

Relaxation Process in Ferroelectrics near the Curie Temperature

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A phenomenological approach is given to the problem of the relaxation process in ferroelectrics near the Curie temperature. It is shown that most of anomalous dielectric behaviours of order-disorder type ferroelectrics can be understood by assuming a distribution of relaxation times and their critical slowing down. A more microscopic approach to the same problem is also made for a specific model of KD_2PO_4 , which is regarded as a kind of Ising spin system with two kinds of nearest neighbour interactions. Dynamical properties of this system are investigated on the basis of the Glauber's equation. In actual calculation, a time-dependent cluster approximation is employed. The system is shown to exhibit a relaxation process with two relaxation times, one tending to infinity as the Curie point is approached, the other being almost constant through the paraelectric phase.

§1. Introduction

In recent years much attention has been paid to the relaxation process in ferroelectric substances, and many experimental works have been published on the frequency and temperature dependences of complex dielectric constant near the Curie points of several ferroelectric crystals. Among all, recent experiment on NaNO_2 by Hatta¹⁾ and its theoretical interpretation by Yamada et al.²⁾ suggest that one can have a fairly simple picture of dielectric relaxation process in the vicinity of the Curie point of order-disorder type ferroelectrics. As a matter of fact, Yamada et al.^{2),3)} have proved that the complex dielectric constant of NaNO_2 in the paraelectric region can be well explained by a monodisperse theory together with the critical slowing down of the relaxation time at the Curie point. The first monodisperse theory of this kind has been presented by Mason in 1947⁴⁾ in order to explain the observed behaviour in Rochelle salt. The Mason's theory could give a qualitative account for the experimental results obtained by Akao and Sasaki,⁵⁾ but still left some gulf between theory and experiment. For instance, the Cole-Cole plot given by Akao et al. clearly shows a deviation from the Debye circle to which the Mason's theory should also be led. This means that a distribution of the relaxation time plays an important role.

There are many other examples in which consideration on the distribution

of relaxation time is indispensable. Hill and Ichiki have shown that TGS and KD_2PO_4 are of such cases.⁶⁾ According to them, the complex dielectric constant of TGS and KD_2PO_4 can be expressed as

$$\epsilon^* = \frac{C}{T - T_c} [f(\nu\tau_0) + ig(\nu\tau_0)], \tag{1.1}$$

$$\tau_0 = \frac{1}{\alpha(T - T_c)},$$

where C and T_c are respectively the Curie constant and Curie temperature, $f(x)$ and $g(x)$ are universal functions common to both the substances, and α is a constant to be chosen properly for each substance. The formula (1.1) is derived by assuming a Gaussian distribution of the relaxation times of the form

$$y(\tau) = \frac{2C\alpha}{\sqrt{\pi}} e^{-\alpha^2\tau/\tau_0^2}. \tag{1.2}$$

In spite of an apparent success of the formula (1.1) in reproducing the experimental results, there seems to exist some systematic discrepancies between their theory and experiment. Furthermore it is a point to be questioned that the distribution function (1.2) concentrates at high temperatures around $\tau=0$ instead of a finite value.

Concerning the temperature dependence of the complex dielectric constant near the Curie point, there is a characteristic difference between the Mason's theory and the Hill-Ichiki's formula. The Mason theory corresponds to take

$$f(x) = \frac{1}{1+x^2} \quad \text{and} \quad g(x) = \frac{x}{1+x^2} \tag{1.3}$$

in (1.1) and hence the real part of ϵ^* becomes

$$\epsilon_1 = \frac{C}{1 + \left\{ \frac{T - T_c}{\alpha(T - T_c)} \right\}^2} \rightarrow 0$$

as $T \rightarrow T_c$. On the other hand, it is known that the real part of (1.1) takes a maximum at $T = T_c$. The origin of this difference in the temperature dependence of ϵ_1 is easily traced back; in monodisperse theory, the critical slowing down of the relaxation time has a dominant effect over the Curie-Weiss law of static dielectric constant, while in Hill-Ichiki theory the distribution function of the relaxation time assumed in (1.2) makes the contribution from infinitely fast process (i.e. $\tau=0$) to ϵ_1 more dominant.

There are actually, however, many cases in which ϵ_1 takes a minimum of finite value at $T = T_c$, being neither zero as in Mason's theory nor

maximum as in Hill-Ichiki theory. Typical examples are the cases of $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_3\text{CO}_2)_6$ ⁷⁾ and Colemanite,⁸⁾ in which the relaxation times seem to distribute in some way different from the law given by (1·2). Thus it becomes highly desirable to develop a new systematic study in order to meet the present experimental situation which manifests a plenty of varieties in the anomalous dielectric behaviours of ferroelectrics near the critical points.

The aim of this paper is to take the first step toward this problem. Very recently Nishikawa⁹⁾ has discussed the polydispersive relaxation process caused by the non-linear effect of the polarization fluctuation. The non-linear effect seems to be very small except for narrow temperature range in the vicinity of the critical point. Kawasaki and Yamada¹⁰⁾ have also discussed the same problem for the Ising spin system with a long range interaction by making use of power series expansion in the inverse of the force range. In this paper two approaches are made to this problem. First, starting from the Kubo formula¹¹⁾ for the dielectric susceptibility, we consider phenomenologically a distribution of relaxation times and their critical slowing down. It is shown that most of anomalous dielectric behaviours of order-disorder type ferroelectrics are well explained in terms of a special distribution with one parameter of the relaxation times (§2). Secondly, as one of the possible origins of a distribution of the relaxation time, the effects of the short range correlation between dipoles are examined for a model of KD_2PO_4 which has been investigated by Tokunaga and Matsubara¹²⁾ (hereafter referred to as T-M). We consider KD_2PO_4 as a kind of Ising spin system with two kinds of nearest neighbour interactions. The dynamics of this system is treated on the basis of a master equation derived by Glauber et al.¹³⁾ (§3). In actual calculation, a time-dependent cluster approximation is employed (§§4 through 5). It is an extension of the static cluster approximation (adopted in T-M) to the dynamical case and also is a generalization of the Mason theory. As a result, a relaxation process is obtained in which two relaxation times appear, one tending to infinity as the Curie point is approached, the other being almost constant throughout the paraelectric phase. The former contributes to the dynamical susceptibility a usual term of the Mason type and the latter an extra new term of finite value at the Curie point. The latter contribution, however, is of negligible order compared with the former in this approximation. A generalization to the higher approximation is shown in §6 and some discussion is given on the interpretation of experimental results.

§2. Phenomenological theory

We start our discussion with the Kubo formula for the dielectric susceptibility. The general theory of linear response has been applied to the special case of dielectric response by Glarum and others.¹⁴⁾⁻¹⁶⁾ For the sake of definiteness, we imagine a spherical sample of volume V suspended in a vacuum.

According to the elementary theory of electromagnetism, the dielectric constant ϵ at sufficiently low frequency ω is related to the polarizability of this sphere by an equation

$$\frac{\epsilon-1}{\epsilon+1} = \frac{4\pi}{3V} \frac{P}{E}, \quad (2.1)$$

where P is the polarization induced by an external electric field E . The general linear response theory (or the fluctuation-dissipation theorem) gives us

$$\frac{P}{E} = \frac{1}{3kT} \langle P(0) \cdot P(0) \rangle - \frac{i\omega}{3kT} \int_0^\infty dt e^{-i\omega t} \langle P(0) \cdot P(t) \rangle. \quad (2.2)$$

$P(t)$ is the total electric moment of the sample at time t . It is convenient to define the relaxation function $\phi(t)$, the response function $\Psi(t)$ and their normalized ones by the equations

$$\begin{aligned} \phi(t) &= \frac{1}{3kT} \langle P(0) \cdot P(t) \rangle = \frac{1}{3kT} \langle P(0) \cdot P(0) \rangle \phi(t), \\ \Psi(t) &= -\frac{d\phi(t)}{dt} = \frac{1}{3kT} \langle P(0) \cdot P(0) \rangle \psi(t), \end{aligned} \quad (2.3)$$

$$\psi(t) = -\frac{d\phi(t)}{dt}.$$

Then (2.1) together with (2.2) are rewritten as

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{9kTV} \langle P(0) \cdot P(0) \rangle \int_0^\infty dt e^{-i\omega t} \psi(t). \quad (2.4)$$

We shall add to this expression the contribution from electronic polarization:

$$\frac{\epsilon-1}{\epsilon+2} = \frac{\epsilon_\infty-1}{\epsilon_\infty+2} + \frac{4\pi}{9kTV} \langle P(0) \cdot P(0) \rangle \int_0^\infty dt e^{-i\omega t} \psi(t). \quad (2.5)$$

For static field $\omega=0$, (2.5) becomes

$$\frac{\epsilon_0-1}{\epsilon_0+2} = \frac{\epsilon_\infty-1}{\epsilon_\infty+2} + \frac{4\pi}{9kTV} \langle P(0) \cdot P(0) \rangle, \quad (2.6)$$

where we have used the relation

$$\int_0^\infty dt \psi(t) = \phi(0) - \phi(\infty) = 1.$$

By making use of Eq. (2.6), the factor $\langle P(0) \cdot P(0) \rangle$ in Eq. (2.5) can be eliminated, the result being

$$\frac{\epsilon-1}{\epsilon+2} = \frac{\epsilon_\infty-1}{\epsilon_\infty+2} + \left(\frac{\epsilon_0-1}{\epsilon_0+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2} \right) L[\psi] \quad (2.7)$$

with

$$L[\psi] \equiv \int_0^\infty dt e^{-i\omega t} \psi(t). \tag{2.8}$$

After some manipulation, Eq. (2.7) is further transformed into a more compact form:

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + [L[\psi]^{-1} - 1] X}, \tag{2.9}$$

$$X = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2}. \tag{2.10}$$

When $\phi(t)$ is approximated by a simple exponential function

$$\phi(t) = e^{-t/\tau_0} \tag{2.11}$$

then

$$L[\psi] = \frac{1}{1 + i\omega\tau_0}$$

and hence

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + i\omega\tau_0 X}. \tag{2.12}$$

This is the well-known Debye formula. In order to extend to the case where $\phi(t)$ is not a simple exponential function but a sum (or an integral) of exponential functions with many different relaxation times, let us take a phenomenological view point. It is known that for many dielectric substances the presence of the distribution of the relaxation time can be described by fairly simple empirical law. For instance there are many expressions for $L[\psi]$ proposed to give an empirical account for experimental data of polydisperse system such as

$$(I) \text{ Cole-Cole law: } L[\psi] = \frac{1}{1 + (i\omega\tau_0)^\beta}, \tag{2.13}$$

$$(II) \text{ Lemniscate law: } L[\psi] = \frac{1}{(1 + i\omega\tau_0)^\beta}. \tag{2.14}$$

If we employ these empirical law (I) or (II) for $L[\psi]$, then Eq. (2.9) becomes respectively

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \begin{cases} \frac{1}{1 + (i\omega\tau_0)^\beta X} & \text{for (I),} \\ \frac{1}{1 + [(1 + i\omega\tau_0)^\beta - 1] X} & \text{for (II).} \end{cases} \tag{2.15}$$

Now we examine the case (I) in detail.¹⁷⁾ From (2.15)

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + (i\omega\tau_0^*)^\beta}, \tag{2.16}$$

$$\tau_0^* = \tau_0 X^{1/\beta}$$

which is again the same Cole's law with the relaxation time τ_0^* modified by the factor X . The real and imaginary parts of $\epsilon = \epsilon_1 - i\epsilon_2$ are given respectively by

$$\frac{\epsilon_1 - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1 + bZ}{1 + 2bZ + Z^2},$$

$$\frac{\epsilon_2}{\epsilon_0 - \epsilon_\infty} = \frac{aZ}{1 + 2bZ + Z^2}, \tag{2.17}$$

where

$$a = \sin \frac{\pi}{2} \beta, \quad b = \cos \frac{\pi}{2} \beta, \quad Z = (\omega\tau_0)^\beta X. \tag{2.18}$$

In the neighbourhood of the Curie temperature T_c of a ferroelectric crystal, the static dielectric constant ϵ_0 takes very large values, following Curie-Weiss law:

$$\epsilon_0 - \epsilon_\infty \simeq \frac{C_\pm}{|T - T_c|}. \tag{2.19}$$

By definition (2.10) X takes also very large values in the same temperature range

$$X \simeq \frac{C'_\pm}{|T - T_c|}, \quad C'_\pm \simeq \frac{C_\pm}{\epsilon_\infty + 2}. \tag{2.20}$$

C_\pm is the Curie constant above (+) or below (-) T_c , respectively. Due to these anomalies in $\epsilon_0 - \epsilon_\infty$ and X , both ϵ_1 and ϵ_2 show anomalous behaviour in the vicinity of T_c . In Fig. 1 the temperature dependence of $\epsilon_1 - \epsilon_\infty$, calculated from (2.17) under the assumptions (2.19) and (2.20) is shown for several β values with $\omega\tau_0$ fixed and in Fig. 2 for different frequencies with β fixed. It is interesting to note that for $1/2 < \beta < 1$, $\epsilon_1 - \epsilon_\infty$ takes a non-zero minimum at T_c while for $\beta \leq 1/2$ it becomes maximum. For $\beta = 1$ the expression is reduced to the Mason's result and $\epsilon_1 - \epsilon_\infty$ vanishes at T_c . The general features of these figures are very similar to those observed in $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_4\text{CO}_2)_8$ and Colemanite (for $1/2 < \beta < 1$) and in KDP and TGS (for $\beta \leq 1/2$).

The above results are interpreted in terms of a distribution of relaxation time. Let $G(\tau)$ be the distribution function of relaxation times. Then for the Cole-Cole law

$$\frac{1}{1 + (i\omega\tau_0^*)^\beta} = \int_0^\infty \frac{G(\tau) d\tau}{1 + i\omega\tau}. \tag{2.21}$$

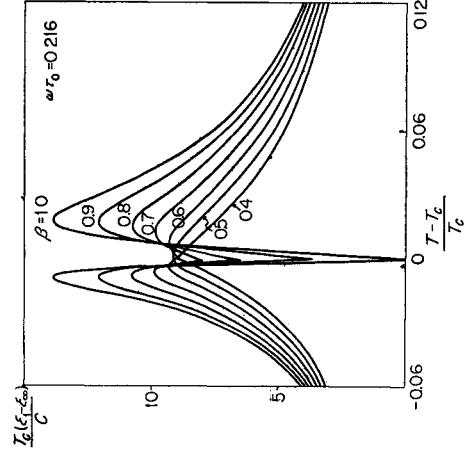


Fig. 1. Temperature dependence of $\epsilon_1 - \epsilon_\infty$ for various values of β with fixed $\omega\tau_0$.

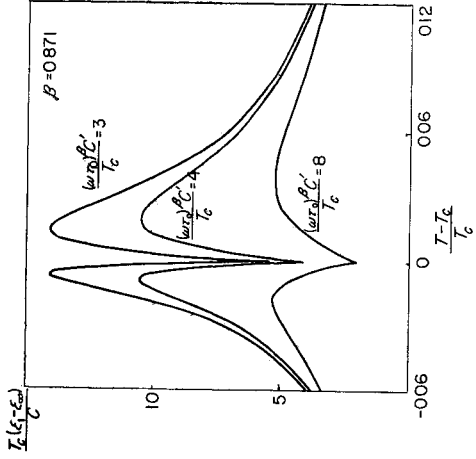


Fig. 2. Temperature dependence of $\epsilon_1 - \epsilon_\infty$ for various values of β with fixed β .

An explicit form of the distribution function $G(\tau)$ which satisfies Eq. (2.21) has been given in the literature.¹⁸⁾ That is

$$y(x) = \tau_0^* G(\tau) = \frac{1}{\pi} \frac{\sin \beta\pi}{x(x^\beta + x^{-\beta} + 2 \cos \beta\pi)} \tag{2.22}$$

with

$$x = \tau / \tau_0^*.$$

This is shown schematically for several β values in Fig. 3. The parameter β is a measure of the width of the distribution. For $\beta = 1$, $y(x)$ is a δ -function and gives the Debye result. As β is decreased the peak of the distribution moves toward smaller τ and finally $y(x)$ concentrates around $\tau = 0$ ($\beta \leq 1/2$). Hence, in spite of the critical slowing down of τ_0^* through the factor X , $\epsilon_1 - \epsilon_\infty$ remains finite at T_c by virtue of the contribution from shorter relaxation times.

On the other hand, the Cole-Cole plot of Eq. (2.17) is similar to the depressed circular arc obtained for $L[\psi]$. Actually, eliminating Z from Eqs. (2.17) we have

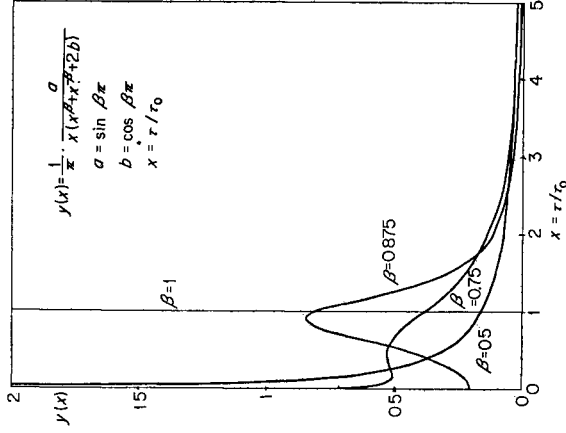


Fig. 3. A distribution function of relaxation times.

$$\left(\frac{\epsilon_1 - \epsilon_0 + \epsilon_\infty}{2}\right)^2 + \left(\epsilon_2 + \frac{b}{a} \frac{\epsilon_0 - \epsilon_\infty}{2}\right)^2 = \left(\frac{\epsilon_0 - \epsilon_\infty}{2a}\right)^2 \quad (2.23)$$

This is the equation of a circle with a center at $((\epsilon_0 + \epsilon_\infty)/2, -b/a(\epsilon_0 - \epsilon_\infty)/2)$ and with a radius $(\epsilon_0 - \epsilon_\infty)/2a$ as is shown in Fig. 4. When β is kept constant, the center of the circle moves along a line as temperature (and hence ϵ_0) is changed. It should be noted, however, that the reduced quantities $(\epsilon_1 - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)$ and $\epsilon_2/(\epsilon_0 - \epsilon_\infty)$ are always on the same circle:

$$\begin{aligned} \left(\frac{\epsilon_1 - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} - \frac{1}{2}\right)^2 + \left(\frac{\epsilon_2}{\epsilon_0 - \epsilon_\infty} + \frac{b}{2a}\right)^2 \\ = \frac{1}{4a^2}. \end{aligned}$$

There are many ferroelectric substances which follow approximately the dielectric behaviours predicted in Eqs. (2.17) through (2.20). We summarize in Table I the β values observed for various substances.

Table I.

Substance	Temperature range	β	Reference
NaNO ₂	$\geq 164^\circ\text{C}$	0.94	1)
Rochelle salt	near upper T_0	variable	19)
HCl	$\leq 98.4^\circ\text{K}$	0.67	20)
HBr	$\leq 89.7^\circ\text{K}$	0.7	21)
DBr	$\leq 93.5^\circ\text{K}$	0.72	22)
HI	$\leq 70^\circ\text{K}$	0.87	22)
DI	$\leq 77.3^\circ\text{K}$	0.81	22)
KNO ₃	paraphase ($\geq 125^\circ\text{C}$)	0.57~0.52	23)
DGN	paraphase	0.64	24)
MASD	paraphase	0.69	25)
Fe-Alum	paraphase	0.96	25)

§3. Kinetic Ising model of KD₂PO₄

In the preceding section we have shown that a distribution of relaxation time accompanied with a critical slowing down well explains the behaviours of the complex dielectric constant in ferroelectrics near the Curie point. It is, therefore, desirable to investigate the origin of a distribution of relaxation times from microscopic point of view.

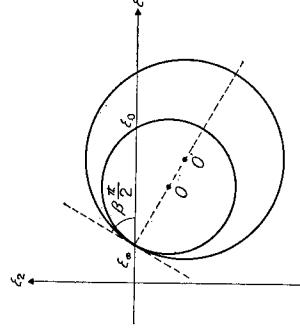


Fig. 4. The Cole-Cole plot of Eq. (2.17) with constant β .

In the following section, as one of possible origins of a distribution, the short range correlation effects between dipoles are examined for a special model of KD_2PO_4 . The study of this model is motivated by the remarkable experimental results reported for this substance (Hill and Ichiki) on one hand and by recent advances in the theoretical works of some simplified model for this substance on the other.

The crystal structure of KH_2PO_4 is shown in Fig. 5. According to Tokunaga and Matsubara (T-M), two possible positions of a proton on hydrogen bond are expressed by two values of the Ising spin $S_j^z(\pm 1/2)$. Then we can consider the system as a kind of Ising spin system whose Hamiltonian is given by

$$\mathcal{H} = -\frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z. \tag{3.1}$$

As has been discussed in detail in T-M, the proton tunneling motion between two positions on hydrogen bond may play an important role, but we discard it in this paper simply because we want to focus our attention on the short range correlation effect for dielectric relaxation. It has been proved in T-M that a suitable choice of J_{ij} reproduces all the energy levels for various proton configurations proposed by several authors including Slater²⁶⁾ and Takagi.²⁷⁾ Now let us pick up a set of four protons ($j=0, 1, 2, 3$) which surround PO_4 group (see Fig. 6). By symmetry, we can choose two parameters U and V for J_{ij} and write the effective Hamiltonian for this cluster as

$$\begin{aligned} H_{\text{eff}}^{(4)} = & -U(S_0^z S_2^z + S_1^z S_3^z) - V(S_0^z S_1^z + S_1^z S_2^z + S_2^z S_3^z + S_3^z S_0^z) \\ & -\mu \bar{E}(t) (S_0^z + S_1^z + S_2^z + S_3^z), \end{aligned} \tag{3.2}$$

where an effective field $\bar{E}(t)$ is introduced to take into account the effect of the interaction from the protons outside the cluster. $\bar{E}(t)$ is assumed equal for four protons. Central problem in this section is to determine $\bar{E}(t)$ self-consistently. To this aim, we take a proton, say $S_j^z, j=0$, out of the cluster and assume that its average motion can be also described by a Hamiltonian

$$H_{\text{eff}}^{(3)} = -\mu \bar{E}_1(t) S_0^z, \tag{3.3}$$

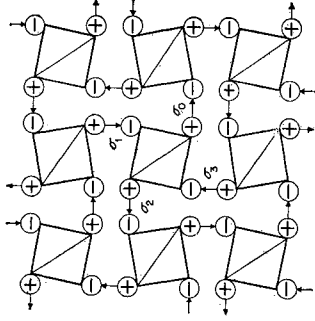


Fig. 5. The crystal structure of KH_2PO_4 .

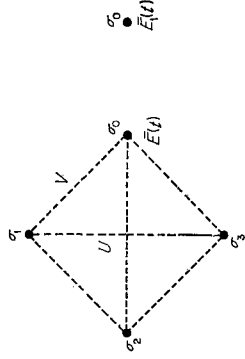


Fig. 6. A cluster of four protons. Dotted lines represent the interaction U or V . $\sigma_j = 2S_j^z$.

where

$$\bar{E}_1(t) = 2\bar{E}(t). \tag{3.4}$$

The factor 2 in (3.4) takes into consideration the fact that the number of interactions exerted to S_0^z is twice of that of the interactions from protons outside the cluster ($S_0^z, S_1^z, S_2^z, S_3^z$). (3.4) is a self-consistency condition which will be used in later stage.

As a basis to discuss the time dependent problem, we shall lay down a fundamental assumption that the time dependent behaviours of the proton system is governed by a law of Markoff processes. To be more specific, we assume that time dependent properties of the proton system can be described in terms of probability density $P(\sigma_1 \cdots \sigma_N; t)$ which satisfies a master equation derived by Glauber et al.:¹³⁾

$$\begin{aligned} \frac{d}{dt} P(\sigma_1 \cdots \sigma_N; t) = & - \sum_j W_j(\sigma_j; \{\sigma\}) P(\sigma_1 \cdots \sigma_N; t) \\ & + \sum_j W_j(-\sigma_j; \{\sigma\}') P(\sigma_1 \cdots, -\sigma_j, \cdots \sigma_N; t). \end{aligned} \tag{3.5}$$

In this equation (3.5), $\sigma_j = \pm 1$ is used in place of S_j^z (i.e. $\sigma_j = 2S_j^z$), and $W_j(\sigma_j; \{\sigma\})$ denotes the probability per unit time such that the j -th proton makes a change of state from σ_j to $-\sigma_j$ under a configuration given by $\{\sigma\} = \sigma_1 \sigma_2 \cdots \sigma_N$, whereas $W_j(-\sigma_j; \{\sigma\}')$ is that of the reversed transition, namely the probability per unit time such that the j -th proton makes a transition from $-\sigma_j$ to σ_j under a configuration given by $\{\sigma\}' = \sigma_1 \sigma_2 \cdots -\sigma_j \cdots \sigma_N$. In order that the master equation (3.5) can provide with an equilibrium solution prescribed by ordinary statistical mechanics, we impose on $W_j(\sigma_j; \{\sigma\})$ a condition of detailed balance:

$$\frac{W_j(\sigma_j; \{\sigma\})}{W_j(-\sigma_j; \{\sigma\}')} = \frac{Z_j(-\sigma_j)}{Z_j(\sigma_j)}, \tag{3.6}$$

where $Z_j(\sigma_j)(Z_j(-\sigma_j))$ is the probability that the j -th proton takes a state $\sigma_j(-\sigma_j)$ at thermal equilibrium. It has been shown that $W_j(\sigma_j)$ is determined from (3.6) in a form

$$W_j(\sigma_j) = \frac{\alpha}{2} \left(1 - \sigma_j \tanh \frac{\beta E_j}{2} \right), \tag{3.7}$$

where $\beta = 1/kT$ and E_j is a local field at the j -th proton given by

$$E_j = \sum_i J_{ij} \frac{\sigma_i}{2}. \tag{3.8}$$

$\alpha/2$ has a meaning of the transition probability of a proton at high temperature limit. Starting with the master equation (3.5), we can easily construct the moment equations. Let us define the n -th order moment by

$$\langle \{\sigma\}_n \rangle = \sum_{\sigma=\pm 1} (\prod_{j=1}^n \sigma_j) P(\sigma_1 \cdots \sigma_N; t) / \sum_{\sigma=\pm 1} P(\sigma_1 \cdots \sigma_N; t).$$

Then the equation of motion satisfied by $\langle \{\sigma\}_n \rangle$ is given by

$$-\frac{1}{\alpha} \frac{d}{dt} \langle \{\sigma\}_n \rangle = \sum_{j=1}^n \left\langle \{\sigma\}_n \left[1 - \sigma_j \tanh \frac{\beta E_j}{2} \right] \right\rangle. \tag{3.9}$$

§4. Equation of motion for a cluster of four protons

We shall apply Eq. (3.9) to a cluster of four protons, whose Hamiltonian is given by (3.2). According to the Slater model proposed for KDP, dipole moment associated with a complex $(\text{H}_2\text{PO}_4)^-$ is assumed to be determined through the configuration of protons attached to it (say $j=0, 1, 2, 3$) and in the language of present theory, therefore, it is a function of $\sigma_0, \sigma_1, \sigma_2, \sigma_3$. We have shown in T-M that the cluster approximation can take account of strong short range correlation among protons and gives satisfactory results for equilibrium properties of KDP. It is natural, therefore, to expect that a dynamical cluster approximation, which is deemed as an extension of the Slater model to time dependent cases, would give a satisfactory explanation of dynamical properties as well.

Before we proceed with the Eq. (3.9), it is necessary to simplify $\tanh(\beta E_j/2)$, using the property $\sigma^2=1$. For instance we shall take $j=0$. From the definition (3.8) and (3.2), E_0 is given by

$$E_0 = \frac{U}{2} \sigma_2 + \frac{V}{2} (\sigma_1 + \sigma_3) + \mu \bar{E}(t) \tag{4.1}$$

and hence

$$\tanh \frac{\beta E_0}{2} = \tanh [A \sigma_2 + B (\sigma_1 + \sigma_3) + C], \tag{4.2}$$

where

$$A = \beta U/4, \quad B = \beta V/4 \quad \text{and} \quad C = \mu \beta \bar{E}(t)/2. \tag{4.3}$$

Since σ_j 's take only two values, the right-hand side of (4.2) takes only 8 different values and may be expressed in a form:

$$\tanh \frac{\beta E_0}{2} = P \sigma_2 + Q (\sigma_1 + \sigma_3) + R \sigma_1 \sigma_2 \sigma_3 + L + M \sigma_2 (\sigma_1 + \sigma_3) + N \sigma_1 \sigma_3. \tag{4.4}$$

Comparisons of eight different values for both (4.2) and (4.4) yield the following relations:

$$P = \frac{1}{8} \{ \tanh(A+2B+C) + 2 \tanh(A+C) + \tanh(A-2B+C) \\ - \tanh(-A-2B+C) - 2 \tanh(-A+C) - \tanh(-A+2B+C) \},$$

$$\begin{aligned}
Q &= \frac{1}{8} \{ \tanh(A+2B+C) - \tanh(A-2B+C) \\
&\quad - \tanh(-A-2B+C) + \tanh(-A+2B+C) \}, \\
R &= \frac{1}{8} \{ \tanh(A+2B+C) - 2\tanh(A+C) + \tanh(A-2B+C) \\
&\quad - \tanh(-A-2B+C) + 2\tanh(-A+C) - \tanh(-A+2B+C) \}, \\
L &= \frac{1}{8} \{ \tanh(A+2B+C) + 2\tanh(A+C) + \tanh(A-2B+C) \\
&\quad + \tanh(-A-2B+C) + 2\tanh(-A+C) + \tanh(-A+2B+C) \}, \\
M &= \frac{1}{8} \{ \tanh(A+2B+C) - \tanh(A-2B+C) \\
&\quad + \tanh(-A-2B+C) - \tanh(-A+2B+C) \}, \\
N &= \frac{1}{8} \{ \tanh(A+2B+C) - 2\tanh(A+C) + \tanh(A-2B+C) \\
&\quad + \tanh(-A-2B+C) - 2\tanh(-A+C) + \tanh(-A+2B+C) \}.
\end{aligned} \tag{4.5}$$

It should be noted that P , Q and R are even functions of C whereas L , M and N are odd functions of C . Therefore when these functions are expanded in powers of C , the former three begin with constant terms while the latter with terms linear in C .

Quite similarly we can obtain the expressions for $\tanh(\beta/2)E_j$, for $j=1, 2$ and 3 . The results are reproduced from (4.4) by changing σ_i in a cyclic order among $(\sigma_0, \sigma_1, \sigma_2, \sigma_3)$. Collecting all these results in (3.9), we have a set of self-contained moment equations.

$$\begin{aligned}
-\frac{1}{\alpha} \frac{d}{dt} \langle \sigma_0 \rangle &= (1-P-2Q) \langle \sigma_0 \rangle - R \langle \sigma_0 \sigma_1 \sigma_2 \rangle - L - 2M \langle \sigma_0 \sigma_1 \rangle - N \langle \sigma_0 \sigma_2 \rangle, \\
-\frac{1}{\alpha} \frac{d}{dt} \langle \sigma_0 \sigma_1 \sigma_2 \rangle &= -(2P+4Q+3R) \langle \sigma_0 \rangle + (3-P-2Q) \langle \sigma_0 \sigma_1 \sigma_2 \rangle \\
&\quad - (2M+N) - 2(L+M+N) \langle \sigma_0 \sigma_1 \rangle - (L+2M) \langle \sigma_0 \sigma_2 \rangle, \\
-\frac{1}{\alpha} \frac{d}{dt} \langle \sigma_0 \sigma_1 \rangle &= -2(L+M+N) \langle \sigma_0 \rangle - 2M \langle \sigma_0 \sigma_1 \sigma_2 \rangle \\
&\quad - 2Q + 2(1-P-R) \langle \sigma_0 \sigma_1 \rangle - 2Q \langle \sigma_0 \sigma_2 \rangle, \\
-\frac{1}{\alpha} \frac{d}{dt} \langle \sigma_0 \sigma_2 \rangle &= -2(L+2M) \langle \sigma_0 \rangle - 2N \langle \sigma_0 \sigma_1 \sigma_2 \rangle \\
&\quad - 2P - 4Q \langle \sigma_0 \sigma_1 \rangle + 2(1-R) \langle \sigma_0 \sigma_2 \rangle, \\
-\frac{1}{\alpha} \frac{d}{dt} \langle \sigma_0 \sigma_1 \sigma_2 \sigma_3 \rangle &= -4(2M+N) \langle \sigma_0 \rangle - 4L \langle \sigma_0 \sigma_1 \sigma_2 \rangle \\
&\quad - 4R - 8Q \langle \sigma_0 \sigma_1 \rangle - 4P \langle \sigma_0 \sigma_2 \rangle + 4 \langle \sigma_0 \sigma_1 \sigma_2 \sigma_3 \rangle,
\end{aligned} \tag{4.6}$$

where use has been made of the fact that in the uniform case, independent correlation functions are

$$\begin{aligned} \langle \sigma_0 \rangle &= \langle \sigma_j \rangle, & j=1, 2, 3, \\ \langle \sigma_0 \sigma_1 \rangle &= \langle \sigma_1 \sigma_2 \rangle = \langle \sigma_2 \sigma_3 \rangle = \langle \sigma_3 \sigma_0 \rangle, \\ \langle \sigma_0 \sigma_2 \rangle &= \langle \sigma_1 \sigma_3 \rangle, \\ \langle \sigma_0 \sigma_1 \sigma_2 \rangle &= \langle \sigma_1 \sigma_2 \sigma_3 \rangle = \langle \sigma_2 \sigma_3 \sigma_0 \rangle = \langle \sigma_3 \sigma_0 \sigma_1 \rangle, \\ \langle \sigma_0 \sigma_1 \sigma_2 \sigma_3 \rangle &. \end{aligned}$$

If we confine ourselves to one proton system described by the Hamiltonian (3.3), only one equation of motion comes out from (3.9):

$$-\frac{1}{\alpha} \frac{d}{dt} \langle \sigma_0 \rangle = \langle \sigma_0 \rangle - \tanh C_1, \tag{4.7}$$

where

$$C_1 = \frac{\mu\beta\bar{E}_1(t)}{2}. \tag{4.8}$$

At this stage we recall the relation (3.4) as a self-consistency condition. Then (4.6) together with (4.7) and (3.4) provide us with sufficient equations to determine unknown quantities $\langle \sigma_0 \rangle$, $\langle \sigma_0 \sigma_1 \rangle$, $\langle \sigma_0 \sigma_2 \rangle$, $\langle \sigma_0 \sigma_1 \sigma_2 \rangle$ and $\mu\bar{E}(t)$.

For simplicity we consider in the following the paraelectric phase above T_c . In this phase C which is proportional to molecular field can be regarded as a small quantity, and all the functions of C such as P , Q , R etc. may be expanded in powers of C . Up to the term linear in C , thus we have

$$\begin{aligned} P &\simeq P_0 = \frac{1}{4} \{ \tanh(A+2B) + 2 \tanh A + \tanh(A-2B) \}, \\ Q &\simeq Q_0 = \frac{1}{4} \{ \tanh(A+2B) - \tanh(A-2B) \}, \\ R &\simeq R_0 = \frac{1}{4} \{ \tanh(A+2B) - 2 \tanh A + \tanh(A-2B) \}, \\ L &\simeq CL_1 = \frac{1}{4} C \{ \operatorname{sech}^2(A+2B) + 2 \operatorname{sech}^2 A + \operatorname{sech}^2(A-2B) \}, \\ M &\simeq CM_1 = \frac{1}{4} C \{ \operatorname{sech}^2(A+2B) - \operatorname{sech}^2(A-2B) \}, \\ N &\simeq CN_1 = \frac{1}{4} C \{ \operatorname{sech}^2(A+2B) - 2 \operatorname{sech}^2 A + \operatorname{sech}^2(A-2B) \}. \end{aligned} \tag{4.9}$$

Substitution of (4.9) into (4.6) give us a set of equations linearized with respect to C . They are, however, still complicated and need further simplification in order that we can easily solve them. Therefore let us assume that

all the moments can be decomposed into their equilibrium values and small fluctuations:

$$\begin{aligned}
 \langle \sigma_0 \rangle &= \langle \sigma_0 \rangle_0 + \eta_1(t), \\
 \langle \sigma_0 \sigma_1 \sigma_2 \rangle &= \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 + \eta_3(t), \\
 \langle \sigma_0 \sigma_1 \rangle &= \langle \sigma_0 \sigma_1 \rangle_0 + \eta_2(t), \\
 \langle \sigma_0 \sigma_2 \rangle &= \langle \sigma_0 \sigma_2 \rangle_0 + \eta'_2(t), \\
 C &= C_0 + \xi(t).
 \end{aligned}
 \tag{4.10}$$

Here C_0 is related to static molecular field E_0 by

$$C_0 = \frac{\mu E_0}{2kT}
 \tag{4.11a}$$

and $\xi(t)$ to fluctuating field $E'(t)$ by

$$\xi(t) = \frac{\mu E'(t)}{2kT}.
 \tag{4.11b}$$

Upon inserting these decomposition (4.10) into the set of linearized equations, the basic equations are separated in two groups, one is to determine the equilibrium values of the moments and other is to give time dependent behaviour of the fluctuating parts. They are summarized in the following matrix form:

$$\begin{pmatrix}
 1 - P_0 - 2Q_0 & -R_0 & -2C_0 M_1 & -C_0 N_1 \\
 -(2P_0 + 4Q_0 + 3R_0) & 3 - P_0 - 2Q_0 & -2C_0(L_1 + M_1 + N_1) & -C_0(L_1 + 2M_1) \\
 -2C_0(L_1 + M_1 + N_1) & -2C_0 M_1 & 2(1 - P_0 - R_0) & -2Q_0 \\
 -2C_0(L_1 + 2M_1) & -2C_0 N_1 & -4Q_0 & 2(1 - R_0)
 \end{pmatrix}
 \begin{pmatrix}
 \langle \sigma_0 \rangle_0 \\
 \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 \\
 \langle \sigma_0 \sigma_1 \rangle_0 \\
 \langle \sigma_0 \sigma_2 \rangle_0
 \end{pmatrix}
 =
 \begin{pmatrix}
 C_0 L_1 \\
 C_0(2M_1 + N_1) \\
 2Q_0 \\
 2P_0
 \end{pmatrix},
 \tag{4.12}$$

$$-\frac{1}{\alpha} \frac{d}{dt} \begin{pmatrix} \eta_1 \\ \eta_3 \\ \eta_2 \\ \eta'_2 \end{pmatrix}
 =
 \begin{pmatrix}
 1 - P_0 - 2Q_0 & -R_0 & -2C_0 M_1 & -C_0 N_1 \\
 -(2P_0 + 4Q_0 + 3R_0) & 3 - P_0 - 2Q_0 & -2C_0(L_1 + M_1 + N_1) & -C_0(L_1 + 2M_1) \\
 -2C_0(L_1 + M_1 + N_1) & -2C_0 M_1 & 2(1 - P_0 - R_0) & -2Q_0 \\
 -2C_0(L_1 + 2M_1) & -2C_0 N_1 & -4Q_0 & 2(1 - R_0)
 \end{pmatrix}$$

$$\begin{pmatrix} \eta_1 \\ \eta_3 \\ \eta_2 \\ \eta_2' \end{pmatrix} - \xi(t) \begin{pmatrix} L_1 + 2M_1 \langle \sigma_0 \sigma_1 \rangle_0 + N_1 \langle \sigma_0 \sigma_2 \rangle_0 \\ 2M_1 + N_1 + 2(L_1 + M_1 + N_1) \langle \sigma_0 \sigma_1 \rangle_0 + (L_1 + 2M_1) \langle \sigma_0 \sigma_2 \rangle_0 \\ 2(L_1 + M_1 + N_1) \langle \sigma_0 \rangle_0 + 2M_1 \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 \\ 2(L_1 + 2M_1) \langle \sigma_0 \rangle_0 + 2N_1 \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 \end{pmatrix} \quad (4.13)$$

Similarly two equations result from (4.7) after linearization and the decomposition:

$$\langle \sigma_0 \rangle_0 = 2C_0, \quad (4.14)$$

$$-\frac{1}{\alpha} \frac{d\eta_1}{dt} = \eta_1 - 2\xi(t), \quad (4.15)$$

where the use has been made of the self-consistency condition (3.4). In the next section we shall examine the solutions of (4.12) ~ (4.15).

§5. Solutions for the paraelectric phase

In the paraelectric phase ($T > T_c$) the static solution should be such that

$$C_0 = \langle \sigma_0 \rangle_0 = \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 = 0. \quad (5.1)$$

Here from (4.12) and (4.13) it follows that

$$\begin{bmatrix} 2(1 - P_0 - R_0) & -2Q_0 \\ -4Q_0 & 2(1 - R_0) \end{bmatrix} \begin{bmatrix} \langle \sigma_0 \sigma_1 \rangle_0 \\ \langle \sigma_0 \sigma_2 \rangle_0 \end{bmatrix} = \begin{bmatrix} 2Q_0 \\ 2P_0 \end{bmatrix} \quad (5.2)$$

and

$$-\frac{1}{\alpha} \frac{d}{dt} \begin{bmatrix} \eta_1 \\ \eta_3 \end{bmatrix} = \begin{bmatrix} 1 - P_0 - 2Q_0 & -R_0 \\ -(2P_0 + 4Q_0 + 3R_0) & 3 - P_0 - 2Q_0 \end{bmatrix} \begin{bmatrix} \eta_1 \\ \eta_3 \end{bmatrix} - \xi(t) \begin{bmatrix} S \\ T \end{bmatrix}, \quad (5.3)$$

$$-\frac{1}{\alpha} \frac{d}{dt} \eta_1 = \eta_1 - 2\xi(t), \quad (5.4)$$

where

$$\begin{aligned} S &= L_1 + 2M_1 \langle \sigma_0 \sigma_1 \rangle_0 + N_1 \langle \sigma_0 \sigma_2 \rangle_0, \\ T &= 2M_1 + N_1 + 2(L_1 + M_1 + N_1) \langle \sigma_0 \sigma_1 \rangle_0 + (L_1 + 2M_1) \langle \sigma_0 \sigma_2 \rangle_0. \end{aligned} \quad (5.5)$$

In order to determine the critical temperature T_c above which $C_0 = 0$, it is more convenient to assume that in (4.12) C_0 is very small but nonzero. Then from (4.12)

$$\begin{bmatrix} 1 - P_0 - 2Q_0 & -R_0 \\ -(2P_0 + 4Q_0 + 3R_0) & 3 - P_0 - 2Q_0 \end{bmatrix} \begin{bmatrix} \langle \sigma_0 \rangle_0 \\ \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 \end{bmatrix} = C_0 \begin{bmatrix} S \\ T \end{bmatrix}. \quad (5.6)$$

Let us define new parameters which have been introduced in T.M:

$$\begin{aligned} U &= -2\epsilon_1, & a &= \exp(-\beta\epsilon_0), \\ V &= 2\epsilon_1 + \epsilon_0, & b &= \exp(-\beta\epsilon_1). \end{aligned} \quad (5.7)$$

After elementary but tedious calculation, the solution of (5.6) can be expressed in terms of a and b as (see Appendix A)

$$\langle \sigma_0 \rangle_0 = \frac{4(1+ab)}{a^2b^4 + 4ab + 2a + 1} C_0, \quad (5.8a)$$

$$\langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 = \frac{4(1-ab)}{a^2b^4 + 4ab + 2a + 1} C_0. \quad (5.8b)$$

On the other hand from (4.14)

$$\langle \sigma_0 \rangle_0 = 2C_0 \quad (5.9)$$

and combining this with (5.8a), we have

$$\langle \sigma_0 \rangle_0 = \frac{2(1+ab)}{a^2b^4 + 4ab + 2a + 1} \langle \sigma_0 \rangle_0. \quad (5.10)$$

We may define the transition point T_c as the temperature at which a non-zero solution $\langle \sigma_0 \rangle_0 \neq 0$ exists. Thus

$$1 = \frac{2(1+ab)}{a^2b^4 + 4ab + 2a + 1} \quad (T = T_c) \quad (5.11a)$$

so that

$$1 - 2a - a^2b^4 = 2ab. \quad (T = T_c) \quad (5.11b)$$

This is exactly the same result as that of T-M. In the similar way, adding an external field E to Eqs. (5.6) and (5.9), we obtain solutions in the presence of E

$$\begin{aligned} \langle \sigma_0 \rangle_0^E &= \frac{\mu E}{kT} \frac{1+ab}{a^2b^4 + 2ab + 2a - 1}, \\ \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0^E &= \frac{\mu E}{kT} \frac{1-ab}{a^2b^4 + 2ab + 2a - 1}. \end{aligned} \quad (5.12)$$

Since the polarization is to be proportional to $\langle \sigma_0 \rangle_0^E$,

$$P = N\mu \langle \sigma_0 \rangle_0^E \quad (5.13)$$

the static susceptibility $\chi_0 = P/E$ is obtained as

$$\chi_0 = \frac{N\mu^2}{kT} \frac{1+ab}{a^2b^4 + 2ab + 2a - 1} \quad (T > T_c)$$

which tends to infinity when T approaches T_c given by (5.11b). This result also agrees with that of T-M.

Now we consider the non-equilibrium case. By equating η_1 and $d\eta_1/dt$ in Eq. (5.3) with those in (5.4), we can determine $\xi(t)$ self-consistently

$$\xi(t) = \frac{(P_0 + 2Q_0)\eta_1 + R_0\eta_3}{2-S}. \tag{5.14}$$

Substituting this into Eq. (5.3), we obtain

$$-\frac{d}{\alpha(dt)} \begin{bmatrix} \eta_1 \\ \eta_3 \end{bmatrix} = M \begin{bmatrix} \eta_1 \\ \eta_3 \end{bmatrix}, \tag{5.15}$$

where M is a 2×2 matrix the elements of which are

$$\begin{aligned} M_{11} &= 1 - \frac{2(P_0 + 2Q_0)}{2-S}, & M_{12} &= -\frac{2R_0}{2-S}, \\ M_{21} &= -\left\{ 2P_0 + 4Q_0 + 3R_0 + \frac{T(P_0 + 2Q_0)}{2-S} \right\}, & & \\ M_{22} &= 3 - \left(P_0 + 2Q_0 + \frac{TR_0}{2-S} \right). & & \end{aligned} \tag{5.16}$$

We note that the static equation (5.6) can be rewritten in terms of the matrix M as

$$M \begin{bmatrix} \langle \sigma_0 \rangle_0 \\ \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 \end{bmatrix} = 0. \tag{5.17}$$

Therefore the transition temperature T_c is also defined in an alternative way by

$$\det |M| = 0. \quad (T = T_c) \tag{5.18}$$

Let us calculate first the relaxation times, which are determined as eigenvalues of the secular equation

$$\det \left| M - \frac{1}{\tau} I \right| = 0. \tag{5.19}$$

There are two relaxation times satisfying a quadratic equation

$$(1/\tau)^2 - (1/\tau) \text{Tr} M + \det |M| = 0. \tag{5.20}$$

One of them τ_1 tends to infinity as T approaches T_c

$$\tau_1 \rightarrow \infty \quad (T \rightarrow T_c)$$

because, by the definition (5.18) of T_c ,

$$\det |M| \rightarrow 0. \quad (T \rightarrow T_c)$$

The explicit expressions for the two roots τ_1 and τ_2 of Eq. (5.20) are much

complicated. Here we show only $\det|M|$ and $\text{Tr}M$ below.

$$\det|M| = \frac{1}{2-S} \frac{8ab(ab^4 + 3ab^3 + 2)(a^2b^4 + 2ab + 2a - 1)}{(ab+1)(b+1)(ab^3+1)(a^2b^4 + 4ab + 2a + 1)}, \tag{5.21a}$$

$$\text{Tr}M = 4 - \frac{4-S}{2-S} \frac{1+3b-2ab+2ab^4-3a^2b^4-a^2b^5}{2(ab+1)(b+1)(ab^3+1)} - \frac{T}{2-S} \frac{(1-b-2ab^2+2ab^3+a^2b^4-a^2b^5)}{2(ab+1)(b+1)(ab^3+1)}$$

with

$$S = \frac{4ab}{a^2b^4 + 4ab + 2a + 1} \left\{ \frac{ab^3}{ab^3 + 1} + \frac{1}{ab + 1} + \frac{2}{b + 1} \right\}, \tag{5.21b}$$

$$T = \frac{4ab}{a^2b^4 + 4ab + 2a + 1} \left\{ \frac{3}{ab + 1} - \frac{2}{b + 1} - \frac{ab^3}{ab^3 + 1} \right\},$$

where a and b are those defined in Eq. (5.7). A numerical calculation of τ_1 and τ_2 has been carried out for the case

$$\eta = \epsilon_1/\epsilon_0 = 5, \tag{5.22}$$

and in Fig. 7 τ_1 and τ_2 are shown as functions of reduced temperature $T^* = kT/\epsilon_0$. The value of the parameter given in (5.22) was the best choice to explain the static properties of KD_2PO_4 , as was discussed in T-M. According to Fig. 7, τ_2 is almost constant throughout the paraelectric phase, in contrast with τ_1 which shows a critical slowing down.

Next we calculate the complex susceptibility $\chi(\omega)$. To do this, we solve the Eq. (5.15) with Eqs. (5.12) as an initial condition to obtain the relaxation function

$$\phi(t) = \frac{N\mu\eta_1(t)}{E} = \chi_1 e^{-t/\tau_1} + \chi_2 e^{-t/\tau_2}. \tag{5.23}$$

χ_1 and χ_2 are shown to be respectively given by

$$\chi_1 = \frac{N\mu}{E} \frac{(M_{11} - 1/\tau_2)\langle\sigma_0\rangle_0^E + M_{12}\langle\sigma_0\sigma_1\sigma_2\rangle_0^E}{1/\tau_1 - 1/\tau_2}, \tag{5.24}$$

$$\chi_2 = -\frac{N\mu}{E} \frac{(M_{11} - 1/\tau_1)\langle\sigma_0\rangle_0^E + M_{12}\langle\sigma_0\sigma_1\sigma_2\rangle_0^E}{1/\tau_1 - 1/\tau_2}$$

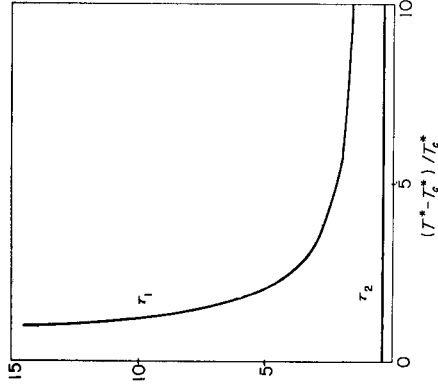


Fig. 7. Temperature dependence of the relaxation time τ_1 and τ_2 .

and satisfy a relation

$$\chi_1 + \chi_2 = \frac{N\mu\langle\sigma_0\rangle_0^E}{E} = \chi_0. \tag{5.25}$$

Then the susceptibility becomes

$$\begin{aligned} \chi(\omega) &= \mathcal{O}(0) - i\omega \int_0^\infty \mathcal{O}(t)e^{-i\omega t} dt \\ &= \frac{\chi_1}{1+i\omega\tau_1} + \frac{\chi_2}{1+i\omega\tau_2}. \end{aligned} \tag{5.26}$$

χ_1 and χ_2 represent the contributions to the static susceptibility χ_0 from the two relaxation modes. Both are the linear combinations of two quantities

$$\begin{aligned} \chi_0 &= \frac{N\mu\langle\sigma_0\rangle_0^E}{E} \\ \chi_0^* &= \frac{N\mu\langle\sigma_0\sigma_1\sigma_2\rangle_0^E}{E}, \end{aligned} \tag{5.27}$$

and

which tend to infinity when T approaches T_c as is seen from (5.12). It is not difficult to confirm that (see Appendix B)

$$\begin{aligned} \chi_1 &\rightarrow \infty \text{ as } T \rightarrow T_c \\ \chi_2 &= \text{finite at } T = T_c. \end{aligned} \tag{5.28}$$

but

The results of numerical calculation for $\chi_1^* = \epsilon_0\chi_1/N\mu^2$ and $\chi_2^* = \epsilon_0\chi_2/N\mu^2$ are shown in Fig. 8 as functions of temperature. From all these results given above, we can conclude the following properties of the susceptibility $\chi(\omega)$ in the present approximation:

- (1) The static susceptibility χ_0 is mainly contributed from χ_1 .
- (2) In the dynamical susceptibility $\chi(\omega)$, the contribution to the real part of $\chi(\omega)$ from the first mode vanishes at $T = T_c$ just as in the Mason theory, because of the fact that

$$\chi_1 \rightarrow \infty, \tau_1 \rightarrow \infty \text{ as } T \rightarrow T_c.$$

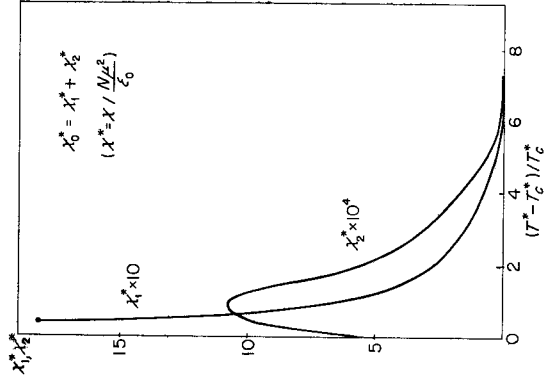


Fig. 8. Temperature dependence of χ_1 and χ_2 ($\epsilon_1/\epsilon_0=5$).

(3) But the contribution to $\text{Re} \chi(\omega)$ from the second mode remains finite at T_c , although its magnitude is of negligible order.

§6. Generalization and discussion

Now we turn our attention to the general features of the results obtained in the preceding sections and make some discussion on a more general case.

To begin with we consider the moment equation (3.9). Let N be the total number of Ising spins in our system, then it is easily verified that the total number of different moments is equal to 2^N , the total number of freedom of the system. It is convenient to arrange the moments in a definite order to define a 2^N dimensional vector \mathbf{m} by

$$\mathbf{m} = \begin{pmatrix} 1 \\ \langle \sigma_1 \rangle \\ \vdots \\ \langle \sigma_N \rangle \\ \langle \sigma_1 \sigma_2 \rangle \\ \vdots \end{pmatrix}. \quad (6.1)$$

By this definition, Eq. (3.9) can be put in a vector form

$$\frac{d\mathbf{m}}{dt} = -D\mathbf{m} \quad (6.2)$$

with an appropriate $2^N \times 2^N$ matrix D . Let us introduce further the Fourier transformation such as

$$\sigma(\mathbf{q}) = \frac{1}{\sqrt{N}} \sum_j \langle \sigma_j \rangle e^{i\mathbf{q} \cdot \mathbf{R}_j} \quad \text{etc.} \quad (6.3)$$

There exists an unitary matrix T which transforms \mathbf{m} into its Fourier transform:

$$\mathbf{m}_F = T\mathbf{m}. \quad (6.4)$$

Then (6.2) becomes

$$\begin{aligned} \frac{d\mathbf{m}_F}{dt} &= -D_F \mathbf{m}_F, \\ D_F &= TDT^{-1}. \end{aligned} \quad (6.5)$$

Through this Fourier transformation, D_F is generally decomposed into several irreducible parts. Since we are mainly interested in a homogeneous polarization which is proportional to $\sigma(0)$, we shall focus our attention on an irreducible part of D_F such that its subspace is spanned by the components of \mathbf{m}_F

$$\eta_1, \eta_2, \dots, \eta_n, \tag{6.6}$$

where $\eta_1 = (1/N) \sum_i \langle \sigma_i \rangle$ is the total polarization and η_2 through η_n are the higher moments which are coupled with η_1 by the matrix D_F . In the paraelectric region above the Curie point, and in the absence of external field, all the moments should vanish except for those of even order. Therefore if we call $\boldsymbol{\eta}$ a vector whose elements are η_1 and other higher moments of odd order coupled with η_1 and define its equilibrium part and fluctuating part by

$$\boldsymbol{\eta} = \bar{\boldsymbol{\eta}} + \boldsymbol{\eta}(t) \tag{6.7}$$

then, on the analogy of the Eqs. (5.17) and (5.15), we can suppose a set of equations for $\boldsymbol{\eta}$ such as

$$M\bar{\boldsymbol{\eta}} = 0, \tag{6.8}$$

$$M\bar{\boldsymbol{\eta}}^E = \frac{\mu E}{kT} \boldsymbol{\alpha}, \tag{6.9}$$

$$-\frac{d}{dt} \boldsymbol{\eta}(t) = M\boldsymbol{\eta}(t). \tag{6.10}$$

In these expressions, M is an $n \times n$ matrix which is connected with an irreducible part of D_F , $\bar{\boldsymbol{\eta}}^E$ is the equilibrium solution under the presence of an external field E and $\boldsymbol{\alpha}$ a vector whose components are given in terms of the even order correlation in equilibrium. We will not enter the details of the last terms. $\bar{\boldsymbol{\eta}}$ is generally zero in the paraelectric region and the transition temperature T_c is defined by the temperature at which Eq. (6.8) has a non-zero solution $\bar{\boldsymbol{\eta}} \neq 0$. This gives a condition to determine T_c :

$$\det |M| = 0. \quad (T = T_c) \tag{6.11}$$

From Eqs. (6.9) and (6.10) we can derive the static susceptibility as

$$\chi_0 = \frac{N\mu\bar{\boldsymbol{\eta}}^E}{E} \tag{6.12}$$

and the relaxation times as roots of the equation

$$\det \left| M - \frac{1}{\tau} \mathbf{1} \right| = 0. \tag{6.13}$$

The last equation proves immediately that one of the relaxation times, say τ_1 , becomes infinite as T approaches T_c .

We are now in a position to calculate the dynamical susceptibility $\chi(\omega)$. For this aim we have to solve Eq. (6.10) with an initial condition

$$\boldsymbol{\eta}(0) = \bar{\boldsymbol{\eta}}^E = \frac{\mu E}{kT} M^{-1} \boldsymbol{\alpha} \tag{6.14}$$

then, using the solution, we have the relaxation function $\boldsymbol{\phi}(t)$ defined by

$$\phi(t) = \frac{N\mu\eta_1(t)}{E} \quad (6.15)$$

to which $\chi(\omega)$ is related through Eqs. (2.2) and (2.3). The calculation can be straightforwardly carried out once the matrix M is diagonalized by a suitable matrix U

$$M' = UMU^{-1} = \begin{pmatrix} 1/\tau_1 & & 0 \\ & \ddots & \\ 0 & & 1/\tau_n \end{pmatrix}. \quad (6.16)$$

The final result may be summarized as follows: Let be

$$\zeta = U\eta, \quad (\zeta_i = \sum_j U_{ij}\eta_j), \quad (6.17)$$

$$\bar{\zeta}^E = U\bar{\eta}^E, \quad (\bar{\zeta}_i^E = \sum_j U_{ij}\bar{\eta}_j^E), \quad (6.18)$$

$$\beta = U\alpha \quad (\beta_i = \sum_j U_{ij}\alpha_j), \quad (6.19)$$

then

$$\phi(t) = \sum_j \chi_j e^{-t/\tau_j}, \quad (6.20)$$

$$\chi(\omega) = \sum_j \frac{\chi_j}{1 + i\omega\tau_j}, \quad (6.21)$$

with

$$\chi_j = \frac{N\mu^2}{kT} (U^{-1})_{1j} \tau_j \beta_j. \quad (6.22)$$

Let us examine the critical behaviours of χ_j near the Curie temperature. For the sake of convenience, we first define the following quantities:

$$\varphi_k \equiv \frac{N\mu\bar{\eta}_k^E}{E} = \frac{N\mu^2}{kT} \frac{1}{\det|M|} \sum_m \Delta_{mk} \alpha_m, \quad (6.23)$$

$$\psi_j \equiv \frac{N\mu\bar{\zeta}_j^E}{E} = \frac{N\mu^2}{kT} \tau_j \beta_j, \quad (6.24)$$

$$\psi_j = \sum_k U_{jk} \varphi_k, \quad (6.25)$$

where Δ_{mk} is (m, k) cofactor of the matrix M . From (6.24) and (6.25) it follows that

$$\chi_j = (U^{-1})_{1j} \psi_j = (U^{-1})_{1j} \sum_k U_{jk} \varphi_k$$

and hence

$$\sum_j \chi_j = \varphi_1 = \chi_0, \quad (6.26)$$

where use has been made of a fact that φ_1 is by definition the static susceptibility χ_0 itself. φ_k ($k \neq 1$) correspond to the linear response of the higher moments of odd order to the external field. Similarly ψ_j may be interpreted as the contribution to the static susceptibility χ_0 from j -th "normal relaxation

mode'. Equation (6.23) tells us that for all k

$$\varphi_k \rightarrow \infty \quad \text{as} \quad T \rightarrow T_c.$$

In spite of the anomaly in φ_k , however, it is quite possible that ψ_j 's (and hence χ_j 's) do not reveal any singularity at T_c except for ψ_1 (and χ_1). This is, indeed, the case for the cluster approximation developed in the previous section where we have seen that

$$\tau_1 \rightarrow \infty \quad \text{as} \quad T \rightarrow T_c$$

and

$$\tau_2 = \text{finite at } T = T_c$$

so that

$$\chi_1 \rightarrow \infty \quad \text{as} \quad T \rightarrow T_c \quad \text{but} \quad \chi_2 = \text{finite at } T_c.$$

We have obtained the relaxation process with two relaxation times by considering the smallest possible cluster. The Mason's results are also derived if we put C_1 in Eq. (4.7) proportional to $\langle \sigma_0 \rangle$, that is, if we confine ourselves within one spin approximation. By making the cluster larger, therefore, we would have a relaxation process with many relaxation times of the form Eq. (6.16). At very high temperatures it is not hard to see that the matrix M tends to a diagonal matrix of the form:

$$M = \begin{bmatrix} 1/\tau_0 & & 0 \\ & 3/\tau_0 & \\ & & \ddots \\ 0 & & & 5/\tau_0 \end{bmatrix},$$

where τ_0 is a time constant and the n -th relaxation time $\tau_n = [\tau_0/(2n+1)]$ repeatedly appears as many times as the number of different $(2n+1)$ -body correlation functions, because they relax independently of τ_1 at high temperatures with the same relaxation time. As temperature is lowered, they begin to couple with τ_1 , and thus a distribution of the relaxation times for polarization seems to come in. In the cluster approximation we have obtained two relaxation times τ_1 and τ_2 of the same order at high temperatures. As temperature approaches T_c only one of them τ_1 tends to infinity. In many mode case, however, it is not yet clear whether the relaxation time of a particular mode (or a few modes) tends to infinity separately from other modes near T_c or all the modes evenly spread toward $\tau = \infty$. In view of the phenomenological theory developed in §2, we are led to the following two possibilities:

- (1) The distribution of relaxation time originates from the interaction which causes the phase transition. This interaction also changes the distribution with temperature.

(2) The distribution originates from some molecular interaction which is not necessarily concerned with the phase transition, and the thermodynamical slowing down related with the appearance of the long range order causes temperature change of the distribution.

Of course these are two extreme cases and the actual situation may be in between them.

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Appendices

(A) A derivation of static solution

Let us first give the relations which connect the parameters P_0, Q_0, \dots, N_1 with a and b defined by

$$\begin{aligned} U &= -2\epsilon_1, & a &= \exp(-\beta\epsilon_0), \\ V &= 2\epsilon_1 + \epsilon_0, & b &= \exp(-\beta\epsilon_1). \end{aligned} \tag{A.1}$$

From the definitions $A = \beta U/4$ and $B = \beta V/4$ together with (A.1) it follows that

$$\begin{aligned} \tanh(A+2B) &= \frac{1-ab}{1+ab}, & \operatorname{sech}^2(A+2B) &= \frac{4ab}{(1+ab)^2}, \\ \tanh A &= \frac{b-1}{b+1}, & \operatorname{sech}^2 A &= \frac{4b}{(b+1)^2}, \\ \tanh(A-2B) &= \frac{ab^3-1}{ab^3+1}, & \operatorname{sech}^2(A-2B) &= \frac{4ab^3}{(ab^3+1)^2}. \end{aligned} \tag{A.2}$$

Therefore we obtain, by putting (A.2) in (4.9),

$$\begin{aligned} P_0 &= \frac{1}{4} \left\{ \frac{1-ab}{1+ab} + 2 \frac{b-1}{b+1} + \frac{ab^3-1}{ab^3+1} \right\}, \\ Q_0 &= \frac{1}{4} \left\{ \frac{1-ab}{1+ab} - \frac{ab^3-1}{ab^3+1} \right\}, \\ R_0 &= \frac{1}{4} \left\{ \frac{1-ab}{1+ab} - 2 \frac{b-1}{b+1} + \frac{ab^3-1}{ab^3+1} \right\}, \\ L_1 &= \frac{ab}{(ab+1)^2} + 2 \frac{b}{(b+1)^2} + \frac{ab^3}{(ab^3+1)^2}, \\ M_1 &= \frac{ab}{(ab+1)^2} - \frac{ab^3}{(ab^3+1)^2}, \end{aligned} \tag{A.3}$$

$$N_1 = \frac{ab}{(ab+1)^2} - 2 \frac{b}{(b+1)^2} + \frac{ab^3}{(ab^3+1)^2}.$$

By making use of these results, we can easily solve Eq. (5.2), where we need to calculate the following determinants:

$$\begin{aligned} \Delta &= \begin{vmatrix} 2(1-P_0-R_0) & -2Q_0 \\ -4Q_0 & 2(1-R_0) \end{vmatrix} = \frac{4b(a^2b^4+4ab+2a+1)}{(ab+1)(b+1)(ab^3+1)}, \\ \Delta \cdot \langle \sigma_0 \sigma_1 \rangle_0 &= \begin{vmatrix} 2Q_0 & -2Q_0 \\ 2P_0 & 2(1-R_0) \end{vmatrix} = \frac{4b(1-a^2b^4)}{(ab+1)(b+1)(ab^3+1)}, \\ \Delta \cdot \langle \sigma_0 \sigma_2 \rangle_0 &= \begin{vmatrix} 2(1-P_0-R_0) & 2Q_0 \\ -4Q_0 & 2P_0 \end{vmatrix} = \frac{4b(1-2a+a^2b^4)}{(ab+1)(b+1)(ab^3+1)}. \end{aligned}$$

Thus

$$\begin{aligned} \langle \sigma_0 \sigma_1 \rangle_0 &= \frac{1-a^2b^4}{a^2b^4+4ab+2a+1}, \\ \langle \sigma_0 \sigma_2 \rangle_0 &= \frac{1-2a+a^2b^4}{a^2b^4+4ab+2a+1}. \end{aligned} \tag{A.4}$$

Next we express the parameters S and T in terms of a and b through the definitions

$$\begin{aligned} S &= L_1 + 2M_1 \langle \sigma_0 \sigma_1 \rangle_0 + N_1 \langle \sigma_0 \sigma_2 \rangle_0, \\ T &= 2M_1 + N_1 + 2(L_1 + M_1 + N_1) \langle \sigma_0 \sigma_1 \rangle_0 + (L_1 + 2M_1) \langle \sigma_0 \sigma_2 \rangle_0. \end{aligned}$$

The results are

$$\begin{aligned} S &= \frac{4ab}{a^2b^4+4ab+2a+1} \left\{ \frac{ab^3}{ab^3+1} + \frac{1}{ab+1} + \frac{2}{b+1} \right\} = \frac{4ab(R_0+1)}{a^2b^4+4ab+2a+1}, \\ T &= \frac{4ab}{a^2b^4+4ab+2a+1} \left\{ \frac{3}{ab+1} - \frac{2}{b+1} - \frac{ab^3}{ab^3+1} \right\} = \frac{4ab(P_0+2Q_0)}{a^2b^4+4ab+2a+1}. \end{aligned} \tag{A.5}$$

The determinants which are necessary to solve Eq. (5.6) are

$$\begin{aligned} A_0 &= \begin{vmatrix} 1-P_0-2Q_0 & -R_0 \\ -(2P_0+4Q_0+3R_0) & 3-P_0-2Q_0 \end{vmatrix} \\ &= (1-P_0-2Q_0-R_0)(3-P_0-2Q_0+3R_0) \\ &= \frac{2ab(3-P_0-2Q_0+3R_0)}{ab+1} = \frac{4ab(ab^4+3ab^3+2)}{(ab+1)(b+1)(ab^3+1)}, \\ A_0 \cdot \frac{\langle \sigma_0 \rangle_0}{C_0} &= \begin{vmatrix} S-R_0 & \\ T & 3-P_0-2Q_0 \end{vmatrix} = \frac{4ab}{a^2b^4+4ab+2a+1} \begin{vmatrix} R_0+1 & -R_0 \\ P_0+2Q_0 & 3-P_0-2Q_0 \end{vmatrix} \\ &= \frac{4ab(3-P_0-2Q_0+3R_0)}{a^2b^4+4ab+2a+1}. \end{aligned}$$

and

$$\begin{aligned} 4_0 \cdot \frac{\langle \sigma_0 \sigma_1 \sigma_2 \rangle_0}{C_0} &= \left| \begin{array}{cc} 1 - P_0 - 2Q_0 & S \\ -(2P_0 + 4Q_0 + 3R_0) & T \end{array} \right| \\ &= \frac{4ab}{a^2b^4 + 4ab + 2a + 1} \left| \begin{array}{cc} 1 - P_0 - 2Q_0 & R_0 + 1 \\ -(2P_0 + 4Q_0 + 3R_0) & P_0 + 2Q_0 \end{array} \right| \\ &= \frac{4ab(1-ab)(3-P_0-2Q_0+3R_0)}{(a^2b^4+4ab+2a+1)(ab+1)}. \end{aligned}$$

From these results we have immediately

$$\begin{aligned} \langle \sigma_0 \rangle_0 &= \frac{4(1+ab)}{a^2b^4+4ab+2a+1} C_0, \\ \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0 &= \frac{4(1-ab)}{a^2b^4+4ab+2a+1} C_0. \end{aligned} \tag{A.6}$$

(B) *The critical behaviours of χ_1 and χ_2 near the Curie point*

First we shall prove that χ_2 is finite at $T = T_c$. By definition (5.24) χ_2 is given by

$$\chi_2 = -\frac{N\mu}{E} \frac{\langle M_{11} - 1/\tau_1 \rangle \langle \sigma_0 \rangle_0^E + M_{12} \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0^E}{1/\tau_1 - 1/\tau_2}, \tag{B.1}$$

where $\langle \sigma_0 \rangle_0^E$ and $\langle \sigma_0 \sigma_1 \sigma_2 \rangle_0^E$ are solution of an equation

$$\begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} \langle \sigma_0 \rangle_0^E \\ \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0^E \end{bmatrix} = \frac{\mu E}{2kT} \frac{1}{2-S} \begin{bmatrix} S \\ T \end{bmatrix}.$$

Hence

$$\begin{aligned} \langle \sigma_0 \rangle_0^E &= \frac{\mu E}{2kT} \frac{1}{(2-S)} |M| \begin{vmatrix} S & M_{12} \\ T & M_{22} \end{vmatrix}, \\ \langle \sigma_0 \sigma_1 \sigma_2 \rangle_0^E &= \frac{\mu E}{2kT} \frac{1}{(2-S)} |M| \begin{vmatrix} M_{11} & S \\ M_{21} & T \end{vmatrix} \end{aligned} \tag{B.2}$$

with

$$|M| = \begin{vmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{vmatrix}.$$

Substituting (B.2) into (B.1), we can rewrite χ_2 in a form

$$\begin{aligned} \chi_2 &= -\frac{N\mu^2}{2kT} \frac{1}{(1/\tau_1 - 1/\tau_2)(2-S)} |M| \left\{ (M_{11} - 1/\tau_1) \begin{vmatrix} S & M_{12} \\ T & M_{22} \end{vmatrix} \right. \\ &\quad \left. + M_{12} \begin{vmatrix} M_{11} & S \\ M_{21} & T \end{vmatrix} \right\}. \end{aligned} \tag{B.3}$$

Since a factor $|M|$ in the denominator of (B·3) vanishes at $T = T_c$, χ_2 will become infinitely large at $T = T_c$ unless the numerator of (B·3) also vanishes at $T = T_c$. Now by simple algebra we find

$$M_{11} \begin{vmatrix} S & M_{12} \\ T & M_{22} \end{vmatrix} + M_{12} \begin{vmatrix} M_{11} & S \\ M_{21} & T \end{vmatrix} = S|M|, \quad (\text{B}\cdot 4)$$

while from (5·20) it holds that

$$\frac{1}{\tau_1} = \frac{1}{\tau_2} = \det |M| \quad (\text{B}\cdot 5)$$

or

$$\frac{1}{\tau_1} = \tau_2 \det |M|.$$

Therefore it is obvious that the expression inside the bracket of (B·3) has a common factor $\det |M|$ which exactly cancels the same factor in denominator. Thus we see that χ_2 remains finite even at $T = T_c$.

On the other hand, the expression for χ_1 similar to (B·3) is given as

$$\chi_1 = \frac{N\mu^2}{2kT} \frac{1}{(1/\tau_1 - 1/\tau_2)(2 - S)|M|} \left\{ (M_{11} - 1/\tau_2) \begin{vmatrix} S & M_{12} \\ T & M_{22} \end{vmatrix} + M_{12} \begin{vmatrix} M_{11} & S \\ M_{21} & T \end{vmatrix} \right\}. \quad (\text{B}\cdot 6)$$

This time, however, the term

$$\frac{1}{\tau_2} \begin{vmatrix} S & M_{12} \\ T & M_{22} \end{vmatrix}$$

remains finite and hence χ_1 tends to infinity as T approaches T_c .

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