On Fluctuations in Cooperative Phenomena

by

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1. Introduction

Previously, in a series of papers, a group including one of the authers has shown that almost all of the conventional theoretical results on fluctuations from the steady state in a nuclear reactor can be obtained more generally by applying Lax's general theory[1] on the fluctuations from steady state to the fluctuation problem in the number of neutrons in the reactor.[2,3,4,5]

On the other hand, in general, most results in statistical mechanics has related to the first moment in the sense of stochastic process and only a few is concerned with the second moment, that is, the fluctuation problem. At present, the interest in the fluctuation problem is rapidly growing in some fields including nucleonics and electronics, in particular, with respect to phenomena involving critical states in some sense.

Here, we consider the order-disorder transition in binary alloys and para-magnetism-ferromagnetism transition in magnetic materials both being typical of phase transition phenomena, by applying Lax's procedure. Though, of course, the famous treatments by Bragg-Williams[6,7] for the former and by Curie-Weiss[8,9] for the later are well known, their treatments are concerned only with the first moment in the above sense. Application of Lax's procedure brings about simultaneously not only the results in complete agreement with them in the first moment but also the fluctuation behaviors in the second moment which they did not consider.

According to Lax's theory, when there is a set of discrete variables $\boldsymbol{a}$ whose steady state values and their fluctuations are $\boldsymbol{a}_0$, and $\boldsymbol{\alpha}$, respectively, if the system

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has the Markoffian charactor, the distribution function $P(\boldsymbol{a}, t)$ of $\boldsymbol{a}$ at time t obeys an equation of the form

$$P(\boldsymbol{a}, t+\Delta t) = \sum_{a} P(\boldsymbol{a}', t)\, P(\boldsymbol{a}' \mid \boldsymbol{a}, \Delta t) \tag{1.1}$$

where, $P(\boldsymbol{a}'|\boldsymbol{a}, \Delta t)$ is the probability of a transition from $\boldsymbol{a}'$ to $\boldsymbol{a}$ in time Δt. The transition probability is assumed known and must obey the normalization and initial conditions

$$\sum_{a} P(\boldsymbol{a}' \mid \boldsymbol{a}, \Delta t) = 1 \tag{1.2}$$

$$P(\boldsymbol{a}' \mid \boldsymbol{a}, 0) = \delta(\boldsymbol{a}, \boldsymbol{a}') \tag{1.3}$$

where $\delta(\boldsymbol{a}, \boldsymbol{a}') = 1$ for $\boldsymbol{a} = \boldsymbol{a}'$ and 0 otherwise is a Kronecker delta function.

As a consequence, any moment of $\boldsymbol{a}-\boldsymbol{a}'$ taken with respect to $P(\boldsymbol{a}'|\boldsymbol{a}, \Delta t)$ vanishes when $\Delta t \to 0$. We assume that the first two moments are expandable in powers of Δt; therefore, for small Δt

$$\sum_{a} P(\boldsymbol{a}' \mid \boldsymbol{a}, \Delta t)\, (\boldsymbol{a} - \boldsymbol{a}') = \boldsymbol{A}(\boldsymbol{a}')\, \Delta t \tag{1.4}$$

$$\sum_{a} P(\boldsymbol{a}' \mid \boldsymbol{a}, \Delta t)\, (\boldsymbol{a} - \boldsymbol{a}')\, (\boldsymbol{a} - \boldsymbol{a}') = 2\boldsymbol{D}(\boldsymbol{a}')\, \Delta t \tag{1.5}$$

then, we obtain

$$\frac{d\langle \boldsymbol{a}(t) \rangle}{dt} = \langle \boldsymbol{A}[\boldsymbol{a}(t)] \rangle \tag{1.6}$$

and,

$$\frac{d\langle \boldsymbol{a}(t)\boldsymbol{a}(t) \rangle}{dt} = 2\langle \boldsymbol{D}(\boldsymbol{a}) \rangle + \langle \boldsymbol{A}(\boldsymbol{a})\boldsymbol{\alpha} \rangle + \langle \boldsymbol{\alpha}\boldsymbol{A}(\boldsymbol{a}) \rangle \tag{1.7}$$

where $<\ldots\ldots>$ represents an ensamble average. Furthermore, if the system can be handled by a quasi-linear treatment, we may write the form by substituting $\boldsymbol{a} = \boldsymbol{a}_0 + \boldsymbol{\alpha}$ to Eqs. (1.6) and (1.7) and retaining only the non-vanishing terms of lowest order,

$$\boldsymbol{A}(\boldsymbol{a}) \simeq \boldsymbol{A}(\boldsymbol{a}_0) - \boldsymbol{\Lambda}\boldsymbol{\alpha} \tag{1.8}$$

$$\boldsymbol{D}(\boldsymbol{a}) \simeq \boldsymbol{D}(\boldsymbol{a}_0) \equiv \boldsymbol{D} \tag{1.9}$$

The steady state values $\boldsymbol{a}_0$ are determined

$$\boldsymbol{A}(\boldsymbol{a}_0) = 0 \tag{1.10}$$

and therefore the first two moments as to $\boldsymbol{\alpha}$ are

$$\frac{d\langle\boldsymbol{\alpha}\rangle}{dt} = -\boldsymbol{\Lambda}\langle\boldsymbol{\alpha}\rangle \tag{1.11}$$

and

$$\frac{d\langle\boldsymbol{\alpha\alpha}\rangle}{dt} = 2\boldsymbol{D} - \boldsymbol{\Lambda}\langle\boldsymbol{\alpha\alpha}\rangle - \langle\boldsymbol{\alpha\alpha}\rangle\boldsymbol{\Lambda}^{\dagger} \tag{1.12}$$

where $\boldsymbol{\Lambda}^{\dagger}$ is the transpose of $\boldsymbol{\Lambda}$. The steady state moments $<\boldsymbol{\alpha\alpha}>$ then can be obtained by solving the equation

$$2\boldsymbol{D} = \boldsymbol{\Lambda}\langle\boldsymbol{\alpha\alpha}\rangle + \langle\boldsymbol{\alpha\alpha}\rangle\boldsymbol{\Lambda}^{\dagger} \tag{1.13}$$

Especially, if the system has microscopic time reversibility from Onsager's relation

$$\langle\boldsymbol{\alpha\alpha}\rangle\,\boldsymbol{\Lambda}^{\dagger} = \boldsymbol{\Lambda}\langle\boldsymbol{\alpha\alpha}\rangle \tag{1.14}$$

then

$$\langle\boldsymbol{\alpha\alpha}\rangle = \boldsymbol{\Lambda}^{-1}\boldsymbol{D} = \boldsymbol{D}(\boldsymbol{\Lambda}^{\dagger})^{-1} \tag{1.15}$$

where $\boldsymbol{\Lambda}^{-1}$ is the reciprocal matrix of $\boldsymbol{\Lambda}$. For those problems in which the transition probability is itself expandable in Δt

$$P(\boldsymbol{a}' \mid \boldsymbol{a}, \Delta t) = \delta(\boldsymbol{a}, \boldsymbol{a}')\,(1 - \Gamma_a \Delta t) + w_{aa'}\Delta t \tag{1.16}$$

we have

$$\boldsymbol{A}(\boldsymbol{a}') = \sum_a (\boldsymbol{a} - \boldsymbol{a}')\,w_{aa'} \simeq \boldsymbol{A}(\boldsymbol{a}_0) - \boldsymbol{\Lambda}(\boldsymbol{a}' - \boldsymbol{a}_0) \tag{1.17}$$

and

$$\boldsymbol{D}(\boldsymbol{a}') = \frac{1}{2}\sum_a (\boldsymbol{a} - \boldsymbol{a}')\,(\boldsymbol{a} - \boldsymbol{a}')\,w_{aa'} \tag{1.18}$$

where $w_{aa'}$ is the transition probability per unit time from state $\boldsymbol{a}'$ to state $\boldsymbol{a}$

$$\Gamma_a = \sum_{a'} w_{a'a} \tag{1.19}$$

is the total transition probability per unit time out of $\boldsymbol{\alpha}$. Then

$$\boldsymbol{A}\boldsymbol{\alpha}' = -\sum_{a} (\boldsymbol{\alpha} - \boldsymbol{\alpha}')\, w_{aa'} \tag{1.20}$$

and

$$\boldsymbol{D} = \frac{1}{2}\sum_{a} (\boldsymbol{\alpha} - \boldsymbol{\alpha}')(\boldsymbol{\alpha} - \boldsymbol{\alpha}')\, w_{aa'} \tag{1.21}$$

are expressible directly in terms of the transition probabilities that describe our stochastic process. Furthermore, substituting Eq. (1.16) to Eq. (1.1)

$$\begin{aligned}\frac{\partial P(\boldsymbol{a}, t)}{\partial t} &= \sum_{a'} w_{aa'} P(\boldsymbol{a}', t) - \Gamma_a P(\boldsymbol{a}, t)\\ &= -\sum_{a'} T(\boldsymbol{a}, \boldsymbol{a}')\,(\boldsymbol{a}', t)\end{aligned} \tag{1.22}$$

where

$$T(\boldsymbol{a}, \boldsymbol{a}') = \Gamma_{a'}\delta(\boldsymbol{a}, \boldsymbol{a}') - w_{aa'} \tag{1.23}$$

The first term of the right-hand side in Eq. (1.22) represents the rate of transitions from any $\boldsymbol{a}'$ into $\boldsymbol{a}$ and the second represents the total transitions out of $\boldsymbol{a}$.

In the case of two states a and a', Eq. (1.22) can be written in the form

$$\frac{\partial P(a, t)}{\partial t} = w_{aa'} P(a', t) - w_{a'a} P(a, t) \tag{1.24}$$

In order to apply Lax's procedure to the fluctuations in the distribution functions in which there are $n(a, t)$ and $n(a', t)$ particles in states a and a' at time t, the rate of transitions per unit time $w_{a'a}$ can be, in accordance with Lax, replaced

$$x(a', a) = [1 + \varepsilon n(a')]\, w_{a'a} n(a) \tag{1.25}$$

where, ε is 1, -1, or 0 depending on the statistics of the particle under consideration.

One is tempted to make the terms on the right-hand side cancel in pairs by detailed balance.

$$\frac{w_{a'a} n_0(a)}{1 + \varepsilon n_0(a)} = \frac{w_{aa'} n_0(a')}{1 + \varepsilon n_0(a')} \tag{1.26}$$

Thus, if the ratio of forward to reverse transition probabilities has the following functional relation

$$f(a', a) = \frac{g(a')}{g(a)} \tag{1.27}$$

then there is a steady state solution of the form

$$\frac{n_0(a)}{1+\varepsilon n_0(a)} = \lambda g(a) \tag{1.28}$$

or

$$n_0(a) = [\{\lambda g(a)\}^{-1} - \varepsilon]^{-1} \tag{1.28$'$}$$

where the proportional constant λ is determined by normalization. Even in the nonequilibrium case, we can choose to define a quasi-Fermi level μ by means of

$$\lambda = \exp\ [\mu/kT] \tag{1.29}$$

Under thermal equilibrium conditions,

$$g(a) = \exp\ [-E(a)/kT] \tag{1.30}$$

and Eq. (1.28) yield the conventional equilibrium result

$$n_0(a) = [-\varepsilon+\exp\{[E(a)-\mu]/kT\}]^{-1} \tag{1.31}$$

2. The Order-Disorder Transition[10] and The Fluctuations in a Binary Alloy

We consider the fluctuations in the case of order-disorder transition in a binary alloy consisting of only a simple cubic lattice. The order-disorder transition problem has been treated, for the first time, by Bragg-Williams, but, by appling Lax's method, we are able not only to obtain the same results, but also to deal with the fluctuations that they did not consider.

First, we shall discuss only a special case that there are two kinds of atoms A and B with an equal number and that the number of α-sites occupied by A atoms is equal to that of β-sites occupied by B atoms. Furthermore, we shall follow the model established by Bragg-Williams and assume, in accordance with them, that each of A atoms can occupy either α-site or β-site having energies $E(\alpha)$ and $E(\beta)$, respectively, their difference being V, that is, $E(\beta) = E(\alpha) + V$.

Now, if N_A and N_B are the number of the A atoms and the B atoms, respectively, and N is the total number of these atoms in the system, we have

$$N_A+N_B=N\,, \quad N_A=N_B=\frac{N}{2} \tag{2.1}$$

Further, if $n(\alpha)$ and $n(\beta)$ are the number of A atoms occupying the α-level and the β-level, respectively, at time t, we have

$$n(\alpha)+n(\beta)=\frac{N}{2}\,, \quad n(\beta)=\frac{N}{2}-n(\alpha) \tag{2.2}$$

Still further we define f_1 as the transition rate of one A atom from the α-level to the β-level and f_2 as that from the β-site to the α-site. Since the number of the B atoms on the α-sites are equal to the number of the A atoms on the β-sites and vice versa, the system can be dealt only with the parameters $n(\alpha)$ and the positions to be occupied by the B atoms may be considered empty.

As a result, the probability $p(\alpha)$ that the α-level is occupied by one A atom is written

$$p(\alpha)=\frac{n(\alpha)}{N/2} \tag{2.3}$$

This coincides with the probability that a given β-site is occupied by the B atom. On the other hand, the probability that one β-site is occupied by one A atom, in other words, the probability $q(\alpha)$ that one α-site is occupied by one A atom is

$$q(\alpha)=1-p(\alpha)=\frac{N/2-n(\alpha)}{N/2} \tag{2.3$'$}$$

This $p(\alpha)$ represents the random variable a in Lax's formulation. If we write, in accordance with Bragg-Williams,

$$p(\alpha)=\frac{1+s}{2} \tag{2.4}$$

where $0\leq p\leq 1$ and $-1\leq s\leq 1$, s is a parameter representing the long-range order.

Now, in order to obtain a better understanding, we shall picture the scheme of what stated above.

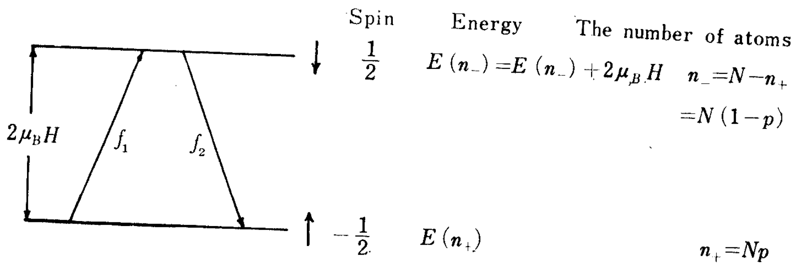

Fig. 2.1

By using Eq. (1.25), the number of the A atoms per unit time from the β-level to the α-level is

$$x(\alpha,\ \beta)=\left[\frac{N/2-n(\alpha)}{N/2}\right]f_2\ n(\beta) \tag{2.5}$$

Similarly, that from the α-level to the β-level is

$$x(\beta,\ \alpha)=\left[\frac{N/2-n(\beta)}{N/2}\right]f_1\ n(\alpha) \tag{2.5$'$}$$

where the terms in either brackets the probability that the forward level is occupied by an unlike atom or vacancy. Representing these equations in terms of the probability, we obtain

$$\left.\begin{aligned} x(\alpha,\ \beta)&=\frac{N}{2}f_2[1-p(\alpha)]^2 \\ x(\beta,\ \alpha)&=\frac{N}{2}f_1[p(\alpha)]^2 \end{aligned}\right\} \tag{2.6}$$

Then, from the combination of Eqs. (1.24) and (1.25), the rate of the increase in the A atoms on the α-level is

$$\frac{dn(\alpha)}{dt}=x(\alpha,\ \beta)-x(\beta,\ \alpha) \tag{2.7}$$

Substituting Eq. (2.5) into this equation

$$\frac{dn(\alpha)}{dt}=\left[\frac{N/2-n(\alpha)}{N/2}\right]f_2\ n(\beta)-\left[\frac{N/2-n(\alpha)}{N/2}\right]f_1\ n(\alpha) \tag{2.8}$$

or in terms of the probability

$$\frac{dp(\alpha)}{dt}=f_2[1-p(\alpha)]^2-f_1[p(\alpha)]^2 \tag{2.8$'$}$$

If we set the right-hand side of Eq. (2.8)′ to zero, we obtain the steady state values as follows

$$0=f_2^0[1-p_0(\alpha)]^2-f_1^0[p_0(\alpha)]^2 \tag{2.9}$$

or

$$\frac{f_2^0}{f_1^0}=\left[\frac{p_0(\alpha)}{1-p_0(\alpha)}\right]^2 \tag{2.10}$$

where the suffix 0 presents the values in the steady state. From Eqs. (2.9) and (2.8)

$$p_0(\alpha)=\frac{1}{1+\sqrt{f_1^0/f_2^0}} \quad \text{and} \quad n_0(\alpha)=\frac{N/2}{1+\sqrt{f_1^0/f_2^0}} \tag{2.11}$$

Thus the values of the steady state are determined.

Further, from the condition of the steady state Eq. (1.28), we have

$$\frac{n_0(\alpha)}{N/2-n_0(\alpha)}=\lambda g(\alpha) \quad \text{or} \quad \frac{p_0(\alpha)}{1-p_0(\alpha)}=\lambda g(\alpha) \tag{2.12}$$

and

$$\frac{n_0(\beta)}{N/2-n_0(\beta)}=\lambda g(\beta) \quad \text{or} \quad \frac{1-p_0(\beta)}{p_0(\beta)}=\lambda g(\beta) \tag{2.13}$$

Combining Eq. (2.12) and (2.13), we obtain;

$$\frac{g(\alpha)}{g(\beta)}=\left[\frac{p_0(\alpha)}{1-p_0(\alpha)}\right]^2 \tag{2.14}$$

By connecting this equation and Eq. (2.10), we have another form of Eq. (2.14)

$$\frac{g(\alpha)}{g(\beta)}=\left[\frac{p_0(\alpha)}{1-p_0(\alpha)}\right]^2=\frac{f_2^0}{f_1^0} \tag{2.14$'$}$$

Let us consider the potential energy under thermal equilibrium conditions. From

Eq. (1.30)

$$\left.\begin{aligned} g(\alpha) &= \exp\left[-E(\alpha)/kT\right] \\ g(\beta) &= \exp\left[-\{E(\alpha)+V\}/kT\right] \end{aligned}\right\} \tag{2.15}$$

and then,

$$\frac{f_2^0}{f_1^0} = \exp\left(V/kT\right) \tag{2.16}$$

where, according to Bragg-Williams, $V = V_0\, s$. By setting $V/kT = x$ and using Eq. (2.16), we obtain

$$\left[\frac{p_0(\alpha)}{1-p_0(\alpha)}\right]^2 = \exp\left(V/kT\right), \quad \frac{1+s_0}{1-s_0} = e^{x/2}$$

and

$$s_0 = \frac{e^{x/2}-1}{e^{x/2}+1} = \tanh\left(\frac{x}{4}\right) = \tanh\left(\frac{V}{4kT}\right) \tag{2.17}$$

This result agrees with the discussion on the equilibrium state by Bragg-Williams.

We return to Eq. (2.8) again,

$$\frac{dp(\alpha)}{dt} = f_2\left[1-p(\alpha)\right]^2 - f_1\left[p(\alpha)\right]^2$$

Considering the deviation from the steady state, and substituting $p = p_0 + \Delta p$, $f_2 = f_2^0 + \Delta f_2$ and $f_1 = f_1^0 + \Delta f_1$, and if we ignore the higher terms than the second order, we obtain

$$\begin{aligned} \frac{d(\varDelta p)}{dt} = {} & \left[f_2^0(1-p_0)^2 - f_1^0 p_0^2\right] - \left[2f_2^0(1-p_0) + 2f_1^0 p_0\right]\varDelta p \\ & + \left[(1-p_0)^2 \varDelta f_2 - p_0^2 \varDelta f_1\right] \end{aligned}$$

Following the previous discussion, the first term of the right-hand side in this equation is equal to zero. And if we use

$$\frac{d(\varDelta p)}{dt} = -\frac{\varDelta p}{\tau}$$

to obtain

$$\frac{1}{\tau}=2f_1^0\frac{p_0}{1-p_0}\left[1-\frac{p_0(1-p_0)}{2}\frac{d}{dp}\left(\ln\frac{f_2}{f_1}\right)\right] \tag{2.18}$$

where τ is a relaxation time. Considering the relation $f_2^0/f_1^0=\exp(V_0 s/kT)$ and the condition Eq. (2.14) in approximation, we obtain Eq. (2.18). Furthermore, by using the following relation,

$$p=\frac{1+s}{2} \quad \text{and} \quad \frac{f_2}{f_1}=\exp(V_0 s/kT)$$

the last term in Eq. (2.18) is evaluated in the form

$$\frac{d}{dp}\left(\ln\frac{f_2}{f_1}\right)=2\frac{d}{ds}\left(\ln\frac{f_2}{f_1}\right)=\frac{2V_0}{kT}$$

By substituting this into Eq. (2.18), we obtain the expected result

$$\begin{aligned}\frac{1}{\tau}&=2f_1^0\frac{p_0}{1-p_0}\left[1-\frac{p_0(1-p_0)}{2}\frac{2V_0}{kT}\right]\\&=2f_1^0\frac{1+s_0}{1-s_0}\left[1-\frac{V_0(1-s_0^2)}{4kT}\right]\end{aligned} \tag{2.19}$$

This result agrees with the discussion in the case of the non-equilibrium state by Bragg-Williams: There is a temperature T_c whereat the relaxation time τ becomes an infinite at $s_0=0$, and from Eq. (2.19)

$$T_c=\frac{V_0}{4k}$$

Thus the critical temperature T_c is determined, while the relaxation time τ becomes an infinite when $T=T_c$, and becomes an infinite on account of the effect of f_1^0 when $T=0$. And it has only a finite value between them. In other words, it takes a long time to establish the degree of order near T_c which has a small value of the degree of order in the equilibrium state, and for a small thermal agitation in the low temperature, the establishment of the equilibrium state requires a long time.

Next, we define $P(n)$ as the probability that there are precisely n A-atoms on the α-level in the system. In order to give a complete description of the stochastic process, we shall put it as follows:

$$\left.\begin{aligned}x(\alpha,\ \beta)&=O(n)\\x(\beta,\ \alpha)&=D(n)\end{aligned}\right\} \tag{2.20}$$

then we can write an equation analogous to Eq. (1.22)

$$\frac{dP(n)}{dt}=D(n+1)P(n+1)+O(n-1)P(n-1)$$
$$-[D(n)+O(n)]P(n) \tag{2.21}$$

and furthermore, this equation can be written in the form

$$\frac{dP(n)}{dt}=-\sum_{n'} T(n, n')\, P(n') \tag{2.22}$$

where

$$T(n, n')=[D(n)+O(n)]\,\delta_{n,n'}-D(n')\delta_{n',n+1}-O(n')\delta_{n',n-1} \tag{2.23}$$

By using the notation

$$\langle f(n)\rangle=\sum f(n')\,P(n') \tag{2.24}$$

we can multiply Eq. (2.22) by n and sum to obtain

$$\begin{aligned}\frac{d\langle n\rangle}{dt}&=-\sum_{n'}\Big[\sum_{n} nT(n, n')\Big]\,P(n')\\&=-\sum_{n'}[D(n')-O(n')]\,P(n')\\&=-\langle D(n)-O(n)\rangle\end{aligned} \tag{2.25}$$

Taking into consideration the deviation from the equilibrium and using $n'=n_0+\Delta n'$, we can linearize the equation

$$\left.\begin{aligned}D(n')&=D(n_0)+D'(n_0)\Delta n'\\O(n')&=O(n_0)+O'(n_0)\Delta n'\end{aligned}\right\} \tag{2.26}$$

$$\begin{aligned}\sum_{n} nT(n, n')&=D(n')-O(n')\\&=D(n_0)-O(n_0)+[D'(n_0)-O'(n_0)]\,\Delta n'\end{aligned} \tag{2.27}$$

By combining Eq. (2.25) and (2.27), and if Λ is regarded as the coefficient of $\Delta n'$, we can obtain the form

$$\frac{d\langle\Delta n\rangle}{dt}=-\Lambda\langle\Delta n\rangle \tag{2.28}$$

Furthermore, it becomes

$$\sum_{n} (n-n_0)^2\, T(n,\, n') = -\,[O(n')+D(n')] \\ +2\,[D(n')-O(n')]\,(n-n_0) \tag{2.29}$$

By substituting Eq (2.26), we obtain

$$\simeq -\,[O(n_0)+D(n_0)] - [D'(n_0)+O'(n_0)]\,\Delta n' \\ +2\,[D(n_0)-O(n_0)]\,\Delta n' + 2\,[D'(n_0)-O'(n_0)]\,(\Delta n')^2 \tag{2.30}$$

The second and the third terms of the right-hand side in this equation are

$$[\{2D(n_0)-D'(n_0)\}-\{2O(n_0)+O'(n_0)\}]\,\Delta n'$$

and using the approximation $D(n_0) \gg D'(n_0)$; $O(n_0) \gg O'(n_0)$

$$2\Delta n'\,[D(n_0)-O(n_0)] = 0$$

Then Eq. (2.30) becomes

$$\sum_{n} (n-n_0)^2\, T(n,\, n') \simeq -\,[O(n_0)+D(n_0)] \\ +2\,[D'(n_0)-O'(n_0)]\,(n'-n_0)^2 \tag{2.31}$$

and

$$\frac{d\langle(\Delta n)^2\rangle}{dt} = \frac{d}{dt}\langle(n-n_0)^2\rangle = \frac{d}{dt}\sum_{n}(n-n_0)^2\, P(n) \\ = \sum_{n}(n-n_0)^2\,\frac{dP(n)}{dt} = -\sum_{n}(n-n_0)^2 \sum_{n'} T(n,\, n')\, P(n') \tag{2.32}$$

By combining Eq. (2.31) and (2.32), it can be written in the form

$$\frac{d\langle(\Delta n)^2\rangle}{dt} = -\sum_{n'}[\sum_{n}(n-n_0)^2\, T(n,\, n')]\, P(n') \\ \simeq -\sum_{n'}[-\{O(n_0)+D(n_0)\}+2\{D'(n_0)-O'(n_0)\}(n-n_0)^2]\, P(n') \\ \simeq [O(n_0)+D(n_0)] - 2A\langle(\Delta n)^2\rangle \tag{2.33}$$

The steady state fluctuations obtained by setting Eq. (2.32) to zero is

$$\langle(\Delta n)^2\rangle \simeq \frac{O(n_0)+D(n_0)}{2A} \tag{2.34}$$

Since $O(n_0)=D(n_0)$ for the steady state, by using Eq. (2.25), Eq. (2.34) becomes

$$\langle(\Delta n)^2\rangle \simeq \frac{D(n_0)}{A} \tag{2.35}$$

Now, let us evaluate each value in the above derived results in terms of the probability. We can write $O(n)$, $D(n)$, in the form

$$\left.\begin{aligned} O(n)&=\frac{N}{2}f_2(1-p)^2=\frac{N}{2}\left[f_2^0(1-p_0)^2-\left\{2(1-p_0)\,f_2^0-(1-p_0)^2\frac{\Delta f_2}{\Delta p}\right\}\Delta p\right] \\ D(n)&=\frac{N}{2}f_1p^2=\frac{N}{2}\left[f_1^0p_0^2+\left\{2p_0f_1^0+p_0^2\frac{\Delta f_1}{\Delta p}\right\}\Delta p\right] \end{aligned}\right\} \tag{2.36}$$

First, the coefficient A of Δn is evaluated

$$\begin{aligned} A&=D'(n_0)-O'(n_0) \\ &=\frac{N}{2}\cdot 2f_1^0\frac{p_0}{1-p_0}\left[1-\frac{p_0(1-p_0)}{2}\frac{d}{dp}\left(\ln\frac{f_2}{f_1}\right)\right] \end{aligned}$$

This agrees with the previously derived result, that is:

$$A=\frac{N}{2}\cdot\frac{1}{\tau} \tag{2.37}$$

Substituting this result into Eq. (2.35)

$$\langle(\Delta n)^2\rangle\simeq\frac{D(n_0)}{A}=\frac{p_0(1-p_0)}{2}\left[1-\frac{p_0(1-p_0)}{2}\frac{d}{dp}\left(\ln\frac{f_2}{f_1}\right)\right]^{-1}$$

and from the result previously obtained, it becomes;

$$\langle(\Delta n)^2\rangle\simeq\frac{1-s_0^2}{8}\left[1-\frac{V_0(1-s_0^2)}{4kT}\right]^{-1} \tag{2.38}$$

By using the relation $\Delta n=(N/2)\cdot\Delta p=(N/4)\cdot\Delta s$, we obtain

$$\langle(\Delta s)^2\rangle\simeq\frac{2}{N^2}(1-s_0^2)\left[1-\frac{V_0(1-s_0^2)}{4kT}\right]^{-1}=\frac{2}{N^2}\cdot\frac{1-s_0^2}{\tau} \tag{2.39}$$

Thus, τ tends to infinity as $T\to T_c$ so that, then, the fluctuations also tend to infinity. On the other hand, owing to the effect of f_1^0 in low temperatures, we have found that τ tends to infinity as $T\to 0$. However it is important to notice the fact that the fluctuations do not include the effect of f_1^0, so that the fluctuations vanishe as $T\to 0$.

By substituting $T_c=V_0/4k$ for Eq. (2.39), we finally obtain the following form

Table 2.1

T/T_c	S_0	$\langle(\Delta S)^2\rangle$
2.00	0	4.0 ($\times 1/N^2$)
1.90		4.2
1.80		4.5
1.70		4.9
1.60		5.3
1.50		6.0
1.40		7.0
1.30		8.7
1.20		12.0
1.10		22.0
1.08		27.0
1.06		35.3
1.04		52.0
1.00	0	∞
0.98	0.25	43.8
0.96	0.33	24.8
0.94	0.39	17.4
0.92	0.45	12.0
0.90	0.50	9.0
0.85	0.61	4.8
0.80	0.71	2.6
0.70	0.83	1.2
0.60	0.90	0.6
0.50	0.95	0.2
0.40	0.98	0.1

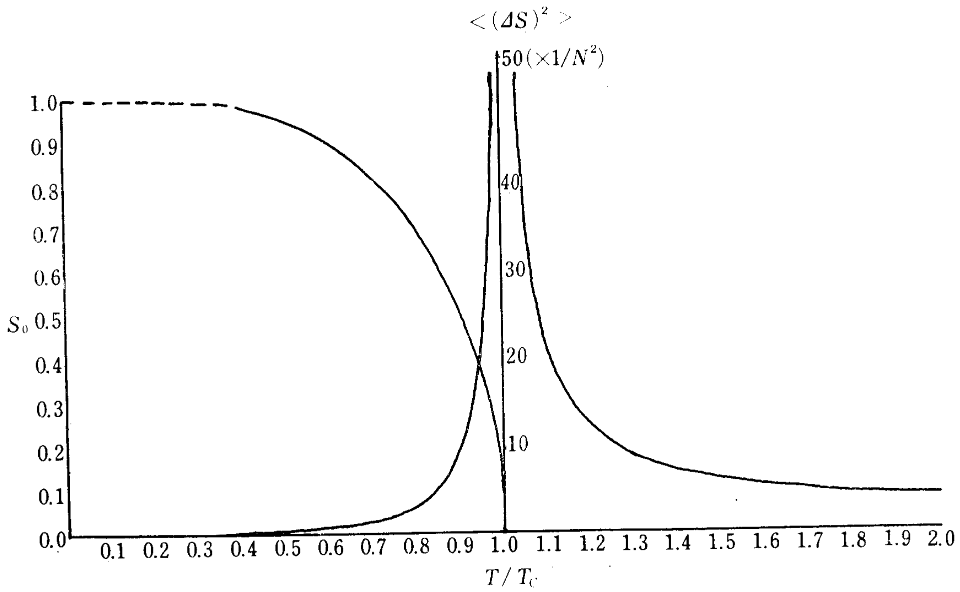

Fig. 2.2

$$\langle(\Delta s)^2\rangle \simeq \frac{2}{N^2} \cdot \frac{1-s_0^2}{1-\frac{T_c}{T}(1-s_0^2)} \tag{2.40}$$

If we use the numerical values by Bragg-Williams, we are able to calculate the fluctuations and to picture the graph as following:

3. The Fluctuations in the Magnetization of a Magnetic Material

We shall investigate the fluctuations in the magnetization of a magnetic material by using the analogous discussion as shown in the preceeding section.

Now, let us consider the random arrangement of magnetic moments without the dependency on the positions as presented in the case of the binary alloy, and treat the magnetization and its fluctuations caused by the spins of angular momentum $\pm 1/2$ in a constant magnetic field H.

Each magnetic moment is disposed on either one of the two energy levels which have energy $E(n_+)$ and $E(n_-)$, respectively and between which the energy difference is $2\mu_B H$ [μ_B is the Bohr magneton and $E(n_-)$ is higher than $E(n_+)$]. In addition, $N = n_+ + n_-$ is the total number of the spins in the system, and n_+, n_- are the populations of the lower and upper levels, respectively. Furthermore, f_1 denotes the transition rate of one spin from the lower level to the higher one and f_2 is defined for the opposite transition. Since the transition of any spin on the one level does not depend on the number of the spins on the other level, the formulation as to the number of transition per unit time between the levels is somewhat different from the previous discussion. Thus we can picture the scheme of what stated above, as follows:

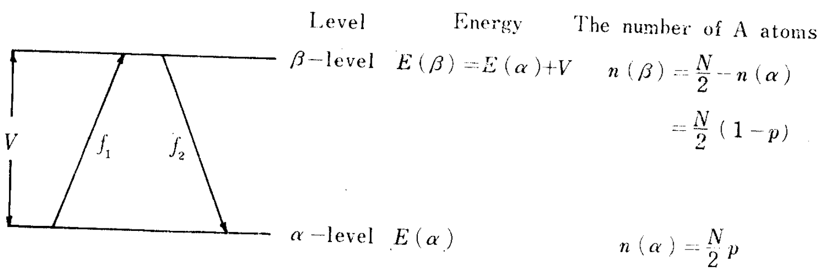

Fig. 3.1

First, according to the assumption, we have

$$N = n_+ + n_- \tag{3.1}$$

And the magnetization is

$$M=\mu_B(n_+-n_-) \tag{3.2}$$

By combining Eq. (3.1) and (3.2), we obtain

$$\frac{1}{2}\left[1\pm\frac{M}{\mu_B N}\right]=\frac{n_\pm}{N} \tag{3.3}$$

If we rewrite,

$$\frac{n_+}{N}=p\,,\quad \frac{n_-}{N}=1-p\,,\quad \frac{M}{\mu_B N}=s,\ \text{and}\ p=\frac{1+s}{2} \tag{3.4}$$

then we can make these parameters correspond to those in the case of the binary alloy. Thus we are able to approach this problem according to the previous discussion.

Now,

$$\left.\begin{aligned} x(n_-,\,n_+)&=f_1 n_+ \\ x(n_+,\,n_-)&=f_2 n_-=f_2(N-n_+) \end{aligned}\right\} \tag{3.5}$$

and substituting this into Eq. (1.24), we obtain

$$\frac{dn_+}{dt}=f_2(N-n_+)-f_1 n_+ \tag{3.6}$$

This equation means that the mean rate of increase in the spins on the lower level is equal to the difference between the mean rates that the down spins change to up and the up spins to down.

Furthermore, by using Eq. (1.30), we have

$$\left.\begin{aligned} n_+^0&=\lambda g(n_+)=\lambda\,\exp\left[-E(n_+)/kT\right] \\ n_-^0&=\lambda g(n_-)=\lambda\,\exp\left[-\{E(n_+)+2\mu_B H\}/kT\right] \end{aligned}\right\} \tag{3.7}$$

And using the probability, it can be written in the form

$$\frac{n_+^0}{n_-^0}=\frac{p_0}{1-p_0}=\frac{g(n_+)}{g(n_-)}=\exp\,(2\mu_B H/kT) \tag{3.8}$$

On the other hand, from the steady state condition, we obtain

$$\frac{f_2^0}{f_1^0}=\frac{n_+^0}{n_-^0}=\frac{p_0}{1-p_0} \tag{3.9}$$

By connecting this and Eq. (3.8)

$$\frac{f_2^0}{f_1^0}=\exp(2x) \quad \text{where } x=\frac{\mu_B H}{kT} \tag{3.10}$$

Then

$$\frac{p_0}{1-p_0}=\frac{1+s_0}{1-s_0}=e^{2x}, \quad s_0=\frac{e^{2x}-1}{e^{2x}+1}=\tanh x.$$

Furthermore, we are able to rewrite in the form

$$\frac{M_0}{\mu_B N}\tanh\left(\frac{\mu_B H}{kT}\right)=\tanh\left(\frac{\mu_B}{kT}\lambda M_0\right) \tag{3.11}$$

where the suffix 0 used here presents the steady state value. And we used $H=0$ in the Weiss theory; i.e. $H=H_e+\lambda M$.

Since $\tanh x \doteqdot x$ for $x \ll 1$, then Eq (3.11) becomes

$$M_0=N\mu_B\frac{\lambda\mu_B}{kT}M_0, \quad T_c=\frac{\lambda\mu_B^2 N}{k} \tag{3.12}$$

This result agrees with that of the usual Curie-Weiss' approach.

Next, in order to obtain the relaxation time τ, if we represent Eq. (3.6) in terms of the probability and consider the deviations from the equilibrium, we can perform just the same procedure as the previous discussion.

$$\frac{dp}{dt}=f_2(1-p)-f_1 p$$

$$\frac{d(\Delta p)}{dt}=-\frac{\Delta p}{\tau}=[(f_2^0+\Delta f_2)\{(1-p_0)-\Delta p\}-(f_1^0+\Delta f_1)(p_0+\Delta p)]$$

If we ignore the higher terms than the second order, we have

$$\frac{\Delta p}{\tau}=f_1^0 p_0-f_2^0(1-p_0)+\left\{f_1^0+f_2^0-(1-p_0)\frac{\Delta f_2}{\Delta p}+p_0\frac{\Delta f_1}{\Delta p}\right\}\Delta p$$

where, from the steady state condition, the first term of the right-hand side in this equation vanishes. Then, the following results,

$$\frac{1}{\tau}=\frac{f_1^0}{1-p_0}\left[1-p_0(1-p_0)\frac{d}{dp}\left(\ln\frac{f_2}{f_1}\right)\right] \tag{3.13}$$

When $H_e=0$, since

$$H=\lambda M=\lambda\mu_B N(2p-1)\,, \quad \frac{dH}{dp}=2\lambda\mu_B N$$

we obtain by the use of the relation $f_2/f_1=\exp(2\mu_B H/kT)$,

$$\frac{d}{dp}\left(\ln\frac{f_2}{f_1}\right)=\frac{2\mu_B}{kT}\frac{dH}{dp}=4\lambda\mu_B\frac{\mu_B N}{kT}$$

Substituting this into Eq. (3.13), it becomes

$$\frac{1}{\tau}=\frac{2f_1^0}{1-s_0}\left[1-\frac{\lambda\mu_B^2 N}{kT}(1-s_0^2)\right] \tag{3.14}$$

There is a critical temperature T_c such that τ tends to infinity as $s_0\to 0$, and it has the form as shown previously;

$$T_c=\frac{\lambda\mu_B^2 N}{k} \tag{3.15}$$

Furthermore, owing to the effect of f_1^0, τ tends to infinity as $T\to 0$, again. Thus this result completely agrees with the discussion in the binary alloy.

Now, we shall calculate the fluctuations in our case by using the discussion after Eq. (2.20).

From Eq. (2.20), we can write $O(n)$, $D(n)$ in the form

$$\left.\begin{aligned} O(n)&=O(n_0)+O'(n_0)\,\Delta n=N\left[f_2^0(1-p_0)-\left\{f_2^0-(1-p_0)\frac{\Delta f_2}{\Delta p}\right\}\Delta p\right]\\ D(n)&=D(n_0)+D'(n_0)\,\Delta n=N\left[f_1^0 p_0+\left\{f_1^0+p_0\frac{\Delta f_1}{\Delta p}\right\}\Delta p\right]\end{aligned}\right\} \tag{3.16}$$

Then Λ can be evaluated immediately;

$$\begin{aligned}\Lambda=D'(n_0)-O'(n_0)&=N\left[f_1^0+f_2^0-(1-p_0)\frac{\Delta f_2}{\Delta p}+p_0\frac{\Delta f_1}{\Delta p}\right]\\ &=N\frac{f_1^0}{1-p_0}\left[1-p_0(1-p_0)\frac{d}{dp}\left(\ln\frac{f_2}{f_1}\right)\right]=N\cdot\frac{1}{\tau}\end{aligned} \tag{3.17}$$

and the fluctuation is

$$\langle(\Delta n)^2\rangle \simeq \frac{D(n_0)}{A} = \frac{p_0(1-p_0)}{\left[1-p_0(1-p_0)\frac{d}{dp}\left(\ln\frac{f_2}{f_1}\right)\right]}$$
$$= \frac{1}{4}\cdot\frac{1-s_0^2}{1-\frac{\lambda\mu_B^2 N}{kT}(1-s_0^2)} \tag{3.18}$$

Furthermore, we can rewrite the above also in the form

$$\langle(\Delta s)^2\rangle \simeq \frac{4}{N^2}\cdot\frac{1-s_0^2}{1-\frac{\lambda\mu_B^2 N}{kT}(1-s_0^2)} = \frac{4}{N^2}\cdot\frac{1-s_0^2}{1-\frac{T_c}{T}(1-s_0^2)} \tag{3.19}$$

that is, by Eq. (3.4)

$$\langle(\Delta M)^2\rangle \simeq 4\mu_B^2\frac{1-\left(\frac{\mu_B N}{M_0}\right)^2}{1-\frac{\lambda\mu_B^2 N}{kT}\left[1-\left(\frac{M_0}{\mu_B N}\right)^2\right]} \tag{3.20}$$

Thus, once the correspondence (as shown in Eq. (3.4)) between the parameters in the case of order-disorder transition and those in the case of magnetization is established, the similar results as to the fluctuations are obtained, though it is necessary to take into account the difference with respect to statistics between Eq. (2.6) and Eq. (3.5).

Conclusion

Lax's procedure, by its application to order-disorder transition and ferromagnetism-paramagnetism transition, results in naturally complete agreement with the results by Bragg-Williams and Curie-Weiss in the first moment, and the fluctuation behaviours, in paticular, in the vicinity of critical point, in the second moment which are of important significance for phase transition phenomena.

These results assures that Lax's theory may be exceedingly useful in the theoretical approach to the phenomena such as those as treated in this paper. That is, it is expected that, based upon more complicated models and elementary processes, more facts already known can be treated in detail, simultaneously making clear the mechanisms participating them. Further, the fluctuations accompanying such mechanisms may be calculated in a comparatively feasible manner. Many phenomena including critical states or threshold situations in which the fluctuations may be exceedingly increased are to be treated by means of Lax's procedure. For example, the theoretical approach to order-disorder problem should be made in which other effects or mechanisms such as short range ordering effect or local disordering by bombardment are included to obtain a more concrete picture corresponding to the actual situations in solids. Then, Lax's procedure will be of great use in that it brings about the kinetics equation (the first moment) as well as the fluctuations (the second moment), as a result, the situation may be discussed in a broader aspect. Based upon the results obtained here, the application of Lax's procedure to order-disorder problem in a more generalized form will be made in the following paper.

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