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†Present address: U. S. Naval Research Laboratory, Washington, D. C. 20390.

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Critical Dynamics of the Order-Disorder Transformation in Ferroelectrics*

D. L. Huber
Physics Department, University of Wisconsin, Madison, Wisconsin 53706
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The dynamic wave-vector-dependent susceptibility of a model order-disorder ferroelectric is studied with particular emphasis on the contributions from the nonlinear terms in the kinetic equation for the fluctuations in the polarization. The Hamiltonian is that of a spin-$\frac{1}{2}$ Ising model in a weak rapidly fluctuating transverse field which simulates the role played by the phonons in bringing about the reorientation of the dipoles. Nonlinear effects are shown to remain small as T approaches T_c+. As a consequence the susceptibility is quite adequately approximated by the Debye form with a width inversely proportional to the static susceptibility. Below the Curie point the nonlinear terms become much more important. The dominant nonlinear process involves the decay into two fluctuations, a process forbidden by symmetry in the disordered state. The results of the theory are compared with experiment. Agreement is found in some cases. Lack of agreement in others is attributed to the shortcomings of the model.

I. INTRODUCTION

In recent years interest has grown in the dynamical properties of systems undergoing second-order phase transitions.[1] Among these are, for example, the magnetic transitions (ferromagnetism and antiferromagnetism), the liquid-gas transition near the critical point, the λ transition in liquid helium, various soft-mode structural transitions, and the displacive and order-disorder transitions in ferroelectrics and antiferroelectrics. In analyzing the dynamics particular attention has been paid to the wave-vector-dependent dynamic susceptibility $\chi(\vec{q}, \omega)$ which is associated with the order parameter for the transition. In many cases detailed information about the susceptibility has come from inelastic neutron scattering studies where the scattering cross section for momentum transfer $\hbar\vec{q}$ and energy transfer $\hbar\omega$ is simply related to $\chi(\vec{q}, \omega)$. Although neutron scattering is a versatile probe, it suffers from the limitation that the measurements are hampered by finite resolution. As a consequence phenomena associated with small $\vec{q}$ and ω are sometimes obscured. This is particularly important near the critical point where there frequently is a "softening" of the character-

istic frequency as well as an increase in the corresponding correlation length.[2] Light scattering and ultrasonic attenuation have also been used to probe the dynamics of the order parameter. In systems where the experiments are feasible, detailed information about the dynamics of the very-long-wavelength fluctuations in the order parameter can often be obtained.

Another method of obtaining information about the critical dynamics of ferroelectric and ferromagnetic systems is to make explicit use of the fact that the polarization or magnetization is the order parameter for the transition. By measuring the zero-field ac susceptibility one obtains $\chi(0, \omega)$ directly. Experiments of this type are particularly valuable in cases where the interesting dynamical features are restricted to frequencies $\lesssim 25$ GHz. At present we are unaware of any measurements in ferromagnets which have focused specifically on the critical point. In ferroelectrics, on the other hand, a great deal is known about the ac susceptibility near T_c. Extensive measurements of the frequency and temperature dependence of $\chi(0, \omega)$ have been reported in the literature.[3]

In interpreting the ac susceptibility measurements it is important to establish that the range of frequencies employed in the experiment spans the important features in the power spectrum of the order parameter. If this is not the case the measurements provide an incomplete picture of the critical dynamics. Such considerations are particularly important for displacive ferroelectrics. In these systems the onset of the transition is signaled by a decrease in the frequency of a zone-center transverse-optical-phonon mode.[4] If the frequency of the optical mode is outside the range of the apparatus, the description of the dynamics which is provided by the measurements may be misleading.

In the case of the order-disorder ferroelectrics the same considerations of course apply. However, in these systems the critical behavior is often limited to comparatively low frequencies which are determined by the relaxation rate for the orientation of the dipoles in the absence of cooperative effects. When this rate lies within the microwave range a rather complete picture of the dynamics can be obtained.

In this paper we will outline a theory for the dynamics of the order-disorder transition in ferroelectrics. It will be applicable both above and below T_c. An important feature of the theory is that it incorporates nonlinear terms in the relevant kinetic equations. These lead to departures from the familiar Debye form for the susceptibility.[5] The importance of the departures is ascertained, and an approximate parametrized expression for $\chi(\vec{q}, \omega)$ in the paraelectric phase is obtained.

The remainder of the paper is divided into two parts. The model Hamiltonian, kinetic equations, and resulting susceptibility are discussed in Sec. II. In Sec. III the predictions of the theory are compared with experiment and with those of other theories.

II. KINETIC EQUATIONS AND DYNAMIC SUSCEPTIBILITY

A. Kinetic Equations

In this section we outline a model calculation of the wave-vector-dependent dynamic electric susceptibility. The analysis begins with a discussion of the model Hamiltonian. Following many authors we approximate the order-disorder ferroelectric by a spin-$\frac{1}{2}$ Ising model, where the $\pm\frac{1}{2}$ eigenvalues characterize the two orientations of the dipole:

$$\mathcal{H}_0 = -\sum_{i,j} J_{ij} S_z^i S_z^j \,. \tag{1}$$

Here the S_z^i are spin operators and the J_{ij} are interaction constants associated with the pair of sites i, j. Typically, in the ferroelectric transition, we expect J_{ij} to have both long- and short-range components.

Since the z components of the spin all commute among themselves the Hamiltonian $\mathcal{H}_0$ is devoid of dynamics. Following Sandy and Jones[6] we introduce time-dependent effects by adding to $\mathcal{H}_0$ a spin-bath coupling of the form

$$\mathcal{H}_1 = \sum_i S_x^i F_i + \mathcal{H}_B \,, \tag{2}$$

where F_i denotes a quasiclassical fluctuating transverse field governed by a Hamiltonian $\mathcal{H}_B$, S_x^i is the x component of the spin, and the sum is over the $\mathcal{N}$ sites. The F_i are postulated to have the properties

$$\langle F_i(t) \rangle_B = 0 \,, \tag{3}$$

$$\langle F_i(t) F_j(t') \rangle_B = \delta_{ij} f(t - t') \,, \tag{4}$$

where

$$F_i(t) = e^{i\mathcal{H}_B t/\hbar} F_i e^{-i\mathcal{H}_B t/\hbar} \,, \tag{5}$$

and the brackets $\langle \cdots \rangle_B$ denote an average over the eigenstates of $\mathcal{H}_B$.

The spin-flipping term is meant to simulate the role played by the phonons in bringing about the reorientation of the dipoles, an effect which can often be interpreted as a thermal activation process. We postulate that the transverse fields are uncorrelated from site to site and that the autocorrelation function $f(t)$ decays in a time which is short in comparison with the characteristic time associated with a spin flip. We also postulate that the spin-bath coupling is sufficiently weak so as to have a negligible effect on the thermodynam-

ic properties of the order-disorder system in the temperature range of interest. In the evaluation of correlation functions involving products of spin and field operators it is assumed that the spins and fields can be treated as independent systems, an approximation which can be expressed symbolically as

$$\langle SF\rangle = \langle S\rangle_0 \langle F\rangle_B \ , \tag{6}$$

where $\langle \cdots \rangle_0$ denotes a thermal average over the eigenstates of $\mathcal{H}_0$.

The calculation of the dynamic susceptibility begins with the appropriate kinetic equations. In a recent paper[7] the author has outlined a general approach to the problem of critical dynamics in easy axis ferromagnets and antiferromagnets. In that paper kinetic equations were obtained for the so-called critical dynamical variables, which involved products of the long-wavelength fluctuations in the order parameter and the energy density. The theory developed in Ref. 7 can be utilized in the present study with only minor modifications.

In its dynamics the order-disorder ferroelectric resembles the antiferromagnet in that in both cases the $\vec{q}=0$ component of the relevant order parameter fails to commute with the full Hamiltonian. There is a difference, however, in that the energy of the antiferrromagnet is approximately constant, whereas the coupling $S_x F$, which leads to time-dependent behavior in the order-disorder system, also allows for the exchange of energy between the dipoles and the bath. In the antiferromagnet the time dependence of the $\vec{q}=0$ component of the order parameter arises from the transverse terms in the exchange interaction, whereas the decay of the $\vec{q}=0$ fluctuations in the energy density is determined by the spin-lattice coupling.

In order to ascertain the importance of this difference it is necessary to compare the decay rate of a fluctuation in the order parameter with the decay rate of a fluctuation in the energy density. We estimate the former from[7]

$$\Gamma_N(\vec{q}) = \chi_T(\vec{q})^{-1} \int_0^\infty dt\, (\dot{N}_{\vec{q}}(t), \dot{N}_{-\vec{q}}), \tag{7}$$

where $N_{\vec{q}}$ denotes the Fourier transform

$$N_{\vec{q}} = \sum_j e^{-i\vec{q}\cdot\vec{r}_j} S_z^j \ , \tag{8}$$

and $\chi_T(\vec{q})$ is the susceptibility associated with the order parameter

$$\chi_T(\vec{q}) = (N_{\vec{q}}, N_{-\vec{q}}) \ . \tag{9}$$

In Eqs. (7) and (9) we have

$$(A, B) = \int_0^{1/KT} d\lambda\, \langle e^{\lambda(\mathcal{H}_0+\mathcal{H}_1)} A e^{-\lambda(\mathcal{H}_0+\mathcal{H}_1)} B\rangle - (1/KT)\langle A\rangle\langle B\rangle \ , \tag{10}$$

where K is Boltzmann's constant and T is the temperature, while in Eq. (7)

$$\dot{N}_{\vec{q}} = (1/i\hbar)[N_{\vec{q}}, \mathcal{H}_1] \ . \tag{11}$$

The evaluation of the relevant commutators together with the approximations reflected in Eqs. (3)–(5) leads to the result

$$\Gamma_N(\vec{q}) = \chi^0(T)/\chi_T(\vec{q})\tau \ , \tag{12}$$

where

$$1/\tau = \hbar^{-2} \int_0^\infty dt\, f(t) \ . \tag{13}$$

The symbol $\chi^0(T)$ denotes the susceptibility of the noninteracting lattice

$$\chi^0(T) = \mathfrak{N}/4KT \ . \tag{14}$$

The calculation of the decay rate for the fluctuations in the energy density proceeds in a similar fashion, i.e., we have[7]

$$\Gamma_E(0) = (TC_V)^{-1} \int_0^\infty dt\, (\dot{\mathcal{H}}_0(t), \dot{\mathcal{H}}_0) \ , \tag{15}$$

where

$$\dot{\mathcal{H}}_0 = (1/i\hbar)[\mathcal{H}_0, \mathcal{H}_1] \ . \tag{16}$$

The symbol C_V denotes the specific heat

$$C_V = (1/KT^2)[\langle \mathcal{H}_0^2\rangle_0 - \langle \mathcal{H}_0\rangle_0^2] \ . \tag{17}$$

From Eqs. (3)–(5), (15), and (16) we obtain the result

$$\Gamma_E(0) \approx C_V^0(T)/C_V\tau \ , \tag{18}$$

where τ is given by Eq. (13). The symbol $C_V^0(T)$ denotes the high-temperature approximation to the specific heat

$$C_V^0(T) = \mathfrak{N} \sum_j J_{ij}^2 / 8KT^2 \ . \tag{19}$$

It should be noted that in evaluating Eq. (15) we have approximated the numerator by its limiting value at high temperatures, which should be satisfactory for qualitative estimates.

Comparing Eqs. (12) and (18) we conclude that at high temperatures the decay rates for the long-wavelength fluctuations in the energy density and the order parameter are roughly comparable. However, in the vicinity of the critical point the divergence in the susceptibility is generally much stronger than the divergence in the specific heat. Thus we have $\Gamma_N(0) \ll \Gamma_E(0)$ for $T \approx T_c$. As a consequence, the fluctuations in the energy density are to be excluded from the set of critical dynamical variables in the order-disorder problem,[8] which is to say that the fluctuations in the order parameter decay isothermally.

The theory of Ref. 7, when transcribed to the order-disorder system, leads to a kinetic equation for the order parameter of the form[9]

$$\frac{dA_{1\vec{q}}}{dt} = -\Gamma_N(\vec{q}) \sum_{\beta,\eta} \hat{\underline{U}}_{1\beta}(\eta_\beta^q)^{-1} A_{\beta\eta} \ , \tag{20}$$

in which the symbols $A_{\beta\eta}$ denote normalized prod-

ucts of β factors of the order parameter $N_{\vec{q}}$. That is, we have

$$A_{1\vec{q}} = A_{1\eta} = \frac{N_{\vec{q}} - \langle N_{\vec{q}} \rangle_0}{[(N_{\vec{q}}, N_{-\vec{q}})_0]^{1/2}} , \tag{21}$$

$$A_{2\eta} = \frac{N_{\vec{q}_1+\vec{q}} N_{-\vec{q}_1} - \langle N_{\vec{q}_1+\vec{q}} N_{-\vec{q}_1} \rangle_0}{[(N_{\vec{q}_1+\vec{q}} N_{-\vec{q}}, N_{-\vec{q}_1-\vec{q}} N_{\vec{q}_1})_0]^{1/2}} , \text{ etc.} \tag{22}$$

For a given β the sum over η involves η_β^q terms, that is, the number of combinations of β factors of the order parameter which have wave vectors which sum to $\vec{q}$.[7] As in Ref. 7 we include only those fluctuations with wave vectors $|\vec{q}| \lesssim K_c$, where K_c is the inverse correlation length associated with $\chi_T(\vec{q})$. The $\hat{U}_{\alpha\beta}$ denote elements of the inverse of the reduced susceptibility matrix. The reduced susceptibility matrix itself is of the form[10]

$$(\hat{U}^{-1})_{\alpha\beta} = \frac{\partial^{\alpha+\beta-1}}{\partial E^{\alpha+\beta-1}} \langle N_0 \rangle_0^E \Big|_{E=0} \times \left(\frac{\partial^{2\alpha-1}}{\partial E^{2\alpha-1}} \langle N_0 \rangle_0^E \Big|_{E=0} \frac{\partial^{2\beta-1}}{\partial E^{2\beta-1}} \langle N_0 \rangle_0^E \Big|_{E=0} \right)^{-1/2} , \tag{23}$$

where the symbol $\langle N_0 \rangle_0^E$ denotes the mean value of the order parameter in the presence of a static external field E whose interaction with the system is written $-EN_0$.

When the terms with $\beta > 1$ are omitted from the right-hand side of Eq. (20) the following linear equation is obtained:

$$\frac{\partial N_{\vec{q}}}{\partial t} = -\Gamma_N(\vec{q}) \hat{U}_{11} N_{\vec{q}} , \quad \vec{q} \neq 0 \tag{24}$$

corresponding to the exponential decay of the fluctuations. Keeping higher-order terms leads to nonlinear effects. As will be discussed in Sec. II B, the importance of these terms depends on the relative magnitudes of the elements of $\hat{U}$. Prior to considering this, however, we should point out that Eq. (20) has a simple physical interpretation. According to the standard arguments[11] we may regard the fluctuations in the polarization as being driven by a time-dependent thermodynamic field $E(\vec{q}, t)e^{i\vec{q}\cdot\vec{r}}$ according to the equation

$$\frac{\partial N_{\vec{q}}}{\partial t} = -\lambda E(\vec{q}, t) . \tag{25}$$

In the linear theory $E(\vec{q}, t)$ and $N_{\vec{q}}(t)$ are related by

$$N_{\vec{q}}(t) = \chi_T(\vec{q}) E(\vec{q}, t) , \tag{26}$$

leading immediately to Eq. (24) with $\hat{U}_{11}\Gamma_N(\vec{q}) = \lambda/\chi_T(\vec{q})$. Viewed in this context Eq. (20) is seen to reflect a more general relationship between E and N which can be written symbolically as

$$E \doteq aN + bN^2 + cN^3 + \cdots . \tag{27}$$

B. Dynamic Susceptibility

As noted above the importance of the nonlinear terms in the kinetic equations depends on the relative magnitudes of the elements of $\hat{U}$. It is apparent that in a loose way we can identify $\hat{U}_{1\beta}$ ($\beta > 1$) as a dimensionless coupling constant characterizing the decay of a fluctuation in the polarization into products of β such fluctuations. In order to obtain quantitative estimates it is necessary to postulate a particular functional relationship between $\langle N_0 \rangle_0^E$ and E. We consider two limiting cases, mean-field theory and the "exact" results for the three-dimensional Ising model. In the former the functional relationship is expressed by the equation

$$\langle N_0 \rangle_0^E = \tfrac{1}{2} \mathfrak{N} \tanh\left(\frac{E + 2\mathfrak{N}^{-1} \langle N_0 \rangle_0^E \sum_j J_{ij}}{2KT} \right) . \tag{28}$$

The elements of $\hat{U}^{-1}$ are then obtained from the coefficients in the expansion of $\langle N_0 \rangle_0^E$ in powers of E. The analogous results for the three-dimensional Ising model follow from the work of Essam and Hunter.[12] Limiting values of $(\hat{U}^{-1})_{1\beta}$ as $T \to T_c\pm$ are given for both models in Table I.

From Table I it is evident that the entries $(\hat{U}^{-1})_{1\beta}$, β even, are zero for $T > T_c$, a result which reflects the symmetry of the disordered state.[7] Furthermore all the entries are temperature independent. As pointed out in Ref. 7 this is a consequence of the singular part of the free energy being a function of the variable $E/|T - T_c|^\Delta$ near T_c. A somewhat surprising feature of Table I is the near equality between the values calculated in the mean-field approximation and the "exact" values for the Ising model with nearest-neighbor interactions.

To obtain an expression for the dynamic susceptibility we must first calculate the relaxation function $(A_{1\vec{q}}(t), A_{1-\vec{q}})$. The imaginary part of $\chi(\vec{q}, \omega)$ is then given by the integral[13]

$$\chi''(\vec{q}, \omega) = \omega \chi_T(\vec{q}) R \int_0^\infty dt\, e^{-i\omega t} (A_{1\vec{q}}(t), A_{1-\vec{q}}) , \tag{29}$$

TABLE I. Limiting values of $(\hat{U}^{-1})_{1\beta}$. MFA denotes mean-field approximation [Eq. (28)]. IM denotes simple-cubic Ising model with nearest-neighbor interactions (Ref. 12).

	$T = T_c+$		$T = T_c-$	
	MFA	IM	MFA	IM
$(\hat{U}^{-1})_{11}$	1	1	1	1
$(\hat{U}^{-1})_{12}$	0	0	$-(\frac{3}{8})^{1/2}$	$-(0.40)^{1/2}$
$(\hat{U}^{-1})_{13}$	$-(\frac{1}{10})^{1/2}$	$-(0.14)^{1/2}$	$(\frac{1}{10})^{1/2}$	$(0.10)^{1/2}$
$(\hat{U}^{-1})_{14}$	0	0	$-(0.025)^{1/2}$	a
$(\hat{U}^{-1})_{15}$	$(\frac{1}{154})^{1/2}$	$(0.01)^{1/2}$	$(0.006)^{1/2}$	a

[a]Not available.

where R denotes real part. Because of the magnitude of $(\underline{\hat{U}}^{-1})_{12}$ the calculation of $(A_{1\vec{q}}(t), A_{1-\vec{q}})$ in the ordered state appears to be prohibitively complex. In the disordered state $(\underline{\hat{U}}^{-1})_{12}$ and $(\underline{\hat{U}}^{-1})_{14}$ are zero and $(\underline{\hat{U}}^{-1})_{15}$ is small. These results suggest that above T_c it is a reasonable approximation to consider only the decay into three modes. In such an approximation we omit all off-diagonal entries in $\underline{\hat{U}}^{-1}$ except $(\underline{\hat{U}}^{-1})_{13}$ and $(\underline{\hat{U}}^{-1})_{31}$. The matrix $\underline{\hat{U}}$ has the form

$$\underline{\hat{U}}=\frac{1}{(1-B^2)}\left(\begin{array}{ccc|c} 1 & 0 & -B & \\ 0 & 1 & 0 & 0 \\ -B & 0 & 1 & \\ \hline & 0 & & I \end{array}\right), \tag{30}$$

where $B=(\underline{\hat{U}}^{-1})_{13}$ and I denotes a unit submatrix.

The equation that results from using the approximate expression for $\underline{\hat{U}}$, Eq. (30), can be written

$$\frac{\partial A_{1\vec{q}}}{\partial t}=\frac{-\Gamma_N(\vec{q})}{1-B^2}A_{1\vec{q}}+\frac{B\Gamma_N(\vec{q})}{(1-B^2)n_3^q}\sum_\eta A_{3\eta}\,. \tag{31}$$

A formal solution to (31) can be obtained by iteration with the zeroth-order solution being $A^0_{1\vec{q}}(t)=A_{1\vec{q}}e^{-\tilde{\Gamma}_q t}$, where $\tilde{\Gamma}_q$ is the renormalized decay rate

$$\tilde{\Gamma}_q=\Gamma_N(\vec{q})/(1-B^2)\,. \tag{32}$$

The relaxation function is then found by taking the inner product of $A_{1\vec{q}}(t)$ with $A_{1-\vec{q}}$. Since the expansion parameter B is fairly small we may obtain a crude approximation to the relaxation function by stopping after the first iteration. The resulting expression then has the form displayed in Eq. (40) of Ref. 7, where the sum over β is limited to one term. The dynamic susceptibility that is obtained by this procedure has an imaginary part which can be written

$$\frac{\chi''(\vec{q},\omega)}{\omega\chi_T(\vec{q})}=\frac{\tilde{\Gamma}_q}{\omega^2+\tilde{\Gamma}_q^2}\left(1+\frac{B^2\tilde{\Gamma}_q}{\bar{\Gamma}_3-\tilde{\Gamma}_q}\right)-\frac{\bar{\Gamma}_3}{\omega^2+\bar{\Gamma}_3^2}\,\frac{B^2\tilde{\Gamma}_q}{\bar{\Gamma}_3-\tilde{\Gamma}_q}\,. \tag{33}$$

In this equation $\bar{\Gamma}_3$ is an effective decay rate which is approximately equal to the zeroth-order rate of decay of $(A_{3\eta}(t), A_{3\eta})$ when all three modes have wave vectors in the vicinity of K_c. Since we have $\Gamma_N(K_c)\gtrsim\Gamma_N(0)$, $\bar{\Gamma}_3$ is at least as large as $3\Gamma_N(0)$. Also, it should be noted that we have made the approximation

$$(A_{3\eta}, A_{1-\vec{q}})\to(\underline{\hat{U}}^{-1})_{31}\,,$$

in evaluating the inner product prior to computing χ''. Such an approximation was made previously in the derivation of Eq. (20).[7]

III. DISCUSSION

The results of Sec. II can be summarized quite briefly. Above the transition temperature the dynamic susceptibility is predicted to have very nearly the Debye form with a width inversely proportional to $\chi_T(\vec{q})$. Nonlinear effects, which reflect multimode decay, remain small in the limit $T\to T_c+$. This happens for two reasons. First, the decay into two fluctuations is forbidden for reasons of symmetry. Second, the quantity $B^2\tilde{\Gamma}_q/(\bar{\Gamma}_3-\tilde{\Gamma}_q)$, which measures the contribution to χ'' from the first allowed nonlinear decay process, is $\lesssim 0.1$. Below T_c nonlinear effects are predicted to be more important since the two-fluctuation decay is no longer forbidden. As a consequence it is expected that $\chi''(\vec{q},\omega)$ will deviate significantly from the Debye form.

The theory outlined in Sec. II is of course based on a particularly simple model of an order-disorder ferroelectric. In order to ascertain the extent to which the theory is applicable to real systems it is necessary to examine the more questionable features of the model in some detail. Especially relevant here is the suitability of the dynamical term $\mathcal{H}_1$ for describing the reorientation of the dipoles. We have assumed that this process could be simulated by a randomly fluctuating transverse field. Such an approximation would appear to be satisfactory as long as the reorientation involves some sort of thermal activation as opposed to unassisted quantum-mechanical tunneling. Also, in a thermally activated process we expect the decay of the fluctuation to take place in a time on the order of the inverse of a thermal phonon frequency which is usually much less than $1/\Gamma_N$, a condition we have assumed in Sec. IIA.

A somewhat more subtle approximation is the assumption that the phonons act as a thermal bath for the order-disorder system. With the particular choice for $\mathcal{H}_1$ it was found that the fluctuations in the polarization decay isothermally near T_c since $\Gamma_N(0)\ll\Gamma_E(0)$. However, if the heat capacity of the phonons is not large in comparison with the heat capacity of the order-disorder system, as may be the case near T_c, the decay is no longer isothermal if the rate of transfer of heat from the dipoles to the phonons greatly exceeds the rate of transfer from the sample to its thermal bath. Very roughly then, within the framework of the model, the conditions necessary for isothermal decay will certainly prevail as long as the fractional increase in the specific heat of the sample relative to its value far away from the critical point is small.

The prediction of an approximate Debye form for $\chi(\vec{q},\omega)$ with a width inversely proportional to $\chi_T(\vec{q})$ is not of course unique to our theory. Early work of Mason[14] and more recent studies of Yamada, Fujii, and Hatta,[15] as well as Sandy and Jones,[6] have led to essentially the same result. The present theory extends the work of these authors in that it attempts to assess the importance of

the nonlinear terms in the relevant kinetic equations. It should be noted that our conclusion is at variance with the theory of Nishikawa which predicts large deviations from the Debye form as $T \to T_c+$.[16] The theoretical approach followed in Ref. 16 is sufficiently different from our own that we have not been able to pinpoint the origin of the discrepancy. Also, Suzuki, Ikari, and Kubo have carried out studies of the dynamics of the two-dimensional Ising model.[17] Starting with the master equation and using the techniques of series expansion they find that as $T \to T_c+$, $\chi(0, \omega)$ has a frequency dependence of form $f(\omega/(T - T_c)^x)$ where $x \approx 2.00 \pm 0.05$. Our theory, applied to that system, leads to $x = \frac{7}{4}$, the exponent of the susceptibility.[18] At present we do not know if the difference in the values of x reflects the use of the fluctuating field as opposed to the master equation or is a consequence of the approximations which were made in obtaining Eq. (33).

As noted in the Introduction zero-field measurements of $\chi(0, \omega)$ near the critical point have been reported for many ferroelectrics. Because of domain effects the interpretation of the data for $T < T_c$ is complicated. Above T_c the over-all shape of $\chi(0, \omega)$ is conveniently characterized by a polydispersive parameter β which measures the deviation from the Debye form[19]

$$\frac{\chi(0, \omega) - \chi(0, \infty)}{\chi(0, 0) - \chi(0, \infty)} = \frac{1}{1 + (i\omega\tau)^{\beta}} , \tag{34}$$

where $\chi(0, \infty)$ denotes the contribution from the atomic polarizabilities. Near T_c, τ varies as $\chi(0, 0) - \chi(0, \infty)$ in almost all instances. With respect to β, however, a significant variation is found from material to material. In agreement with our theory, there are a number of systems where β is approximately one. These include Rochelle salt ($\beta \approx 1$),[6] $NaNO_2$ ($\beta = 0.94$),[20] and NH_4Fe-alum ($0.95 \lesssim \beta \lesssim 1$).[21] On the other hand in KNO_3 we have $\beta \approx 0.57$,[22] which appears to be in disagreement with the theory.[23,24] Although speculations on the origin of the discrepancy are risky, we suspect it has to do with the suitability of our model Hamiltonian. As discussed in Ref. 22 there is a strong dipole-lattice coupling in KNO_3 which is believed to reduce the transition from second to first order. Such an effect is of course absent in our model. Because of this it is our opinion that future progress in understanding the critical dynamics of the order-disorder ferroelectrics lies in working with more realistic Hamiltonians rather than in refining calculations based on simple models.

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[23]Using the functional form for χ given in Eq. (33) we have calculated a corresponding value of β by fitting it with a function of the form $[1 + (i\omega\Gamma_0^{-1})^{\beta}]^{-1}$. With $B^2 = 0.10$ and $\bar{\Gamma}_3 = 3\bar{\Gamma}_0$, we obtain the value $\beta = 0.99$.

[24]According to a table prepared by E. Nakamura *et al.* [J. Phys. Soc. Japan Suppl. 26, 174 (1969)], other systems with comparatively small values of β include colemanite ($\beta \approx 0.62$), diglycine nitrate ($\beta \approx 0.64$), and $K_4Fe(CN)_6 \cdot 3H_2O$ ($\beta \approx 0.74$).