quad \text{where} \quad C = \frac{Ng^2\beta^2}{2k_B}.$$

While substantiated only in ferroelectric crystals, from the above discussion we have the reason to believe that the Weiss field is a real internal field in the mean-field accuracy in ordered magnetic crystals as well.

We have so far reviewed statistical theories of binary ordering with the mean-field approximation, which can be described in terms of the Ising spin  $\sigma_m$  located at a lattice site  $m$ . It is noted that such statistical variables defined at lattice points may not necessarily be periodic functions of the lattice if their correlations are insignificant. Furthermore, in the mean-field theory, all  $\sigma_m$  are represented by the spatial average  $\langle \sigma_m \rangle_s$ , making the crystal of a uniform substance, thereby their ordering appears to have nothing to do with the lattice structure. In this section, we have in fact shown that binary values of the  $\langle \sigma_m \rangle_s$  are determined the Boltzmann probabilities, implying that the ordering is a thermal process at a given temperature. Although the role of lattice is implicit in the statistical argument, we realize that the thermal accessibility of these states should be attributed to random collisions with phonons, thereby contributing to the free energy as expressed by  $TdS$  under a constant-volume condition.

On the other hand, the failure of the mean-field theory in the critical region signifies that the ordering process is slow in the timescale of observation, where the probability cannot be a meaningful concept. Instead, in so-called *displacive* systems, collective displacements prevail in the critical region, as will be discussed in Chapter 3. Unlike the Ising spin  $\sigma_m$  for probabilities, such displacement vectors at lattice sites can violate translational symmetry of the lattice, generating strains if they are correlated *incommensurately* and, hence, responsible for a symmetry change at  $T_c$ . Below  $T_c$ , the free energy should, therefore, change by an internal *mechanical work*  $dW$ , resulting in the ordered crystal with a deformed lattice.

In the lattice dynamical theory, it is known that in normal crystals, there are three independent acoustic modes at long wavelengths, in addition to a large number of high-frequency modes, representing thermal vibrations of the lattice. In this context, these lattice modes in different categories can be responsible for a change of the Gibbs free energy under given external variables  $p$  and  $T$ , where mechanical and thermal contributions are expressed by the terms  $dW$  and  $TdS$ , respectively. We discuss such order variables in displacive systems in Chapter 3.



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